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Interpretation of X-ray Absorption Spectroscopy in the Presence of Surface Hybridization

Katharina Diller*,^{a)} Reinhard J. Maurer,^{b)} Moritz Müller,^{c)} and Karsten Reuter
Department Chemie, Technische Universität München, D-85747 Garching, Germany

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X-ray absorption spectroscopy yields direct access to the electronic and geometric structure of hybrid inorganic-organic interfaces formed upon adsorption of complex molecules at metal surfaces. The unambiguous interpretation of corresponding spectra is challenged by the intrinsic geometric flexibility of the adsorbates and the chemical interactions at the interface. Density-functional theory (DFT) calculations of the extended adsorbate-substrate system are an established tool to guide peak assignment in X-ray photoelectron spectroscopy (XPS) of complex interfaces. We extend this to the simulation and interpretation of X-ray absorption spectroscopy (XAS) data in the context of functional organic molecules on metal surfaces using dispersion-corrected DFT calculations within the transition potential approach. On the example of X-ray absorption signatures for the prototypical case of 2H-porphine adsorbed on Ag(111) and Cu(111) substrates, we follow the two main effects of the molecule/surface interaction on XAS: (1) the substrate-induced chemical shift of the 1s core levels that dominates spectral changes in dominantly physisorbed systems and (2) the hybridization-induced broadening and loss of distinct resonances that dominates in more chemisorbed systems.

I. INTRODUCTION

Adsorption of organic molecules at single-crystal metal surfaces yields well-defined models for interfaces in hybrid inorganic-organic systems (HIOS). A detailed understanding of the geometric and chemical structure, of the electronic level alignment and reactivity of the adsorbates¹⁻⁶ provides thus important information for the application of HIOS in organic solar cells, organic light-emitting diodes (OLEDs) or other molecular electronics devices.⁷⁻¹¹ X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine-structure (NEXAFS, often also referred to as XANES) spectroscopy represent some of the most popular techniques to study the electronic structure and (with polarization-dependent NEXAFS) the adsorption geometries¹². For XPS, and even more so for NEXAFS, the interpretation of the spectroscopic signatures is a challenge though, and disentangling effects of electronic structure and adsorption geometry of complex functional adsorbates purely from experiment can be close to impossible.

The principles of XPS¹³ and NEXAFS¹⁴ are depicted in Fig. 1: The sample is irradiated by an X-ray beam, leading either to the emission of photoelectrons from a core level (XPS) or the excitation of core electrons to higher, unoccupied levels (NEXAFS). In both cases experimental spectra are acquired by scanning over an energy range: kinetic energies for XPS (which are linked

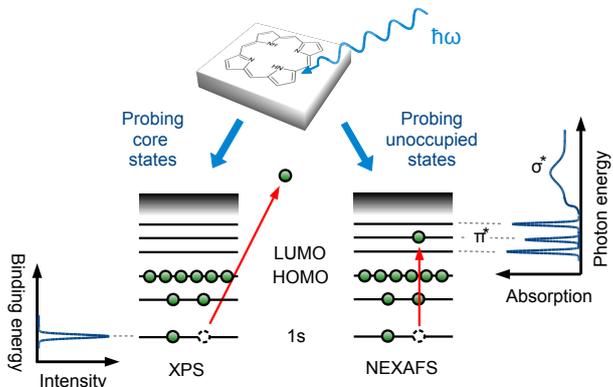


FIG. 1. Principle of XP and NEXAFS spectroscopy. Absorption of X-ray radiation leads either to emission of core electrons (XPS) or to excitation into unoccupied molecular π^* and σ^* states (NEXAFS). The schematic spectra indicate the relation between adsorbate states and peaks in the spectra.

via the photon energy to electron binding energies) and photon energies for NEXAFS (to probe resonant excitations). Ideally, the measured spectrum exhibits sharp signatures which can be directly assigned to originate from individual core levels (XPS, Fig. 1 left) or from transitions between core levels and unoccupied states (NEXAFS, Fig. 1 right). Correspondingly, changes in the chemical environment are reflected in (i) the position of the spectral features, as well as (ii) their shape and intensity. A full understanding of these signatures is therefore the key to understand the chemistry and the electronic properties of the combined molecule/surface system.

