NEAR-EDGE X-RAY ABSORPTION FINE-STRUCTURE STUDIES OF RING MOLECULES ADSORBED ON SINGLE CRYSTAL SURFACES

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To cite this version:
M. Bader, J. Haase, K.-H. Frank, C. Ocal, A. Puschmann. NEAR-EDGE X-RAY ABSORPTION FINE-STRUCTURE STUDIES OF RING MOLECULES ADSORBED ON SINGLE CRYSTAL SURFACES. Journal de Physique Colloques, 1986, 47 (C8), pp.C8-491-C8-496. <10.1051/jphyscol:1986892>. <jpa-00226223>

HAL Id: jpa-00226223
https://hal.archives-ouvertes.fr/jpa-00226223
Submitted on 1 Jan 1986

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NEAR-EDGE X-RAY ABSORPTION FINE-STRUCTURE STUDIES OF RING MOLECULES ADSORBED ON SINGLE CRYSTAL SURFACES

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Abstract
Near edge X-ray absorption fine structure (NEXAFS) has been used to establish the orientation of the six-membered ring molecules benzene, pyridine, pyrazine and s-triazine adsorbed on Cu and Ag single crystal surfaces. For submonolayer coverages of pyridine on Ag(ll1) an orientational phase transition has been observed with NEXAFS in real time.

1. Introduction
The determination of the structure of adsorbed species on surfaces is a key problem in surface science and during the last few years considerable progress has been made. With near edge X-ray absorption fine structure (NEXAFS) spectroscopy /1/ a technique now is available which yields information on the orientation of molecules on surfaces in an easy and straightforward way. In the present study we have investigated the molecular orientation of the six-membered ring molecules benzene (C6H6), pyridine (C5H5N), pyrazine (C4H4N2) and s-triazine (C3H3N3) on Cu(ll0), Cu(ll1) and Ag(ll1) single crystal surfaces by analysing the polarization dependence of the π resonance intensities in their NEXAFS spectra. Our special interest was focused on pyridine adsorption which could have model character for determining the relative contributions of nitrogen lone-pair and π bonding to the chemisorption bond. In particular we were interested in showing that with high-brightness storage rings and advanced grazing-incidence monochromators structural phase transitions - as they were found in the pyridine/Ag(ll1) system /2/ - can be observed by NEXAFS in real time.

2. Experimental
The experiments were performed at the Berlin storage ring for synchrotron radiation, BESSY, using the plane-grating grazing-incidence monochromator SX-700 /3/ with a 1200 l/mm-grating. The data were taken in the partial electron-yield mode /4/ running the monochromator with a sweep rate of 30 eV/min. Spectra shown are background corrected (covered/clean). The NEXAFS was studied at the C and N K-edges. The X-ray incidence angle on the sample could be varied from near grazing incidence (θ = 20°) to normal incidence (θ = 90°). The Cu and Ag crystals, mechanically and chemically polished, were cleaned by Ar⁺ bombardment and subsequent annealing at ~ 600 K. Good p(1x1) LEED patterns were obtained. The surface cleanliness was checked by AES. During exposure and measurement the crystals were held at a temperature of ~ 100 K.
3. Results and Discussion

3.1 Peak assignment

Characteristic K-edge NEXAFS spectra of six-membered ring molecules condensed on Cu(110) are shown in Fig. 1. The benzene (left) and pyridine (right) spectra were taken at the C and N K-edge, respectively. Both spectra have the same main structures labeled A – D.

