Surface Extended X-Ray-Absorption Fine Structure of Low-Z Adsorbates Studied with Fluorescence Detection

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Comparison of x-ray-fluorescence-yield and electron-yield surface extended x-ray-absorption fine-structure spectra above the S *K* edge for $c(2\times2)$S on Ni(100) reveals an order-of-magnitude higher sensitivity for the former technique. Thiophene (C_4H_4S) chemisorption on Ni(100) is studied with S coverages down to 0.08 monolayer. The molecule dissociates at temperatures as low as 100 K by interaction with fourfold hollow Ni sites. Blocking of these sites by oxygen leaves the molecule intact.

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Surface extended x-ray-absorption fine-structure (SEXAFS) and near-edge x-ray-absorption fine-structure (NEXAFS) studies of chemisorbed species on surfaces are usually carried out by means of electron-yield (EY) detection.[1] As a result of the convenient ultrahigh-vacuum (UHV) compatibility of electron detectors and the inherent surface sensitivity of electron detection techniques little effort has been made to use other schemes.[2]

It is known that the detection of the characteristic x-ray *fluorescence* signal from atoms diluted in solids or liquids is a powerful method of obtaining their local structure by means of EXAFS.[3] Recently, fluorescence-yield (FY) EXAFS has also been used as a probe for certain surface problems, i.e., the structure of high-*Z* adsorbates (e.g., Au) on low-*Z* substrates (e.g., Si).[4] However, since the FY strongly decreases with decreasing atomic number *Z*,[5] FY detection has been thought to be ill suited for obtaining the SEXAFS of low-*Z* adsorbates on high-*Z* subtrates. This case is of extreme importance because the interaction of low-*Z* molecules with metal surfaces is the heart of heterogenous catalysis. It is clear that FY EXAFS studies on such systems, if possible, could revolutionize traditional surface science in that they would allow the study of samples under UHV as well as "real" nonvacuum conditions.

Here we report SEXAFS and NEXAFS studies by means of FY detection above the *K* absorption edge (2470 eV) of sulfur,[6] at submonolayer coverage on Ni(100). We find that FY detection is not only feasible but, surprisingly, offers an order-of-magnitude higher sensitivity than any EY detection mode.[7] We also find a significantly reduced background in our soft x-ray FY studies as compared to previous FY studies at higher x-ray energies.[3,4] It is, therefore, unnecessary to utilize grazing x-ray incidence schemes.[4] NEXAFS and SEXAFS spectra obtained by FY detection are used to study the dissociation of thiophene (C_4H_4S) on Ni(100). A site-dependent desulfurization process is proposed.

Experiments were performed at the Stanford Synchrotron Radiation Laboratory with use of the "Jumbo" monochromator.[8] With Ge(111) monochromator crystals and storage-ring currents of 50 mA, we obtained a flux of about 2×10^{10} photons/sec at the S *K* edge in a $2\times4\text{-mm}^2$ spot.[8] The S *K* (2.3-keV) fluorescence from the sample was recorded with a proportional counter[9] which was mounted in the horizontal plane, perpendicular to the x-ray beam, and collected a solid angle of 10% of 4π sr. A 127-μm-thick Be window (40% transmission) of 5-cm diameter was used to separate the UHV sample chamber from the P10 detector gas. The energy resolution of our counter was approximately 1 keV and a discriminator window was centered on the S *K* peak. The NEXAFS and SEXAFS spectra were recorded for 20° grazing (**E** vector close to the sample normal) and 90° normal (**E** in the surface plane) x-ray incidence angles. The Ni(100) single crystal was cleaned by Ar^+ bombardment and oxygen heat treatments.[10] To obtain a sharp $c(2\times2)$ LEED pattern from atomic S on Ni(100) the clean annealed surface was dosed with 5 L [1 langmuir (L) corresponds to 10^{-6} Torr sec exposure] H_2S at 100 K and then shortly heated to 420 K. Thiophene was adsorbed on the clean or oxygen-predosed [20 L at 300 K, $c(2\times2)$ LEED pattern] Ni(100) surface at 100 K. All spectra were recorded at 100 K.

The $c(2\times2)$S on Ni(100) surface, corresponding to half monolayer (ML) coverage, was used to compare Auger-yield (AY)[10] and FY detection. Figure 1 shows SEXAFS spectra recorded with both techniques at grazing x-ray incidence and with use of the same data acquisition time (10 sweeps, 400 sec/sweep). Spectra obtained at normal incidence gave similar results with a reduction in count rate by a factor of 2.5 for both detection modes.