Unfortunately the inherent multi-peak structure in NEXAFS (Fig. 1b) makes interpretation difficult. Already for simple organic molecules containing only a single carbon atom (such as CO) or only a single dis-

^{a)} Author to whom correspondence should be addressed. Electronic mail: katharina.diller@tum.de; current address: Institute of Physics, École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland

^{b)} current address: Department of Chemistry, Yale University, New Haven CT 06520, USA

^{c)} current address: CIC nanoGUNE Consolider, Tolosa Hiribidea 76, E-20018 Donostia - San Sebastián, Spain

tinguishable chemical carbon species (such as C₂H₄ or benzene) the carbon K-edges are non-trivial and interpretation is vastly aided by simulations.^{15–18} Organic adsorbates currently studied in the context of molecular nanotechnology are considerably more complex. Molecules such as pentacene derivatives and alkanethiols,¹⁹ alkynes,²⁰ porphyrins,^{1,21} or azobenzene derivatives^{22,23} have a high molecular flexibility and their conformation on surfaces depends on many factors. Polarization-dependent NEXAFS is commonly used to derive adsorption geometries,^{12,19,24} but the results are only reliable when all peaks are correctly assigned to subgroups of the molecule, obtained e.g. by comparison to (polarization dependent or independent) simulations. Complex organic adsorbates contain many chemically inequivalent carbon atoms. The measured C K-edge is thus composed of several non-trivial contributions, which not only differ in shape and position, but may each react differently to the presence of the surface.

First-principles NEXAFS simulations of complex interfaces (including the substrate) may prove indispensable, but became computationally feasible only recently. In contrast, single-molecule calculations using time-dependent DFT, as well as the here employed transition potential (TP) approach^{25,26} are well established and generally reproduce experimental gas-phase and multilayer data very well.^{27–29} Relaxation effects in the TP approximation are taken into account by including half a core hole, and the excitations at different atomic centers allow the direct assignment of spectral features to individual atoms and transitions. This approach (which we will use in the following as described in the methods section) has been successfully employed in single-molecule simulation for reproducing the near-edge region of experimental K-edge data with high accuracy (for details see for example works on the C edge of anthracene,³⁰ the F edge of perfluoropentacene,³¹ or the C³² and the O edge³³ of phenyl-C60-butyric acid methyl ester performed with the DFT cluster code StoBe), which then allows a detailed fitting of the measured fine structure.³⁴ However, such single-molecule calculations lack the perturbing effect of the substrate on the signatures of adsorbates in the monolayer, i.e. they neglect the effects that define the electronic and optical properties of the HIOS interface. In this work we assess the role of such molecule/substrate interaction in the interpretation of NEXAFS signatures using dispersion-corrected DFT in combination with the TP approach. Explicitly accounting for the extended metal surface (similar to the study of Baby et al.³⁵ and in contrast to finite cluster calculations, as used for example in refs. 36 and 37), we study the XPS and NEXAFS signatures of two prototypical showcases for HIOS, free-base porphine (2H-P, Fig. 3a) on Ag(111) and Cu(111). 2H-P represents the most basic compound in the group of porphyrins; molecules which attract large interest due to their ubiquitous presence in biology and their large chemical flexibility and versatility.^{1,21} In a recent study³⁸ we found that the molecule-

surface binding is dominated by dispersion interactions on both substrates. However the charge rearrangement and surface hybridization is more physisorption-like on Ag(111) and more chemisorption-like on Cu(111).³⁸ As we will show below, this subtle difference for otherwise equivalent features makes these systems an ideal showcase for the study of surface-interaction effects on NEXAFS signatures.

II. COMPUTATIONAL DETAILS

All DFT calculations have been performed using the pseudopotential plane wave code CASTEP 6.0.1³⁹ and employing standard library ultrasoft pseudopotentials (USPPs)⁴⁰ for the geometry optimizations and the generation of the molecular orbital projected density of states (MO-PDOS). Electronic exchange and correlation were treated with the semi-local PBE functional⁴¹ and a plane wave cutoff of 450 eV (400 eV) was used for the calculation of the adsorbates (isolated molecule). As adsorbate structures are strongly governed by van-der-Waals interactions, the semi-local functional was augmented with the pairwise-additive dispersion correction scheme vdWsurf of Tkatchenko and co-workers.^{42,43} All calculations were performed with (6 × 6) (111) four-layered surface slabs of Ag and Cu with PBE-optimized lattice constants of 4.14 Å (bulk Ag) and 3.63 Å (bulk Cu). The vacuum was chosen to exceed 20 Å and Brillouin-zone sampling was done with a 2×2×1 (4×4×1) Monkhorst–Pack grid⁴⁴ for geometry optimizations (electronic structure calculations). All molecular degrees of freedom were fully relaxed until residual forces fell below 0.025 eV/Å. The energetically most favored adsorption sites were on both substrates the bridge sites (with respect to the center of the molecule). The porphine molecules adsorb parallel to the surface with only minor deformations. The difference in maximum pyrrole tilt angle between porphines adsorbed onto Cu and Ag is less than 4°. A more detailed description of the optimized geometries, as well as an analysis of the adsorption energies can be found in ref. 38