In benzene, peaks A and B correspond to transitions of 1s electrons into two unfilled \( \pi^* \) orbitals with \( e_{2u} \) and \( b_2g \) symmetry, respectively, separated by 3.7 eV /5//. In pyridine the degenerate \( e_{2u} \) orbital of benzene is split by 0.6 eV into two levels of \( b_1 \) and \( a_2 \) symmetry /5/, which in this experiment were not resolved because the monochromator resolution was set at 1.2 eV (N K-edge). The measured energy separation between peaks A and B is (3.7 ± 0.2) eV for benzene and (3.8 ± 0.2) eV for pyridine. In pyrazine spectra (not shown here) peak A clearly has a shoulder in agreement with the much larger splitting of the \( e_{2u} \) orbital into two levels of \( b_{3u} \) and \( a_u \) symmetry /5/. In general, peaks A and B show the same polarisation dependence. In the remainder of the paper we will analyse only peak A and refer to it as the "\( \pi \) resonance". There is no disagreement in the literature about the assignment of peak D as a \( \sigma \) resonance corresponding to transitions of 1s electrons into \( \sigma^* \) orbitals. In inner-shell EELS measurements of benzene /6/ peak C, however, was assumed to be a shakeup structure, whereas recent multiple scattering calculations for benzene /7/ suggest that peak C is also a \( \sigma \) resonance. Fig. 2 shows NEXAFS spectra for a submonolayer coverage of benzene adsorbed on Cu(110). The spectra were taken at normal (\( \theta = 90^\circ \)) and near grazing (\( \theta = 20^\circ \)) incidence and are identical in both azimuths \( \langle 001 \rangle \) and \( \langle 110 \rangle \). Whereas the intensities of peaks A, B and D show the expected large polarisation dependence of a flat lying molecule the intensity of peak C stays nearly constant. Hence, the dominant contribution to peak C cannot have \( \sigma \) resonance character.

3.2 Benzene, pyridine and pyrazine on Cu(110)

NEXAFS spectra for benzene have already been shown in Fig. 2. As the \( \pi \) resonance intensity varies with the angle \( \gamma \) between the \( \mathbf{E} \) vector and the normal to the molecular plane, \( \hat{n} \) (see inset in Fig. 2), according to /8/

\[
I_\pi \propto \cos^2 \gamma
\]

the analysis yields an angle \( \alpha \) between the ring plane and the surface of \( \alpha = 0 \pm 10^\circ \). The benzene molecule is thus lying flat on the Cu(110) surface and is therefore predominantly \( \pi \)-bonded to it. This is in agreement with NEXAFS results for benzene on Pt(111) /9/ and in agreement with the results of numerous other surface science techniques.
For pyridine the π resonance intensities are plotted as a function of the polar angle θ in Fig. 3. The analysis of the angular dependence in the [110] azimuth yields α = 90° ± 10° whereas the constant intensity in [001] indicates that the ring plane lies parallel to [001]. This finite intensity in [001] is due to imperfect (≈85%) source polarisation as expected [10]. Our data are in agreement with angle-resolved photoemission results on the same system [11] which indicated that pyridine adsorbs with its aromatic ring perpendicular to the surface. This latter study also proved that the adsorbate/substrate interaction occurs through the lone-pair of the nitrogen atom.

The analysis of our NEXAFS data for pyrazine yields α = 90° ± 10° with the ring plane of pyrazine aligned along the [001] direction. This result is identical to that for pyridine.

Also, measurements at the C and N K-edge for the nitrogen containing molecules pyridine and pyrazine yield exactly the same α-values.
3.3 Benzene, pyridine, pyrazine and s-triazine on Cu(111)

On fcc(111) surfaces the π resonance intensity for molecules with the ring plane tilted by an angle θ with respect to the surface is given by /12/

\[ I_\pi = P(\sin^2 \alpha \sin^2 \theta + 2\cos^2 \alpha \cos^2 \theta + (1-P)\sin^2 \alpha) \]  

(2)

where P is the degree of linear polarisation of the synchrotron radiation. Our data for submonolayer coverages of the ring molecules adsorbed on Cu(111) have been analysed according to equ. (2). The determined tilt angles θ are summarised in Table 1 together with the measured θ-values for adsorption on the Cu(110) and Ag(111) surfaces.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Cu(110)</th>
<th>Cu(111)</th>
<th>Ag(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0 \pm 10°</td>
<td>0 \pm 10°</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>90° \pm 10°</td>
<td>70° \pm 5°</td>
<td>45° \pm 5°  (low coverage)</td>
</tr>
<tr>
<td>Pyrazine</td>
<td>90° \pm 10°</td>
<td>58° \pm 10°</td>
<td>70° \pm 5°  (monol. coverage)</td>
</tr>
<tr>
<td>s-Triazine</td>
<td></td>
<td></td>
<td>58° \pm 10°</td>
</tr>
</tbody>
</table>

