



HAL
open science

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

Fatah Chiter, Dominique Costa, Vincent Maurice, Philippe Marcus

► **To cite this version:**

Fatah Chiter, Dominique Costa, Vincent Maurice, Philippe Marcus. DFT investigation of 2-mercaptobenzothiazole adsorption on model oxidized copper surfaces and relationship with corrosion inhibition. Applied Surface Science, 2021, 537, 10.1016/j.apsusc.2020.147802 . hal-03453309

HAL Id: hal-03453309

<https://hal.science/hal-03453309>

Submitted on 17 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Fatah Chiter*, Dominique Costa**, Vincent Maurice, Philippe Marcus

PSL Research University, CNRS – Chimie ParisTech, Institut de Recherche de Chimie Paris (IRCP), Physical Chemistry of Surfaces Group, 11 rue Pierre et Marie Curie, 75005 Paris, France

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

*Corresponding author: fatah.chiter@chimieparistech.psl.eu

**Corresponding author: dominique.costa@chimieparistech.psl.eu

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,

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

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

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

68 The surface state of copper has an impact on MBT adsorption. Chadwick
69 and Hashemi [15] demonstrated the influence of the oxidation state on MBT
70 adsorption. Kazansky et al. [20] suggested that a thin Cu_2O layer is required
71 for the formation of the MBT layer, which thickness would depend on the
72 immersion time in neutral phosphate media. Recently, Chen and Erbe. [25]
73 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 formation 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 addressed 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)

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

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

165 2.1. Passivated surface model

166 Fig.1 shows the constructed model of the passivated surface as derived
167 from experimental data [75, 76, 77, 78, 79]. The model elaborated for
168 the oxidized $\text{Cu}(111)||\text{Cu}_2\text{O}(111)$ surface consists of the $\text{Cu}(111)$ metal sub-
169 strate covered by the stoichiometric $\text{Cu}_2\text{O}(111)$ oxide film in parallel epitaxy:
170 $\text{Cu}(111)[110]||\text{Cu}_2\text{O}(111)[110]$. Because of the perfect fit between the oxide
171 and metal substrate lattices over a coincidence length of 17.87 \AA [76, 79], we
172 use the lateral dimensions of the supercell of 17.81 \AA in both x and y di-
173 rections, which corresponds to (7×7) and (6×6) supercells for $\text{Cu}(111)$ and
174 $\text{Cu}_2\text{O}(111)$, respectively.

