

## Photon stimulated ion desorption studies from polypyrrole film doped with $[\text{Ni}(\text{dmit})_2]^{2-}$ anion following S K-edge excitation

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### INTRODUCTION

The synthesis and characterization of polypyrrole (PPy) doped with metal complexes based on dmit (1,3-dithiole-2-thione-4,5-dithiolate) has been reported very recently [1, 2]. Although the conducting polymers based on PPy can offer a combination of the properties that make them attractive alternatives for certain technological application, the physical and chemical effects of the soft x-ray irradiation of theirs have been evaluated for photon energies just above C and N 1s binding energies [3]. Thus, it is important to perform other studies about the interaction of high energy photons with these materials, which are not fully understood. In this work, we have performed NEXAFS and photon stimulated ion desorption (PSID) studies following sulphur K-shell excitation on PPy doped with  $[\text{Ni}(\text{dmit})_2]^{2-}$  as counter anion.

### EXPERIMENT

The PSID measurements were performed in a PPy/ $[\text{Ni}(\text{dmit})_2]^{2-}$  film deposited onto FTO (fluor-tin-oxide) [2], using SXS beamline operating in a single-bunch mode. The experimental set up includes a sample manipulator and a TOF spectrometer (TOF-MS) housed in an UHV chamber with a base pressure of about  $10^{-9}$  Torr. The pulsed synchrotron radiation (SR) was used both a trigger for the experiment and as the start signal for the Time-to-Digital Converter (TDC). The desorbed positive ions were extracted from the sample biased at + 1.5 kV through the entrance grid of the TOF-MS placed at - 2.0 kV and with the lens potential at - 2.0 kV. They were further collimated and transmitted through the 25 cm drift tube, which was kept at a potential of - 3.0 kV. Finally, the ions were detected by the MCP, biased at - 4.6 kV. The mass assignment was performed by simulation of the ion flight time with the program SIMION 3D 6.0 and using a procedure described in detail elsewhere [4]. The photoabsorption spectra were recorded by measuring the electron current at the sample (total electron yield), simultaneously with a photon flux monitor (Au grid). The final data was normalized by this flux spectrum to correct for fluctuations in beam intensity.

### RESULTS AND DISCUSSION

In the Figure 1 is showed the NEXAFS spectrum of PPy/ $[\text{Ni}(\text{dmit})_2]^{2-}$  film obtained following the sulphur K-

edge, covering from 2450 to 2540 eV photon energy.

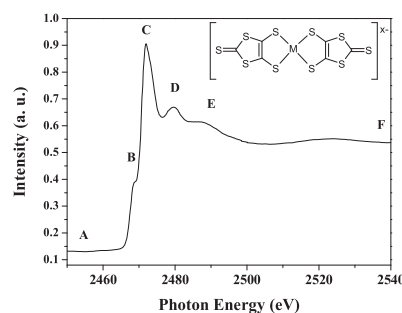


FIG. 1: NEXAFS spectrum of the polymeric film at the sulphur K-edge.

The electronic transitions from 1s electron to unoccupied molecular orbitals were labelled (B-E). In the absence of theoretical calculations, we suggest that the sharp peak C at 2471.8 eV and the shoulder D could be associated to the S 1s to  $\pi^*$  and  $\sigma^*$  (S-C) transition, respectively, in analogy to the thiophene molecule [5]. The less intense structure at 2468.6 eV (peak B) may correspond to a transition from S 1s electron to an orbital possessing (S-Ni) character. The other features may be associated to transitions to higher energy excitations, probably containing Rydberg character, and to  $\sigma^*$  shape resonance. In order to gain insight into the ionic desorption process from this polymeric system at the sulphur K-edge, PSID spectra were obtained at the energies labelled A-F in Figure 1. The corresponding PSID spectra are presented in Figure 2.

