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DFT investigation of 2-mercaptobenzothiazole adsorption on model oxidized copper surfaces and relationship with corrosion inhibition

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Abstract

2-mercaptobenzothiazole (MBT) is known as an efficient corrosion inhibitor for copper. In the present work, we performed quantum chemical DFT calculations of the interaction of MBT on Cu(111) surfaces covered by an ultrathin Cu₂O(111) film, in order to bring atomic scale insight on the corrosion inhibition properties of MBT on oxidized copper surfaces. Thione and thiolate forms of MBT are found to interact strongly with the oxidized surfaces. The formation of a monolayer at full coverage is favored over single molecular adsorption at low coverage with the molecules adopting a perpendicular orientation. Thione binds strongly via covalent bonding between the exocyclic sulfur atom and the under coordinated Cu site, and additional H-bonding between the NH group and surface oxygen atoms (NH...O H-bond). Thiolate binds more strongly via a second covalent bond between the N atom and saturated Cu site. Bonding interaction is confirmed by the electronic structure analysis and charge transfer. The adsorption process leads to the reconstruction of the topmost oxide surface. The calculations suggest that both forms of MBT may substitute H₂O and OH at the Cu₂O film surface, and thus may form a protective layer on oxidized copper surfaces in aqueous environment.

Keywords: 2-mercaptobenzothiazole, Copper, Oxide, Corrosion, Organic inhibitor, DFT

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1. Introduction

Corrosion of metals and alloys is an ubiquitous phenomenon with huge economic impact, which affects many industrial sectors. Its prevention is thus a crucial issue. One of the solutions to mitigate corrosion is the use of organic corrosion inhibitors [1, 2, 3], that are considered as promising candidates to replace chromate-based coatings [4, 5, 6]. Various organic compounds containing nitrogen, oxygen and sulfur heteroatoms, polar functional groups, and conjugated double bonds are used to prevent the corrosion of copper [7, 8, 9, 10, 11, 12, 13, 14].

Among these organic molecules, 2-mercaptobenzothiazole (MBT) has been shown to improve the corrosion resistance of copper in various conditions. Indeed, MBT exhibits different active sites and may have different types of interaction with the surface (H-bonding, electrostatic, covalent bonding). Still, the question of the detailed interaction and monolayer formation of MBT in its various forms (thiol, thione, anionic) on copper surfaces in metallic or oxidized or passivated states, remains opened.

Several experimental works showed that MBT exhibits corrosion inhibition efficiency on copper. Chadwick and Hashemi [15] studied the corrosion inhibition of copper by MBT and MBI (2-mercaptobenzoimidazole) in different experimental conditions (pH, immersion time and presence of Cl and copper ions) using X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger spectroscopy (X-AES). They found that the formation of a Cu-MBT film is possible under all conditions and that the organic film thickness depends on the pH of the treatment solution, which reflects the stability and thickness of the Cu₂O passivating surface oxide. In the Cu₂O stability domain (pH>4), the thickness of organic films cannot exceed the monolayer without copper ions in the solution, whereas, in the Cu₂O instability domain (pH<3), the thickness of the organic film may be increased to any desired value. Ohsawa and Suetaka [16] used various spectroscopy techniques in order to clarify the mechanism of corrosion inhibition of Cu by MBT and showed the formation of a surface film that acts as barrier isolating the metal from the corrosive media. The mechanism would consist of the surface reaction of cuprous ions with adsorbed MBT and not of a complex precipitated from bulk solution and involving the ionized thiol form and copper ions in ethanol solution [17]. Because corrosion processes are highly sensitive to pH,

Ramírez-Cano et al. [18] imaged in situ the pH distributions produced in the surrounding electrolyte by the interaction of MBT with copper by using scanning electrochemical microscopy (SECM) in potentiometric mode. They concluded that the presence of an adsorbed MBT film on Cu shifts the pH towards more alkaline values in a small volume of NaCl solution.

Some studies also investigated the adsorption sites and film formation in different experimental conditions. Finšgar and Merl [19] showed using electrochemical techniques that in chloride media MBT acts as mixed-type (i.e. anodic and cathodic) inhibitor on copper. The surface layer thickness was estimated to be 1.5 ± 0.5 nm and the adsorption of the thione form (MBTH) via the N and exocyclic S atoms to Cu was concluded from XPS measurements. Kazansky et al. [20] determined similar adsorption mechanism of MBT in neutral phosphate media. However, Woods et al. [21] investigated by Surface Enhanced Raman Spectroscopy (SERS) the interaction of MBT with copper, silver and gold surfaces. They found that MBT chemisorption on all three metals involves bonding between the exocyclic S and metal atoms. They concluded using XPS, that the surface layer is of monolayer thickness. In contrast, Shahrabi et al. [22] reported that the adsorption of inhibitors (MBT, MBI and MBO) on copper in sulphuric acid solution is physical via electrostatic interaction and that no covalent bonding between inhibitor molecule and metal surface is established.

The synergistic effect of MBT with other species has been established. He et al. [23] investigated the corrosion inhibition of MBT with and without the presence of halide ions on copper in sulfuric acid solution. They concluded that the growth kinetics of the Cu-MBT film depends on the concentration of ions and that I^- promotes the synergistic formation of the protective film. Bao et al. [24] used MBT to develop antibacterial coatings, aiming to solve microbiologically influenced corrosion (MIC) problems. MBT doped chitosan/11-alkanethiolate acid composite coating was found to improve copper protection (anticorrosion and antibacterial) in NaCl solution and in the presence of sulphate reducing bacteria (SRB). Moreover, the MBT molecule inhibited both anodic and cathodic reactions [17, 18, 22, 24].

The surface state of copper has an impact on MBT adsorption. Chadwick and Hashemi [15] demonstrated the influence of the oxidation state on MBT adsorption. Kazansky et al. [20] suggested that a thin Cu_2O layer is required for the formation of the MBT layer, which thickness would depend on the immersion time in neutral phosphate media. Recently, Chen and Erbe. [25] reported using in situ infrared and Raman spectroscopy that in reducing con-

74 ditions in alkaline electrolyte, MBT forms a monolayer on the oxide free Cu
 75 surface and prevents oxide formation. The inhibiting effect of a pre-adsorbed
 76 monolayer of MBT on oxide fomation is also found from studies of adsorption
 77 from the gas phase on surfaces prepared in well-controlled conditions under
 78 ultra low pressure [26, 27]. Thus, it appears that the oxidation state of the
 79 Cu surface (metallic or covered by an oxide layer) is a determining factor in
 80 the interaction of MBT with copper.

81 MBT also interacts with other metal and metallic alloy surfaces and
 82 can be used for the protection against corrosion of aluminum and its al-
 83 loys [28, 29, 30, 31, 32, 33, 34], steel [35, 36, 37, 38, 39, 40], brass [41, 42] and
 84 nanocomposite [43]. Others studies investigated the corrosion and lubrica-
 85 tion properties of MBT on bronze [44] and self-healing coatings properties on
 86 magnesium and its alloys [45, 46]. The adsorption geometries of MBT mono-
 87 layers on zinc [47], silver [21, 48, 47] and gold [21, 49, 50, 51] surfaces and gold
 88 nanoparticles (AuNPs) [52] were also investigated by various experimental
 89 techniques.

90 Thus, although corrosion inhibition is well established, the adsorption
 91 mechanisms of MBT, including the role of the surface oxide, are still subject
 92 to discussion and theoretical calculations are missing to clarify the MBT-
 93 copper interaction. Quantum calculations approach can help us to under-
 94 stand how inhibitors build up protective barriers against corrosion by inves-
 95 tigating the interaction mechanisms on metallic and oxidized surfaces at the
 96 atomic and sub-atomic scales.

97 Very few quantum chemical studies adressed the MBT molecule and its
 98 adsorption. Theoretical calculations of the molecular properties showed that
 99 the molecule can exist in different forms in solution [39] and suggested that
 100 the thione form is a better inhibitor for steel than the thiol form. Cen et
 101 al. [35] proposed that MBT adsorbs via N and exocyclic S atoms on carbon
 102 steel (Fe). The combined first-principles and experimental study of Zhang
 103 et al. [53] showed that MBT is more able to protect Cu(220) and not able
 104 to protect Cu(200) and Cu(111) surfaces in the metallic state at low Cl
 105 concentration. MBT was found to adsorb via physical bonding on Cu(200)
 106 and Cu(111), while it chemically bonds via two sulfur atoms on Cu(220).
 107 The highest chemical activation of the (220) face would drive the better
 108 anti-corrosive ability than on the (200) and (111) faces. Vernack et al. [54]
 109 studied MBT (thiol, thione, thiolate) adsorption on Cu(111) surfaces in the
 110 metallic state. They found that the most stable configuration is that of a
 111 monolayer of the thiolate form in a perpendicular orientation and adopting a

112 ($\sqrt{7} \times \sqrt{7}$) R19° superstructure, the molecules being bonded to the Cu atoms
 113 via the exocyclic S atoms on Cu(111) surface. Bonding to Cu atoms via the
 114 S atoms was confirmed by an experimental study of the adsorption of MBT
 115 from the gas phase on oxide-free Cu(111) surfaces controlled at the atomic
 116 scale [26, 27].

