



# Tetrathia- and tetraselenafulvalene adsorbed on Ag(110): A theoretical study

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## ABSTRACT

We have studied the adsorption properties of the  $\pi$ -donor molecule TXF, where X stands for the chalcogens sulfur and selenium [TTF = tetrathiafulvalene, TSF = tetraselenafulvalene], respectively, on the (110) surface of silver by means of periodic plane-waves based DFT (Density Functional Theory) calculations using slab models. We have determined and characterized the stable adsorption sites and have evaluated the charge transfer from TXF molecules into the surface. The simulation of the vibrational spectra for TXF and the fully deuterated TXF species has permitted to identify the fingerprints of both molecules on this surface.

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## 1. Introduction

Despite the vast amount of information, both from the experimental and theoretical points of view, existing on molecular organic materials based on functionalized derivatives of the  $\pi$ -donor molecules TTF and TSF [1–6], surprisingly little work has been devoted to the interaction of such molecules with ordered surfaces. TXF (see Fig. 1) is the core building block of a host of molecular materials exhibiting complex and extremely rich phase diagrams with a variety of ground states: metallic, Mott–Hubbard, spin–Peierls, antiferromagnetic, spin and charge density wave, and superconducting.

The interest on interfaces involving TXF-derivatives primarily arises from the intrinsic two-dimensional (2D) character of most molecular materials, where molecules organize in segregated planes with a periodic distribution of alternate molecular planes containing either donor or acceptor molecules in charge transfer salts, or donor and anions in radical cation salts. Such a distribution justifies the use of the term chemically constructed multilayers [7].

One of the most prominent derivatives of TXF is TMTSF, tetramethyl-tetraselenafulvalene, base of the celebrated Bechgaard salts, quasi-one-dimensional (1D) organic mixed-valence radical cation salts with the general formula (TMTSF)<sub>2</sub>Y, where Y stands for a monovalent anion. The first compound exhibiting a metal–superconductor transition was (TMTSF)<sub>2</sub>PF<sub>6</sub>, with a transition temperature  $T_c = 0.9$  K above  $P = 1.2$  GPa [8] and (TMTSF)<sub>2</sub>ClO<sub>4</sub> was the first ambient pressure organic

superconductor, with  $T_c = 1.4$  K [9]. The isostructural salts based on TMTTF [tetramethyl-tetrathiafulvalene] are called Fabre salts.

To our knowledge, only a few studies have been devoted to the formation of layers of TTF-derivatives on crystalline surfaces. The first one was a combined Scanning Tunnelling Microscopy and DFT study of TTF on Au(111) in the submonolayer regime, where it was shown that at low coverages (below 0.2 ML), in absence of short-range attractive lateral interactions, charge transfer from TTF into the surface induces coulombic long-range repulsive interactions, leading to the formation of 1D Wigner crystals [10]. The adsorption of TTF on gold and silver surfaces has been investigated by means of DFT simulations, revealing the nonplanarity of the molecule and its ability to transfer part of the electronic density to the surface [11,12]. Moreover, the comparison of IR spectra for gas phase TTF and TTF adsorbed on silver and gold surfaces indicates the small geometric distortions of the molecule upon the adsorption process [12]. On the other hand, exTTF layers grown on Au(111) have been characterized from the experimental and theoretical points of view, where exTTF stands for 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole, a derivative of TTF with a butterfly shaped nonplanar structure [13]. In this case only one of the two dithiole rings is in close contact with the surface due to conformational reasons, in contrast with TTF on Au(111), where both dithiole groups interact with the gold surface.

The aim of the present work is to compare the adsorption properties of TTF [12] and TSF on Ag(110). We have structured it in two parts. First, we compare the geometrical parameters and vibrational IR spectra for TTF and TSF in the gas phase. Then, these organic moieties are adsorbed on the Ag(110) surface and their adsorption properties such as structural parameters, Reflection Absorption Infrared (RAIR) spectra and charge transfer into the surface are contrasted.