As can be seen from this Figure,  $\text{H}^+$  is the main ionic species to desorb after photon excitation followed by other heavier fragments with lower intensities. In the Figure 2, it can be observed the appearance of the peaks associated with the sulphur species  $\text{S}^+$  and  $\text{S}^{2+}$  at the energies corresponding to peaks B, C and D of the NEXAFS spectrum, i.e., they are not observed below the S K-edge. Especially strong is the contribution of the main peak (C) to the desorption of the  $\text{S}^+$  ion. The other structures seem to present no dependence on the photon energy and were tentatively assigned as illustrated in Figure 2. Desorption ion yields for  $\text{S}^+$  and  $\text{S}^{2+}$  ions are presented as a function of the photon energy in Figure 3. They were calculated with respect to the total ion yields. The desorption curve for  $\text{S}^+$  has a maximum at the first S 1s resonance while for  $\text{S}^{2+}$  its maximum appears associated to a higher energy transition (peak D), in the vicinity of the ionization threshold. In the present case, a sulphur KLL Auger process will probably end up in a double S (LVV) process as a result

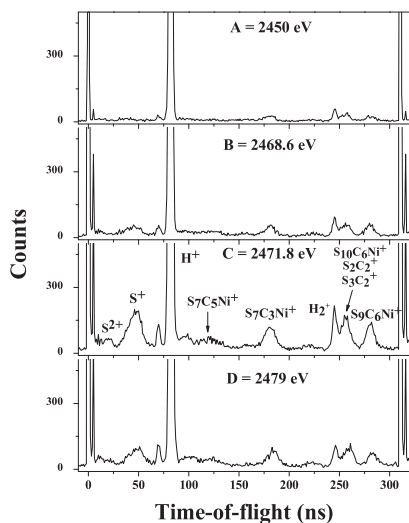


FIG. 2: PSID spectra of polymeric film as a function of photon energy.

of cascading Auger mechanisms giving raise to the following scenarios: a) a final state of the type  $v^4\pi^*/v^{-4}\sigma^*$  (spectator Auger process), and b) a final state given by  $v^4$  (normal Auger process), where  $v^{-4}$  represents four holes in valence orbitals. In the first case, the aromatic character associated to this state would hinder the specificity of the transition while the excess of positive charges characteristic of the second case would favour the ejection of multiply charged species.

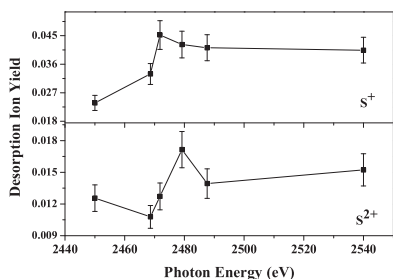


FIG. 3: Desorption ion yield of the selected ions desorbed at the S K-edge.

Indeed, if we compare the ratios between the intensity signals above and below the absorption edge (edge-jump) with the electron yield (NEXAFS spectrum) and the ion yield, it

shows that at the first resonance no enhancement of the  $S^+$  ion yield occurs. This could suggest that the XESD mechanism is responsible for  $S^+$  desorption. However, since no desorption of  $S^+$  was observed below the sulphur K-shell excitation region, the XESD mechanism has to be ruled out. The unspecific bond breakage reflecting in the  $S^+$  yield at the first resonance may be due to the delocalised (aromatic)  $\pi$ -bonding character associated to this transition. This could explain a weaker contribution of  $v^{-4}\pi^*/v^{-4}\sigma^*$  final state resulting from a spectator Auger decay process to the  $S^+$  desorption.

## CONCLUSION

PSID and NEXAFS studies have been performed on  $PPy/[Ni(dmit)_2]^{2-}$  systems at the sulphur 1s-edge. The Auger process seems to play an important role in the desorption of  $S^+$  and  $S^{2+}$  species at the S 1s-edge. Although no enhancement in the  $S^+$  ion yield was observed at the first resonance, the spectator Auger process was used to interpret the results, since no desorption of  $S^+$  was observed below the sulphur K-edge. Furthermore, for the  $S^{2+}$  ion an enhancement at higher photon energies suggests that the normal Auger process dominate. On the other hand, the production of  $H^+$  and molecular fragments seem to be induced by both XESD and ASID mechanisms.

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