117 From the examination of literature data, it thus appears that the adsorp-
 118 tion of organic inhibitors on metal and alloy surfaces and the formation of
 119 protecting layers is well established. The affinity of MBT with the metallic
 120 Cu surface has been clearly demonstrated by experimental [26, 27, 25] and
 121 theoretical [54] data. However, to the best of our knowledge, no theoretical
 122 studies of MBT adsorption on oxidized copper surfaces has been performed
 123 to complement the experimental knowledge. Indeed, depending on pH and
 124 potential, the Cu surface will be oxidized or reduced [55].

125 Here we report a Density Functional Theory (DFT) study of the adsorp-
 126 tion of MBT on an oxidized Cu surface. Modeling a metal surface covered
 127 by a ultrathin oxide layer is a challenging task. Most often, the strategy is
 128 either to use a metal surface covered by an oxygen or water overlayer, or
 129 the termination of a bulk oxide. On Cu(111), Gharachorlou et al. [56] mod-
 130 eled one monolayer of Cu₂O on the Cu surface and Park et al. [57] modeled
 131 only a mildly oxidized (p4:O/Cu(111)) copper surface, while other groups
 132 [58, 59, 60] modeled oxidized Cu surfaces by considering the termination of
 133 a Cu₂O bulk structure.

134 Here we use a much more realistic model for the Cu surface passivated
 135 by a surface oxide (Cu(111)||Cu₂O(111)) derived from experimental studies.
 136 In order to better understand the role of the oxide layer, two thicknesses
 137 were considered. On these models, the MBT molecule was adsorbed and the
 138 molecular coverage, molecular conformer and energies of adsorption were sys-
 139 tematically investigated. The adsorption of MBT is compared to water and
 140 OH adsorption in order to investigate in which conditions MBT is adsorbed
 141 at the solid/liquid interface with the passivated surface.

142 2. Computational details

143 All calculations were performed in the framework of DFT with the peri-
 144 odic plane-wave basis set code VASP (Vienna Ab initio Simulation Package)[61,
 145 62, 63, 64]. All results reported have been obtained with projector-augmented-
 146 wave potentials using a 450 eV plane-wave cut-off [65, 66]. The Gener-
 147 alized Gradient Approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)

functional was used for the exchange-correlation term [67, 68]. We used a Methfessel–Paxton smearing [69]. Because of the large unit cell size used in calculations, the Brillouin-zone sampling was restricted to the Γ -point [70]. Van der Waals contributions were considered in the local van der Waals density functional scheme proposed by Dion et al [71] and Klimeš et al [72, 73, 74] and calculations were carried out using OptB86b-vdw level [73]. Atomic positions were relaxed with the conjugate gradient (CG) algorithm until forces on each moving atom were less than $0.02 \text{ eV}\text{\AA}^{-1}$.

In the unit cell, the substrate is represented by four layers of copper metal having the (111) orientation and covered by a (111)-oriented Cu_2O ultrathin oxide film with thickness of 5.89 or 11.07 \AA . The detailed description (construction, optimisation, energetic and electronic properties and reactivity with water and OH groups) of the model will be presented in a separate article. Only a summary is given below. The MBT molecules were adsorbed on top of the oxide layer. The vacuum region was set at more than 18 \AA to minimize the interactions in the z direction between periodic images of the system.

2.1. Passivated surface model

Fig.1 shows the constructed model of the passivated surface as derived from experimental data [75, 76, 77, 78, 79]. The model elaborated for the oxidized $\text{Cu}(111)||\text{Cu}_2\text{O}(111)$ surface consists of the $\text{Cu}(111)$ metal substrate covered by the stoichiometric $\text{Cu}_2\text{O}(111)$ oxide film in parallel epitaxy: $\text{Cu}(111)[110]||\text{Cu}_2\text{O}(111)[110]$. Because of the perfect fit between the oxide and metal substrate lattices over a coincidence length of 17.87 \AA [76, 79], we use the lateral dimensions of the supercell of 17.81 \AA in both x and y directions, which corresponds to (7×7) and (6×6) supercells for $\text{Cu}(111)$ and $\text{Cu}_2\text{O}(111)$, respectively.

The two studied thicknesses of the oxide structure, 5.89 \AA and 11.07 \AA , correspond to two and four $\text{Cu}_2\text{O}(111)$ layers, respectively. The oxide layers are kept free to move. The two bottom layers of the $\text{Cu}(111)$ metal are fixed and two interface layers are kept free to move, aiming to optimize the interface interaction with the oxide film.

For the adsorption of the organic molecule, we considered three surface states of the oxide layer as shown in Fig.1. In the dry surface state, the bare $\text{Cu}_2\text{O}(111)$ surface exhibits two distinct copper sites: coordinatively saturated (*csa*) and coordinatively unsaturated (*cus*) Cu atoms, labeled as Cu_{csa} and Cu_{cus} , respectively. It contains also two distinct oxygen sites:

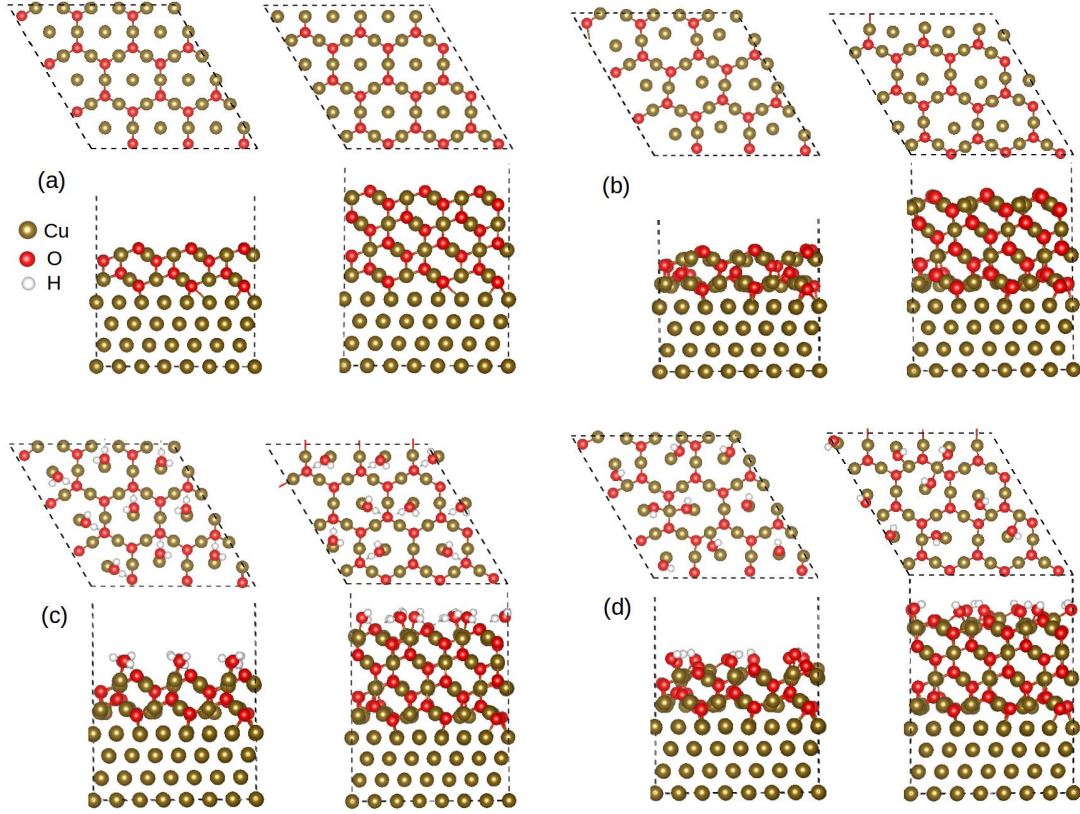


Figure 1: Snapshots of Cu(111) covered by two or four $\text{Cu}_2\text{O}(111)$ oxide layers with different oxide surface states (top view and side view). Before relaxation (a) and after relaxation in the (b) dry, (c) hydrated and (d) hydroxylated surface states.

185 saturated and unsaturated oxygen ions, labeled (O_{dn}) and (O_{up}), respectively,
 186 where the subscripts indicate that they are located below (dn) and above
 187 (up) the surface Cu layer, as illustrated in Fig.2. The high symmetry of
 188 the unsaturated copper atoms is broken by lateral relaxation toward one or
 189 two adjacent saturated copper ions, which can affect the molecule adsorption
 190 topologies.

191 We also investigated the adsorption of the molecules on the hydrated
 192 and hydroxylated surfaces. Indeed, in contact with an aqueous solution,
 193 the surface can be covered by a layer of water molecules or by OH groups.
 194 On the hydrated surface, the water molecules bind on top of Cu_{cus} sites
 195 via the oxygen atom and form H-bonds with adjacent O_{up} oxygen. The
 196 adsorption energy is -1.10 eV/mol at saturation of the Cu_{cus} sites . On the

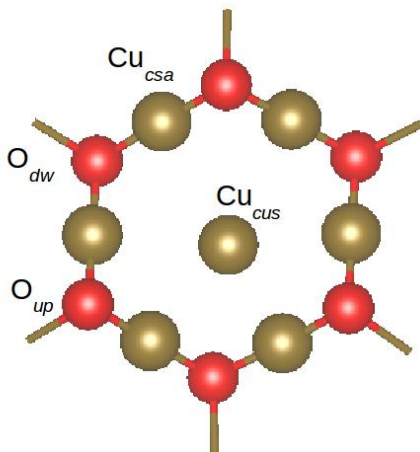


Figure 2: Surface sites of $\text{Cu}_2\text{O}(111)$. Cu_{cus} and Cu_{csa} correspond to unsaturated and saturated copper surface sites, respectively. O_{up} and O_{dn} correspond to unsaturated and saturated oxygen surface sites, respectively.

hydroxylated surface, two types of OH bonding, named μ_1 -OH and μ_2 -OH groups are found. μ_1 -OH corresponds to OH adsorbed on top of Cu_{cus} atom, whereas μ_2 -OH corresponds to OH adsorbed in bridge mode between Cu_{cus} and adjacent Cu_{csa} copper atoms. The adsorption energy at saturation is -3.72 eV/mol.

