

The Electronic Structure of Thiophene Adsorbed on Cu(110)

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A adsorção de tiofeno sobre uma superfície de Cu(110) foi estudada através das técnicas de fotoemissão com resolução angular (ARUPS) e fotoemissão inversa (IPES). Os Resultados de ARUPS indicam que as moléculas de tiofeno adsorvem inclinadas em relação à superfície na fase $c(2 \times 2)$, com o plano perpendicular ao plano molecular principal alinhado ao longo da direção da superfície de cobre. Os orbitais moleculares não ocupados de tiofeno foram investigados através de IPES, obtendo-se boa concordância com resultados obtido, em fase gasosa.

Angle-resolved photoemission with synchrotron radiation has been used to study monolayer of thiophene adsorbed on Cu(110). A parallel adsorption geometry could not be derived from the photoemission results. The molecules are tilted away from the surface normal and are azimuthally oriented with the mirror plane (plane perpendicular to the principal molecular plane) aligned along the direction in the $c(2 \times 2)$ phase. The unoccupied molecular orbitals of thiophene were investigated by inverse photoemission, where good agreement were found with electron transmission and optical measurements.

Key words: *thiophene monolayer; photoelectron spectroscopy; inverse photoemission.*

Introduction

The adsorption of thiophene on single crystal surfaces has been the subject of a number of investigations¹⁻¹³. The interest in these adsorption systems is motivated primarily by the need to understand the industrially important hydrodesulphurisation (HDS) process¹⁴. The adsorption of thiophene also serves as a model system for the investigation of the interaction of cyclic aromatic molecules with metal surfaces. Furthermore, thiophene derivatives form the basis of a variety of organic conducting polymers¹⁵.

In this paper we have investigated the adsorption of thiophene on Cu(110) surface using angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) and inverse photoemission spectroscopy (IPES). Adsorption of thiophene on Cu(110) at 150 K results in monolayer coverage and a $c(2 \times 2)$ overlayer structure has been identified by LEED. Additional dosing at this temperature results in no differences in the ARUPS spectra or LEED pattern.

Experimental

The ARUPS experiments were performed at the synchrotron radiation source BESSY in Berlin using an UHV system specially designed for the preparation and characterization of organic molecule samples^{16,17}. It consists of two UHV chambers connected by a sample transfer system. The measuring chamber is equipped with a commercial 180° hemispherical analyser (R = 50 mm) in connec-

tion with a position sensitive detector for multichannel operation (Vacuum Science Workshops Ltd.). The analyser is mounted on a two-axis-goniometer to detect photoelectrons at different polar angles θ relative to the sample surface normal. The second chamber is designed for sample preparation with various gas inlet systems and sublimation ovens.

Tunable radiation was provided by the toroidal grating monochromator TGM 1 ($4 \leq h\nu \leq 125$ eV). The overall resolution including the monochromator and electron energy analyser was set to about 0.3 eV for the photon energy range used in this experiment. The IPES measurements were performed in a UHV chamber described elsewhere¹⁸. The inverse photoemission system detects photons of $h\nu = 9.5$ eV with a resolution (electron source plus photon detector) of 0.35 eV. The Cu(110) surface was cleaned by repeated cycles of Ar sputtering and annealing at 500°C. Thiophene vapour was introduced by means of a leak valve while the Cu(110) sample was maintained at 150 K.

Results and Discussion

Photoelectron spectra ($h\nu = 35$ eV) of a monolayer of thiophene adsorbed on Cu(110) are presented as a function of electron emission angle, θ in Fig. 1. the angle of incidence of the radiation (α) was set at 70° and the electrons were detected in the plane defined by the surface normal and the incoming radiation, which was parallel to the $\langle 001 \rangle$ azimuth. The binding energies are referenced to the

vacuum level ($E_{\text{vac}}=0$), which was determined by correcting the work function of the clean surface by the adsorbate induced work function change. An exposure of 10 L (1 L = 1×10^{-6} Torr.s) induces a work function change of $\Delta\phi = -0.7$ eV, which results in a work function of the thiophene/Cu(110) system of $\phi = 3.8$ eV (having taken $\phi = 4.48$ eV for clean Cu(110))¹⁹. The gas phase photoelectron lines of thiophene²⁰ is also shown in the form of a bar diagram in Fig. 1. The spectra of gaseous and monolayer phases have been energetically aligned at the $4a_1$ orbital. The assignment of the ionization potentials (IP) of the gas phase spectrum from the calculations of von Niessen et al.²¹ are also given. An average relaxation shift of $\Delta E = 1.4$ eV was determined by comparing the IP's of the adsorbed and gaseous phases.

