DFT calculations of XPS/NEXAFS and IR spectra to elucidate the reaction products of acetonitrile with Si(0 0 1)-2 × 1

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Abstract

NEXAFS data [S. Rangan et al., Phys. Rev. B 71 (2005) 165319] and FTIR data [M.P. Schwartz, R.J. Hamers, Surf. Sci. 601 (2007) 945] apparently do not converge in the identification of the reaction products of acetonitrile (CH_3CN) with Si(0 0 1)-2 × 1 at room temperature. Using DFT calculations of core-excited/core-ionized spectra and of IR vibrational frequencies and intensities, we show the consistency of the body of experimental data. Three species are present on the surface in equivalent amounts, a C=N moiety, a pendent C≡N and a C=C=N ketenimine submitted to a strong twist imposed by the Si bond directionality. More generally, the paper shows the usefulness of spectroscopic data simulations in the elucidation of complex surface chemistry problems.
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1. Introduction

The adsorption of nitrile compounds – acetonitrile [1–3], allylcyanide [4,5], acrylonitrile [2,4,6,7] and benzonitrile [8,9] – on Si(0 0 1)-2 × 1 surface has attracted the attention of many surface science groups, due to potential applications in the field of hybrid organic/inorganic structure fabrication. A comparative review of the reactivity of these molecules, focusing on the contribution of X-ray photoemission spectroscopy (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS) has appeared recently [10]. For all the studied molecules the adsorption at room temperature leads to multiple bonding geometries, as kinetics dominates over thermodynamics. Surprisingly, despite its *apparent* simplicity in terms of available reactive

groups, the chemisorption of acetonitrile (CH_3–C≡N:) leads also to several products at 300 K, as shown by our experimental XPS/NEXAFS study combined with calculated core-ionized/excited sates using the density functional theory (DFT) approach [3,10]. Two "chemical units" have been identified unambiguously. The first one, is a C=N unit, characterized by a N 1s NEXAFS transition energy *hv* of 397.85 eV (Fig. 1) and a N 1s XPS binding energy[1] of 397.8 eV. The dichroic behavior[2] of the NEXAFS spectra shows that the π system of the C=N unit is contained

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[1] To ease comparison with other published XPS binding energies, note that the Si $2p_{3/2}$ core-level peak is at 99.5 eV in Ref. [3].
[2] Due to the dipolar selection rules, K-edge NEXAFS probes the unfilled states of p symmetry. The absorption has a characteristic $\cos^2(\delta)$ dependence, where δ is the angle between the p orbital axis and the polarization vector **E** of the synchrotron radiation. Therefore the direction of bonds having a characteristic symmetry (π, σ) can be inferred from the experimental dichroic absorption spectra.

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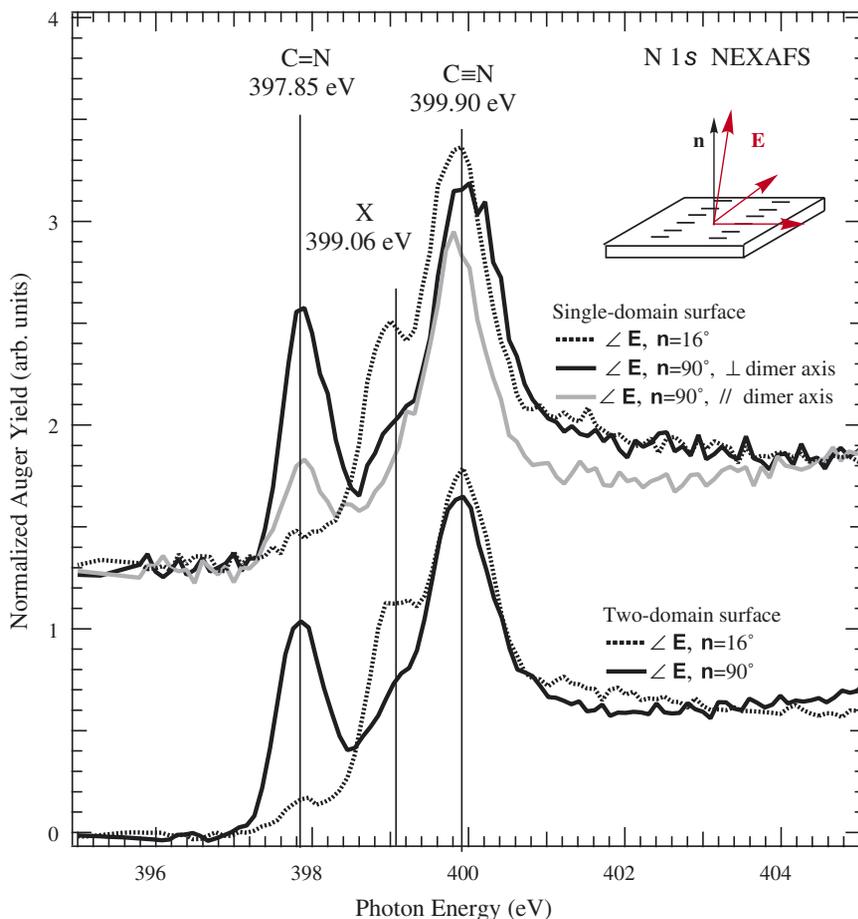*E-mail address:* roch@ccr.jussieu.fr (F. Rochet).