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

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

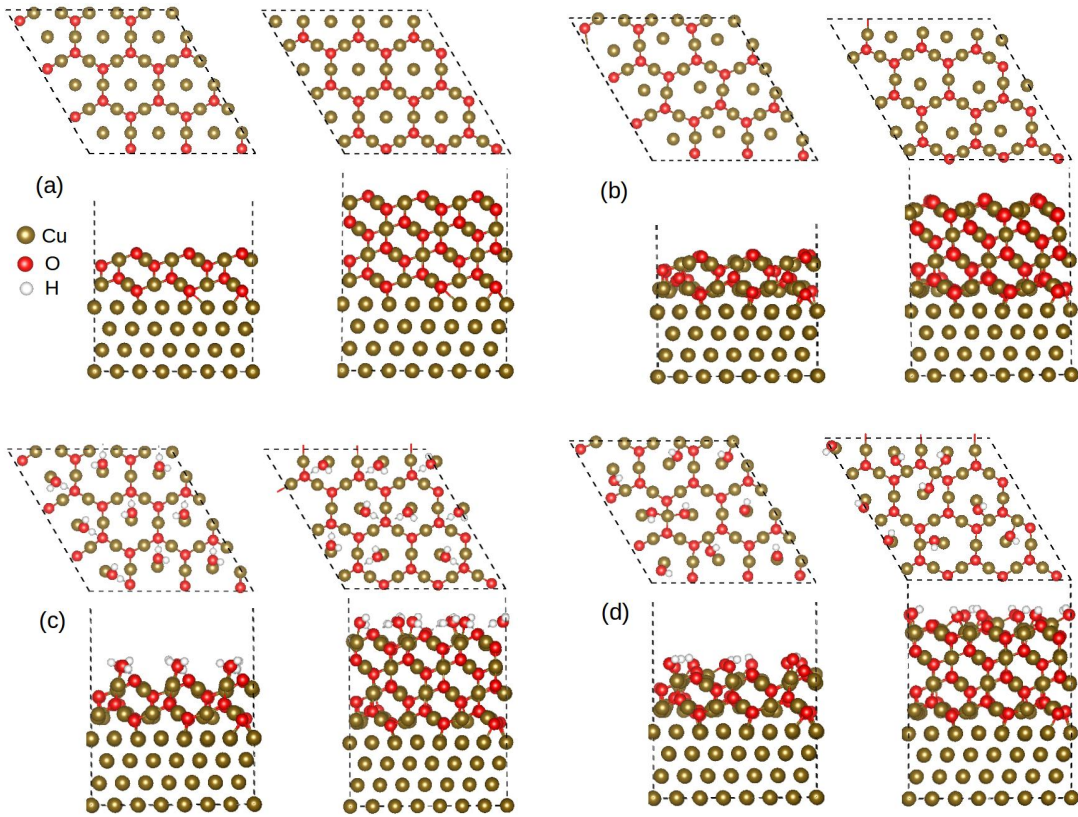


Figure 1: Snapshots of Cu(111) covered by two or four Cu₂O(111) oxide layers with different oxide surface states (top view and side view). Before relaxation (a) and after relaxation in the (b) dry, (c) hydrated and (d) hydroxylated surface states.

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

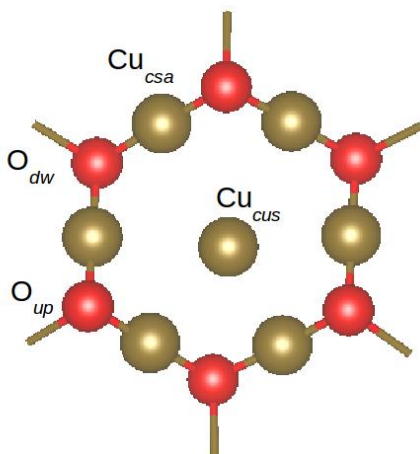


Figure 2: Surface sites of $\text{Cu}_2\text{O}(111)$. Cu_{cus} and Cu_{csa} correspond to unsaturated and saturated copper surface sites, respectively. O_{up} and O_{dn} correspond to unsaturated and saturated oxygen surface sites, respectively.

197 hydroxylated surface, two types of OH bonding, named μ_1 -OH and μ_2 -OH
 198 groups are found. μ_1 -OH corresponds to OH adsorbed on top of Cu_{cus} atom,
 199 whereas μ_2 -OH corresponds to OH adsorbed in bridge mode between Cu_{cus}
 200 and adjacent Cu_{csa} copper atoms. The adsorption energy at saturation is
 201 -3.72 eV/mol.

202 The supercell described here allows us to study MBT adsorption at low
 203 (0.37 mol/nm²) and high coverage (3.27 mol/nm²). The low coverage corre-
 204 sponds to one molecule per supercell and the high coverage to nine molecules
 205 per supercell, i.e. one molecule is adsorbed on each unsaturated copper site.

206 2.2. Molecules

207 The MBT molecule was modeled in thione (MBTH) and radical thiolate
 208 (MBT°) forms (Fig.3). The properties of the MBT molecule have been de-
 209 scribed in the literature. In the crystal structure, the molecules form centro-
 210 symmetric hydrogen bonded dimers [80, 81]. In dilute solution, MBT ex-
 211 ists as thione monomer and cyclic dimer [82, 83]. Experimental [82, 44]
 212 and theoretical [54, 83] works revealed that the thione form is more stable
 213 than the thiol form, and thus the thiol form was not modeled in the present
 214 work. The isolated molecules were optimised in a box with dimensions of
 215 $20\text{\AA} \times 20\text{\AA} \times 20\text{\AA}$ in x, y, and z directions, using the same computational con-
 216 ditions described above. For the radical MBT° form, spin polarization was
 217 implemented to get the energy minimum.

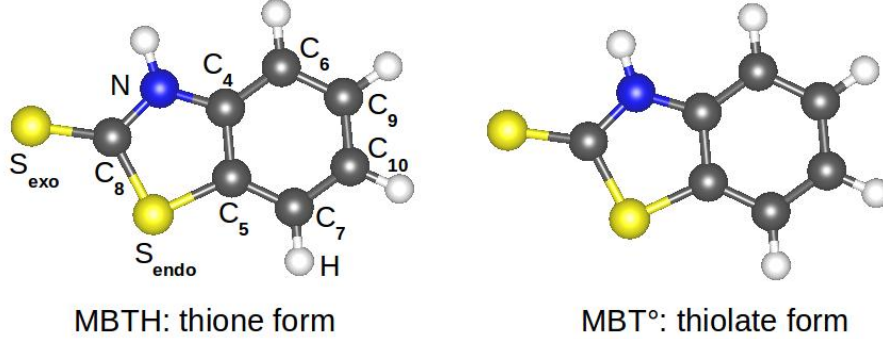


Figure 3: Isolated MBT molecule under the thione (MBTH) and thiolate (MBT°) forms modeled in this work