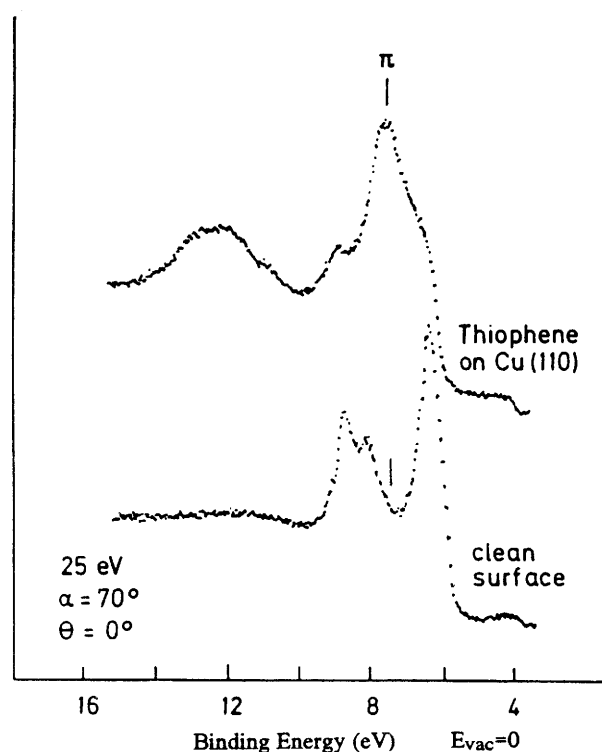


Figure 1. Intensity variation of the angle-resolved photoelectron spectra for a thiophene monolayer on Cu(110) as a function of polar emission angle θ . The gas phase photoelectron results of thiophene²⁰ is also shown. The MO assignments are given in molecular C_{2v} symmetry²¹.

Between 6 eV and 10 eV strong emission from the Cu 3d-bands overlap with the first two thiophene induced peaks. At lower photon energy, however, they are detected. This is shown in Fig. 2 where a photon energy of 25 eV was used. These features lie at 7.4 eV relative to E_{vac} in the monolayer phase and correspond to emission from the $1a_2$ and $2b_1$ π molecular orbitals of thiophene. Comparison of gaseous and adsorbed phase spectra shows that the π orbitals are relatively shifted to lower binding energy in the adsorbed phase indicating that there is no stabilization of these orbitals due to the interaction with the metal surface. A similar relative shift of the $1b_1$ orbital is also expected. The shift of the π orbitals to relative lower binding energy as shown in Figs. 1 and 2 contrasts strongly with benzene

adsorption on a variety of metal surfaces²² as shifts to relative higher binding energy have been observed due to the interaction with the surface in the parallel adsorption geometry. Thus it seems more likely that thiophene is adsorbed on Cu(110) via the S lone-pair orbital ($6a_1$) and that the molecule is not oriented in a parallel configuration. Our preliminary NEXAFS (near-edge X-ray absorption spectroscopy) results confirm the non parallel adsorption of thiophene on Cu(110). They show that the molecular plane of thiophene is tilted by 30° from the surface. Evidence for an inclined geometry of thiophene on metal surfaces has already been reported^{3,7,8,10}.