Fig. 1. Normalized Auger yield N 1s NEXAFS spectra of a single-domain and a two-domain Si(0 0 1)-2×1 surface exposed to acetonitrile at 300 K (10^{-7} mbar for 600 s). **E** and **n** are the radiation polarization and surface normal (parallel to [0 0 1]), respectively. **E** is either nearly collinear with **n** (∠**E,n** = 16°) or contained in the (0 0 1) surface plane (∠**E,n** = 90°). For a single-domain surface, **E** can be oriented either perpendicular or parallel to the dimer axes (see inset). The two-domain surface comprises two equivalent domains of dimer orientations, rotated by 90° with respect to one another. A strong absorption dichroism is observed for C=N and X peaks. The C=N π* bond is contained within the surface plane, with the p-like orbitals perpendicular to the silicon dimer axis, as expected for a Si–C=N–Si unit. The X peak is polarized normal to the surface. The non-dichroic signal of the C≡N π* bond can be explained by the rotation of the Si–CH₂C≡N moiety around the Si–C axis. The figure gathers spectroscopic data previously published in Ref. [3].

within the (0 0 1) plane, with most of the species having their CN axis parallel[3] to the silicon dimer axis (as depicted in Fig. 2**a**). Note that the species of Fig. 2**a′** is a variant of that of Fig. 2**a**, corresponding to a 1,2-H transfer, leading to a more stable geometry. The second well-defined chemical unit is a "free" C≡N group (i.e. not datively bonded to an electrophilic "down" Si dimer atom). It is characterized by a NEXAFS transition energy of 399.9 eV (Fig. 1) and an XPS binding energy of 399 eV. Due to the acidity of the αH, we have proposed that *one* H from the methyl group is abstracted, leading to the formation of a cyanomethyl/silicon monohydride pair, possibly on the same silicon dimer, as shown in Fig. 2**b**. As it can bee seen in Fig. 1, a third structure (labeled X) – strongly polarized perpendicularly to the surface – appears at a photon energy of ~399 eV. This NEXAFS transition energy is close to

that of the *main* N 1s π* transition of the C=C=N chemical block (398.8 eV) formed when Si(0 0 1) is exposed to acrylonitrile (non dissociative adsorption) and allylcyanide (dissociative adsorption via αH transfer to Si) [10]. Moreover the experimental XPS N 1s binding energy of C=C=N is at ~398.9 eV, nearly degenerate with that of C≡N, as shown by a DFT calculation of their ionization potentials[4] (IP) [3] and a comparative approach [10]. Due to possible C–H bond cleavage, a ketenimine-like product (Si–N=C=CH₂) *plus* a silicon monohydride (Fig. 2**c**) was envisaged for acetonitrile, and its geometry was calculated [11]. As in the ketenimine molecule (H₂C=C=NH), the C=C=N block is characterized by two *orthogonal* π$_{C=C}$ and π$_{C=N}$ bonds [3]. However, the calculated N 1s NEXA-

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[3] A single-domain vicinal surface (miscut by 5°) was used.

[4] The binding energies are measured experimentally with respect to the Femi level. The IP takes the vacuum level as the reference energy. The IP is simply equal to the sum of the binding energy (referenced to the Fermi level) plus the work function.