The supercell described here allows us to study MBT adsorption at low (0.37 mol/nm²) and high coverage (3.27 mol/nm²). The low coverage corresponds to one molecule per supercell and the high coverage to nine molecules per supercell, i.e. one molecule is adsorbed on each unsaturated copper site.

2.2. Molecules

The MBT molecule was modeled in thione (MBTH) and radical thiolate (MBT[•]) forms (Fig.3). The properties of the MBT molecule have been described in the literature. In the crystal structure, the molecules form centrosymmetric hydrogen bonded dimers [80, 81]. In dilute solution, MBT exists as thione monomer and cyclic dimer [82, 83]. Experimental [82, 44] and theoretical [54, 83] works revealed that the thione form is more stable than the thiol form, and thus the thiol form was not modeled in the present work. The isolated molecules were optimised in a box with dimensions of 20Å×20Å×20Å in x, y, and z directions, using the same computational conditions described above. For the radical MBT[•] form, spin polarization was implemented to get the energy minimum.

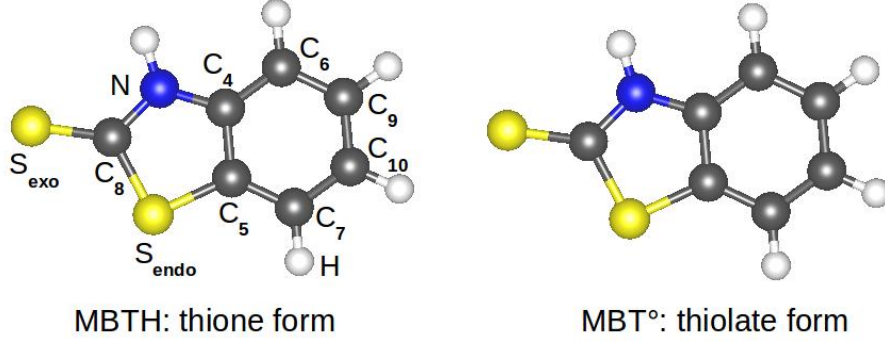


Figure 3: Isolated MBT molecule under the thione (MBTH) and thiolate (MBT°) forms modeled in this work

2.3. Energetics

The adsorption energy of the thione form (MBTH) was calculated as:

$$E_{ads} = [E(\text{slab}/\text{MBTH}) - E(\text{slab}) - nE(\text{MBTH})]/n \quad (1)$$

where $E(\text{slab}/\text{MBTH})$ is the total energy of the system with MBTH adsorbed on the slab surface. $E(\text{slab})$ and $E(\text{MBTH})$ are the energies of the bare, relaxed Cu(111)||Cu₂O(111) slab and of the free MBTH molecule optimized in vacuum, respectively. n is the number of molecules on the surface.

The adsorption energy for the radical thiolate form (MBT°) was calculated as:

$$E_{ads} = [E(\text{slab}/\text{MBT}^\circ) - E(\text{slab}) - nE(\text{MBT}^\circ)]/n \quad (2)$$

where $E(\text{slab}/\text{MBT}^\circ)$ is the total energy of the system with MBT° adsorbed on the slab surface. $E(\text{MBT}^\circ)$ is the energy of the free radical MBT° optimized in vacuum and n is the number of radical adsorbates on the surface.

In order to compare the stability of the formation of dense layer at full coverage with the adsorption at low coverage, we normalized the adsorption energy per unit area as follows:

$$\varepsilon_{norm} = E_{ads} \times \theta \quad (3)$$

where E_{ads} is the adsorption energy per molecule and $\theta = \frac{n}{A}$ is the coverage, defined as the number of adsorbed molecules (n) per area (A) of the slab.

237 We evaluated the interaction of MBTH and MBT° with the hydrated
 238 surface considering a substitution reaction, where MBT replaces H_2O on the
 239 surface covered initially by water molecules and water molecules are released
 240 after adsorption. The reaction is:



241 where H_2O_{ads} stands for adsorbed H_2O molecules and MBT_{ads} for ad-
 242 sorbed MBT molecules (MBTH or MBT° form). The corresponding substi-
 243 tution energy is calculated as:

$$\Delta E_{subst} = [E(slab/MBT) + nE(H_2O) - E(slab/H_2O) - nE(MBT)]/n \quad (5)$$

244 where $E(slab/MBT)$ is the total energy of the system with MBT (MBTH
 245 or MBT°) adsorbed on the slab surface. $E(H_2O)$ is the energy of a water
 246 molecule calculated in the vacuum. $E(slab/H_2O)$ and $E(MBT)$ are the en-
 247 ergies of the optimized structures with the water molecules adsorbed on the
 248 surface and the free MBTH or MBT° form optimized in vacuum, respectively.
 249 n is the number of adsorbed (or released) molecules.

250

251 We also evaluated the interaction of the thione form (MBTH) with the hy-
 252 droxylated surface. The following condensation reaction (replacement of an
 253 OH group by the MBT° form and release of water molecule) was considered:



254 where OH_{ads} stands for a surface OH group and MBT_{ads} for an adsorbed
 255 molecule under thiolate form after reaction. The corresponding condensation
 256 energy is calculated as:

$$\Delta E_{cond.} = [E(slab/MBT^\circ) + nE(H_2O) - E(slab/OH) - nE(MBTH)]/n \quad (7)$$

257 where $E(slab/MBT^\circ)$ is the total energy of the system with MBT thio-
 258 late (MBT°) adsorbed on the oxide surface. $E(H_2O)$ is the energy of a water
 259 molecule calculated in the vacuum. $E(slab/OH)$ and $E(MBTH)$ are the en-
 260 ergies of the optimized hydroxylated slab surface and the free MBTH thione
 261 form optimized in vacuum, respectively. n is the number of adsorbed MBT
 262 molecules.

263 *2.4. Electronic and charge analysis*

264 We plotted the charge density difference expressed as follows:

$$\Delta\rho(r) = \rho(r)_{slab/mol} - (\rho(r)_{slab} + \rho(r)_{mol}) \quad (8)$$

265 where $\rho(r)_{slab/mol}$ is the charge density distribution on the adsorbed sys-
266 tem, $\rho(r)_{slab}$ and $\rho(r)_{mol}$ are the charge density distributions on the isolated
267 slab and the molecule for the geometry after adsorption, respectively.

268 The net charge variation was determined on each atom by:

$$\Delta Q(x) = Q_{ads}(x) - Q_{vac}(x) \quad (9)$$

269 where $Q_{ads}(x)$ and $Q_{vac}(x)$ are the net charges on each atom (Bader pop-
270 ulation analysis) [84] of the adsorbed and free molecule, respectively.

271 **3. Results and discussion**

272 *3.1. Adsorption topologies and energetics*

273 The main question to answer is whether the molecules may adsorb on the
274 oxidized surface and what are the most favored configurations obtained for
275 a full MBT layer. The molecules were adsorbed on the dry, hydrated and
276 hydroxylated surfaces.

277 A wide range of configurations were tested, considering: i) the different
278 possible adsorption sites present on the topmost surface plane; ii) the differ-
279 ent reactive sites of the molecule, which are the exo (S_{exo}) and endo (S_{endo})
280 cyclic sulfur, and the nitrogen atoms; iii) the orientation of the molecule with
281 respect to the surface plane. We considered perpendicular, tilted and parallel
282 orientations. Among all adsorption configurations investigated in this study,
283 we discuss here the most relevant ones. An intuitive nomenclature is used
284 to describe the adsorbed configurations. For example (S_{exo} - Cu_{cus} , NH - O_{up})
285 means that MBTH forms two bonds, one between the exocyclic sulfur (S_{exo})
286 atom and the unsaturated copper (Cu_{cus}) atom, the other one between the
287 NH function and the oxygen atom located "up" (O_{up}) in the topmost oxide
288 plane.

289
290 The energetics of MBTH and MBT° adsorption at low and high coverages
291 is compiled in Table 1. As we did not find any difference for the adsorption
292 mode of MBT on the models with two or four oxide layers, we discuss here
293 in details only the case where Cu(111) is covered by two $Cu_2O(111)$ oxide
294 layers. The adsorption energy as function of the number of oxide layers is
295 reported in each Figure.

