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N 1*s* x-ray absorption study of the bonding interaction of bi-isonicotinic acid adsorbed on rutile TiO_2(110)

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N 1*s* x-ray absorption spectra of bi-isonicotinic acid (2,2′-bipyridine–4,4′-dicarboxylic acid) on rutile TiO_2(110) have been studied experimentally and quantum chemically. Differences between multilayer and monolayer spectra are explained by the adsorbate bonding to the substrate. A connection to the electronic coupling in dye-sensitized electrochemical devices is made. © *2000 American Institute of Physics.* [S0021-9606(00)70709-4]

INTRODUCTION

Dye-sensitized electrochemical devices, such as the Grätzel solar cell, have developed rapidly during the last decade.[1,2] In these devices it is important to understand the interactions between the dye and the semiconductor on a molecular level. To this end, we recently investigated the adsorption geometry of bi-isonicotinic acid (2,2′-bipyridine–4,4′-dicarboxylic acid) on rutile TiO_2(110) using a combined experimental and theoretical approach.[3,4]

X-ray absorption spectroscopy (XAS) is a powerful technique to study the local electronic structure of molecules. In particular it provides a probe of the unoccupied valence orbitals.[5] In the present work we combine experimental and theoretical N 1*s* near-edge XAS spectra to elucidate bonding effects on the electronic structure of bi-isonicotinic acid on rutile TiO_2(110). In particular, we focus on how the surface affects the bound unoccupied molecular orbitals of the adsorbate which are involved in the current-generating photo-induced charge separation in the Grätzel cell.[2] Nitrogen was selected as a probe because of its importance in the charge separation process[6] and as it presents the simplest XAS spectra.

From a fundamental perspective on the exploitation of XAS it is important to understand the changes of the valence orbital structure induced by the core hole. In addition to the final-state calculations used to calculate the XAS spectra, we therefore present results from ground state calculations on the isolated and the adsorbed bi-isonicotinic acid, which are used to analyze the XAS spectra with respect to core hole effects.

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EXPERIMENTAL AND THEORETICAL DETAILS

The experiments were performed at Beamline 22 of the MAX I synchrotron storage ring at MAX-Lab in Lund, Sweden.[7] The polarization dependence of XAS was used to confirm the π^* character of the levels studied.[4] The photon energy scale was calibrated using first and second order light. The relative intensities of the different π^* XAS peaks were found not to depend significantly on the angle of photon incidence,[4] and the presented spectra are representative. Further information regarding the experimental procedure is given in Ref. 4. We define one monolayer to be the saturation coverage. Multilayers were studied as an approximation to isolated molecules, and should be representative for this type of van der Waals-bonded system.

Calculations were performed at the restricted Hartree–Fock level using the semiempirical INDO/S program package ZINDO[8] which has been used to interpret many core hole spectra, e.g., Refs. 9, 10, and 11, including the XAS spectra of C_{60}.[12] ZINDO has also been used to study clusters and model surfaces containing transition metal atoms,[13,14] including TiO_2.[15]

The XAS spectrum of isolated bi-isonicotinic acid was calculated for the *cis* and *trans* conformers, as well as for a 90° twisted bi-isonicotinic acid molecule. No significant differences were found, and only the results for the *cis* conformer are shown. The calculations of the adsorbed bi-isonicotinic acid were performed using a $Ti_{18}O_{36}$ cluster model of the surface (Fig. 1). 66 point charges were located at surrounding crystal atomic positions (44 O and 22 Ti). The magnitudes of these point charges are not uniquely defined, as the calculated degree of ionicity depends on the kind of population analysis used, but the calculated XAS spectra were found to vary insignificantly over a wide range of values from $-0.5/+1.0$ to $-1.7/+3.4$ for the O/Ti point

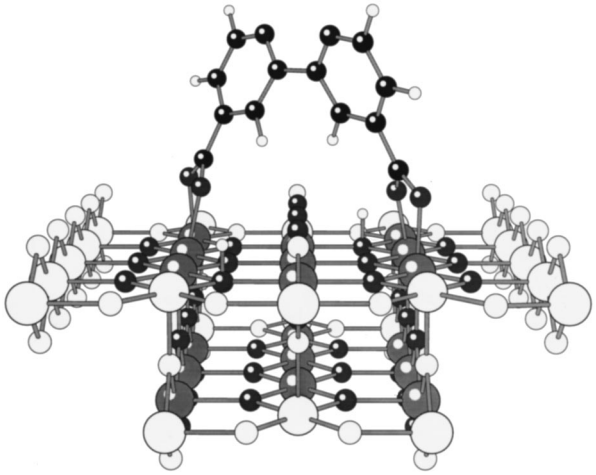

FIG. 1. Cluster geometry for bi-isonicotinic acid adsorbed on a $Ti_{40}O_{80}$ model of the rutile $TiO_2(110)$ surface. In the surface, the small shaded spheres represent oxygen atoms, and the large shaded spheres represent titanium atoms; the white spheres represent corresponding point charges.