Core-Level spectroscopy simulations have been performed using the ELNES module in CASTEP⁴⁵, a self-written post-processing tool, and on-the-fly generated core-hole excited USPPs including a full (half) core hole for the simulation of the XPS (NEXAFS) spectra. XPS energies for each chemical species have been calculated as the difference in total energies between core hole-excited and ground-state calculations. The XPS intensity is simply given by stoichiometry, assuming ideal and species-independent generation of photoelectrons. The NEXAFS simulations are performed using the transition potential (TP) approximation,²⁵ where the occupation of the initial state orbital (here: C 1s) is set to 0.5 (see also refs. 30,31). This allows to calculate all transition energies in a single DFT calculation by determining the difference

175 between the eigenvalue of the state with $n = 0.5$ and
 those of the unoccupied orbitals. The number of simu-
 180 lations is therefore the same for the simulation of XPS
 and NEXAFS spectra. To facilitate comparison to the
 experiment, spectra were then broadened with Gaussian
 functions of varying width: Up to 5 eV over the first
 transition a broadening σ of 0.2 eV was used, followed
 185 by a linear increase to 2.0 eV up to 15 eV over the first
 transition to account for the reduced lifetime of the σ^*
 resonances which leads to increasing widths.¹⁴ The sum
 of the shifted and broadened contributions resulted in
 the spectra displayed in Fig. 2 and Fig. 3. The spec-
 tra in Figs. 2 and 3 are referenced with respect to the
 first feature of lowest-energy species (marked in black).
 Further details on the calculations can be found in the
 190 Supplemental Material.

III. RESULTS AND DISCUSSION

Figure 2b shows the experimental C K-edge NEXAFS
 multilayer spectra for 2H-P on Ag(111).⁴⁶ The spectrum
 is well reproduced by single-molecule calculations em-
 195 ploying DFT cluster codes with the TP approach⁴⁷ and
 equally by our here employed pseudopotential plane-wave
 dispersion-corrected DFT calculations (Fig. 2a) using a
 periodic supercell (cf. Methods and SI). The agreement²³⁰
 between simulations and experiment allows for a direct
 assignment of the measured features in terms of transi-
 tions between core-levels and unoccupied molecular or-
 bitals (MOs), cf. Fig. 3b. Peak A is generated by transi-
 tions from the 1s levels to the π^* lowest unoccupied MOs²³⁵
 (LUMOs) in the presence of the respective core holes of
 the outer C-C bound carbon atoms. Peak B originates
 205 from the 1s \rightarrow LUMO transition of the carbon atom at-
 tached to the iminic nitrogen atom, and peak C is a mix
 of several components (in agreement with previous single-²⁴⁰
 molecule simulations⁴⁷).

For 2H-P directly adsorbed on Ag(111) (Fig. 2d, ref.
 46) the spectrum is very similar to that of the multi-
 layer/isolated molecule. Only the second peak (peak²⁴⁵
 B') seems shifted upwards leading to a broadening of
 the third (peak C'), and a reduction of the first peak
 215 (peak A'). In contrast, the strong modifications intro-
 duced by direct adsorption to Cu(111) (structures D, E
 in Fig. 2e, refs. 47,48) pose a challenge for any such inter-²⁵⁰
 pretation. Just on the basis of the measured spectrum,
 it is not possible to unambiguously conclude whether all
 features are still present, but broadened; whether only
 the first peak is quenched due to an electron transfer to
 the LUMO⁴⁹; whether the first peak is shifted upwards²⁵⁵
 and the third one downwards; or even if the molecule is
 decomposed⁵⁰. Using the detailed information on geome-
 220 try, electronic structure, and individual atomic contribu-
 tions provided by the first-principles calculations allows
 instead to clearly separate the spectral changes into two²⁶⁰
 distinct effects: (i) chemical shifts of the 1s core levels
 (i.e., the XPS energies) which govern the onset of the