	Low coverage (0.37 mol/nm ²)			Full coverage (3.27 mol/nm ²)				
	Fig.	E_{ads} (eV/mol)	ε_{norm} (J/m ²)	Fig.	E_{ads} (eV/mol)	ε_{norm} (J/m ²)	$\Delta E_{subst.}$ (eV/mol)	$\Delta E_{cond.}$ (eV/mol)
MBTH	Fig.4	-3.40	-0.20	Fig.5(a)	-2.71	-1.42	-1.61	-
MBT ^o	Fig.6	-4.60	-0.27	Fig.7(b)	-2.96	-1.55	-1.87	-1.35
				Fig.7(d)	-2.94	-1.54	-1.84	-1.33
				Fig.8(a)	-3.11	-1.63	-2.01	-1.50

Table 1: Energetics of MBT adsorption at low and full coverage on Cu(111) covered by two layers of Cu₂O(111). E_{ads} is the adsorption energy on the dry surface, calculated with Equations 1 and 2, ε_{norm} is the adsorption energy normalized per unit area, calculated with Equation 3. $\Delta E_{subst.}$ is the energy of substitution on the hydrated surface (Equation 5) and $\Delta E_{cond.}$ the energy of condensation on the hydroxylated surface (Equation 7).

3.1.1. Adsorption of thione form (MBTH) at low and full coverage

Fig.4 shows the most stable configuration obtained at low coverage. The molecule is tilted toward the surface (meaning rings nearly parallel to the surface). The adsorption energy is -3.40 eV/mol and ε_{norm} is -0.20 J/m². MBTH binds via the S_{exo} atom to a Cu_{cus} atom with a bond length of 2.17 Å. A NH...O hydrogen bond with an O_{up} atom is also formed and the distance NH...O is 1.61 Å. In addition, two carbon atoms of the aromatic ring are involved in the interaction mechanism. These carbon atoms (corresponding to C₆ and C₉ in Fig.3) are bonded to adjacent Cu_{cus} atoms with C-Cu bond lengths of 2.16 Å and 2.19 Å.

At high coverage, the molecules stand perpendicular to the surface in the most stable configuration (Fig.5(a)). The S_{exo} atom and the NH group are directed toward the surface. MBTH forms a covalent bond between the S_{exo} and a Cu_{cus} atoms with a bond length of 2.15 Å and an H-bond between the NH group and an unsaturated oxygen (O_{up}) surface atom (1.38 and 1.70 Å for NH...O). The adsorption direction from Cu_{cus} to O_{up} on the surface is favored over Cu_{cus} to O_{dn} by the formation of the H-bond (Fig.5 (a) and (b)). The adsorption energy is -2.71 eV/mol and less favorable than at low coverage. However, the normalization of the adsorption energy to a unit area, $\varepsilon_{norm} = -1.42$ J/m², shows that the formation of a full monolayer is much favored compared to the adsorption at low coverage. The adsorption of the molecule via both the exo and endocyclic sulfur atoms is less stable as shown in Fig.5 (c) and (d).

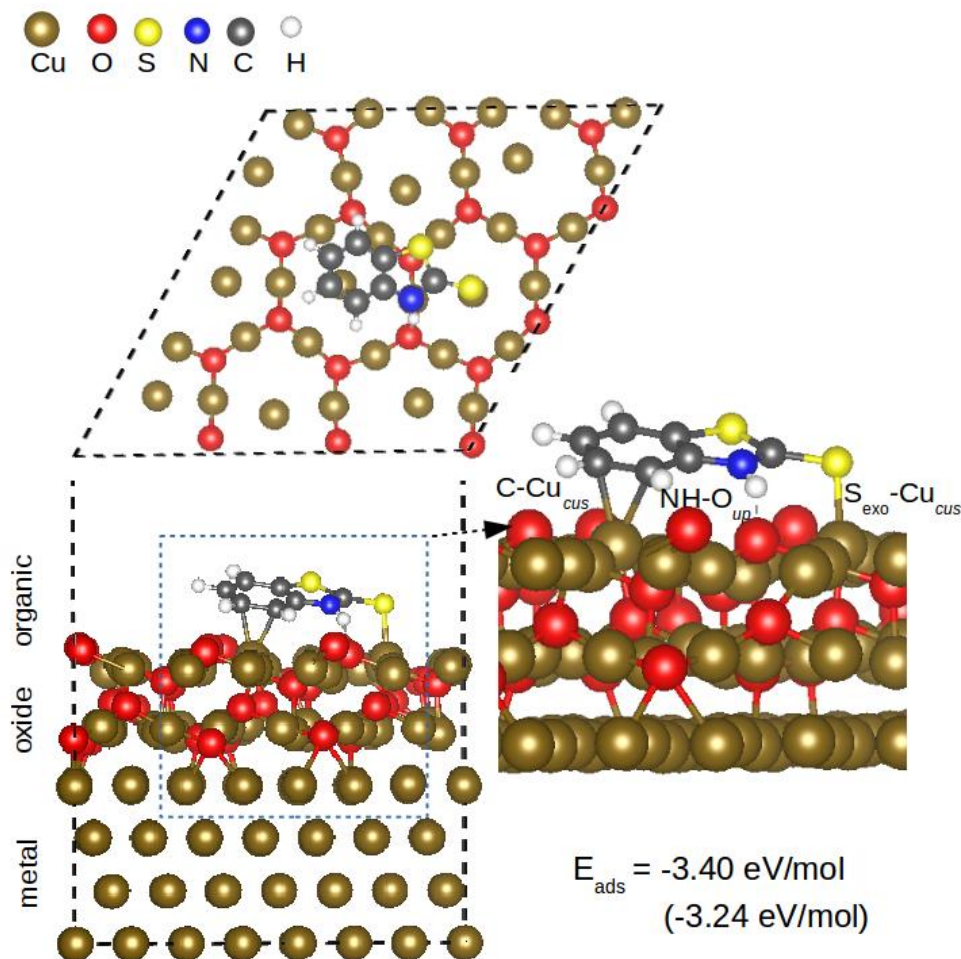


Figure 4: Snapshot and adsorption energy of the most stable adsorbed configuration of thione form (MBTH) at low coverage. E_{ads} value in brackets corresponds to the adsorption energy of MBTH adsorbed on Cu(111) covered by four Cu₂O(111) oxide layers.

3.1.2. Adsorption of thiolate form (MBT[°]) at low and full coverage

The situation for the thiolate is different since the molecule cannot form a H-bond with a surface oxygen. However, the nitrogen atom can interact directly with surface copper atoms. In addition, the reactivity of the molecule may be different in the radical form as compared to the neutral form.

The most stable adsorption configuration of MBT[°] at low coverage is a tilted orientation toward the surface (meaning rings nearly parallel to the surface), like for MBTH form (Fig.6(a)). Indeed, MBT[°] binds via the exo-

