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Photoelectron spectroscopy (PES) study of gas-phase 2,5-(2, 2'-dithienyl)diethynyl-thiophene (TRIM): an experimental and theoretical study

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Abstract

The X-ray photoelectron spectra of gaseous 2,5-(2,2'-dithienyl)diethynyl-thiophene (TRIM) in the C 1s and S 2p core level regions have been recorded by means of synchrotron radiation (SR) at ELETTRA. For all the non-equivalent carbon atoms of TRIM, Δ SCF calculations of the C 1s photoelectron spectra, have also been performed. All the carbons of the aromatic rings are perturbed by an electron charge withdrawing. The ethyne carbon atoms are negatively shifted in energy. The relative broadening of the S 2p accounts for the presence of two non-equivalent sulphur atoms. The S 2p_{3/2} ionization potential value is lowered with respect to thiophene by –0.63 eV. © 2001 Published by Elsevier Science B.V.

1. Introduction

There has been great interest in polymeric organic and organometallic compounds showing electronic and optical properties. Among others, π -conjugated materials, such as the polyyne polymers containing transition metals in the main chain, have received great attention because of their importance for molecular electronics [1–3]. These materials show several physical properties arising by the delocalized π -electrons system in-

volving also the metal orbitals, as for instance third-order non-linearity [4], photoluminescence [3,5] and alignment in a magnetic and electrical field [6], properties.

Recently, application of metal-polynes Pd-DEBP and Pt-DEBP, respectively, poly[palladium-bis(tributylphosphine) diethynylbiphenyl] and poly[platinum-bis(tributylphosphine) diethynylbiphenyl], $[-\text{Me}(\text{PBU}_3)_2-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-]_n$, Me=Pd, Pt has been investigated and Pd-DEBP employed as a sensitive membrane in a surface acoustic waves (SAW) device gave a satisfactory response to relative humidity variations [7].

Polarization-dependent near edge X-ray absorption fine structure (NEXAFS) investigations

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revealed the presence of a preferential alignment of the polymeric chain when spin-deposited as thin films even in the multilayer regime [8]. It is well established that orientation effects are important to get fast and high response from materials with non-linear optical (NLO) properties. It is also believed that orientation of polymer chains can improve the acoustic phase velocity variations in organometallic polymer-based gas sensors.

In order to evaluate the changes in properties of the organometallic polymers induced by substituting the conjugated organic spacer, a series of organometallic systems containing thiophene and ethyne alternate groups have been synthesized [9]. The electronic band structure, and in turn the properties of these compounds, depend on the nature of the transition metal (Pt, Pd), its coordination and the conjugation of the π -system. In addition, the hetero-aromatic containing spacers were chosen because thiophene can work as an electron donating group and enhance the third-order NLO properties of macromolecular materials. Two different organic spacers characterized by the presence of an increasing number of thiophenes and triple bond units (DET' and TRI', Fig. 1) were chosen. The Pd(0) catalysis was exploited for the constructions of the thiophene ethynylated spacers [10]; the related organometallic materials were obtained by different reaction conditions, that is Heck [11] and a new *extended one pot* version [9] of the modified Stille coupling procedures [12].

In the characterization of polymeric materials for molecular electronics, small organic molecules are convenient models that can supply helpful information for understanding the properties of polymeric systems. The use of simplified systems allows for a better insight into the electronic structure of the atoms in their chemical environment and the changes occurring as a consequence of insertion of new chemical groups in close proximity or directly bonded to them. In this framework we have begun the investigation of simple organic molecules, that can be taken as models for the organometallic polymers reported in Fig. 1, by photoemission spectroscopy at the C K-edge and at the S L-edge in gas phase conditions. As a starting model molecule, the TRIM oligothienylene-ethynylene molecule has been chosen, because it can be

considered a suitable model for the organic spacers DET' and TRI' (see molecular structures in Fig 1). The C 1s and S 2p photoelectron spectroscopy (PES) study of TRIM carried out in gas phase provided us unique informations about the electronic structure of this oligothienylene-ethynylene molecule, which is representative of the organic part of related organometallic polymers, evidencing charge density variations around the studied atomic species arising from the bonding to chemically different groups.