218 *2.3. Energetics*

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

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

220 where $E(\text{slab}/\text{MBTH})$ is the total energy of the system with MBTH ad-
 221 sorbed on the slab surface. $E(\text{slab})$ and $E(\text{MBTH})$ are the energies of the
 222 bare, relaxed Cu(111)||Cu₂O(111) slab and of the free MBTH molecule opti-
 223 mized in vacuum, respectively. n is the number of molecules on the surface.

224
 225 The adsorption energy for the radical thiolate form (MBT°) was calcu-
 226 lated as:

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

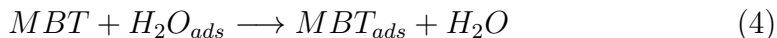
227 where $E(\text{slab}/\text{MBT}^\circ)$ is the total energy of the system with MBT° ad-
 228 sorbed on the slab surface. $E(\text{MBT}^\circ)$ is the energy of the free radical MBT°
 229 optimized in vacuum and n is the number of radical adsorbates on the surface.

230
 231 In order to compare the stability of the formation of dense layer at full
 232 coverage with the adsorption at low coverage, we normalized the adsorption
 233 energy per unit area as follows:

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

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

237 We evaluated the interaction of MBTH and MBT^o with the hydrated
 238 surface considering a substitution reaction, where MBT replaces H₂O on the
 239 surface covered initially by water molecules and water molecules are released
 240 after adsorption. The reaction is:

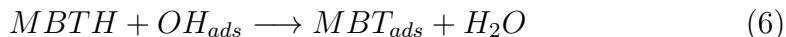


241 where H₂O_{ads} stands for adsorbed H₂O molecules and MBT_{ads} for ad-
 242 sorbed MBT molecules (MBTH or MBT^o form). The corresponding substi-
 243 tution energy is calculated as:

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

244 where E(slab/MBT) is the total energy of the system with MBT (MBTH
 245 or MBT^o) adsorbed on the slab surface. E(H₂O) is the energy of a water
 246 molecule calculated in the vacuum. E(slab/H₂O) 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^o 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^o 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:

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

257 where E(slab/MBT^o) is the total energy of the system with MBT thio-
 258 late (MBT^o) adsorbed on the oxide surface. E(H₂O) 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)	ΔE _{subst.} (eV/mol)	ΔE _{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. ΔE_{subst.} is the energy of substitution on the hydrated surface (Equation 5) and ΔE_{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, ε_{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).