Whereas benzene lies flat on Cu(111) as on Cu(110), the measured tilt angles for the other six-membered ring molecules differ from those measured on Cu(110). The measured tilt angle of θ = 70° \pm 5° for pyridine is in agreement with nearly all results of NEXAFS /9/ or of other surface science techniques /13 - 15/ applied to pyridine adsorbed on different (111) surfaces, which indicated more or less upright standing pyridine molecules. There is even quantitative agreement with NEXAFS data on Pt(111) (high-temperature state) /9/ and with ESDIAD data on Ir(111) /13/. The only known results /2/ at variance with our data are discussed in chapter 3.4. The measured tilt angle of θ = 58° \pm 10° for pyrazine, however, is in conflict with EELS data /16, 17/ taken on Ag(111) which indicated flat lying molecules. The agreement with θ = 55° measured by ellipsometry on pyrazine condensed on Ni(111) /18/ might only be accidental.

We should stress here that in no case has a phase transition been observed for submonolayer coverages of the investigated ring molecules on Cu(111).

3.4. Phase transition in the system pyridine/Ag(111) /12/

The normalized nitrogen K-edge π resonance intensity for normal incidence (θ = 90°), I_90, and the intensity ratio I_20/I_90 as a function of dose during permanent adsorption of pyridine (∼0.1 L/min) on Ag(111) is shown in Fig. 4. The ratio I_20/I_90 is constant at doses lower than ∼4 L. According to equ. (2) it corresponds to a tilt angle of θ = 45° \pm 5°. Between 4 and 5.5 L the ratio I_20/I_90 decreases drastically and steadily increases at higher doses. The minimum value of I_20/I_90 corresponds to θ = 70° \pm 5°. Finally I_20/I_90 = 1 for a randomly oriented condensed multilayer is approached. We therefore assign a monolayer to an exposure of approximately 5.5 L in agreement with inverse photoemission, UPS, and work-function results /14/. Hence, we observed an orientational phase transition for a submonolayer coverage in agreement with the vibrational EELS (VEELS) data /2/. The measured tilt angles compare well with those found by NEXAFS for pyridine on Pt(111) /9/ where a temperature dependent phase transition was observed. The tilt angle of 45° measured for the low-coverage, low-temperature phase of pyridine on Ag(111), however, is at variance with
that indicated by VEELS for the same system. Further careful VEELS and NEXAFS studies on identical systems should help to solve the obvious discrepancies /12/. Our NEXAFS results suggest that even at low coverages N lone-pair bonding occurs.

Fig. 4: N K-edge π resonance (peak A) intensity for normal incidence (θ = 90°), \( I_{90} \) (full circles), and the intensity ratio \( I_{20}/I_{90} \) (crosses) as a function of dose during permanent adsorption of pyridine (≈0.1 L/min.) on Ag(111) at 100 K. The \( I_{20}/I_{90} \) data points with error bars were independently measured at fixed pyridine doses. There is a phase transition near 4.5 L.

4. Conclusions

With NEXAFS the orientation of molecules on single crystal surfaces can be determined in an easy and straightforward way. Our NEXAFS results on six-membered ring molecules adsorbed on Cu and Ag surfaces show: While benzene lies flat on both Cu(110) and Cu(111) surfaces, and pyridine and pyrazine stand upright on Cu(110) with the ring plane aligned along the [001] direction, pyridine, pyrazine and s-triazine are more or less tilted (45° ≤ \( \alpha \) ≤ 70°) on Cu(111) and Ag(111) surfaces. It has been shown that NEXAFS can detect orientational phase transitions in real time. Such a phase transition was observed at a submonolayer coverage in the system pyridine/Ag(111).

Acknowledgements

The authors are pleased to acknowledge the support of the Bundesministerium für Forschung und Technologie under Grant No. 05 238 JH.

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