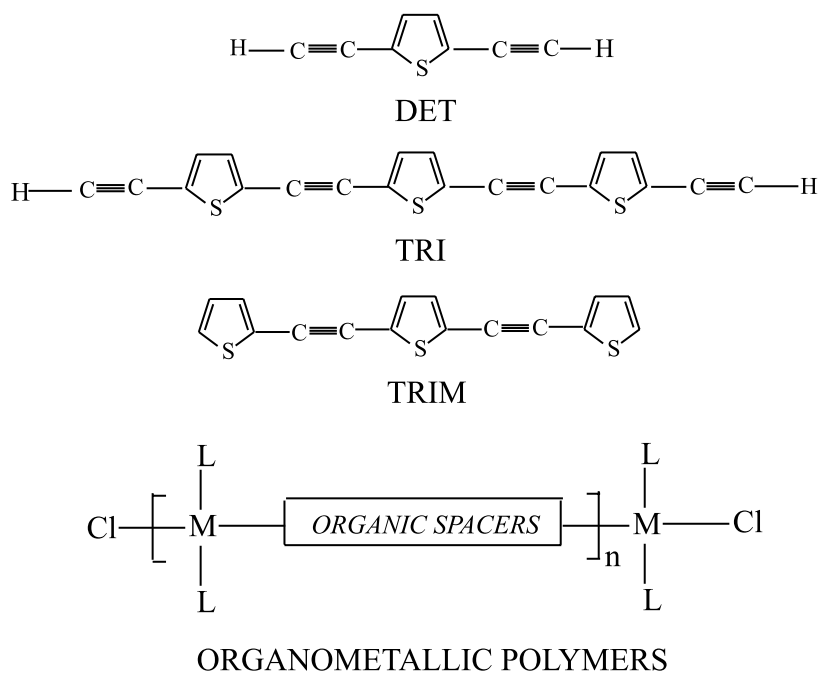
The knowledge of the difference in energy between the carbon atoms in different chemical environments can be also a valid guide for the interpretation of the C K-edge absorption spectra and the assignment of the resonances related to the organic backbone of the polymeric materials containing thiophene reported in Fig. 1, in the π^* resonances region.

Core-level photoemission spectroscopy has been one of the major spectroscopic techniques used to characterize the electronic structure of atoms and molecules. With the use of tunable SR the photon energy can be easily varied, moreover the performance that can be obtained has evolved tremendously due to the rapid development in 'light sources'. The availability of highly monochromatized intense photon beams over a broad spectral range makes it possible to study a great variety of problems by the use of PES.

In this framework we have already performed photoemission [13] and NEXAFS spectroscopy measurements on the synthesized organometallic macromolecular systems. In this Letter, we report a gas-phase photoemission investigation, by SR and by *ab initio* calculation, of the molecule TRIM that is a convenient model for highly ethynylated organic and organometallic materials. The study yielded interesting results allowing a better insight into the electronic structure of such organic spacers and their influence on the whole structure of the organometallic species.

2. Experimental

The synthesis of TRIM has been performed by applying a *one pot procedure* based on the Stille



