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Diethynyl-thiophene adsorbed on Cu(100) investigated by NEXAFS and XPS

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Abstract

Studies on the chemical stability and interface interaction of diethynyl-thiophene (DET) condensed multilayer at 90 K on Cu(100) are reported. The temperature influence in the multilayer and monolayer range has been investigated by means of near edge X-ray absorption fine structure (NEXAFS) spectroscopy at the C K-edge. The NEXAFS spectra were recorded at 90 K, 150 K, 200 K, 245 K and 298 K. Comparison with X-ray photoemission spectroscopy (XPS) data, collected on DET at similar temperatures, has also been accomplished. NEXAFS spectra recorded for the multilayer show a strong similarity with those of our previous NEXAFS theoretical and experimental investigations in gas-phase. The multilayer spectra appear affected by the temperature from 90 K to 155 K, while after desorption a broadening of the main π^* region occurs, indicative of interaction with the substrate. XPS data at the S2p core level suggests a partial desulphurization reaction that takes place at nearly room temperature with the S–C replaced by a Cu–C bond.

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1. Introduction

The study of the electronic structure of penta-atomic aromatic heterocyclic compounds is of prime importance since these are the starting base for the synthesis of several organic conducting polymers [1]. Related materials are conjugated organometallic polymers, such as poly-ynes containing bonded transition metals in the chain, that also show interesting properties due to the mixing between the metal and ligand orbitals. It is well known that the π -conjugation of the σ -bonded acetylenic spacer is preserved

through the metal [2–4], giving rise to third-order non-linearity (NLO) [5], phosphorescence [6], liquid crystal behaviour [7] and possibility of alignment in electric [8] and magnetic field [9]. A series of Pt and Pd containing polymers and oligomers with different organic spacers have been synthesized. Diethynyl-butoxybenzene (DBOB), diethynyl-hexadecyloxybenzene (DHDOb), diethynylbiphenyl (DEBP) and diethynyl-thiophene (DET) were used as organic moieties, and the materials were routinely characterised [4,10,11]. A Pt–DET oligomer was investigated as sensitive membrane for chemical sensors [12] using metal wires as transducers. The here reported investigation is related to the polymer/metal interaction that is important for the performance of electronic devices.

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DET is a relative of thiophene, the precursor of polythiophene, and the chemical structure of the two molecules can be usefully compared. The electrodonating ability of aromatic thiophene is well established [13], leading to third-order NLO properties of the corresponding polyene. It is also stated that molecular orientation effects can play a major role for the achievement of fast and good response from NLO materials. Within this family of molecules, several oligomers and polymers of thiophene have been synthesized and investigated, and new synthetic methods have been developed for conjugated polymers with thiophene linked by ethynyl groups [11,14]. For a deeper knowledge of the electronic properties of polymers, a reliable approach is the investigation of the constituent building blocks, i.e. the precursors or small model molecules. In this research program, DET was previously investigated by XPS and NEXAFS at the C1s and S2p edges in gas-phase and experimental results have been compared with calculated data [15]. NEXAFS is suited for the study of molecular and electronic structures and molecular orientation of adsorbed molecules by recording spectra at normal and grazing incidence of the linearly polarized photon beam. The resonance intensity at a K-edge depends on the relative orientation of both the excited molecular orbital and the polarization direction of the radiation; the intensity is maximum for the **E**-vector parallel to the main axis of the examined orbital. In this paper we present C K-edge NEXAFS measurements of DET multilayer and monolayer adsorbed at 90 K on Cu(100) and their temperature dependence. Comparisons with XPS data and with previous NEXAFS investigations in gas-phase, by experiment and theory, are also discussed. Similarly to thiophene, this molecule can be damaged by the X-radiation [16]. Therefore, in this paper we present preliminary data concerning NEXAFS at the C K-edge and XPS at the S2p core level experiments, while further investigations are planned.