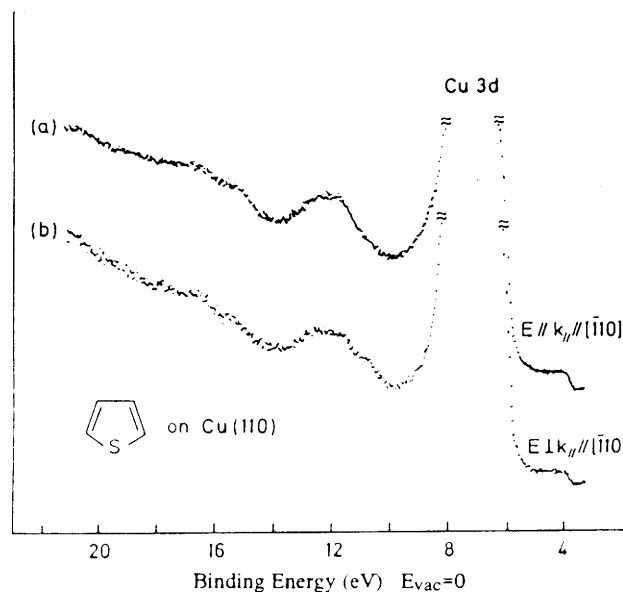


Figure 2. Photoemission spectrum of thiophene on Cu(110) at a photon energy of 25 eV.

For an inclined geometry, the symmetry of the adsorbate/substrate complex is reduced from C_{2v} in the gas phase to C_s . In C_s symmetry the thiophene molecule has only one mirror plane that is perpendicular to the principal molecular plane. The orbitals in C_{2v} symmetry that are symmetric with respect to this plane (a_1 and b_1 orbitals) will transform into the a' representation of the C_s point group. The antisymmetric orbitals (a_2 and b_2) will belong to the a'' representation. The binding energies of the features and the corresponding assignments are given in Table 1.

The investigation of the azimuthal ordering can be carried out in ARUPS by placing the detector along or azimuth of the $\langle 001 \rangle$ or $\langle \bar{1}10 \rangle$ azimuth of the Cu(110) surface and taking spectra with normal incident radiation with the electric field vector of the incoming beam parallel and perpendicular to the emission plane. The emission intensity from a totally symmetric state should be zero when for s-polarised light the photoemitted electrons are detected in a plane perpendicular to the plane defined by the \mathbf{E} vector and the surface normal ($\mathbf{E} \perp \mathbf{k}_{\parallel}$). The results for emission in the $\langle \bar{1}10 \rangle$ and $\langle 001 \rangle$ azimuth are shown in Fig. 3 and Fig. 4, respectively.

In spectrum (a) of Fig. 3 the electric field vector \mathbf{E} is aligned parallel to the $\langle \bar{1}10 \rangle$ azimuth and $\mathbf{E} \parallel \mathbf{k}_{\parallel}$. In this

Table 1. Valence binding energies (in eV of monolayer thiophene on Cu(110)). The gas phase ionization potentials and symmetry assignments are also given. The binding energies are given with respect to the vacuum level E_{vac} .

C_{2v}	C_s	Gas phase (eV)	$c(2 \times 2)$ $\phi = 3.8$ eV
$1a_2 \pi$	a''	8.9	7.4
$2b_1 \pi$	a'	9.5	7.4
$6a_1 n$	a'	12.1	(11.3)*
$1b_1 \pi$	a'	12.7	10.6
$4b_2$	a''	13.3	12.0
$5a_1$	a'	13.9	12.6
$3b_2$	a''	14.3	12.6
$4a_1$	a'	16.6	15.2
$2b_2$	a''	17.6	16.6
$3a_1$	a'	18.3	16.6

*weak structure

allowed geometry only initial states of a' symmetry will be detected. In spectrum of Fig. 3 (b) we have the forbidden geometry ($E \perp k_{||}$). The spectra have been magnified to a better identification of the intensity variations of the deeper lying orbitals. The intensity of the $4a_1$ orbital (a' in C_s symmetry) that has no overlap with other emissions is almost the same in both measuring geometries of Fig. 3. In both cases emissions from a' and a'' orbitals can be identified. This indicates that there is no mirror plane in the $\langle 110 \rangle$ azimuth.