Clearly, the AY and FY spectra in Fig. 1 have comparable signal-to-noise (STN) ratios. However, the *STN ratio* is the figure of merit only if the noise of the data is purely statistical. With decreasing adsorbate coverage a measurability limit will be set by instrumental noise or structures, e.g., arising from normalization problems, which are independent of counting time. In this case, the criterion of merit is no longer the STN but rather the signal-to-background (STB) ratio, defined as the ratio of the edge jump over the signal before the edge. Figure 1 shows that the FY technique offers an 8 times larger STB or sensitivity for S. A similar enhancement is observed at 90° x-ray incidence. This surprising result is due to a much-reduced background from the substrate relative to all EY techniques. The background is also significantly smaller than in typical FY measurements at higher x-ray energies.[3,4] Reasons for the enhanced STB are as follows:

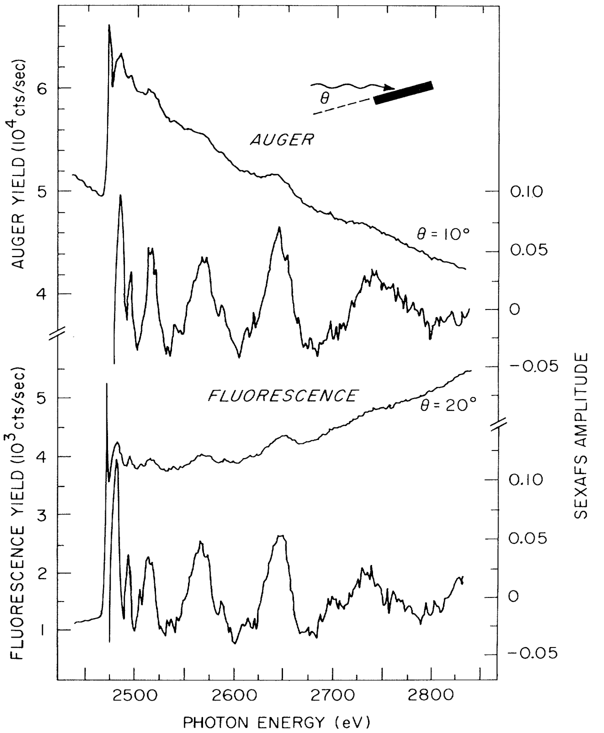

FIG. 1. Auger-electron-yield (Ref. 10) and x-ray-fluorescence-yield SEXAFS spectra above the S K edge for $c(2\times2)$S on Ni(100) corresponding to half a S monolayer. Both spectra were recorded at grazing x-ray incidence. Underneath each spectrum the SEXAFS oscillations after background subtraction are shown enlarged.

(1) In contrast to the Auger peak which sits on a significant inelastic electron background,[7] the fluorescence line has almost no background originating from *inelastic* x-ray scattering events.

(2) The *elastically* scattered x-ray background from the substrate strongly decreases with decreasing photon energy. The increased x-ray-absorption cross section at low photon energies results in a reduced scattering volume in the substrate. Also, at low photon energies the short wave vector of the incident radiation reduces the accessible volume in reciprocal space. Finally, at soft x-ray energies the Bragg scattering condition is not fulfilled for most crystalline substrate materials.

(3) Energy discrimination and windowing of the characteristic fluorescence line does not suffer from similar interference problems as AY detection which for low-Z atoms is often rendered useless by a superposition of Auger and photoemission peaks.[2]

We have used the high sensitivity of the FY technique to study the interaction of thiophene with Ni(100).[11] Because such studies involved S coverages of less than 0.1 ML (1 layer of thiophene corresponds to ~ 1 ML of S) they are presently not feasible with EY detection. Figure 2 shows NEXAFS spectra for thiophene chemisorbed on clean and $c(2\times2)$O-predosed Ni(100) recorded at normal x-ray incidence. The spectra have been scaled as indicated to reveal the S coverage which is proportional to the edge jump. Using the 0.5-ML $c(2\times2)$S on Ni(100) surface as a reference we find that on clean Ni(100) a thiophene exposure of 1 L produces a S coverage of 0.08 ML. The NEXAFS spectrum [Fig. 2(a)] is dominated by a threshold peak A and a broader structure C. For exposures in excess of 2 L another peak B appears which is accompanied by a broader structure D. These structures dominate in the 12-L spectrum shown in Fig. 2(b) which corresponds to a thin multilayer. Heating the sample diminishes structures B and D until they vanish at around 180 K. At higher temperatures ($T < 600$ K) the spectra, including that for a $p(2\times2)$ LEED pattern which develops around 540 K, look like that shown in Fig. 2(c) which was recorded after heating to 270 K. When the Ni(100) surface is precovered with a $c(2\times2)$ O layer the NEXAFS spectra for 1- and 2-L thiophene exposure at 100 K are almost identical and consist of peaks B and D only [Figs. 2(d) and 2(e)]. These peaks which are characteristic of the thiophene molecule[12] disappear after heating to higher temperatures [Fig. 2(f)].