2. Experimental

NEXAFS experiments were performed at LURE Super ACO at the SACEMOR experimental station connected to the beam line SA72. The line uses a TGM with a resolution of 150 meV at the carbon edge. SACEMOR is built up with three main vacuum chambers connected by gate valves and the base pressure is 3×10^{-10} mbar. NEXAFS spectra were recorded by means of two channeltrons collecting the partial secondary electron emission of a clean reference gold grid I_0 and by the sample **I**, in the total yield mode; **I** was then normalized with respect to I_0 . For angular dependence the C K-edge spectra were taken at normal (90°) and grazing (30°) incidence angles of the photon beam on the sample surface, with the **E**-vector parallel and nearly normal to the surface respectively. Reference C K-edge spectra of the clean Cu surface were also taken at the above cited angles in the same conditions for the adsorbed DET. The photon energy has been calibrated at the C K-edge using the small feature at 284.6 eV, due to weak contamination

of the light optics, in the I_0 spectrum. Normalization was performed by subtracting the contribution due to the reference spectra of the clean metal surface. The spectra were then normalized by subtracting a straight line that fits the part of the spectrum below the edge and assessing to 1 the value at 320 eV.

2,5-Diethynyl-thiophene ($\text{H}-\text{C}\equiv\text{C}-\text{C}_4\text{H}_2\text{S}-\text{C}\equiv\text{C}-\text{H}$, DET; $\text{C}_4\text{H}_2\text{S}$ = thiophene) was synthesized following a specific procedure [11]. DET was stored in a series of dark glass vials at -60°C . Before the experiments was introduced into a CF16-flanged glass vessel fixed to the gas-line by a leak valve. DET, which is solid below 0°C , albeit with a high vapor pressure, was kept at liquid nitrogen temperature for all the experiments. Several cycles of pumping and cooling down allowed to remove all the contaminants; DET purity was checked by mass spectrometry. The Cu(100) crystal was cleaned by several cycles of heating to 400°C , and sputtering and checked by LEED and C K-edge and O L-edge NEXAFS, after cooling to 90 K. DET was deposited onto Cu(100) at 90 K, by exposure at 2.4×10^{-7} mbar. The temperature of the crystal, checked by a thermocouple, was controlled by a cryostat. Synchrotron radiation-induced (SR) XPS measurements were carried out at ELETTRA using the SuperESCA beamline and relative experimental station built on three levels. The beamline is connected to an undulator front-end and brings a SX700 monochromator, a custom designed electron analyzer and a multichannel plate detector. Two hundred and eighty electron volts photons were used for recording the S2p core spectra, and the measurements were performed in the fixed analyser transmission mode with 50 eV pass energy.

3. Results and discussion

We have previously discussed XPS and NEXAFS investigations concerning experiment and theory relative to DET in gas-phase [15]. The assignment of the main spectral features of the C K-edge spectrum was based mainly on STEX calculations and according to the molecular structure depicted in Fig. 1(a). For the discussion of the present data we refer to the previous gas-phase assignments, also reported for comparison in Table 1, while the gas-phase spectrum and the multilayer spectrum collected at normal photon beam incidence are reported in Fig. 1(b). Fig. 1(a) shows the chemical structure of DET, where $\text{C5}\equiv\text{C7}$ and $\text{C6}\equiv\text{C8}$ are ethynyl bonds, is used to identify the excitation site among the four chemically inequivalent carbon atoms. S2p XPS spectra of DET multilayer deposited onto Cu(100) at ~ 130 K have also been collected. The behaviour of both multilayer and monolayer films will be discussed here.

3.1. NEXAFS measurements of DET multilayer

C K-edge NEXAFS spectra for DET multilayer freshly deposited onto Cu(100) at 90 K were measured at normal