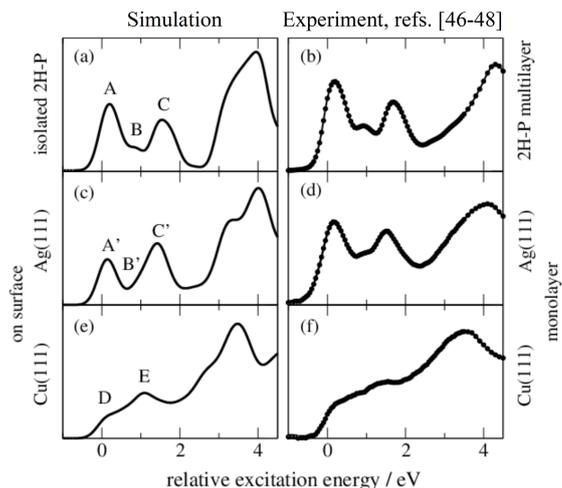


FIG. 2. Comparison of simulated (left) and experimental (taken from refs. 46–48) C K-edge NEXAFS spectra of 2H-P (top), 2H-P on Ag(111) (middle), and 2H-P on Cu(111) (bottom). For ease of comparison both experiment and simulation have been shifted to align the leading edge with 0 eV, corresponding to an alignment to the lowest C-CN transition (cf. Fig. 3).

NEXAFS curves of the different carbon species (cf. Fig. 3), and (ii) the electronic structure of the frontier MOs, which determines the shape of the individual spectral components (cf. Fig. 4).

In the 2H-P XPS signature (Fig. 3a) the main low-energy feature is generated by purely carbon-coordinated C species, while the contributions from N-coordinated and NH-coordinated C species are clearly separated at higher binding energies. Upon adsorbing the molecule onto Ag(111) (Fig. 3c) and Cu(111) (Fig. 3e) the two groups separate more and more, up to the point of two displaced peaks in the case of 2H-P on Cu(111) (for a comparison to experimental literature XPS data see Fig. S1). Accordingly, the first peak of the 2H-P gas-phase NEXAFS curve originates from purely C-bonded carbon, the second peak from the C-N species, and the third is a mixture. The calculation confirms that the second peak (C-N component) is indeed shifted upwards upon adsorption on Ag(111) (Fig. 3d). On Cu(111) (Fig. 3f), however, the strong spectral changes can no longer be explained on the basis of chemical shifts alone.

This leads us to discuss the second adsorption-induced effect on the spectra that is not captured by single-molecule simulations: the variation of the shape of the individual spectral components arising from surface hybridization of the involved frontier MOs. To illustrate this, Fig. 4 compares the simulated NEXAFS spectra with the MO-projected partial density of states (MO-PDOS). For clarity we show only the component arising from one of the C-bonded species (blue dashed component in Fig. 3), the others show the same behavior. In the MO-PDOS the frontier orbitals of isolated 2H-P

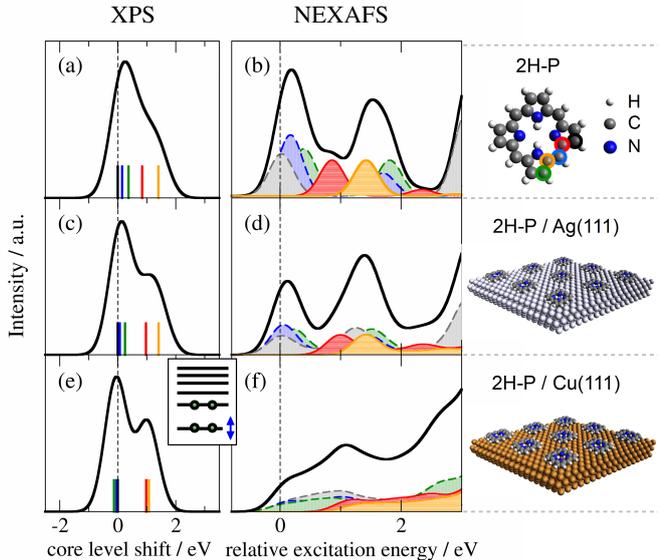


FIG. 3. Comparison of simulated C1s XP (left) and C K-edge NEXAFS (middle) signatures of isolated 2H-P (top) with those of 2H-P adsorbed on Ag(111) (middle) and Cu(111) (bottom) surfaces. The color code of individual spectral components indicates the coordination of the corresponding C atom as indicated in the top right panel: C-bonded (black, blue, green dashed lines), N-bonded (red continuous line) and NH-bonded (orange continuous line). Total spectra (black lines) and NEXAFS components are broadened for visual clarity. For better comparison all spectra are aligned to the lowest C-CN transition (black component).

