

# Adsorbed molecular shuttlecocks: An NIXSW study of Sn phthalocyanine on Ag(1 1 1) using Auger electron detection

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## Abstract

Normal incidence X-ray standing wave (NIXSW) spectroscopy has been used to determine the orientation of Sn phthalocyanine (SnPc) molecules in a highly ordered, but incommensurate, monolayer on the Ag(1 1 1) surface. Our sample preparation procedure differs from that used in previous work on this system [C. Stadler, S. Hansen, F. Pollinger, C. Kumpf, E. Umbach, T.-L. Lee, J. Zegenhagen, Phys. Rev. B 74 (2006) 035404] and leads to a different unit cell with basis vector lengths of  $\sim 15.0$  Å and  $15.3$  Å ( $\gamma = 98^\circ$ ) which is oriented at an angle of  $\sim 5^\circ$  to the underlying Ag(1 1 1) lattice. Structural parameters extracted from Sn MNN NIXSW spectra indicate that SnPc, a buckled, ‘shuttlecock’ phthalocyanine, adsorbs in a Sn-down geometry with the Sn atom approximately  $2.3$  Å above the Ag(1 1 1) surface plane. Despite the incommensurate nature of the overlayer, we find a surprisingly high coherent fraction for standing wave data taken for the  $(\bar{1} 1 1)$  reflection and argue that this arises from the small domain size of the superstructure.

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## 1. Introduction

The desire for increased computational power at an ever-reducing physical size per gigaflop is pushing state-of-the-art nanoscale science and technology into the domain of molecular electronics. Organic molecules lend themselves well to the requirements of building electronic circuits not only in terms of their ability to form novel self-assembled structures [1] but also because individual molecules can be used as discrete circuit elements (switches, wires, etc.) [2].

One set of molecules of particular importance in molecular electronics is the phthalocyanine family [3]. Metal phthalocyanines (MePc) are generally planar organic molecules comprising of a central metal atom surrounded by a porphyrin-like unit that in turn is surrounded by four aromatic rings (see inset to Fig. 1). Phthalocyanines are structurally similar to important biomolecules such as haemoglobin and chlorophyll and are commonly used in industry for pigmentation. They have been the focus of intense interest due to their electrical and (non-linear) optical properties. Selection of the central metal atom allows the molecular properties to be tuned *without the addition of functional groups*. For example, by increasing the size of the metal atom the molecule distorts and becomes aplanar [4], as in the case of SnPc which appears shuttlecock shaped with the Sn out of the molecular plane.

Fundamental understanding of molecule–molecule and molecule–surface interactions is important when attempting to determine the charge transport characteristics of metal phthalocyanines. For instance, the adsorption of CuPc on a rough substrate results in the molecular axis aligning perpendicular to the surface. If, however, the molecule is

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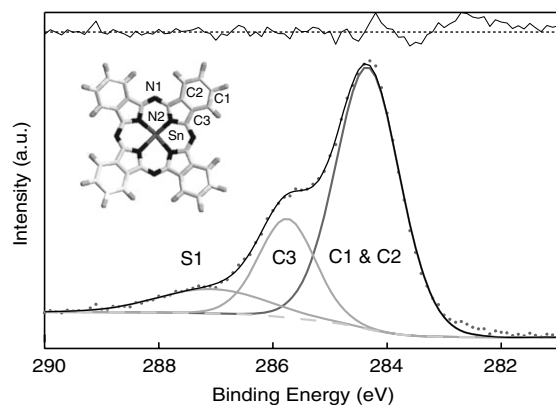


Fig. 1. C 1s XPS spectrum for a thick SnPc film. The fitting parameters are given in Table 1. Inset: The structure of tin phthalocyanine. Labels are defined in the text.

adsorbed on an atomically flat substrate the molecular axis lies parallel with the surface plane [5]. This can have a considerable impact on the efficiency of photovoltaic and other organic devices [6].