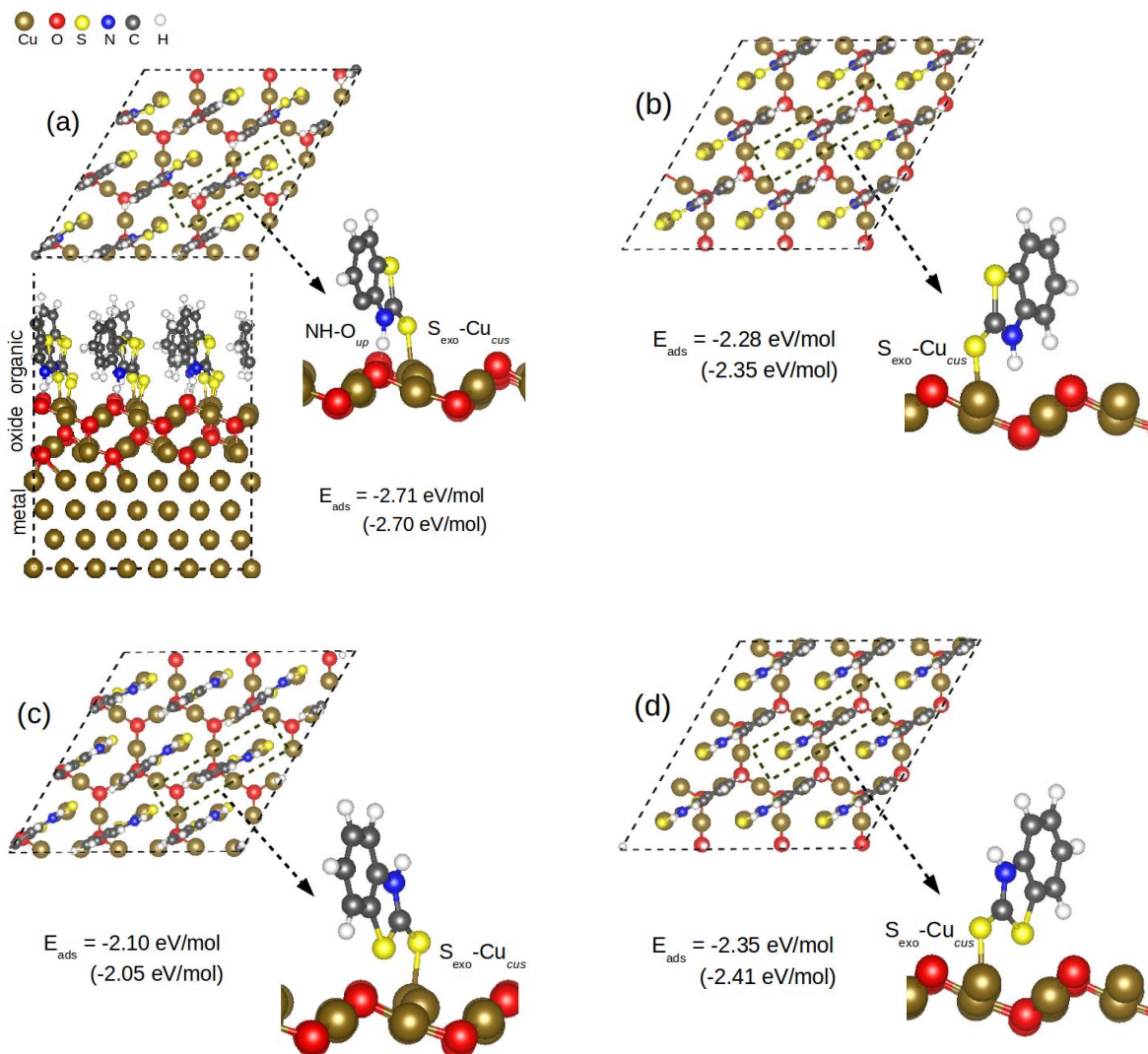


Figure 5: Snapshots and adsorption energies of different adsorption configurations of MBTH form at full coverage and illustration of the adsorption mode. Top, adsorption through exocyclic sulfur atom and NH functional group and orientation relative to the surface sites, (a): (S_{exo} - Cu_{cus} bond; $NH-O_{up}$ bond) and (b): (S_{exo} - Cu_{cus} bond; $NH-O_{dn}$ orientation). Bottom, adsorption through exo and endocyclic sulfur atoms and orientation relative to the surface sites, (c): (S_{exo} - Cu_{cus} bond; $S_{endo}-O_{up}$ orientation) and (d): (S_{exo} - Cu_{cus} bond; $S_{endo}-O_{dn}$ orientation). E_{ads} values in brackets correspond to the adsorption energy of MBTH adsorbed on Cu(111) covered by four $Cu_2O(111)$ oxide layers.

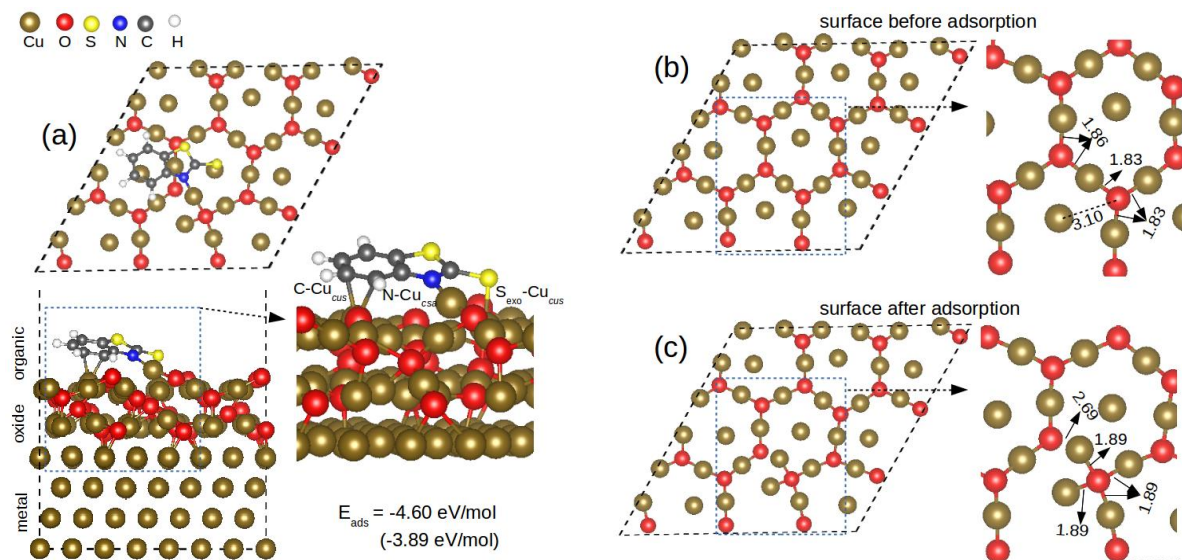


Figure 6: Snapshots and adsorption energy of the most stable adsorption configuration of thiolate form (MBT°) at low coverage (a) and surface structure of Cu₂O(111) film after adsorption (b) and before adsorption (bare surface) (c). E_{ads} value in brackets corresponds to the adsorption energy of MBT° adsorbed on Cu(111) covered by four Cu₂O(111) oxide layers.

328 cyclic sulfur to an unsaturated copper atom with a bond length of 2.18 Å.
 329 Two carbon atoms (C₆ and C₉ in Figure 3(b)) are also involved in the inter-
 330 action mechanism with bond lengths C...Cu_{cus} of 2.11 Å and 2.14 Å. MBT°
 331 also forms a covalent bond via the nitrogen atom with a saturated copper
 332 atom with a bond length of 1.91 Å. The adsorption energy is -4.60 eV/mol
 333 ($\epsilon_{norm} = -0.27$ J/m²), which is more stable by 1.20 eV/mol than for MBTH.
 334 However, the competitive adsorption of both forms under the following mech-
 335 anisms (MBTH + * \rightarrow MBT_{ads} + $\frac{1}{2}$ H₂ or MBTH + * \rightarrow MBT_{ads} + H_{ads})
 336 showed that MBTH is more favored by 0.35 and 0.23 eV/mol, respectively.
 337 The results reveal that the competitive adsorption of MBT° is favored only
 338 in the presence of both species (thione and thiolate) in the same solution.

339
 340 The surface atoms involved in the interaction undergo reconstruction (
 341 Fig.6(c)) as compared to the bare surface before adsorption (Fig.6(b)). De-
 342 hydrogenation of the molecule (MBT°) makes the nitrogen more reactive
 343 towards the substrate surface. The saturated copper atom is pulled out by
 344 breaking of the O_{dn}...Cu_{csa} bond due to the formation of the N...Cu_{csa} bond,

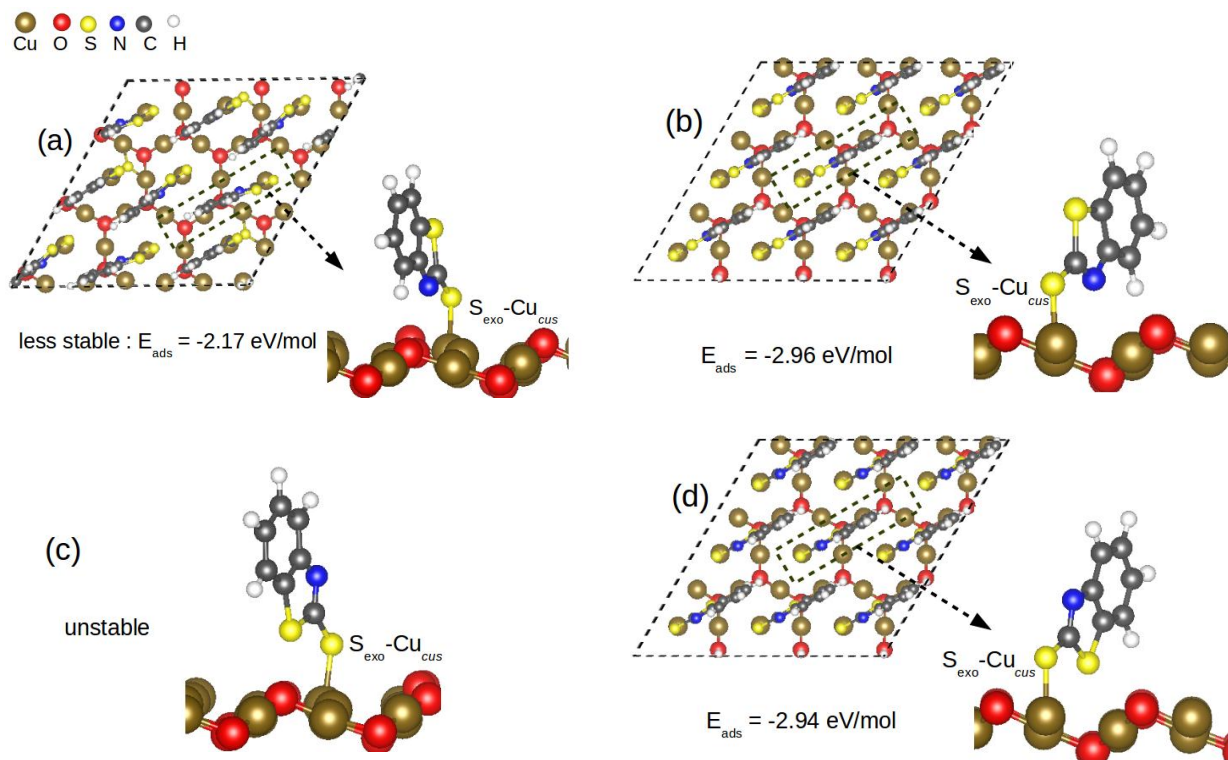


Figure 7: Snapshots and adsorption energies of different adsorption configurations of MBT^o form at full coverage and illustration of different adsorption modes. Top, adsorption through exocyclic sulfur and nitrogen atoms and orientation relative to the surface sites, (a): (S_{exo} - Cu_{cus} bond; N- O_{up} orientation), (b): (S_{exo} - Cu_{cus} bond; N- O_{dn} orientation). Bottom, adsorption through exo and endocyclic sulfur atoms and orientation relative to the surface sites, (c): (S_{exo} - Cu_{cus} bond; S_{endo} - O_{up} orientation), (d): (S_{exo} - Cu_{cus} bond; S_{endo} - O_{dn} orientation).

