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To cite this version:

HAL Id: jpa-00226154
https://hal.archives-ouvertes.fr/jpa-00226154
Submitted on 1 Jan 1986
A NEW TECHNIQUE FOR SUBMONOLAYER NEXAFS: FLUORESCENCE YIELD AT THE CARBON K EDGE

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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 JR due to reduction in background intensity the fluorescence yield method is shown to be the most reliable. The values obtained for JR are: JR(FY) = 10, JR(AEY) = 0,6, JR(PEY) = 0,17 and JR(TEY) = 0,05. Submonolayer spectra of C2H2, C2H4, C2H6 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 ls 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 JR, which is defined as the count rate difference above and below the edge, normalized to the pre-edge back-
A typical value of $J_R$ for one layer of hydrocarbons (such as C$_2$H$_4$) 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 $2 \times 10^{10}$ photons/sec (400 mA current), with an energy resolution of 1 eV. The sample was cleaned by Ar$^+$ bombardment, annealed to 300°C and checked using LEED and Auger spectroscopies. Spectra were recorded on the Au$_x$ partial, total electron yield modes as before /6/, as well as the fluorescence yield mode. The experimental details of the UEV compatible proportional counter are given elsewhere /5/. The solid angle was 5% of 4 π sr with an energy resolution of 280 eV FWHM at the C K$_\alpha$ line (277 eV). By using a multichannel analyser, a window was set around the C K$_\alpha$ 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 $J_R$.

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 ($L_p > 1000 \AA$) is much larger than the one of the electrons ($L_e > 10 \AA$). We have chosen $\beta = 0^\circ$ and $\alpha = 0^\circ$ for normal X-ray incidence.](image)
Table 1: Estimated and measured fluorescent yield count rates at the S/3 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 ($\approx 10^{-3}$). 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).

*Estimated using TDS spectroscopy  
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 (~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(1ο) initial state to a final $\pi^*$ 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(1ο) to $\pi^*$ 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 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 $\sigma$-shape.
resonance. A complete discussion about the orientation of the molecules is given elsewhere /8/. In this case, the sharp π resonance of C₂H₂ 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 C₂H₂ transforms to C₂H₆. This decrease in π intensity is easily understood as the C₂H₆ 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: C₂H₂ 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.

Acknowledgements

We acknowledge the help of D.A. Fischer during the early stage of the experiment. The work was supported by BMFT under grant no. 0233 BB.

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