Absence of resonance B in Fig. 2(a) suggests that on

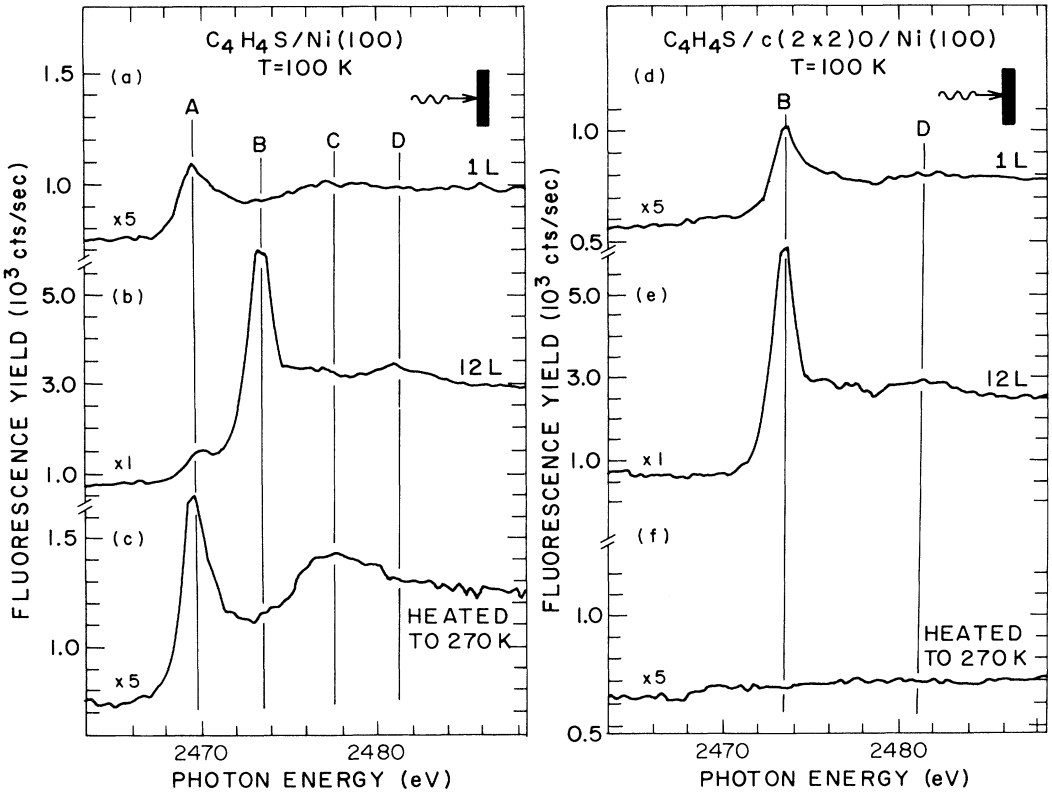

FIG. 2. Fluorescence-yield NEXAFS spectra for thiophene on clean and oxygen-predosed [$c(2\times2)$ overlayer] Ni(100) at various exposures and temperatures: (a) 1-L exposure at 100 K on Ni(100); (b) 12-L exposure at 100 K on Ni(100); (c) sample in (b) heated to 270 K; (d) 1-L exposure at 100 K on $c(2\times2)$O/Ni(100); (e) 12-L exposure at 100 K on $c(2\times2)$O/Ni(100); (f) sample in (e) heated to 270 K.

clean Ni(100) thiophene dissociates at temperatures as low as 100 K. Resonance B is known to be characteristic of the S-C bond from the multilayer thiophene spectra [Figs. 2(b) and 2(e)], gas-phase spectra of various molecules with S-C bonds,[12] and from $X\alpha$ multiple-scattering calculations.[13] Peaks A and C are associated with S-Ni bonds since they are also observed for the $p(2\times2)$ and $c(2\times2)$ atomic-S overlayers on Ni(100).[9,10] For the oxygen-predosed surface only resonances B and D are observed. This and the fact that no S remains on the surface after heating [Fig. 2(f)] unambiguously proves that thiophene does not dissociate on the $c(2\times2)$O-covered Ni(100) surface.