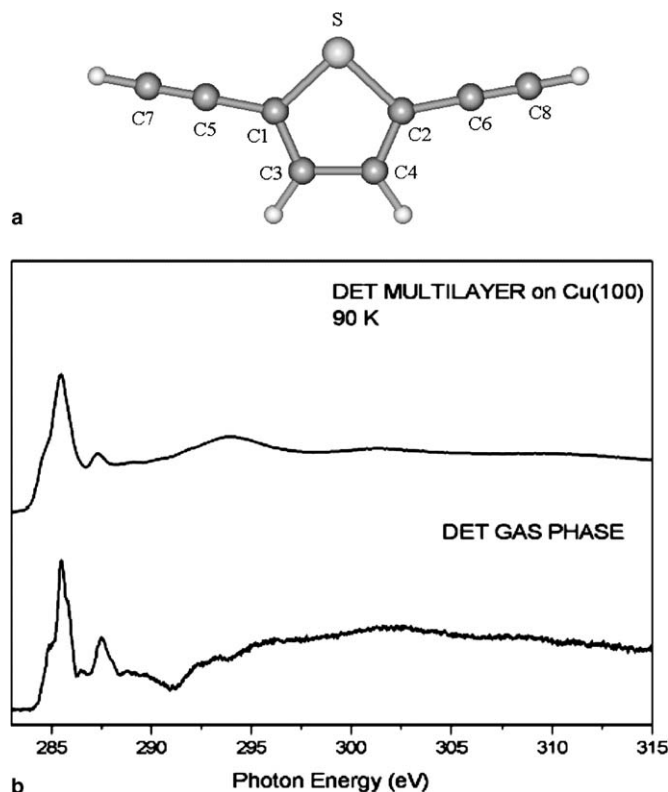


Fig. 1. (a) Chemical structure of diethynyl-thiophene (DET); C5≡C7 and C6≡C8 are ethynyl bonds; (b) C K-edge NEXAFS spectra for DET in gas-phase and for the DET multilayer on Cu(100) at 90 K as measured at normal photon beam incidence.

Table 1
Features assignment for both gas-phase and solid state DET C K-edge NEXAFS spectra

Resonance position [film on Cu(111)] (eV)	Resonance position [gas-phase] (eV)	Assignments
284.7	284.6	C1s → π^* orbitals of terminal acetylenic C (C7)
	284.9	C1s → π^* orbitals of C in the ring not bonded to S (C3)
285.6	285.6	C1s → π^* orbitals of C bonded to S (C1)
	285.8	C1s → π^* orbitals of internal acetylenic C (C5)
286.4	286.4	C1s → π^* orbitals of C acetylene moieties (C7 and C5)
287.5	287.4	C1s → σ^* orbitals of C–S bonds
~296	~295	C1s → σ^* orbitals of C–C bonds
~302	~302	C1s → σ^* orbitals of C=C bonds
~309	~310	C1s → σ^* orbitals of C≡C bonds

and grazing photon beam incidence. The two spectra and their difference are reported in Fig. 2(a). The spectrum difference evidences the resonances with non-isotropic character. Features assignment is reported in Table 1, and a good data matching between gas-phase and solid spectra is observed, although, due to solid state effects, the resonances in Fig. 2(a) are less resolved compared to the gas-

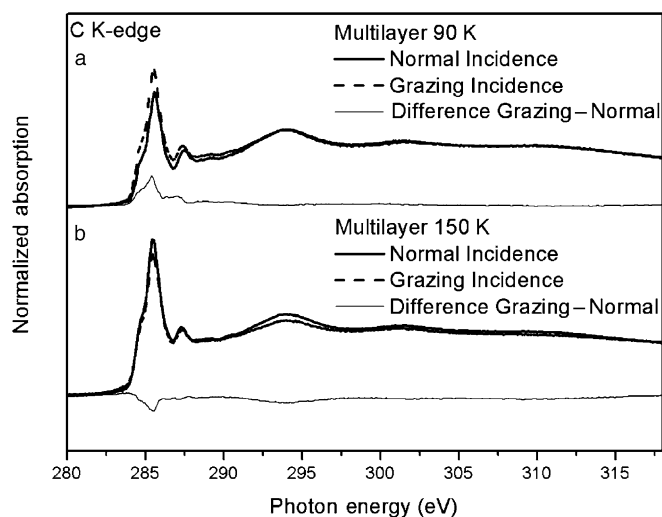


Fig. 2. (a) C K-edge NEXAFS spectra for DET multilayer freshly deposited onto Cu(100) at 90 K as measured at normal and grazing photon beam incidence, and their difference. The spectrum difference evidences the resonances with non-isotropic character; (b) C K-edge NEXAFS spectrum recorded after heating the sample from 90 K to 150 K.

phase features. The π^* resonances region show one shoulder at ~284.7 eV that corresponds to the peak previously associated to C1s → π^* transitions at C7 + C3 (284.76 eV) [15] and one main resonance at 285.6 eV, which includes both the second and third features, resolved in the gas-phase but overlapping in the solid spectrum, that are assigned to π^* excitations at C1 + C5 and C7 + C5 respectively (285.45 + 285.73 eV). By comparison with the STEX calculations, the first two features were assigned to *out of the molecular plane* transitions, while the third one to *in the molecular plane* transitions. Looking at Table 1, for gas-phase DET we have found respectively 284.76, 285.45 and 285.73 eV values for the three bands. The σ^* region contains, as previously shown for the gas-phase, six main resonances, at 287.43 eV, 292–293 eV, 296 eV, 302 eV and 309 eV, due to C1s- σ^* excitations at the C–S, C–C, C=C and C≡C carbons, respectively.