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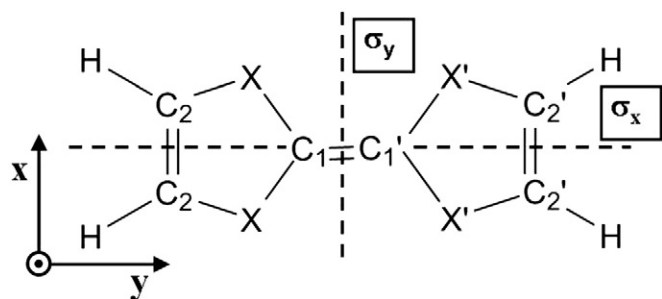


Fig. 1. Scheme of TXF (X=S, Se) showing the labeling used and the mirror planes of symmetry  $\sigma_x$  and  $\sigma_y$ .

## 2. Computational details

In this study we have performed periodic slab calculations in the DFT framework using the Vienna Ab Initio Simulation Package (VASP) [14–16]. To solve the Kohn–Sham equations, this code makes use of a development of the one-electron wave function in a basis of plane-waves. The effect of the core electrons on the valence electrons is described by the projector augmented wave (PAW) method [17,18]. The plane-wave expansion was converged with a cut-off of 500 eV. The generalized gradient approximation (GGA) was used with the functional of Perdew and Wang (PW91) [19]. The 2D Brillouin integrations were carried out on a  $6 \times 4 \times 1$  Monkhorst-pack grid.

Based on our previous work [12] we used a 10 Å cubic unit cell to perform the calculations for the gas phase. In order to check the effect of the box size in our calculations, we increased the cubic unit cell to 20 Å. The use of a 20 Å unit cell has no effect either in the energies or in the geometrical structure of TTF and TSF. For TTF, the difference in energy between the two unit cells was less than 1 kJ mol<sup>-1</sup>; for TSF this difference was slightly higher (3 kJ mol<sup>-1</sup>). Such differences are below the precision limit of the method used, which is estimated to be about 5 kJ mol<sup>-1</sup>. The differences in geometrical parameters were less than 0.01 Å in bond distances and less than 0.1° in bond angles. The calculated vibrational frequencies and vibrational normal modes (VNM) were also independent of the unit cell used: frequencies had variations of less than 5 cm<sup>-1</sup> and VNM were the same for both unit cells. However, dipole moments (and, as a direct consequence, IR intensities) changed with the use of the larger unit cell, in a strong way for TSF, and in a more limited way for TTF. For this reason, we only report here results for the 20 Å unit cell.

The (110) surface of Ag has been modeled by a 2D slab in a 3D periodic cell generated by introducing a vacuum width in the perpendicular direction to the surface (~17.5 Å, equivalent to eleven metal layers). The slab contains four atomic metal layers with the donor molecule adsorbed on one side of the slab. The Ag–Ag interatomic distance was optimized for the bulk, being the resulting calculated value 2.94 Å, which is larger than the experimental value of 2.89 Å [20], as expected because the known trend of GGA functionals to overestimate interatomic distances [21,22]. We have considered a  $2 \times 4$  unit cell, associated with the low molecular coverage of 1/8 ML. The optimization of the geometry included all degrees of freedom of the adsorbed molecule and the uppermost atomic metal layer. The three lower metal planes were kept fixed at the optimized bulk geometry. In all calculations, the position of the ions was relaxed by a conjugate-gradient algorithm until the forces were smaller than 0.02 eV Å<sup>-1</sup> setting the electronic convergence criterion to 10<sup>-6</sup> eV. Once the equilibrium geometry of each system was obtained, the vibrational frequencies and the corresponding normal modes were calculated using the harmonic approach. The Hessian matrix elements were obtained by numerical differences of the analytical gradients, with two displacements of 0.02 Å for each atomic Cartesian coordinate. In order to simplify the treatment, the coupling of the molecular vibrations and the surface phonons was neglected, as in a recent study