345 and the $O_{dn}...Cu_{csa}$ distance increases from 1.86 to 2.69 Å. Another change
 346 in the surface structure concerns the neighboring unsaturated copper atom,
 347 which moves and binds with the unsaturated oxygen (O_{up}) atom, the distance
 348 decreasing from 3.10 to 1.89 Å.

349
 350 Different adsorption configurations studied at full coverage are shown in
 351 Fig.7 and Fig.8. In order to compare with the interaction of MBTH (Fig.5),
 352 we addressed similar adsorption configurations of MBT^o bonded to Cu and
 353 O surface atoms as shown in Fig.7. The most stable configuration of MBT^o
 354 is in Fig.8(a). The unstable (Fig.7(c) and Fig.8(b)) and less stable (Fig.7(a))

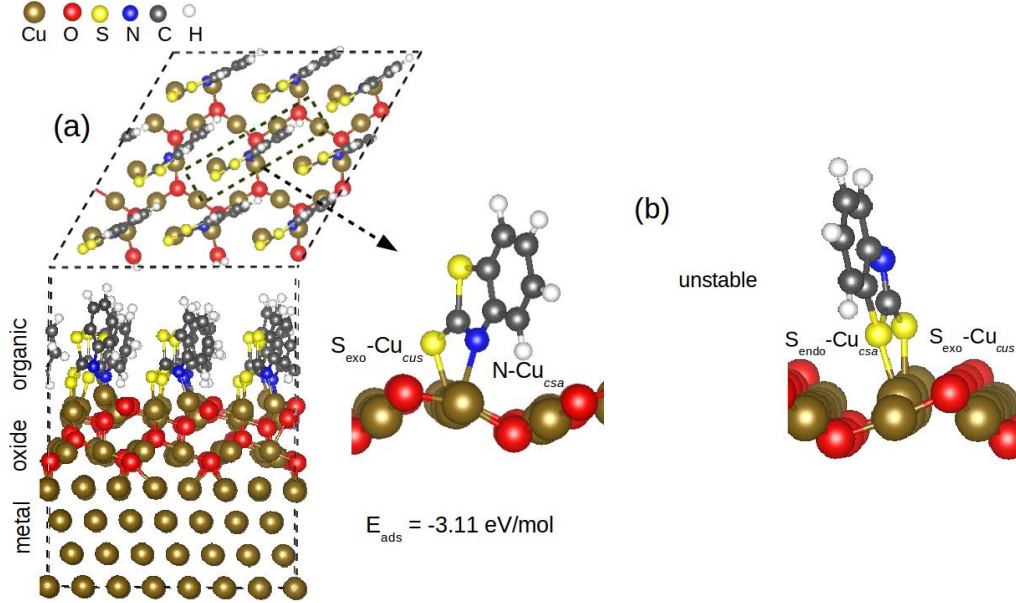


Figure 8: Snapshots and adsorption energy of different adsorption configurations of MBT° at full coverage and illustration of different adsorption modes. (a) adsorption through exocyclic sulfur and nitrogen atoms and orientation relative to the surface sites (S_{exo} - Cu_{cus} bond; N - Cu_{csa} bond). (b) adsorption through exo and endocyclic sulfur atoms and orientation relative to the surface sites (S_{exo} - Cu_{cus} bond; S_{endo} - Cu_{csa} bond).

configurations are not further discussed below.

At full coverage, MBT°, like MBTH, adsorbs in a perpendicular orientation. Interestingly, the adsorption via S_{exo} and N atoms or via S_{exo} and S_{endo} atoms, noted (b) and (d) in Fig.7, respectively, are iso-energetic. The adsorption energy is -2.95 ± 0.01 eV/mol ($\varepsilon_{norm} = -1.55$ J/m²) and more stable by 0.25 eV/mol than for MBTH. This competitive adsorption is valid only in the presence of both species (thione and thiolate) in the same medium, as explained for low coverage case. MBT° binds only via S_{exo} atom to an unsaturated copper atom, with a bond length of 2.12 Å. The distance from the S_{endo} and N atoms to the O_{dn} atom is 3.15 ± 0.03 and 4.48 ± 0.03 Å, respectively. These MBT° adsorbed configurations are oriented from Cu_{cus} to O_{dn} direction, whereas it is from Cu_{cus} to O_{up} direction for the most stable configuration of MBTH.

The most stable adsorbed configuration of MBT°, noted (a) in Fig.8, has an adsorption energy of -3.11 eV/mol ($\varepsilon_{norm} = -1.63$ J/m²). The normalization to the unit area shows again that the full monolayer adsorption is favored

371 compared to the low coverage adsorption. MBT° binds via S_{exo} atom to an
 372 unsaturated copper atom, with a bond length of 2.12 Å. In addition, MBT°
 373 forms a covalent bond via its nitrogen atom with a saturated copper surface,
 374 with a bond length of 1.98 ± 0.04 Å.

375

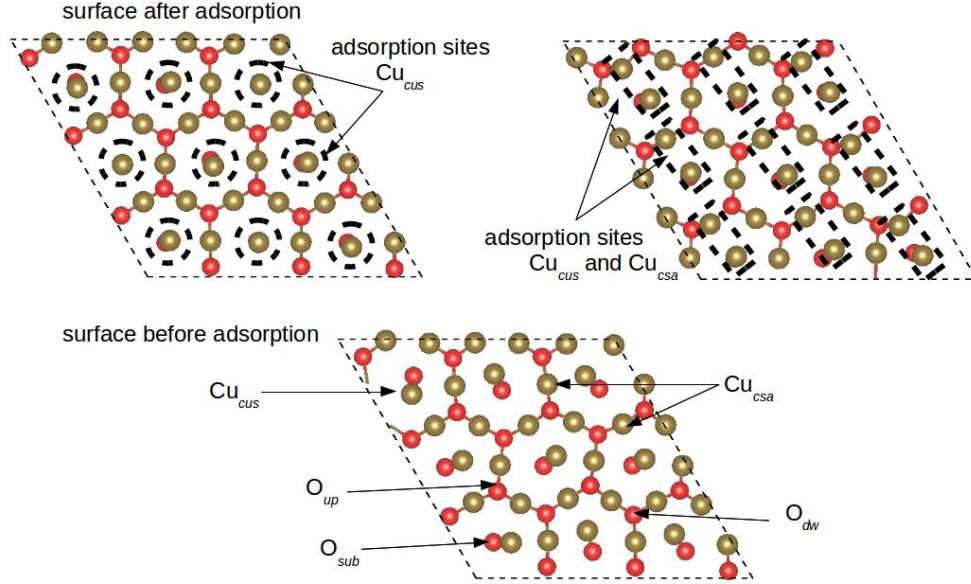


Figure 9: Surface structure after adsorption of MBT (top) compared to bare surface structure (bottom). Top left corresponds to all adsorption configurations of MBTH and MBT° with one covalent bond of the molecule to the Cu_{cus} atom (circled). Top right corresponds to the configuration in Fig8(a) with two covalent bonds of the molecule to the Cu_{cus} and Cu_{csa} atoms (circled).

376 We recall that on bare $\text{Cu}_2\text{O}(111)$ surface the high-symmetry of the Cu_{cus}
 377 atom is broken due to lateral relaxation towards adjacent Cu_{csa} ions. At full
 378 coverage, the adsorption of the molecule under MBTH and MBT° forms on
 379 top of the Cu_{cus} atoms lifts the reconstruction of the bare surface (Fig.9)
 380 and the bulk high-symmetry is recovered. Thus both forms of molecule sta-
 381 bilize the Cu_{cus} sites. However, for the most stable adsorbed configura-
 382 tion of MBT° shown in Fig.8(a), the Cu_{csa} atoms are also involved in the inter-
 383 action mechanism. The nitrogen atom pulls out the Cu_{csa} atom with elongation
 384 of the $\text{O}-\text{Cu}_{csa}$ distance (average of $\Delta d = 0.12$ Å), indicating a quasi-bond
 385 breaking ($\text{Cu}_{csa} \dots \text{O}_{dn}$ or $\text{Cu}_{csa} \dots \text{O}_{up}$) compensated by bond-making between
 386 Cu and N atoms ($\text{Cu}_{csa} \dots \text{N}$).

387

388 Comparison of the adsorption energies (E_{ads}) calculated by Equations 1
 389 and 2, and substitution energy (E_{subs}) calculated by Equation 5, from the
 390 mechanism defined by Equation 4, shows that the formation of an MBTH or
 391 MBT° adsorbed monolayer at full coverage is much more exothermic than
 392 that of a molecular water layer (Table 1). Indeed, we calculated substitution
 393 energies of -1.61 and -2.01 eV/mol for the most stable monolayer configura-
 394 tion of MBTH (Fig.5 (a)) and MBT° (Fig.8 (a)), respectively. This means
 395 that in both forms the MBT molecule is able to substitute a water monolayer
 396 on the hydrated copper oxide surface. However, the substitution mechanism
 397 of hydroxyl groups, $OH_{ads} + MBT \rightarrow MBT_{ads} + OH$, is unfavored for
 398 both the MBTH and MBT° forms. For these reasons, we considered the
 399 condensation reaction of MBT° (Equation 6) with the corresponding energy
 400 calculated by Equation 7. The results show that this condensation reaction
 401 is very exothermic with calculated energies of -1.34 ± 0.01 eV/mol for (b) and
 402 (d) configurations in Fig.7 and -1.50 eV/mol for (a) configuration in Fig.8.
 403 These calculations suggest that the MBTH form would be able to replace
 404 surface OH groups by forming adsorbed MBT° and releasing water but that
 405 the MBT° form would not be able to directly substitute surface OH groups.