M= Pd, Pt
L= PBu₃

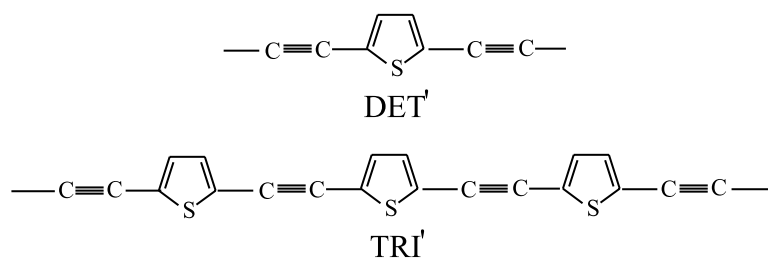


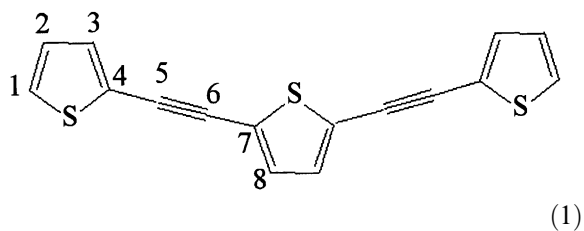
Fig. 1. Chemical structure of DET, TRI and TRIM model molecules, of the organometallic polymers and of DET' and TRI' organic spacers.

coupling. Details of the reaction procedure and characterization will be reported in a forthcoming paper [9] where the chemical structure of the molecule is attributed by ¹H NMR, IR and UV–VIS spectroscopies.

A high purity sample of TRIM was obtained by sublimation at 95°C/4.5 × 10^{−6} mbar, cooling the cold finger to −10°C.

For the purpose of this spectroscopic investigation a freshly synthesized sample has been purified by sublimation, stored in a vessel filled with

argon and introduced into the vacuum chamber. The chemical structure of TRIM is reported here.



The gas-phase PES measurements above the C 1s and S 2p edges were performed at the third generation storage ring ELETTRA (Trieste-Italy), at the Gas-Phase Beamline [14]. The experimental station consists of one 500 mm I.D. cylindrical main vacuum chamber, lined with a double μ -metal shield, connected to the beamline. Gaseous and volatile liquid or solid samples can be introduced into the ionization region through a hypodermic needle mounted on an XYZ manipulator. An efficient pumping system is realized by a 1000 l/s turbomolecular pump resistant to chemicals and a liquid helium cryo pump mounted on large flanges. Differential pumping using several stages of capillary tubing allowed to achieve 4–5 orders of magnitude of difference in pressure between the experimental chamber and the beamline, reducing the risk of contamination of the optical elements. In addition, the molecules–beam interaction region can be enclosed by a liquid-nitrogen-cooled jacket. One 50 mm mean radius VSW emispherical analyzer, with a four-element lens system, has been used for the measurements with one single channeltron electron multiplier, giving a total instrumental (monochromator plus electron analyzer) resolution of 0.4 eV. The analyzer has been used in the constant pass energy mode, with the pass energy set to 25 eV. Before the measurements, the molecular sample was introduced into a resistively heated stainless steel furnace enclosed in a cooled jacket, and left outgassing for several hours at room temperature. For the measurements the crucible, with a small hole on its top, is placed just below the photon beam while the analyzer is set to the magic angle ($\approx 55^\circ$). The high photon flux generated by the third generation storage ring ELETTRA allowed us to get resolved spectra despite the elemental species under analysis was carbon, which is well known to be the main contaminant on the surface of the light optics. The intensity of the C 1s signal was relatively low despite of the high photon flux provided by the undulator beam line and the choice of the low photon energy with respect to conventional XPS laboratory studies. Check of the purity of the sample was performed by analysis of the valence photoelectron band using photons of $h\nu = 25.0$ eV. Photons of 336.9 eV energy have been used for

the measurements, with the monochromator entrance and exit slits fixed at 30 and 120 μm , respectively. The sulphur 2p PES was recorded using 190 eV photons. The sample temperature was kept constant at 72 $^\circ\text{C}$. The base pressure of the chamber without any sample reached the low 10^{-7} Torr range. The collected spectra were energy referenced to the Ar 2p_{3/2} ionization at 248.4 eV and measured simultaneously with the C 1s level. A curve fitting analysis of the C 1s core level bands, shown in Fig. 2, was performed using Gaussian curves as fitting functions.