charges. The experimental bulk geometry of the surface was assumed, and the bridge-binding adsorbate geometry was taken from our previous work on this system.[3,4]

The XAS spectra were calculated using the $Z+1$ approximation to model the core hole, and using a one-center approximation to calculate the intensities. The intensity of an excitation of a 1*s* electron to a valence orbital i is to a first approximation given by an expression of the form:[12]

$$I(i) \propto |c^i_{2p_x}|^2 + |c^i_{2p_y}|^2 + |c^i_{2p_z}|^2, \tag{1}$$

where $c^i_{2p_x}$ is the coefficient of the $2p_x$ orbital on the core hole atom in the valence orbital i, etc. The $Z+1$ approximation is here equivalent to the use of a so-called ''ionic Hamiltonian,'' [16] which can be formally derived from a configuration interaction involving all single excitations from the core hole.[17] The usefulness of the $Z+1$ approximation for calculating XAS spectra has been demonstrated for C_{60},[12] and later also for graphite[18] and, more recently, again for C_{60} within the DFT approximation.[19] In a more accurate treatment, the intensities obtained from (1) should be corrected by projecting the relaxed final state orbitals on the initial state orbitals,[20] which by necessity will decrease all intensities. However, since the present goal is an interpretation of the experimental results rather than a quantitative agreement between theory and experiment, the simpler estimates obtained from (1) are used in Tables I and II, and the discussion below. The theoretical XAS spectra have been aligned to the

TABLE I. Summary of the analysis of the N 1*s* XAS data for multilayer of bi-isonicotinic acid on rutile $TiO_2(110)$. All excitations are to π^* orbitals.

Property	Peak A	Peak B
E (expt.)/eV	398.79±0.06	402.43±0.06
E (calc.)[a]/eV	398.79	402.29
I (expt.)/%	100	15
I (calc.)/%	100	30

[a]The theoretical spectrum is aligned to the experimental spectrum using the first π^* resonance.

TABLE II. Summary of the analysis of the N 1*s* XAS data for monolayer of bi-isonicotinic acid on rutile TiO_2 (110). All excitations are to π^* orbitals.

Property	Peak 1	Peak 2	Peak 3
E (expt.)/eV	398.74±0.06	400.73±0.06	402.41±0.06
E (calc.)[a]/eV	398.74	400.74	402.64
I (expt.)/%	100	6	7
I (calc.)/%	100	25	23
ads. contribution/%	97	69	85
TiO_2 contribution/%	3	31	15

[a]The theoretical spectrum is aligned to the experimental spectrum using the first π^* resonance.

corresponding experimental spectra using the first π^* resonance, but no energy scaling factors,[12] were used. To facilitate comparison of the spectra, the theoretical peaks have been convoluted with 0.7 eV FWHM gaussians.

For free bi-isonicotinic acid, the changes in the unoccupied valence molecular orbitals induced by the core hole were studied quantitatively by calculating the overlaps, $O(i,j)$, between the ith orbital $\psi_{\mathrm{ch}}(i)$ of the core-excited state and the jth orbital $\psi(j)$ of the ground state from their AO expansion coefficients $c_{\mathrm{ch}}(i,k)$ and $c(j,k)$, respectively:

$$O(i,j) = \sum_k c_{\mathrm{ch}}(i,k) * c(j,k). \tag{2}$$

For adsorbed bi-isonicotinic acid the degree of mixing between the relevant adsorbate orbital with the substrate conduction band was used as a measure of the bonding effects of adsorption. Weights of the orbitals on the adsorbate and substrate parts were calculated as partial orbital densities from the atomic orbital expansion coefficients of that orbital. While the numbers obtained may depend somewhat on, e.g., the choice of cluster, we feel that this analysis is useful for identifying qualitative features and trends of the investigated orbitals.

RESULTS

The experimental bi-isonicotinic acid N 1*s* XAS spectra in the π^* region for multilayer and monolayer adsorption are shown in Fig. 2(a). We have labeled the peaks for the multilayer A and B, and for the monolayer 1, 2, and 3, as shown in Fig. 2. Results of the experimental analysis of these data are listed in Tables I and II.

The theoretical N 1*s* XAS spectrum for an individual bi-isonicotinic acid molecule, shown in Fig. 2(b), agrees well with the experimental spectrum for the multilayer. A detailed comparison is summarized in Table I. Peak A is found to correspond to the $11\pi^*_{\mathrm{ch}}$ LUMO orbital predominantly located on the pyridine ring containing the N 1*s* core hole, whereas Peak B is due to the $15\pi^*_{\mathrm{ch}}$ orbital delocalized on the two rings (see Fig. 3). One of the orbitals ($17\pi^*_{\mathrm{ch}}$) contributing weakly to the theoretical spectrum in the region around 403 eV, but which is important for Peak 2 in the monolayer case, is also shown in Fig. 3.