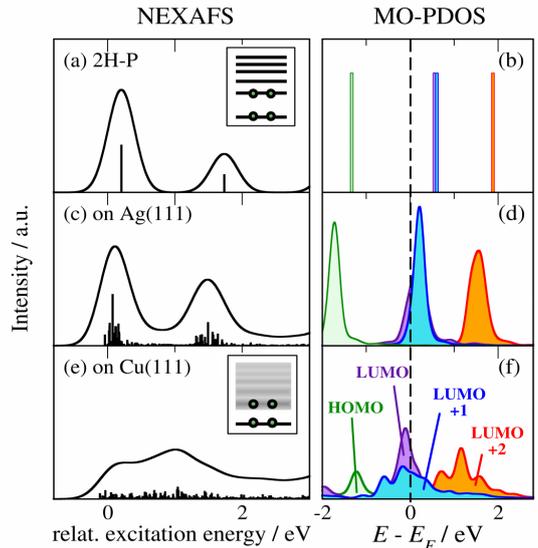


FIG. 4. (Left) Simulated NEXAFS component originating from one C-bonded species (cf. blue dashed lines in Fig. 3) for isolated 2H P (a), 2H-P on Ag(111) (c), and on Cu(111) (e). Bars denote the calculated transitions. The continuous black line results after broadening. To increase visibility, bars in (c) and (e) are scaled by a factor of four compared to (a). (Right) The changes of the NEXAFS signatures reflect the differing hybridization in the molecular states as evidenced by the MOs projected from the total density of states (see text). Considering the discrete spectrum of isolated 2H-P, no broadening was applied in (b).

(Fig. 4b) are projected onto the final eigenstates of the adsorbed system. The MO-PDOS thus exclusively reflects the changes of the frontier orbitals upon adsorption (see SI for more details). Figure 4b shows the discrete frontier MOs of the isolated molecule. The corresponding NEXAFS spectrum in Fig. 4a is governed by single transitions into the LUMO and LUMO+2. Due to the missing overlap between the 1s orbital and the LUMO+1 derived using the TP method (cf. Supporting Information, Fig. S3) the corresponding transition has close to zero intensity. For 2H-P on Ag(111) this discrete peak structure is mostly preserved, as well as the near-degeneracy of LUMO and LUMO+1. However, small hybridization effects already lead to broadened molecular states, and a partial shift below the Fermi level indicates an onset of charge transfer (which we recently confirmed using a range of charge partitioning schemes³⁸). This change in electronic structure carries over to the NEXAFS spectrum by replacing the delta-peak transitions of the isolated molecule with narrow distributions. The MO-PDOS alone, however, while reflecting the influence of the surface on the molecular states, is not sufficient for a detailed interpretation of the spectral changes. In Fig. S4 we compare the experimental data to the summed up MO-PDOS shown in Fig. 4, which was multiplied by a step function to consider only the unoccupied states.

The trends are well reproduced, but the near-edge fine-structure is not, which underlines the need for the inclusion of the core hole (in agreement with the results for single-molecule simulations presented for examples in refs. 30,31. The analysis of the experimental data in ref. 46 let not unambiguously decide whether the minimal changes in spectral shape of the experimental NEXAFS data of 2H-P adsorbed on Ag(111) compared to isolated 2H-P are caused by a reduction of the first peak caused by charge transfer or a shift of the individual contributions. The here presented TP calculations show that the spectrum is not only governed by a relative peak shift, but also by a slight reduction of intensity in the first peak that stems from a charge transfer. The latter effect is evidenced by the MO-PDOS and the partial shift of the LUMO below the Fermi level (Fig. 4d). In general, however, the quantification of transferred charge is not easy, as our employed computational setup (i.e., using the semi-local PBE functional) is not able to capture all possible effects such as the occurrence of integer charge transfer.⁵¹ For a more detailed discussion of the amount of partial charge transfer between the Ag(111) and Cu(111) surfaces and the porphine molecule, the values obtained with different methods and the influence of the molecular coverage we refer to ref. 38.