2.1. Computational

Ab initio calculations of the ionization potentials (IPs) were also carried out for a detailed assignment of the unresolved peaks. The molecular geometry has been computed by means of SCF optimization using GAMESS [15] and Pople's N-31G split valence basis set. The molecule appears to be planar (point group (C_{2v})) with an angle C_6-C_7-S (see figure in the previous section) of about 120° ; there are eight non-equivalent carbon atoms, indicated by labels C_1-C_8 in the figure. A theoretical model neglecting correlation and vibrational effects but including the electronic relaxation around the core hole, may be considered suitable for the analysis of the main features of a

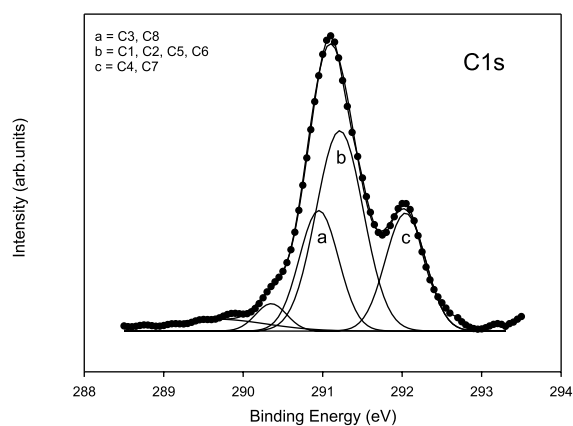


Fig. 2. Curve fitting analysis of the experimental SR-induced C 1s photoemission spectrum detected in gas phase, for the TRIM molecule. Dots represent the experimental spectrum, the continuous lines the fitting components **a**, **b**, **c** and their sum.

molecular core photoelectron spectrum. With this assumption we calculated the IP for each non-equivalent carbon atom (C_1 – C_8) by the Δ SCF procedure, i.e. as the difference between the ground state and the localized core-hole state energies both obtained by direct SCF calculations using DALTON [16]. In order to improve convergence to the correct core-hole state, the initial guess of the half-occupied orbital in the core-hole SCF calculation was obtained from the ground state orbitals by a localization procedure around the ionization site of interest. All calculations for the core-hole states have been performed at the ground state geometry using contracted Gaussian basis sets of triple zeta (TZ) quality consisting of 5s, 3p functions for C and 7s, 5p functions for S, and of double zeta quality for H. Δ SCF calculations of IPs for organic molecules of similar size [17] using the basis sets employed here and a larger one obtained from TZ by adding a polarization d function on the heavy atoms and a third s function on H, have shown that the basis set dependence of the results can be simply described by a small common shift of all IPs. Because the overall shape of the simulated spectrum as well as the assignment of the observed spectral features do not change substantially, we avoided the long CPU demanding calculations with the larger basis set for TRIM. In order to simulate the XPS spectrum, at least the relative intensity of each ionization process should also be computed. This difficult task, requiring the evaluation of a dipole matrix element between the ground state and the final continuum state, can be avoided here because, for X-ray excitation highly above the ionization thresholds as in the present measurements, the variation of such dipole matrix element for the different ionization sites is negligible. We can then assign the same nominal value (1) of intensity to each ionization process and present the theoretical spectrum (arbitrary units) as a bar diagram (see Fig. 3), where the intensity of each peak is simply proportional to the multiplicity of the ionization site. In order to have an easier comparison with the experimental spectra the bar diagram was also convoluted with a Gaussian function of full width at half maximum (FWHM) = 0.5 eV that is intended to reproduce the broadening of the exper-

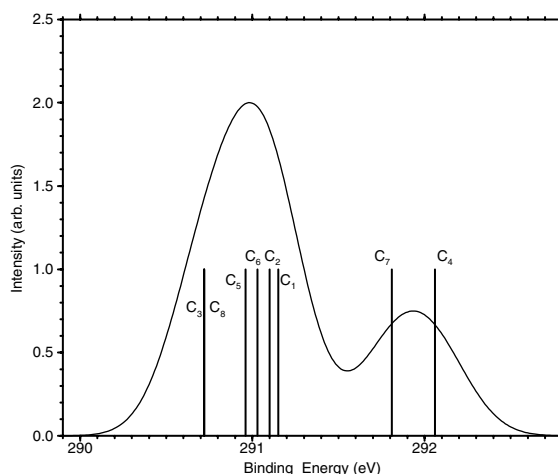


Fig. 3. Calculated (bar diagram) photoemission spectrum of TRIM as obtained from the ionization potential of each chemically different carbon atom computed by the Δ SCF method. The continuum line is a Gaussian convolution (FWHM = 0.5 eV) of the different contributions.