406

407 We can conclude that whatever the surface state of the $Cu_2O(111)$ oxide
 408 film on Cu(111) (anhydrous, hydrated or hydroxylated) the adsorption of
 409 MBT (under thione and thiolate forms) is favored and MBT can form dense
 410 and ordered monolayer with a density of 3.27 mol/nm^2 , which could explain
 411 the experimental results on the formation of the protective film on copper
 412 under different conditions [15, 16]. However, the adsorption mode depends on
 413 the thione or thiolate form of the MBT molecule and the copper surface state
 414 (covered or not by oxide). The thione form (MBTH) is adsorbed via covalent
 415 bonding of the S_{exo} atom on $Cu(111)||Cu_2O(111)$ surfaces, which corresponds
 416 to the bonding reported from experimental measurement on oxidized copper
 417 by Woods et al. [21]. The thiolate form (MBT°) is adsorbed via covalent
 418 bonding of both the N and S_{exo} atoms on $Cu(111)||Cu_2O(111)$ surfaces, in
 419 agreement with the bonding reported from XPS measurements by Kazansky
 420 et al. [20] and Finšgar and Merl [19]. On the metallic surface not covered by
 421 any oxide, the adsorption via covalent bonding of both exo and endocyclic
 422 S atoms was calculated to take place on metallic copper [54] and observed
 423 experimentally by XPS [26, 27]. This type of bonding was also observed on
 424 metallic gold by STM measurements [49].

425 *3.2. Electronic structure analysis*

426 Electronic structure analysis provides more details about the molecule-
427 surface interaction. This can be done using the density of states (DOS),
428 the projected density of states (PDOS), the integral local density of states
429 (ILDOS) and the visualization of the molecular orbitals. It can be also done
430 by analysis of the charge density variation ($\Delta\rho(r)$) and charge transfer (Δ
431 Q) as defined in Equations 8 and 9, respectively. A combined analysis of
432 all these data brings relevant information useful to understand the nature
433 of the reactive sites involved in the binding process, the amount of charge
434 transferred from/to the surface, and the reactivity of the molecules towards
435 substrate surfaces.

436
437 *3.2.1. Isolated species (before adsorption)*

438 The total density of state (DOS) analysis of the isolated thione (MBTH)
439 form is shown in Fig.10 (middle). There are several S, N, C and H atoms
440 in the molecule, and hence, we projected the density of states (PDOS) for
441 every type of atom, as shown in Fig.10 (bottom). The molecular orbitals of
442 the isolated molecules and the integral range are shown in Fig.10 (top). We
443 represented the highest occupied molecular orbitals (HOMO-1 and HOMO)
444 and lowest unoccupied molecular orbitals LUMO and LUMO+1, with iso-
445 surface of $+0.004 \text{ e}/\text{\AA}^3$.

446
447 The DOS shows that the HOMO is located near the Fermi level of the
448 slab at about -0.40 eV and that the LUMO is located 2.70 eV above the
449 Fermi level. These HOMO and LUMO alignments relative to the Fermi level
450 suggests that MBTH can easily exchange electrons with the surface and be-
451 haves more as an electron donor than electron acceptor during the adsorption
452 process. The PDOS reveals that the occupied states near the Fermi level are
453 dominated by the contribution of the exocyclic sulfur orbitals (green line).
454 Thus, the exocyclic sulfur atom is the most reactive species and it is the most
455 likely site for the interaction with the surface copper atoms. We also observe
456 a small contribution of nitrogen and endocyclic sulfur atoms to the DOS,
457 which is visible at HOMO and HOMO-1 levels. The LUMO and LUMO+1
458 levels show the contribution of all atomic orbitals of the molecule in the
459 unoccupied states. Analysis for the isolated thiolate anion shows similar
460 characteristics.

461

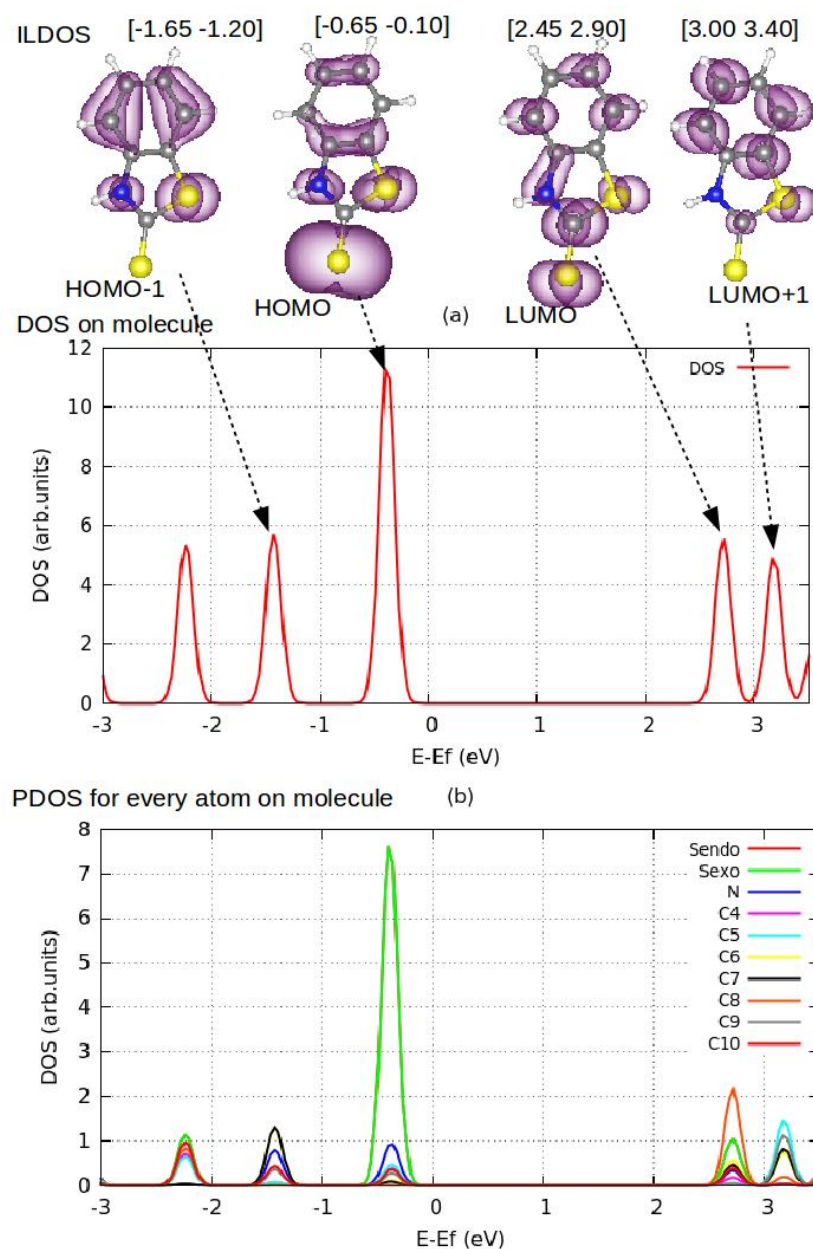


Figure 10: Electronic structure analysis of the isolated MBTH form of MBT: integral local density of states (ILDOS, top), density of states (DOS, middle) and projected density of states (PDOS, bottom).

3.2.2. Adsorbed molecules at full coverage

Fig.11 depicts the ILDOS (top) at different integral range, the PDOS on the molecule (middle) and for every atom (bottom) for MBTH adsorbed at full coverage. It corresponds to the most stable adsorbed configurations in Fig.5(a).

The comparison of the ILDOS and DOS projected on the molecules before and after adsorption, reveals drastic changes in the electronic structure of the molecule, indicating a strong molecule-surface interaction. We observe peak shifting, peak broadening, and the appearance of new peaks in the density of states after adsorption. Two peaks located below the Fermi energy at -1.50 eV and -3.60 eV are dominated by the DOS of the exocyclic sulfur atom. The ILDOS reveals that the peak at -1.50 eV is similar to the sulfur contribution at HOMO before adsorption and that the peak at lower energy (-3.60 eV) is associated to the sulfur-copper binding. It can be concluded that the interaction via the exocyclic sulfur with the copper atom is very strong and it is the only atom involved in the covalent binding of MBTH on Cu(111)||Cu₂O(111) surface.

More details on the molecule-surface binding are provided by the charge density difference analysis. Fig.12 show the charge density difference ($\Delta\rho(r)$), plotted with an isosurface of ± 0.001 e/ \AA^3 for the most stable configuration at full coverage of MBTH. For better visualization of the isosurface, we represented only one molecule on the surface in the same adsorption topology as at full coverage.