For the only modestly more reactive Cu(111) surface the MO-PDOS loses this discrete peak structure and in-

stead exhibits band-like features due to hybridization³⁷⁰ with substrate states (Fig. 4f). Rather than mere energetic shifts and significant broadening these features show a pronounced sub-structure with multiple peaks due to the splitting of MOs. These complex shapes again carry directly over to the NEXAFS spectrum (Fig. 4e). The³⁷⁵ availability of a continuum of molecular states leads to a continuum of transitions with non-zero transition probability. In their superposition these transitions give rise to new features in the resulting spectrum that resemble peaks or shoulders. However, as is clear from the³⁸⁰ present analysis any association of these features to (predominant) transitions to specific resonant MOs would be unjustified, if not misleading: Neither can the spectral change be assigned to quenching of the first peak due to charge transfer alone, the molecule is neither decomposed³⁸⁵ nor deprotonated, nor is there a strong selective binding that would lead to a pronounced geometric deformation – as could all have been deduced by traditionally interpreting the spectrum in Fig. 3f in terms of strong “shifts” or “quenching” of one or more of the three principal peaks³⁹⁰ of the gas-phase spectrum in Fig. 3b. In fact, with the exception of the overall vertical adsorption height, the calculations yield only minimal differences in the optimized geometric structure of 2H-P on Ag(111) and Cu(111), with the difference in maximum pyrrole tilt angle being³⁹⁵ less than 4° .³⁸

IV. CONCLUSIONS

To summarize, we studied the influence of molecule-substrate interactions on X-ray absorption spectra of⁴⁰⁰ large organic adsorbates by using dispersion-corrected density-functional theory combined with the transition potential approach. For the example of free-base porphine adsorbed on the commonly employed substrates⁴¹⁰ Ag(111) and Cu(111), this approach results in an excellent agreement between our X-ray absorption spectroscopy simulations and experimental literature data, with modest computational costs equivalent to commonly employed XPS simulations. By comparing the⁴⁰⁵ spectra of the adsorbed molecules to the spectra of the gas-phase reference (i.e., simulation of an isolated molecule), we could show that the implicit assumption of a small metal surface-induced perturbation of molecular states fails completely for the adsorption on copper.⁴¹⁵ However also on the silver surface, typically considered as rather inert, assignment of all spectral changes necessitates simulation of the combined adsorbate/substrate⁴²⁰ system. For both HIOS we followed the two effects that shape the final C K-edge NEXAFS spectrum of the adsorbate: (1) Chemical shifts that are induced by the substrate-induced potential and (2) the broadening, splitting and complex shape of transitions into strongly⁴²⁵ hybridized frontier orbitals. The first effect can in principle be interpreted using a discrete MO picture, the sec-

ond effect can not. While a surface-imposed broadening of molecular resonances is generally not surprising, its strength for a moderately reactive surface such as Cu(111) and an organic adsorbate that is predominantly bound by dispersive interactions is. The hybridization of the states modifies the NEXAFS spectrum up to the point where only a continuum of states is found. As illustrated by the showcase 2H-P on Cu(111), what appear to be discernible spectroscopic signatures may then merely emerge from the superposition of a continuum of transitions with non-zero transition probability. This calls for utmost caution in the interpretation of adsorbate X-ray absorption spectra. Typical peak assignments in terms of adsorbate orbital symmetries (π^* , σ^*) or fitting procedures including only a few Gaussian or Lorentzian line shapes in such cases would not reflect the correct chemistry and could only be a rough approximation. Ideally, spectroscopic assignment should be supported by first-principles spectroscopic calculations that explicitly consider the effect of an extended surface. In lieu of such calculations, detailed XPS data can be equally helpful. Measured core-level shifts provide information about the energetic position of NEXAFS spectral components due to individual species. Even if nothing else is known about the hybridization and concomitant shape of the frontier orbitals, interpretation can then at least proceed in terms of atomic species.

SUPPLEMENTARY MATERIAL

Additional computational information, a comparison to experimental XPS data, the total DOS, the final states orbitals, and a comparison between the experiment and the MO-PDOS are provided as Supporting Information.

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