imental peaks due mostly to molecular vibrations and limited instrumental resolution. The use of a Gaussian function here, as well as in the inverse process of the curve fitting analysis of the experimental spectrum, is evidently arbitrary. The effective vibrational lineshape of an XPS peak can certainly be more complex and asymmetric and give origin to a substantially different distribution of intensity, compared to that described by a Gaussian function. However, because the measured spectrum shows large unresolved peaks and detailed information on the vibrational motion of this large molecule is not available, we believe that a Gaussian function may be considered a reasonable compromise.

3. Results and discussion

3.1. C 1s experimental spectrum of TRIM

In Fig. 2 the experimental C 1s spectrum (dots) of the gas phase TRIM molecule is reported, together with the fit results. A main and rather broad peak is evident at a binding energy (b.e.) value just below 291 eV; a well resolved but lower in intensity

component occurs at higher b.e. in close proximity of 291.5 eV and is interpreted as due to more positive carbon atoms. The signal splitting as well as the broadening of the first peak are due to the presence of different IPs of the eight inequivalent carbon atoms of TRIM.

The weak feature at low b.e. values appears quite separated in energy from the main line, in a position where no contributions from the examined molecule are expected. We believe it is probably due to a small amount of impurities present in the residual gas of the analysis chamber used for the experiment.

For the thiophene molecule studied by photoemission spectroscopy the shift in energy between the contribution by the α and β carbon atoms (i.e. bonded to sulphur and not) was reported as being 0.34 eV [18]. This splitting was found somewhat smaller than the 0.59 eV, separation obtained from ab initio calculations performed by Gelius et al. [19], but larger than the results coming from ab initio calculations of Clark and Armstrong discussed by Clark and Lilley [20], who also reported an experimentally determined value of energy shift equal to 0.1 eV. In our case we should take into consideration that the central thiophene brings two chemically bonded ethyne groups on each side of the ring, while the two terminal heteroaromatic rings are linked to only one $\text{—C}\equiv\text{C—}$ group. This is expected to produce a perturbation on the charge distribution around the thiophene ring.

In the present case, the assignment of the different contributions to the experimental spectrum has been performed on the basis of spectroscopic evidence and mainly considering the results obtained from the calculations carried out on purpose on the TRIM molecule. The theoretical

values (ΔSCF) for the ionization potential of each carbon atom of the molecule have been obtained at the ground state optimized molecular geometry.

3.2. Comparison of experimental results with theoretical calculations

The theoretical IPs values have been obtained by the ΔSCF method, subtracting the SCF energy of the ground state of the neutral molecule from the SCF energy of the core-hole state of the ionized molecule for each core orbital of the inequivalent carbon atoms. This approach takes into account fully the electronic relaxation of the system in the presence of the core hole, but does not include the electronic correlation. By this procedure the differences among the ΔSCF IPs (chemical shifts) may be considered as being more accurate than the absolute values. The calculated IPs for TRIM are collected in Table 1.