Some differences between both geometries is found

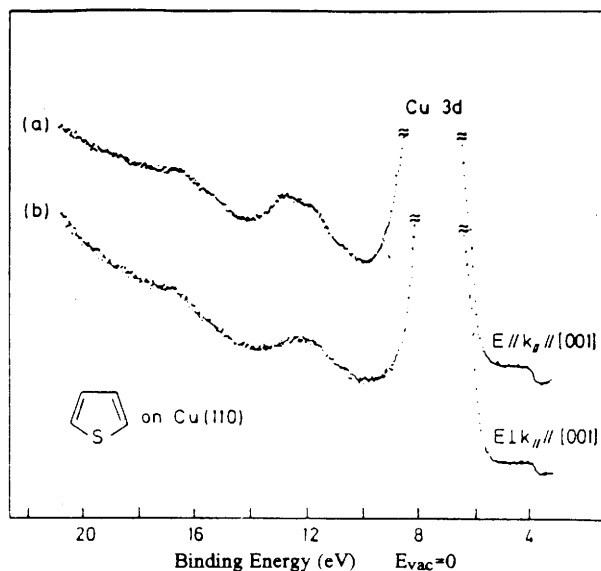


Figure 3. Photoemission spectra of thiophene on Cu(110) recorded in the $\langle 110 \rangle$ crystal azimuth. The photon polarization vector was aligned parallel (spectrum a) and perpendicular (spectrum b) to the corresponding azimuth.

however for the azimuth. This is shown in Fig. 4. When the E vector is aligned parallel to the direction (Fig. 4a) emission from the $4a_1$ and $3a_1$ orbitals (a' representations in C_s) is observed. With E perpendicular to the emission azimuth (Fig. 4b) the a' feature ($4a_1$) is not detected. The appearance of the emission at 16.6 eV in spectrum (b) can be explained by the contribution by the $2b_2$ (a'') orbital as expected from MO-calculations²¹. Moreover, it is clear that in the forbidden geometry (spectrum b) the emission of the a' component ($5a_1$) at 12.6 eV is missing. From the results presented in Figs. 3 and 4 it is concluded that thiophene is azimuthally oriented at monolayer coverage in the $c(2 \times 2)$ phase. The mirror plane is perpendicular to the principal molecular plane and aligned parallel to the $\langle 001 \rangle$ azimuth, i.e.

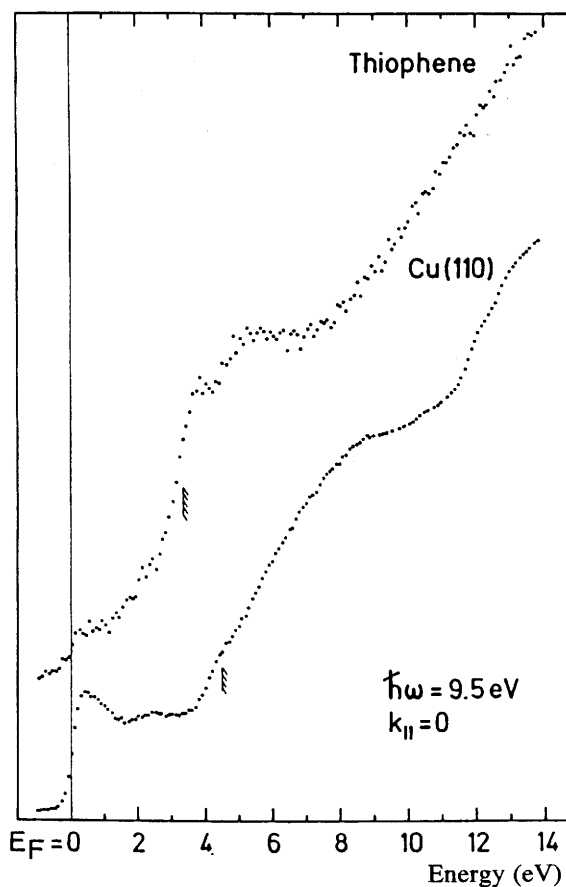


Figure 4. Photoemission spectra of thiophene on Cu(110) recorded in the $\langle 001 \rangle$ crystal azimuth. The photon polarization vector was aligned parallel (spectrum a) and perpendicular (spectrum b) to the corresponding azimuth.

perpendicular to the close-packed row of the (110)-surface.