of propyne on copper surfaces [23]. The IR intensities have been calculated using the IRIAN external code especially developed for this purpose [24,25]. The VASP code computes the dipole moment ( $\mu$ ) components at each nuclear configuration used for the construction of the Hessian matrix. The IRIAN code computes a numerical estimate of the dipole moment derivatives,  $\partial\mu/\partial r$ , on the basis of the atomic Cartesian displacements. Then, the dynamic dipole moments of the vibrational modes ( $\partial\mu/\partial Q_k$ , first derivative of the dipole moment with respect to the normal mode  $Q_k$ ) are also computed to estimate the intensities (I) of the IR spectra ( $I \propto \partial\mu/\partial r$ ) or RAIR spectra ( $I \propto \partial\mu_z/\partial r$ ), where  $\mu_z$  stands for the z component of  $\mu$ . We have also obtained the spectra of the fully deuterated molecules, TTF-D4 and TSF-D4, using the IRIAN code, since experimentalists often obtain deuterated spectra in order to facilitate the assignment of the bands. Finally, we have rounded the vibrational frequencies off to multiples of 5, since the precision limit of the method is 5 cm<sup>-1</sup>, as mentioned above.

The adsorption energy,  $E_{ads}$ , is defined as the difference between the energy of the adsorbed molecule system,  $E_{adsorbate-slab}$  and the sum of the energy of the bare surface,  $E_{slab}$ , and the energy of the gas phase molecule,  $E_{gas-phaseTXF}$ ,  $E_{ads} = E_{adsorbate-slab} - (E_{slab} + E_{gas-phaseTXF})$ . A negative value indicates an exothermic adsorption process.

Bader's charge analysis was performed using the code developed by Henkelman et al. for this purpose from the charges calculated by VASP [26–28]. The analysis was carried out with the total charge density, i.e. including the core and valence electrons.

## 3. Results and discussion

### 3.1. TTF and TSF in the gas phase

The optimized structures of TTF and TSF in the gas phase are given in Table 1. The ideal configuration of the TXF molecule corresponds to a flat geometry, thus belonging to the  $D_{2h}$  point group (see Fig. 1). However, the molecule is distorted which leads to a point group with a lower symmetry ( $C_{2v}$ ). C–H and external C–C bonds are equal for both moieties, 1.09 and 1.34 Å, respectively, being the inner counterpart slightly shorter, 0.01 Å, for TSF than TTF (1.35 and 1.36 Å, respectively). These distances are similar to those of ethene (1.34 Å), indicating the existence of double C–C bonds and no aromaticity in the molecules. As expected from the difference in covalent radii between S and Se (0.15 Å) evaluated in a recent paper of Cordero et al. [29], the Se–C distances are between 0.13 and 0.15 Å larger than for S–C, being the C<sub>1</sub>–Se bond 0.02 Å larger than the C<sub>2</sub>–Se contact (1.92 and 1.90 Å, in each case). The bond angles show small variations between both molecules, corresponding the largest one to the C<sub>1</sub>–Se–C<sub>2</sub> angle, which is 4° smaller for TSF (92° and 96°, respectively). This is expected from the larger Se covalent radius with respect to S. The most changing parameter is the bending angle of the

Table 1

Geometrical parameters and adsorption energies ( $E_{ads}$  in kJ mol<sup>-1</sup>) of TTF and TSF in the gas phase and adsorbed on Ag(110). d (Å),  $\alpha$  and  $\theta$  (degrees) correspond to the distance, angle and bending angle, respectively, while X = S or Se.

	TTF [12]		TSF	
	Gas	Adsorbed	Gas	Adsorbed
d(C <sub>1</sub> –C <sub>1</sub> )	1.36	1.36	1.35	1.35
d(C <sub>1</sub> –X)	1.77	1.76	1.92	1.92
d(X–C <sub>2</sub> )	1.77	1.75	1.90	1.91
d(C <sub>2</sub> –H)	1.09	1.09	1.09	1.09
d(C <sub>2</sub> –C <sub>2</sub> )	1.34	1.34	1.34	1.34
$\alpha$ (C <sub>1</sub> –C <sub>1</sub> –X)	123	123	123	122
$\alpha$ (C <sub>1</sub> –X–C <sub>2</sub> )	96	94	92	92
$\alpha$ (X–C <sub>2</sub> –C <sub>2</sub> )	117	117	120	120
$\alpha$ (X–C <sub>2</sub> –H)	119	117	116	116
$\theta$	14	11	22	11
d(X–Ag)	–	2.73	–	2.76
$E_{ads}$	–	–86	–	–101

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