An attempt to estimate the presence of an angular dependence has been performed considering the main π^* resonance. Unfortunately, as we stated above, the feature at 285.6 eV contains two contributions arising by *out of the molecular plane* and *in the molecular plane* transitions, which show opposite angular effects. Due to the very close energy values of these resonances, it was impossible to achieve a spectral resolution. As a result, we were not able to carry out a quantitative evaluation of the angular dependence of the NEXAFS spectra.

Thiophene in gas-phase, solid and monolayer adsorbed on Pt(111) was studied by ISEELS and NEXAFS [17]. Either for gas and solid thiophene, one main π^* resonance was detected at 285.4 eV and assigned as deriving by both α and β carbons; one feature at 287.1 eV was assigned to the overlapping between σ^* (C–S) and π^* (C–C), and the shoulders at 288 eV and 289.3 eV were assigned to transitions to 3p and 4p levels, respectively. Our data are generally in

agreement with these assignments and the differences derive by the presence of two ethynyl groups, in DET, which give additional contributions, highlighted in the low energy region with two extra features in gas-phase at 284.76 eV and 285.73 eV. The ethyne carbons C5 and C7 undergo π^* level splitting, as we have already discussed [18,19] because of the symmetry reduction of free acetylene when bonded to thiophene. Free acetylene has degenerate π^* orbitals, but the interaction with the thiophene ring originates two energy splitted orbitals. This effect is displayed in the calculated spectra for C5 and C7, where a 0.6 eV splitting goes together with a relative variation in intensity thought as deriving from the delocalization of the virtual orbitals [15].

The molecular orientation and the effect of temperature were already investigated for thiophene adsorbed on Pt(111) [17]. Two monolayer phases were detected by annealing the condensed phase to 150 K and 180 K, the first one made by close packed molecules tilted at about 40° to the surface and a second one “relaxed” with thiophene lying flat on the Pt surface. A change in the chemisorption geometry and cleavage of the C–S bond was previously reported [20] as occurring for Pt during desorption, while for Cu the absence of bond breaking has been assigned to the reduced interaction between copper and thiophene [21,22]. The C K-edge spectrum for thiophene and bithiophene multilayer condensed on Ag(111), in conjunction with X α -SW calculations data was discussed [23]. One main feature at 285.9 eV was assigned to excitation into the LUMO by both C α and C β carbons, while the resonance at 287.6 eV was considered as due to superposition of excitation to the second π^* orbital and the C α –S σ^* orbital; the feature at 289.5 eV was considered as a mixed valence-Rydberg excitation. For thiophene two types of monolayer were identified as “compressed” and “relaxed”, coexisting over a wide range of coverages with no C–S bond breaking.

In Fig. 2(b), the C K-edge NEXAFS spectrum recorded after heating the sample from 90 K to 150 K is reported. Within this temperature range no appreciable desorption has been observed; some changes are however detectable in the differential intensity and probably connected to some kind of molecular rearrangement.

3.2. Monolayer at 200 K, 245 K and 298 K

The NEXAFS spectra related to the sample warmed to 200 K, 245 K and 298 K are reported in Fig. 3(a), (b) and (c), respectively. The multilayer desorption starts above 160 K, as detected by the pressure change; from a coarse analysis of the desorption curve (pressure versus temperature), we can roughly deduce that the monolayer regime occurs at nearly 200 K. The NEXAFS spectra of DET monolayer are somehow comparable to the multilayer ones, displaying the main features in the same positions. The main change detectable by comparison between Figs. 2 and 3 is the occurrence of a broadening of the first band envelope centered at about 285.6 eV. Such an effect is usu-