The analysis performed on the experimental spectrum, considering a set of Gaussian curves, is displayed in Fig. 2, while the energies of the features and proposed assignments are listed in Table 1. Three Gaussian functions denoted as **a**, **b** and **c**, have been used for the fit, respectively at energies of 290.33, 290.59 and 291.43 eV with a % area corresponding to 22.61:45.13:22.61, respectively. Although each core ionization process may have a different vibrational structure and therefore a different broadening of the peak, a first estimate based on the computed C 1s ionization potentials for the eight carbons of the molecule and on the measured band intensity gives a ratio of 2:4:2 in agreement with the molecular structure. The peaks width, reported in Table 1, is different (**b** > **c** > **a**) due to the band broadening introduced by the increasing separation between the different con-

Table 1

Comparison between experimental and calculated IPs for the three spectral bands (**a**, **b**, **c**, see Fig. 2) attributed to the eight chemically different types of carbon atoms of TRIM^a

Peak Type	Experimental IP	Calculated IP	FWHM (eV)	% Area
a C3, C8	290.33	290.72, 290.72	0.55	22.61
b C1, C2, C5, C6	290.59	291.15, 291.10, 290.96, 291.03	0.66	45.13
c C4, C7	291.43	292.06, 291.81	0.61	22.61

^a Data are in eV. Intensity of bands **a**, **b**, **c** are also given in %.

tributions, as determined by the calculations of the IPs and discussed in the following.

In Fig. 3 the calculated bar spectrum (eight inequivalent carbons) of TRIM is reported; the bars have been labeled with the number of the corresponding carbon atoms, while the continuum line is a convolution of the bars spectrum with a Gaussian function (FWHM = 0.5 eV).

A good agreement between experiment and theory is observed by comparing the spectra of Fig. 2 (experimental) and Fig. 3 (calculated) both for the position of the bands and for their intensity ratios that are fairly similar. The assignment of the peaks, made on the basis of both the IPs calculations and the chemical structure, is given in Table 1, with details about the different components of the line as derived from calculation of the theoretical spectrum and deconvolution of the experimental one.

Comparing the C 1s b.e. values determined for C α and C β in thiophene as 290.5 and 290.2 eV [18] respectively, with the theoretical IPs value here reported it is clear that all the carbon atoms of the thiophene rings in the TRIM molecule are perturbed by the presence of the two ethyne groups. A positive shift occurs for all of them even if to a different extent, as shown in the following: C1 (+0.65 eV), C2 (+0.90 eV), C3 (+0.52 eV), C4 (+1.56 eV), C7 (+1.35 eV) and C8 (+0.52 eV). This comparison is reasonable since for benzene Gelius et al. [18] reported a C 1s b.e. of 290.2 eV and we experimentally find a C1s b.e. value of 290.16 eV for the benzene-like carbons of phenylacetylene and 290.39 eV by Δ SCF calculations [17]. The energy shifts reported above result markedly higher for carbon atoms C4 and C7, which are bonded both to the sulphur and to the ethynyl group. At the same time, by comparison with the C 1s b.e. value (291.47 eV) calculated for acetylene [17], a negative shift occurs for the IPs of the acetylenic carbons in TRIM, C5 (−0.51 eV) and C6 (−0.44 eV) resulting from a more effective electron relaxation around these two core holes due to an electron charge withdrawing from the thiophene units. This effect is stronger for C5, bonded to the terminal thiophene ring. A parallel antiscreening effect occurs for the thiophenic carbon C7 and more markedly for C4 (highly antiscreened).

The carbon atom C1 bonded to sulphur shows lower charge density than expected on the basis of literature reports concerning thiophene [18]. The differentiation in b.e. between C α and C β found for thiophene is essentially removed in the TRIM molecule. In the case of the carbon atoms C1 and C2 it is only 0.05 eV while between C1 and C3 we still detect a difference of 0.43 eV. Comparing the separation in energy between C α and C β thiophenic carbons measured for TRIM with the values predicted by previous investigations on thiophene [18], we find that the differentiation disappears between C1 and C2, while in some way it is still preserved between C1 and C3, despite that the local atomic charge density is lowered for all of them. The IPs of the ethyne groups are also a little bit higher (0.27 eV) than the most negative carbons (C3 and C8). From the above analysis we can conclude that the molecule experiences a dramatic reorganization of charge density around the carbon atoms due to electron charge withdrawing and to conjugation. The effects of such reorganization on the core electronic structure, and on the IPs of the different atoms cannot be easily predicted by considering the chemical structure and adopting a simple building block approach. Such effects are sometimes surprising and only calculations performed using appropriate methods can help in fully elucidating them.