The unoccupied molecular orbitals of thiophene adsorbed on Cu(110) have been studied using IPES. Fig. 5 shows the inverse photoemission spectrum of a monolayer thiophene and for comparison the IPES-spectrum of clean Cu(110) is also presented. The features in the Cu(110) spectrum are assigned to bulk transitions^{23,24}. The energies are referenced to the Fermi level (E_F). The vacuum level of the adsorbate system was determined by monitoring the work function change after adsorption and it is also shown in Fig. 5. Due to electron bombardment the thin thiophene film

was rapidly damaged. The IPES-spectrum represents the sum of only three scans that were taken at different positions of the sample surface. Therefore, the statistics of the spectrum in Fig. 5 are relatively poor.

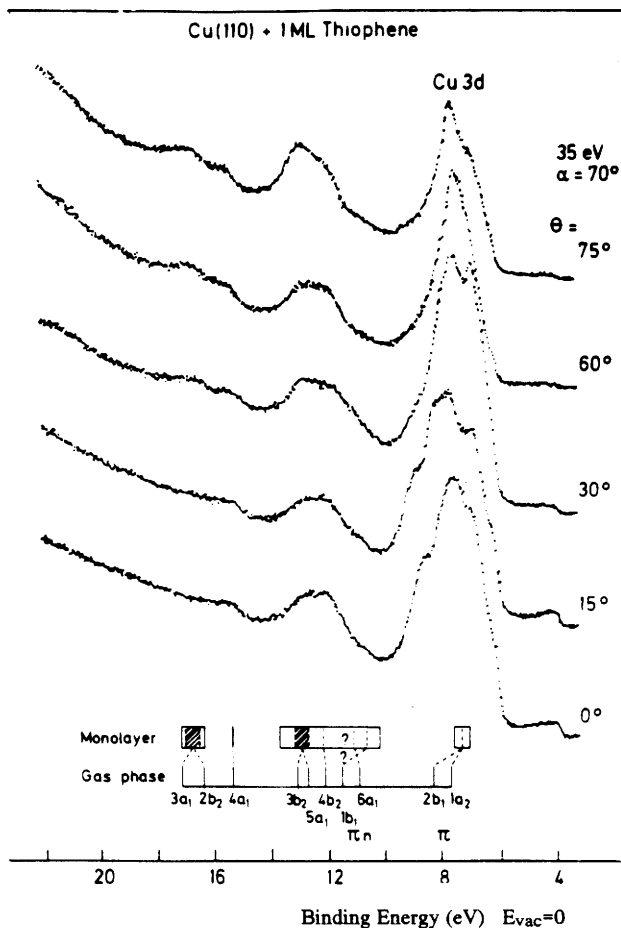


Figure 5. Isochromat inverse photoemission spectrum of thiophene adsorbed on Cu(110) taken at normal electron incidence. For comparison the spectrum of the clean Cu(110) surface is also shown.

Two adsorbate induced bands can be observed at 3.9 eV and at approximately 5.3 eV above E_F (relative to the vacuum level they appear at 0.5 eV and 1.9 eV, respectively). The gas phase electron transmission data^{25,26} also show two peaks that are lying at 1.15 eV and 2.63 eV. Using the results of HAM/3²⁷ and Green function CNDO²⁸ calculations they were assigned to the $3b_1$ and $2a_2 \pi^*$ molecular orbitals. Comparing these results with or IPES data good agreement was found concerning the energy difference between the measured peaks. Optical transition results show the energy difference between the $2b_1(\pi) \rightarrow 3b_1(\pi^*)$ and $2b_1(\pi) \rightarrow 2a_2(\pi^*)$ transitions to be 1.5 eV²⁹, which also supports our assignment of these features.

Conclusions

Angle-resolved photoelectron spectra of thiophene monolayer on Cu(110), measured with synchrotron radiation, were presented and discussed. The thiophene molecules are tilted away from the surface normal and are

azimuthally oriented with the mirror plane aligned along the $\langle 001 \rangle$ direction in the $c(2 \times 2)$ phase. The unoccupied molecular orbitals of thiophene were investigated by IPES. A complete picture of the occupied and unoccupied valence bands of the thiophene/Cu(110) system was obtained. This example also demonstrates the ability of IPES in investigating the unoccupied energy levels of adsorbate-covered surfaces.

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