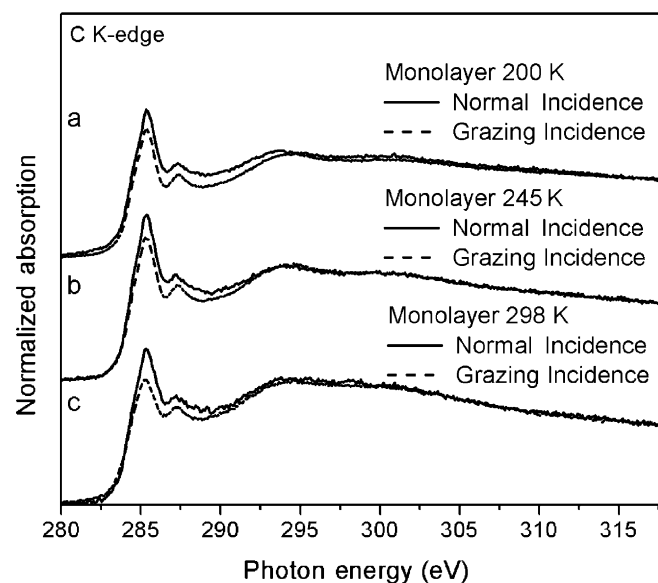


Fig. 3. C K-edge NEXAFS spectra related to the sample warmed to 200 K, 245 K and 298 K.

ally ascribed to a strong interaction with transition metals. The consequent strong hybridization of molecular π^* orbitals with metal d- π orbitals leads to the formation of new unoccupied π^* states with a larger energy distribution [24]. The formation of such new states arising from π -metal bonding have been observed for benzene adsorbed on Mo(110) [25] and for metallocene sandwich compounds for Fe, Co and Ni in gas-phase, investigated by ISEELS [26]. From these considerations, it comes out that the more flat is the molecule on the metal surface, the stronger is the orbital overlapping and therefore, the band broadening.

We suppose that the interaction with the Cu substrate with involvement of the side acetylene groups and/or with opening of the C–S bond, for a fraction of the molecules, could be responsible for this behaviour. The second hypothesis is confirmed by our XPS analysis, as reported in the following paragraph. Stöhr et al. [20] have discussed the C–S bond cleavage for thiophene on Pt, suggesting the sulphur substitution with Pt in the ring for a fraction of the thiophene molecules and giving also evidence for the molecule with its plane close to the Pt surface at 180 K. For thiophene on Cu(111), Cu(100) and Ag(111) [21–23], no C–S bond breaking has been observed. These results, including the present ones, suggest a difference in reactivity given by the transition metal/aromatic molecule interaction and by the chemical nature of the molecule itself as well. The molecular structure, i.e. in this case the presence or absence of acetylenic groups, affects the reactivity as well as the self-assembling tendency in the monolayer regime. As we have stated above for the NEXAFS spectra, the acetylene carbons are strong electron acceptors; giving rise to a weakening of the adjacent C–S bond, then leading to bond cleavage even when deposited onto those substrates where the thiophene is known to show stability. The mentioned difference between the electronic

structure of DET and thiophene, due to the $\text{C}\equiv\text{C}$ moieties, can justify the observed different behaviour of the two materials deposited on similar substrates. As for the molecular arrangement, angular dependent NEXAFS measurements do not give unambiguous indication for a flat orientation. The side acetylene substituents on thiophene can play a role about this regard, influencing somehow the DET organization since the possibility for a side interaction triple bond/metal cannot be excluded; at the present stage of the research we have no evidence for this, and further experiments are planned to achieve a better knowledge about this topic.

3.3. XPS measurements

The temperature influence on the molecular arrangement and chemical state of the adsorbate has also been investigated by means of SR-induced XPS. The $\text{S}2\text{p}$ core levels spectra were collected for a thick DET film deposited on $\text{Cu}(100)$ at 130 K and in the monolayer regime after desorption.

3.4. $\text{S}2\text{p}$ core level spectra

In Fig. 4, $\text{S}2\text{p}$ core level XPS spectra are reported for the experiments performed at two selected temperatures. The spectrum collected at 177 K shows one signal (two spin–orbit splitted peaks, $\text{S}2\text{p}_{3/2,1/2}$) assigned to the sulphur atom in the intact DET molecule; the $\text{S}2\text{p}_{3/2}$ peak occurs at a binding energy (b.e.) of 164.4 eV. Our finding is in agreement with literature reports; in fact a value of 164.5 eV was assessed for intact thiophene on $\text{Ag}(111)$ by Baumgaertner et al. [27]. As the temperature rises above 177 K, multilayer desorption occurs leading to a monolayer adsorbed regime. The room temperature $\text{S}2\text{p}$ spectrum, of the monolayer sample, shows two $\text{S}2\text{p}$ doublets occurring at different