The theoretical N 1*s* XAS spectrum for a bi-isonicotinic acid molecule adsorbed on a rutile (110) TiO_2 surface is shown in Fig. 2(c). There are three resolved peaks with significant intensity, matching the experimental monolayer

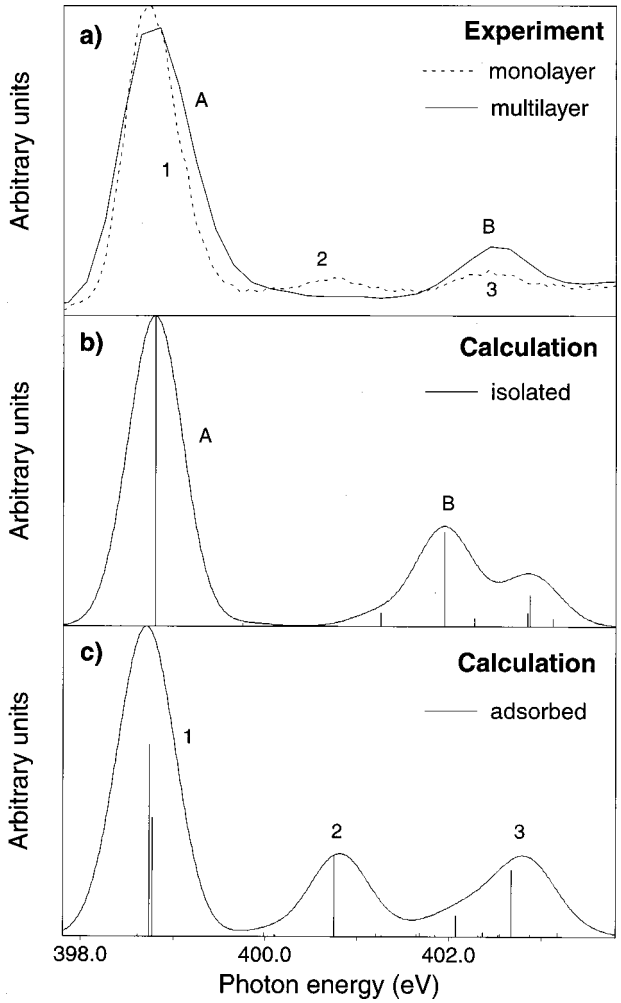

FIG. 2. (a) Experimental, (b) theoretical isolated molecule, and (c) theoretical monolayer N 1*s* XAS spectra for bi-isonicotinic acid on rutile $TiO_2(110)$. The theoretical spectra have been aligned with the corresponding experimental spectra using the first π^* resonance, and the theoretical peaks convoluted with a gaussian.

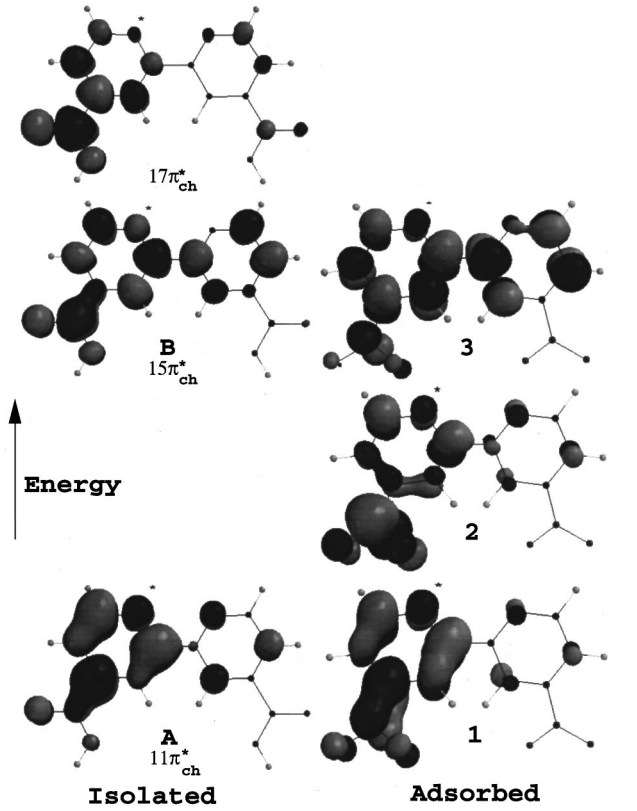

FIG. 3. Calculated molecular orbitals involved in the XAS transitions for the isolated and adsorbed bi-isonicotinic acid molecules. N 1*s* core-hole atoms are marked with a star (∗). For the adsorbate case, only the bi-isonicotinic acid part of the orbital is shown, and the nature of the orbitals 1, 2, and 3 is described further in the text.