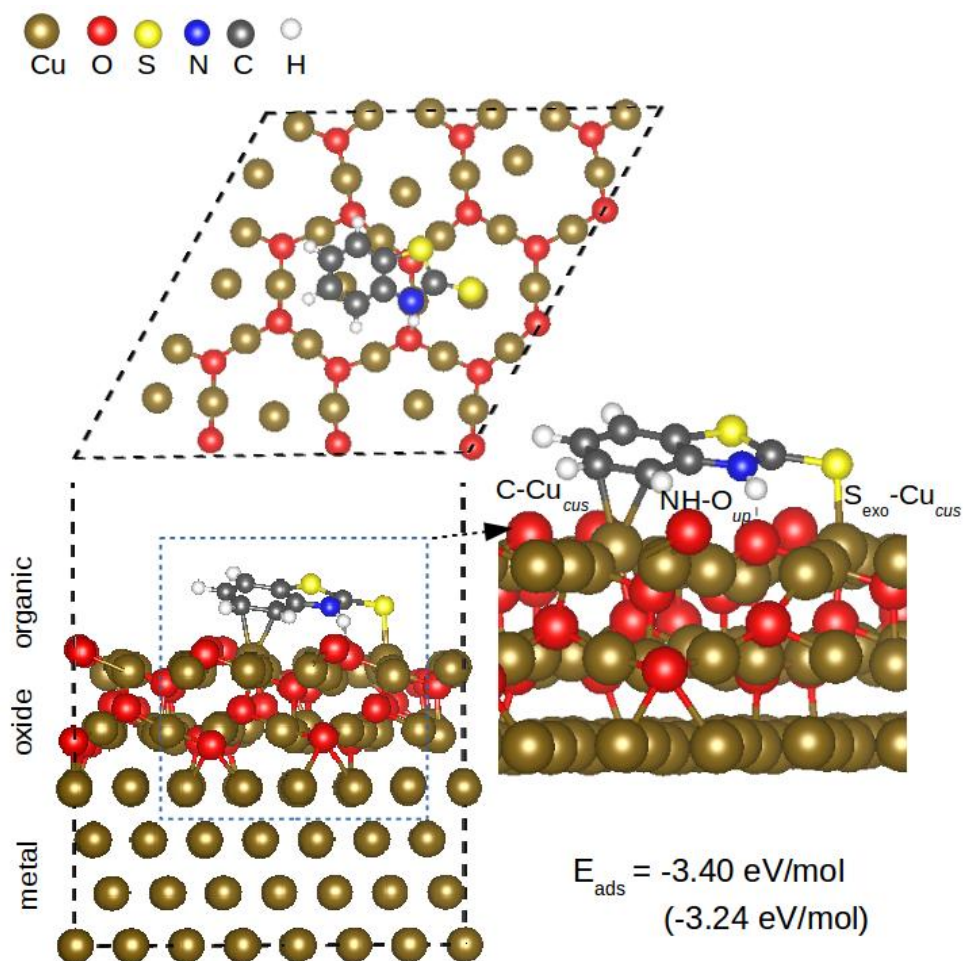


Figure 4: Snapshot and adsorption energy of the most stable adsorbed configuration of thione form (MBTH) at low coverage. E_{ads} value in brackets corresponds to the adsorption energy of MBTH adsorbed on Cu(111) covered by four Cu₂O(111) oxide layers.