$\Delta\rho(r)$ shows charge density accumulation between the exocyclic sulfur atom and one unsaturated copper. In addition a charge density deficit is observed on the S_{exo} and Cu_{cus} atoms, confirming again the formation of a covalent bond between these atoms. We also observe charge density accumulation on one unsaturated oxygen atom and charge density deficit on the hydrogen of the NH group confirming the H-bonding NH...O.

The Bader charge analysis for MBTH form reveals an electron transfer from the organic layer to the oxide. We calculated the values of 0.15 e/molecule at full coverage. The electrons were redistributed in the oxide, whereas the electrons distribution after adsorption remains unchanged in the metallic part of the slab substrate. The electrons redistribution on the

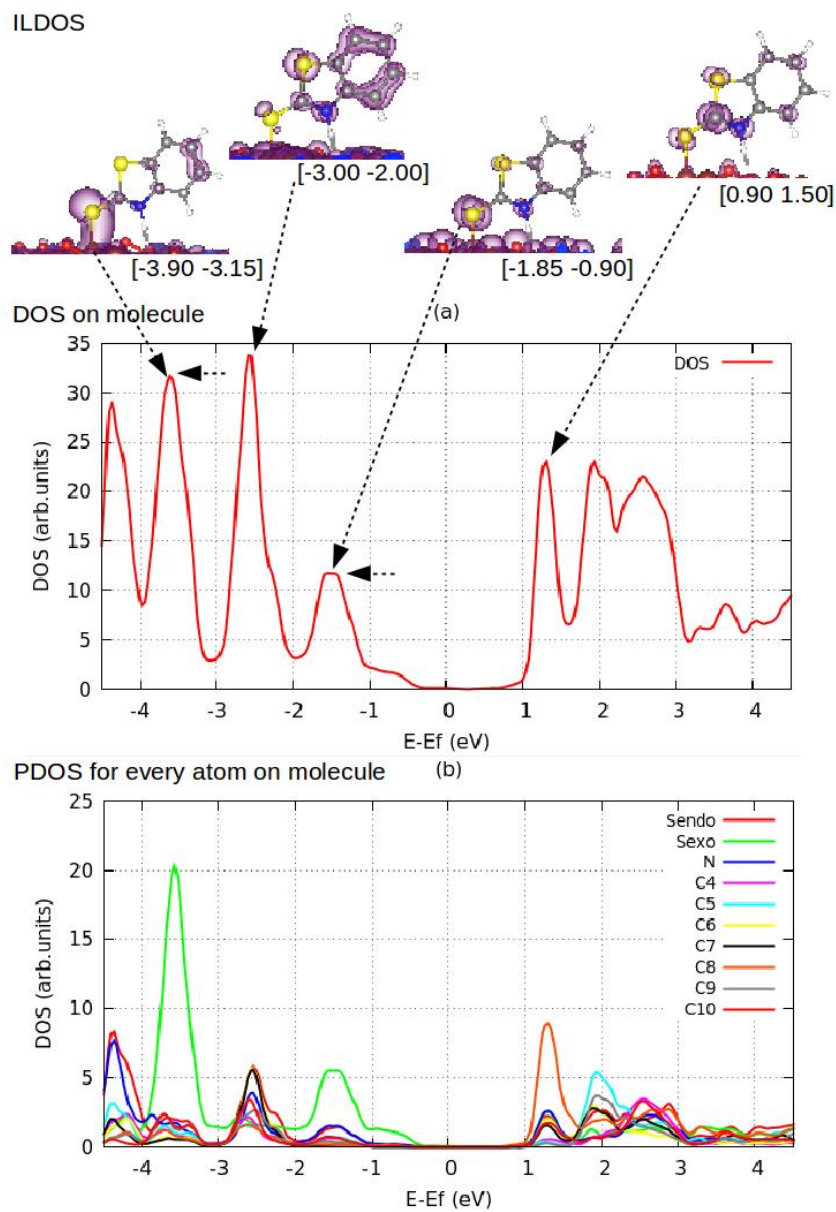


Figure 11: Electronic properties of adsorbed MBTH at full coverage: visualisation of integral local density of states (ILDOS, top), projected density of states on the molecules (PDOS, middle) and projected density of states for every atom of the molecule (PDOS, bottom).

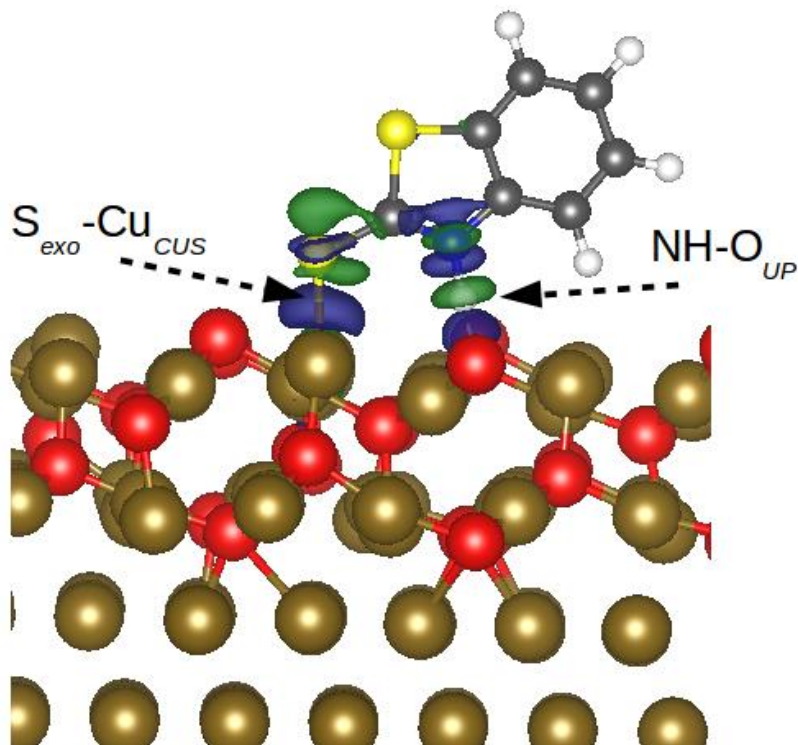


Figure 12: Charge density difference analysis for most stable full coverage adsorbed configuration of MBTH. Blue and green color correspond to accumulation and deficit of charge density, respectively

499 molecules concerns all atoms. The exocyclic sulfur atoms lose electrons,
 500 whereas endocyclic sulfur atoms gain electrons and the nitrogen atom charge
 501 remains unchanged before and after adsorption. Analysis for the most stable
 502 form of adsorbed thiolate at full coverage also confirms the nature of covalent
 503 bonding between the S_{exo} and Cu_{cus} atoms and between the N and Cu_{csa}
 504 atoms.

505

506 4. Conclusion

507 The interaction of the organic inhibitor 2-mercaptobenzothiole (MBT)
 508 under thione (MBTH) and thiolate (MBT°) forms with an oxidized copper
 509 surface modeled by a $Cu(111)||Cu_2O(111)$ slab was investigated by DFT.
 510 We analyzed the structural and energetic trends to determine the most sta-

ble adsorption configuration, and more details about the molecule-surface interaction were provided by the electronic structure analysis.

Two thicknesses of the oxide overlayer were considered (5.89 and 11.07 Å) and gave similar results. The oxide surface was considered in the dry, hydrated and hydroxylated states at full coverage.

At low coverage, the molecules are in tilted adsorption mode. Both forms of MBT bind via S_{exo} atom to Cu_{cus} and two carbon atoms in the aromatic ring are bonded with adjacent Cu_{cus} . In addition MBT° binds via N atoms to Cu_{csa} , instead of $NH...O_{up}$ H-bonding for MBTH.

At full coverage, the molecules can form a dense and ordered monolayer by standing perpendicular to the surface. The $S_{exo}-Cu_{cus}$; $NH-O_{up}$ and $S_{exo}-Cu_{cus}$; $N-Cu_{csa}$ orientations are favored for MBTH and MBT° forms, respectively. For both forms, the exocyclic sulfur atom is more reactive and binds covalently to Cu_{cus} . In the thiolate form, the nitrogen is more reactive and binds covalently to Cu_{csa} , whereas in the thione form, a $NH...O_{up}$ H-bond is formed.

The adsorption of the molecules leads to recover the high symmetry of the Cu_{cus} sites broken on the bare $Cu_2O(111)$ surface. Thus both forms of the molecule are able to stabilize the surface by bond-making between the S_{exo} and Cu_{cus} atoms. However, for MBT° , bond making between the N and Cu_{csa} atoms leads to the surface reconstruction of Cu_{csa} sites by bond elongation with the adjacent O atoms.

The adsorption energy shows strong interaction of MBT with the $Cu(111)||Cu_2O(111)$ surface and a similar trend for the two studied Cu_2O layer thicknesses.

The normalization of the adsorption energy to a unit area shows that the full layer formation is favored as compared to the single molecule adsorption. The high adsorption energy is confirmed by the electronic analysis, which evidences the formation of strong bonds between the molecule and the oxidized copper surface. Our calculations suggest that the substitution of water or OH groups by MBT molecule is exothermic, the adsorption of MBT is favored whatever the surface state of the oxide film. All these results suggest that MBT strongly adsorbs on copper covered by an ultra thin oxide film and contribute to explain the corrosion protection efficiency of MBT molecule.

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