SEXAFS measurements on the low-coverage samples provide further information as shown in Fig. 3. The Fourier transform for 1 L thiophene adsorbed at 100 K on clean Ni(100) is dominated by the same peak as that for $c(2\times2)$S on Ni(100), corresponding to the S-Ni nearest-neighbor distance. Analysis of the polarization dependence of the 1-L spectrum reveals that S sits in the fourfold hollow (FFH) site with a distance of 2.22 ±0.02 Å, indistinguishable within experimental error[14] from $p(2\times2)$[9,15] and $c(2\times2)$[10,16] S on Ni(100). In contrast, for the oxygen-predosed surface a 1-L thiophene exposure shows a peak in the transform at nearly the same position (1.3 Å) as the thiophene multilayer and (not shown) thiophene gas.[12] Using the S-C bond length $R=1.714$ Å in the thiophene molecule as a reference we obtain a distance of 1.71 ±0.02 Å for multilayer thiophene and 1.74 ±0.04 Å for 1 L thiophene on O-predosed Ni(100). This clearly demonstrates that on the O-predosed surface the molecule remains undissociated upon chemisorption. In contrast, thiophene dissociation on the clean surface is proven by the absence of a S-C bond-related peak around 1.3 Å in Fig. 3(b).

Our FY NEXAFS and SEXAFS studies suggest the existence of a site-dependent desulfurization process. On the clean Ni(100) surface, S is broken out of the thiophene ring by bonding to FFH Ni sites. This occurs already at a remarkably low temperature of 100 K. The dissociated thiophene layer passivates the surface such that with increasing coverage, the molecules remain undissociated in the second and higher layers. For the $c(2\times2)$O-precovered surface, O atoms occupy

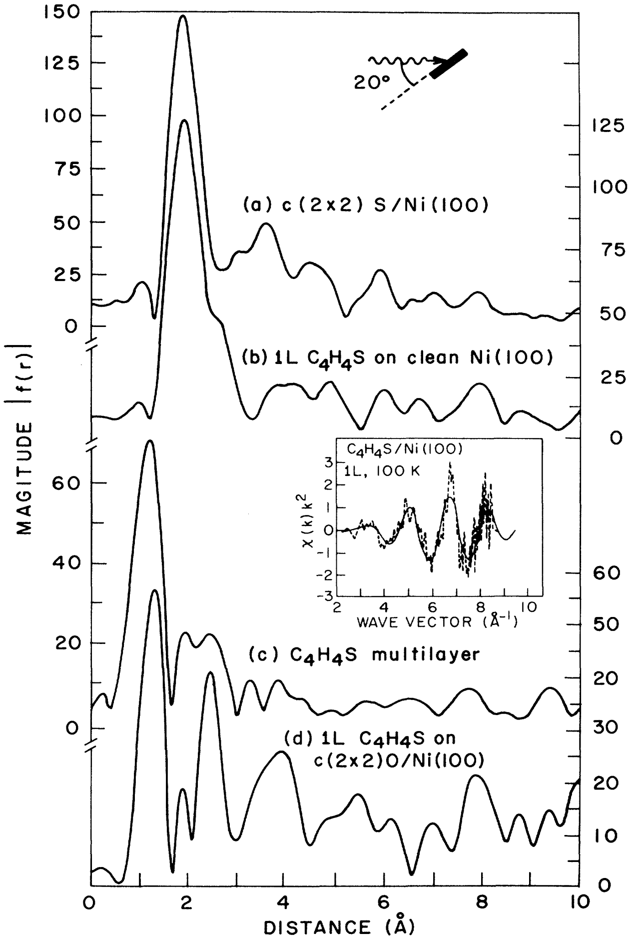

FIG. 3. Absolute Fourier transforms of fluorescence-yield (S)EXAFS spectra for four selected cases. (a) $c(2\times2)$S on Ni(100); 0.5 ML of atomic S. (b) 1 L thiophene on Ni(100) at 100 K; 0.08 ML of S. The inset shows the original SEXAFS data (dashed line) for case (b) and the back-transformed SEXAFS signal (solid line) of the filtered peak around 2 Å in (b). (c) Thiophene multilayer ($\sim$7 layers) condensed on $c(2\times2)$O/Ni(100). (d) 1 L thiophene on $c(2\times2)$O/Ni(100) at 100 K; 0.08 ML of S.

the active FFH Ni sites[16] and thus prevent thiophene dissociation.

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