For these reasons, a number of groups have focussed on elucidating the interactions of phthalocyanine molecules with metal, semimetal, and semiconductor surfaces. SnPc has attracted attention due to its aplanar character and its adsorption on a variety of substrates including graphite [7], Au [7], Ag [8], and InSb [9] has thus been examined. Of particular importance to the present study, the SnPc/Ag(111) system has very recently been investigated with normal incidence X-ray standing wave spectroscopy (NIXSW) [10,11] by Stadler et al. [12] who found that the incommensurate lattice formed by annealing a multilayer film at a temperature of  $\sim 290^\circ\text{C}$  comprised molecules adsorbed in a Sn-down geometry. Importantly, a variety of coverage-dependent incommensurate superstructures have been observed in, as yet, unpublished SPA-LEED measurements for SnPc/Ag(111) [40]. The observation of this range of structures highlights the importance of intermolecular interactions (and the balance of intermolecular and molecule–substrate forces) in the SnPc/Ag(111) system.

Stadler et al.'s NIXSW investigation used photoelectron emission from the Sn 3d core-level as the probe of adsorption of the X-ray standing wavefield by the tin atom at the centre of the phthalocyanine molecule. As is now well-established [13], the extraction of structural parameters from NIXSW data can be complicated by a number of phenomena, depending on the signal used to monitor X-ray absorption. With photoelectron yield, the contribution of higher order (multipole) contributions beyond the standard dipole approximation must be taken into consideration [14]. This is, perhaps surprisingly, the case even for the relatively low photon energies typically used in XSW (a few keV). (As pointed out by Woodruff [15], the conventional view for quite some time was that non-dipole effects were significant only for much harder X-rays ( $>20$  keV).) As discussed briefly below, the asymmetry in photoelectron emis-

sion arising from the higher order components of the electromagnetic field – in particular, the *cross terms* involving the electric quadrupole and magnetic dipole terms,  $E1 \cdot E2$  and  $E1 \cdot M1$  – can be formally taken into account using an asymmetry parameter,  $Q$  [14,16].

Auger electron emission does not suffer from the non-dipole asymmetry problem. One might then imagine that Auger-based NIXSW is rather better suited to the robust determination of accurate structural parameters. Unfortunately, however, for emission involving relatively shallow core-levels, Auger-based XSW is plagued by a different experimental artifact: the excitation of adsorbate Auger emission by inelastic and secondary electrons from the bulk crystal. The energy ‘threshold’ at which the dominant contribution to the adsorbate Auger signal becomes the excitation by the incident X-ray wavefield remains ill-defined. Although some authors suggest that the threshold energy should occur in the range 500–1000 eV [19,15], it is clear that further work on a diverse range of systems is required to clarify the importance of “bulk-excited” Auger contributions to the XSW signal. An interesting element of the study reported here is that for the Sn MNN Auger emission used to acquire our XSW data, the Sn  $M_4$  binding energy is 498 eV, very close to the threshold suggested by some authors [19].

We note at this point that, for reasons described in the following section, it was not possible to apply the “ratioing” method previously put forward by Woicik et al. [17] to extract “pure” surface-related information from the total (i.e. bulk + surface) XSW signal. (Indeed, and as we shall discuss in a later paper [38], the Woicik et al. method is not generally well-suited to the extraction of quantitative structural parameters from XSW data.) Importantly, and notwithstanding the possible contribution of bulk-excited electrons to our Sn MNN spectra, we find that the structural parameters derived from our Auger XSW study largely agree within experimental error with those determined from XSW measurements of SnPc/Ag(111) based on Sn 3d photoemission signals [12]. An important exception is the observation of a rather higher coherent fraction for the  $(\bar{1}11)$  which we argue arises from a relatively small SnPc domain size.

## 2. Normal incidence X-ray standing wave spectroscopy

NIXSW is a powerful technique for the determination of adsorption sites [10,11,15,21] and has been used to study a variety of adsorbed molecules on a range of substrates. Using a single crystal substrate, backscattered X-rays will occur at the Bragg condition for normal incidence. The superposition of illuminating and reflected X-rays produces a standing wave field which has a periodicity in intensity equal to that of the scattering planes. Varying the incident photon energy within the reflectivity range moves the standing wave nodal and anti-nodal planes with respect to the crystal lattice. An atom ‘bathed’ in the wavefield will

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