b.e. values with different intensity. A difference in energy indicates a difference in electron density and therefore a different chemical state. For the $\text{S}2\text{p}_{3/2}$ signal we find values of 161.9 eV and 164.4 eV in the monolayer regime and respectively 164.4 eV in the multilayer regime. While the 164.4 eV value is associable to the sulphur bonded to C_1 in the intact molecule, the first one (161.9 eV) can be assigned to sulphur no longer covalently bonded to a carbon atom in DET, possibly elemental sulphur whose b.e. value is expected around 162 eV [27,28]. The presence of these two chemically different sulphur atoms supports our hypothesis of a C–S bond breaking, as reported for thiophene adsorbed on $\text{Pt}(111)$ [20]. For DET we observe that at room temperature a cleavage of the C–S bond occurs for a high fraction of the adsorbate; this result is quite similar to that discussed in [20] but different from that observed for thiophene adsorbed on copper [21,22]. An explanation for the presently observed behaviour takes into account the charge withdrawal by the ethynes with a reduction of the C–S bond strength. The XPS study at the sulphur edge provides then additional information about the physical–chemical aspects of the adsorption process. A progressive desorption of the condensed multilayer takes place by increasing the temperature; the interaction with the substrate, more relevant for the first layer, produces a perturbation of the C–S bond with an extended orbital overlap from the metal, influencing mainly C_1 . The C–S bond undergoes cleavage and a Cu–C bond formation possibly occurs.

4. Conclusions

DET multilayer was deposited on $\text{Cu}(100)$ at 90 K. The influence of the temperature on the molecular and electronic structure was investigated by NEXAFS spectroscopy at 90 K, 150 K, 200 K, 245 K and 298 K. In the multilayer regime the aromatic ring is intact. From 90 K up to 155 K a molecular orientational rearrangement probably occurs. Above 160 K desorption starts and a monolayer film is expected to be formed at nearly 200 K. NEXAFS spectra taken at 200 K, 245 K and 298 K, display a band broadening giving an unambiguous indication for a strong interaction with the substrate that could produce a cleavage of the C–S bond and a likely replacement of sulphur with copper.

The XPS $\text{S}2\text{p}$ spectra collected for the condensed multilayer show one single spin–orbit doublet indicating that the molecule is still intact before the desorption starts. The XPS analysis at room temperature indicates, instead, the presence of two $\text{S}2\text{p}$ spin–orbit doublets, assigned to sulphur atoms in the intact DET molecule and to atomic sulphur respectively; the second one appear as the predominant species. The XPS spectrum in the monolayer regime confirms the hypothesis of a strong chemical interaction between Cu and DET giving origin, for a large portion of the adsorbate, to the cleavage of the C–S bond replaced by a Cu–C bond with a partial desulphurisation.

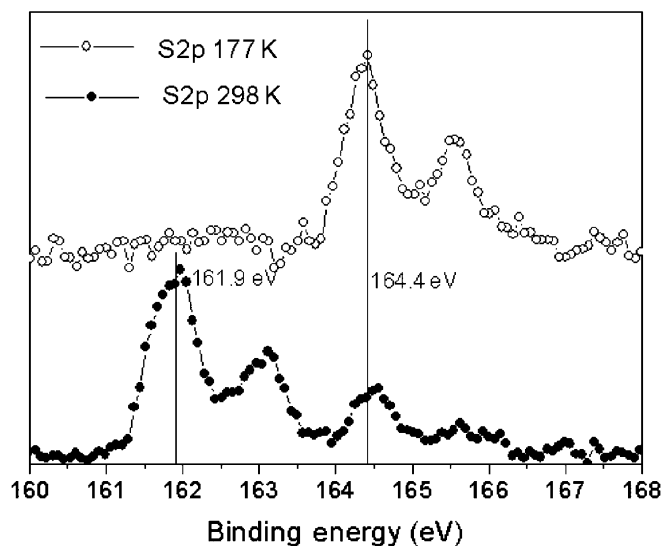


Fig. 4. $\text{S}2\text{p}$ core level XPS spectra for the experiments performed at two selected temperatures, i.e. 177 K and 298 K.

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