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A NEW TECHNIQUE FOR SUBMONOLAYER NEXAFS : FLUORESCENCE YIELD AT THE CARBON K EDGE

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Resumé: La structure fine au voisinage du seuil d'absorption X (NEXAFS) K du carbone est mesurée pour de molécules d'hydrocarbures linéaires sur du Cu(100) à 60 K. Quatre modes possibles de detection sont comparés: yield en fluorescence (FY), yield électronique en mode Auger (AEY), partiel (PEY) et total (TEY) sous les mêmes conditions expérimentales. On prouve que la fluorescence est la technique la plus fiable, à cause du rapport accru signal sur fond $J_R:J_R(FY) = 10$, $J_R(AEY) = 0,6$, $J_R(PEY) = 0,17$ et $J_R(TEY) = 0,05$. Des spectres en sous-monocouche de C_2H_2 , C_2H_4 , C_2H_6 sur du Cu(100) sont présentés.

Abstract: Near Edge X-ray Absorption Fine Structure (NEXAFS) measurements at the C K edge are used to investigate linear hydrocarbon molecules on Cu(100) at 60 K. Four different detection modes are compared under the same experimental conditions: fluorescence yield (FY), Auger electron yield, (AEY), partial electron yield (PEY) and total electron yield (TEY). Because of an increase of the edge jump ratio J_R due to reduction in background intensity the fluorescence yield method is shown to be the most reliable. The values obtained for J_R are: $J_R(FY) = 10$, $J_R(AEY) = 0,6$, $J_R(PEY) = 0,17$ and $J_R(TEY) = 0,05$. Submonolayer spectra of C_2H_2 , C_2H_4 , C_2H_6 on Cu(100) are presented.

I. Introduction

The Near Edge X-ray Absorption Fine Structure (NEXAFS) of a molecule contains useful information about the orientation with respect to the substrate and intra-molecular bond lengths /1/. Many studies that measure the electron yield associated to the Auger deexcitation of the created 1s core hole have been carried out in the past for monolayer coverages on metal surfaces /1,2/ above the oxygen and nitrogen K edges. For many chemical studies, the carbon K edge is the most important one. But around the carbon K edge, the strongly energy dependent transmission function of all monochromators, caused by contamination of the optical elements, limits the surface sensitivity which can be reached by means of the electron yield techniques.

A standard figure of merit for any detection scheme at an adsorbate edge is the edge jump ratio J_R , which is defined as the count rate difference above and below the edge, normalized to the pre-edge back-

ground /3/. A typical value of J_R for one layer of hydrocarbons (such as C_2H_4) on a metal surface is on the order of only 1% for the partial electron yield mode /4/. It is therefore worthwhile to develop alternative detection schemes that offer a larger J_R and an ultimately higher surface sensitivity.

Recently, fluorescence yield detection at the C K edge /5/, has demonstrated the advantage of a larger J_R , compared to electron detection. Here we illustrate the actual status of this technique through measurements on linear hydrocarbons on submonolayer coverages on a Cu(100) surface at 60 K. These experiments illustrate the possibilities of the technique at the C K edge, which is important because of the importance of carbon in surface physics and chemistry.

This technique opens new fields of investigation, due to the big escape depth of photons (figure 1), as interlayer studies, measures at higher pressures under reaction conditions. It is also suitable for the study of insulating materials, as it is not directly sensitive to charging effects.

II. Experimental

The experiments were performed at the storage ring BESSY in Berlin, using the SX-700 plane grating monochromator. The flux around the C K edge was about $2 \cdot 10^{10}$ photons/sec (400 mA current), with an energy resolution of 1 eV. The sample was cleaned by Ar^+ bombardement, annealed to 300°C and checked using LEED and Auger spectroscopies. Spectra were recorded on the Auger, partial, total electron yield modes as before /6/, as well as the fluorescence yield mode. The experimental details of the UHV compatible proportional counter are given elsewhere /5/. The solid angle was 5% of 4π sr with an energy resolution of 280 eV FWHM at the C K_{α} line (277 eV). By using a multichannel analyser, a window was set around the C K_{α} peak to limit the effects of electronic noise on the low energy side and the possibly second order excited Cu L edges at the high energy side /5/. In an electron yield experiment, the possibly higher harmonics excited channels would give a background contribution and further decrease J_p .

All detectors were positioned at grazing angles with respect to the sample surface (figure 1, $\beta = 0^\circ$). The specularly reflected X-ray beam from the sample and the fluorescence detector are at normal angles to each other at normal X-ray incidence (figure 1, $\alpha = 0^\circ$). In that geometry the background due to the substrate is reduced and J_R is maximized.