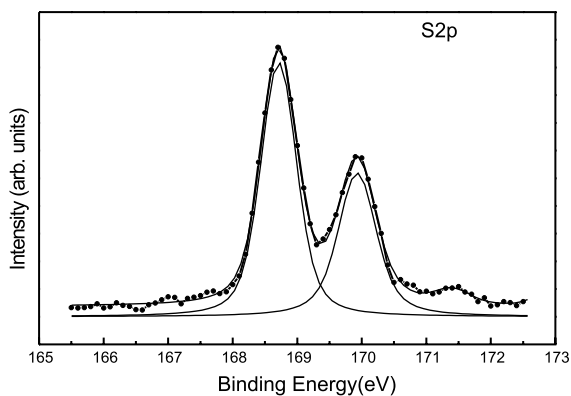


Fig. 4. S 2p experimental spectrum as measured by SR-induced photoemission in gas phase of TRIM. Dots represent the experimental spectrum, the continuous lines the fitting components and their sum.

For the purpose of completeness the S 2p spectrum was also recorded. The $2p_{3/2}$ and $2p_{1/2}$ spin-orbit components are resolved, as can be seen in Fig. 4, where the deconvolution of the two contributions is also shown. The S 2p spectrum was calibrated in the same way as the carbon spectrum, by using the Ar $2p_{3/2}$ line at 248.4 eV. The measured S $2p_{3/2}$ core level b.e. value is 169.27 eV. The value measured for this sulphur line is lower than the value of 169.9 eV reported by Gelius et al. [18] for thiophene in gas phase, resulting in a shift of 0.63 eV towards lower b.e. values. Apparently the normal electron charge withdrawing effect exerted by sulphur toward the ring carbons, is enhanced by the presence of ethyne bridging groups. This result is in some way surprising and not predictable on the basis of simple models considering the molecular structure of TRIM and the expected chemical behavior of these chemical species. Therefore, considering the observed effects on the whole molecule we can deduce that the electron charge perturbation involves all the atoms of the molecule and finally that charge delocalization occurs involving all the different units of TRIM (thiophene and acetylene).

The line width of the two S 2p peaks is found to be 0.7 eV and their separation 1.15 eV. The latter value is similar to those reported in the literature for solid thiophene (1.25 eV [18] and 1.0 eV [21]), for polythiophene solid films (1.2 eV [22]) or to the value (1.3 eV) found by our group for the corresponding organometallic polymers [13]. The observed 0.7 eV line width value might be considered a little higher than expected; this could be justified by the presence of two inequivalent sulphur atoms in the TRIM molecule.

4. Conclusions

The carbon 1s core level spectrum has been acquired for the molecule TRIM in the gas phase Δ SCF calculations with basis set of TZ quality were carried out for all the chemically inequivalent carbon atoms of the TRIM molecule. Curve fitting analysis of the experimental spectrum allowed to compare experiment and theory. The overall agreement between theoretical and spectroscopic

results was excellent. The results give a complete picture of the electronic charge perturbation caused by linking thiophene units by means of ethyne bridging groups. A significant increase of the ionization potentials for the thiophenic α carbon atoms bonded to the ethynes, by about 1.56 eV for C4 and 1.35 eV for C7 is observed. The electronic charge reorganization effect extends all over the thiophene rings; the β carbons are affected as well, but to a minor extent. The S 2p core level photoelectron spectrum does not show clearly the presence of two chemically different sulphur atoms, that could be expected on the basis of chemical structure considerations. If present, the effect is below the energy resolution achieved in the present experiment. However, since the line width of the sulphur line appears a little higher than expected, this can account for the presence of two inequivalent sulphur atoms. The measured IP for the S $2p_{3/2}$ core level gives an indication of a small increase of local charge density with respect to thiophene resulting from a more effective charge withdrawing from the neighboring carbon atoms.

Acknowledgements

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