spectrum well. A detailed comparison is summarized in Table II. In Fig. 3, we show the orbital corresponding to Peak 1, which closely resembles the one corresponding to Peak A of the isolated molecule. There is a weak coupling to the substrate conduction band, splitting the peak in two components which are calculated to be 0.03 eV apart. Together these components have 97% weight on the adsorbate. Peak 2 corresponds to an orbital which is a mixture of several orbitals of the isolated molecule, with a resemblance in the surface binding region to the $17\pi^*_{ch}$ orbital located around 2.5 eV higher in the spectrum of the free molecule. The strong mixing of orbitals arises from the strong interaction with the conduction band of the TiO_2 substrate, as seen from the population analysis, which locates 69% of the weight on the adsorbate and 31% in the Ti($3d$) conduction band. We attribute the strong interaction to the significant portion of the orbital located on the surface-binding carboxyl oxygens, which bind directly to surface Ti atoms. The interaction of the valence orbital corresponding to Peak 3 with the semiconductor conduction states is intermediate compared to the first two peaks, with 85% of the orbital located on the adsorbate.

A projection of the $11\pi^*_{ch}$ LUMO orbital manifested in Peak A of the isolated bi-isonicotinic acid molecule with a core hole, in terms of the molecular orbitals of the ground state, $i\pi^*$, gives

$$11\pi^*_{ch} = 0.74*11\pi^* - 0.53*12\pi^* - 0.17*13\pi^* + 0.17*15\pi^* + \cdots .$$

According to this, the $11\pi^*_{ch}$ orbital is essentially a combination of the $11\pi^*$ and $12\pi^*$ ground state orbitals, localizing the $11\pi^*_{ch}$ orbital to the core excited half of the bi-isonicotinic acid, and consistent with the core hole effects in aromatic hydrocarbons, see, e.g., Refs. 21, and 22. Peak B originates from the $15\pi^*_{ch}$ orbital which is calculated to be a mixture of several unoccupied ground state π^* orbitals, with the strongest contribution (60%) from the $15\pi^*$ and $16\pi^*$ orbitals. Similarly, the $17\pi^*_{ch}$ orbital is a mixture of several unoccupied ground state π^* orbitals with ca. 60% in the $17\pi^*$ and $18\pi^*$ orbitals. The analysis shows that the bi-isonicotinic acid XAS spectrum retains a significant amount of information about the unoccupied valence orbitals of the ground state, with only small contributions ($\leqslant 2\%$) from occupied ground state π orbitals.

For the ground state of the surface-adsorbate system, the first unoccupied orbital with significant adsorbate character

lies within the Ti($3d$) conduction band, and has a population on the bi-isonicotinic acid part of only 58%. It is identified as most closely resembling the bi-isonicotinic acid orbital responsible for Peak 1 in the core hole calculation. The low population on the adsorbate is an indication of strong mixing with the substrate conduction band, not seen for the corresponding core hole orbital discussed above. Thus this orbital which in the ground state lies within the conduction band, is pulled below the band edge of the present cluster system by the core hole potential. Recent experimental results[23] support the view that the final-state orbital corresponding to Peak 1 has little or no interaction with the TiO_2 conduction band. A ground state orbital, with similar appearence as the final-state orbital responsible for Peak 3 in the adsorbed case, is found with an adsorbate population of 84%, closely matching the population of the Peak 3 orbital discussed above. We thus find that the strength of the adsorbate-surface mixing is similar for the ground state and the core hole cases within the conduction band.

We have shown in some detail that the adsorbate orbital shape and energy (relative to the substrate bands) can strongly affect the adsorbate–substrate interaction strength. This has implications for the charge injection process important in dye-sensitized electrochemical devices such as the Grätzel solar cell.[24,25] Of direct importance is that the XAS excitations involve final state orbitals which are closely related to ground state orbitals, which enables one to use XAS to gain an understanding of charge transfer processes upon valence excitation.

CONCLUSIONS

In this paper experimental and theoretical N 1*s* XAS spectra for both multilayer and monolayer bi-isonicotinic acid on rutile (110) TiO_2 are presented. The experimental and the theoretical spectra are in reasonable agreement for both cases. Significant differences between the multilayer and monolayer cases are observed, and the differences are here interpreted in terms of the interaction of the bound unoccupied adsorbate valence molecular orbitals with the substrate conduction band. The agreement found here suggests that a similar level of understanding can be extended to more complicated systems, e.g., the full dye complex in the Grätzel solar cells.

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