Fig. 1: Fluorescent photons and Auger electrons are created by filling a deep core hole created by a photon. The escape depth of the photons ($L_p \approx 1000 \text{ \AA}$) is much larger than the one of the electrons ($L_e \approx 10 \text{ \AA}$). We have chosen $\beta = 0^\circ$ and $\alpha = 0^\circ$ for normal X-ray incidence.

	c(2 x 2) S/Ni(100)	10 L C ₂ H ₄ on Cu(100)
Photon flux (ph/sec)	$2 \cdot 10^{10}$	$\gtrsim 1 \cdot 10^{10}$
Atoms/cm ²	$8 \cdot 10^{14}$	$\lesssim 3 \cdot 10^{15}$ *
K edge cross-section (cm ² /atom) **	$6 \cdot 10^{-20}$	$8,4 \cdot 10^{-19}$
K edge fluoresc. yield **	$8 \cdot 10^{-2}$	$1,5 \cdot 10^{-3}$
Solid angle fraction	0,1	0,05
Window transmission	0,4	0,25
Detector efficiency	≈ 1	≈ 1
Estimated counts/s	3070	470
Measured counts/s	3000	400

*Estimated using TDS spectroscopy

**CRC Handbook of Spectroscopy, Vol. 1, J.W. Robinson Edt. 1974

Table 1: Estimated and measured fluorescent yield count rates at the S 2p and C K edges. A small count rate is expected in our case due to the small fluorescence deexcitation probability with respect to the Auger process ($\sim 10^{-3}$). The experimental conditions are comparable. Here the sample is looking to the detector ($\alpha = 70^\circ$) at grazing X-ray incidence. The count rate is decreased at normal X-ray incidence with $\alpha = 0^\circ$ (see text).

Fig. 2: Raw, unnormalized, spectra of fluorescence (a), Auger (b) and partial electron (c), yields, of 10 L C₂H₄ (~ 2 ML), at normal X-ray incidence on Cu(100) at 60 K.

Fig. 3: Comparison of fluorescence yield with the three electron yield detection modes /5/. a,b,c) Normal X-ray incidence. d) 20° Grazing X-ray incidence. All spectra are normalized: covered/clean.

a factor 4 in the adsorbate due count rate. This decrease can be understood in terms of scattered radiation from the substrate.

Because of the low counting rate, the statistical noise is much bigger in the case of the fluorescence and the Auger yield modes. But as one decreases the concentration of the adsorbate atoms, what determines the surface sensitivity and reliability of a detection scheme is J_R . For $J_R < 0,01$ one has often observed features related to incomplete normalization of the spectra.

Fluorescence yield submonolayer spectra for C_2H_2 , C_2H_4 and C_2H_6 are shown in Fig. 4. The coverages are estimated by TDS spectroscopy. The statistics do not allow the determination of the position of the σ -shape

III. Results and discussion

The raw, unnormalized, spectra for 10 L C_2H_4 at normal X-ray incidence on Cu(100) at 60 K are shown for three detection modes in figure 1. The partial electron yield spectrum (figure 1c, regarding voltage: -220 V) gives the transmission function of the monochromator. No specific features due to the C_2H_4 molecules on the surface ($\sim 2ML$) can be detected, as the Auger KVV peak is sitting on an inelastic electron background /7/. This spectrum has to be normalized in order to separate the adsorbate contribution, and yields $J_R = 0,17$ (figure 3). If only the Auger electrons are detected, as we did using a CMA, the contribution of the background electrons is reduced. Then a peak can be identified on the spectrum (figure 2b at ~ 285 eV) that corresponds to the transition from the $C(1\sigma)$ initial state to a final π^* molecular state. The valence bands of Cu, are swept through the window of the analyser below the C K edge.

Figure 2a shows the fluorescence yield mode. The pre-edge background is reduced to ~ 10 counts/sec, which is constant over the pre-edge region caused by electronic noise /5/. Once the Auger channel is opened, one can also follow the transmission curve of the monochromator. Then, the $C(1\sigma)$ to π^* transition is much more visible. $J_R = 10$ for that mode, which confirms that fluorescence is the more reliable and sensitive detection scheme. The large value for J_R can be understood in terms of a small background. At 20° grazing X-ray incidence (figure 1, $\alpha = 70^\circ$), J_R decreases to 0,2 in spite of an increase by

resonance. A complete discussion about the orientation of the molecules is given elsewhere /8/. In this case, the sharp π resonance of C_2H_2 can be used to determine the chemical transformation of that species when the temperature of the substrate is raised. At ~ 110 K (figure 5), the height of the π resonance decreases. A check using TDS showed that C_2H_2 transforms to C_2H_6 . This decrease in π intensity is easily understood² as the C_2H_6 molecule presents no π bonding.

Fig. 4: Submonolayer spectra at normal X-ray incidence for linear hydrocarbon on Cu(100) at 60 K using the fluorescence yield mode.

Fig. 5: C_2H_2 spectra at submonolayer coverages and normal X-ray incidence. a) 0,5 L fluorescence yield at 60 K, b) 0,25 L partial electron yield at 60 K c) same as a) warmed up to ~ 110 K. d) same as b), warmed up to ~ 130 K.

These test experiments demonstrate the utility of fluorescence yield detection, even when the absorbate edge is for an element with a low atomic number. With synchrotron facilities of the second generation having one to three orders of magnitude higher photon flux, fluorescence should be the method of choice for surface science investigations.

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