320 *3.1.2. Adsorption of thiolate form (MBT^o) at low and full coverage*

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

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

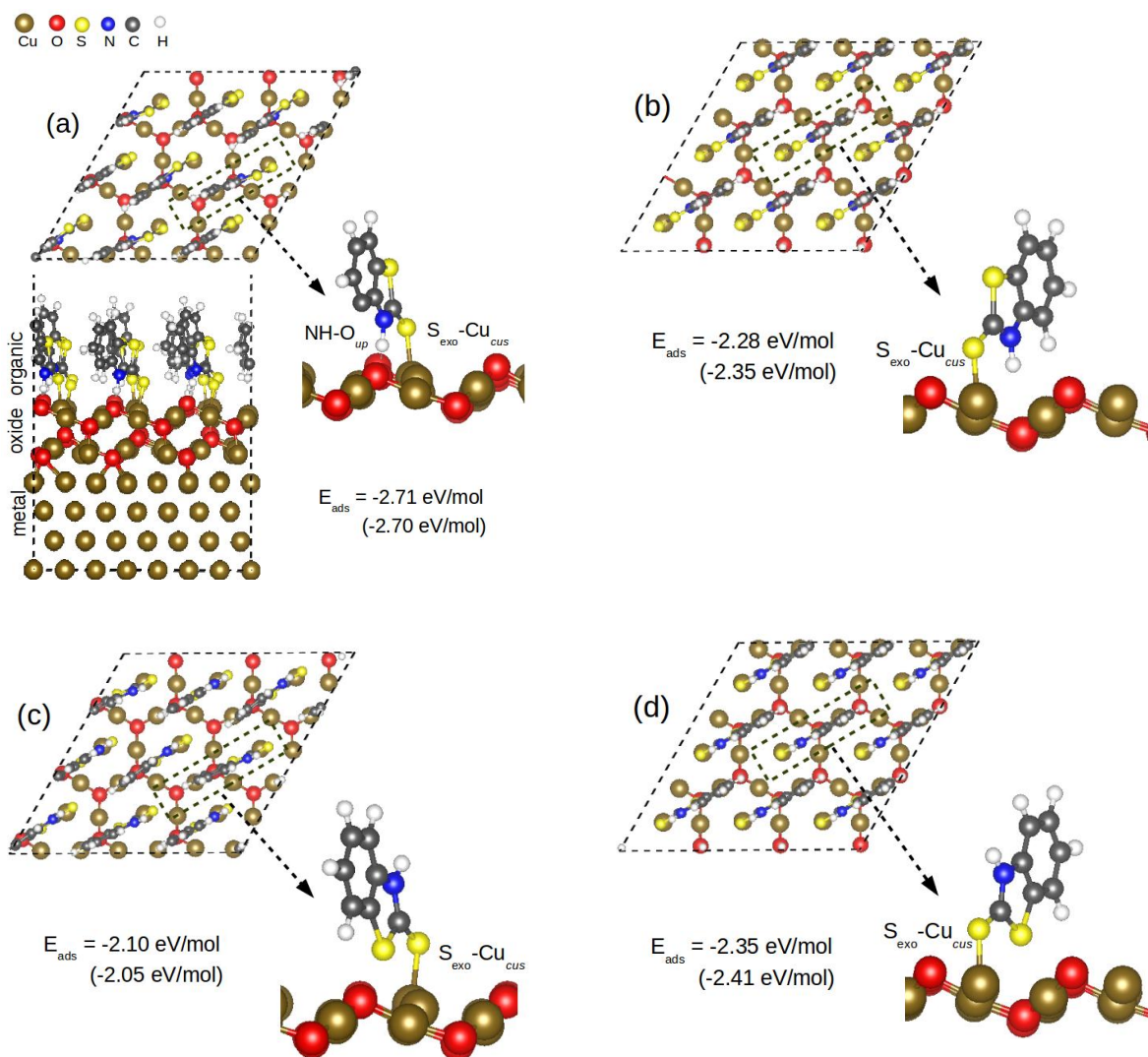


Figure 5: Snapshots and adsorption energies of different adsorption configurations of MBTH form at full coverage and illustration of the adsorption mode. Top, adsorption through exocyclic sulfur atom and NH functional group and orientation relative to the surface sites, (a): ($S_{\text{exo}}\text{-Cu}_{\text{cus}}$ bond; NH-O_{up} bond) and (b): ($S_{\text{exo}}\text{-Cu}_{\text{cus}}$ bond; NH-O_{dn} orientation). Bottom, adsorption through exo and endocyclic sulfur atoms and orientation relative to the surface sites, (c): ($S_{\text{exo}}\text{-Cu}_{\text{cus}}$ bond; $S_{\text{endo}}\text{-O}_{\text{up}}$ orientation) and (d): ($S_{\text{exo}}\text{-Cu}_{\text{cus}}$ bond; $S_{\text{endo}}\text{-O}_{\text{dn}}$ orientation). E_{ads} values in brackets correspond to the adsorption energy of MBTH adsorbed on Cu(111) covered by four $\text{Cu}_2\text{O}(111)$ oxide layers.

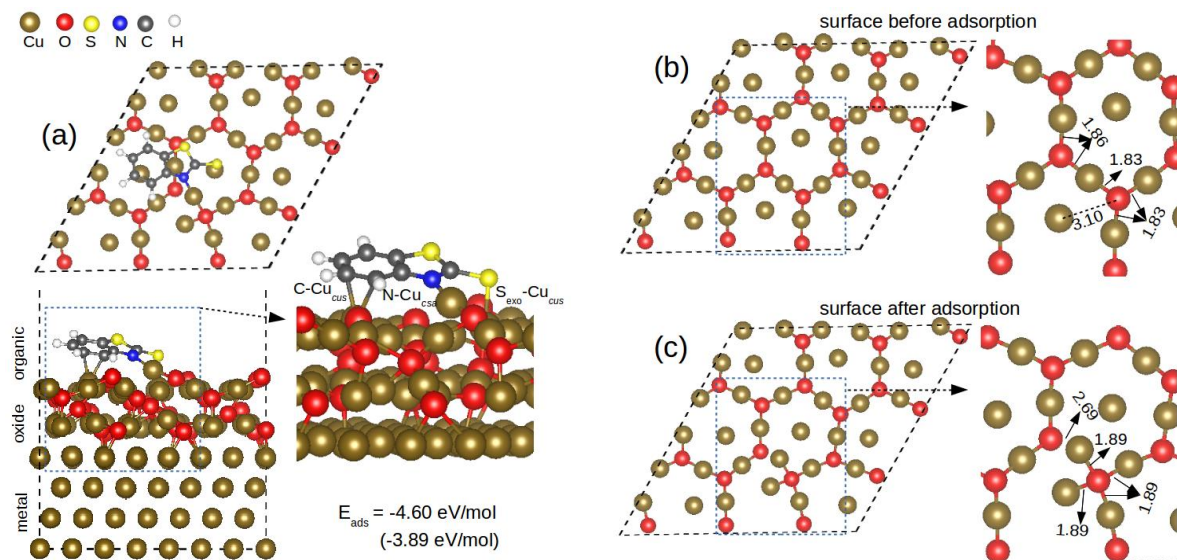


Figure 6: Snapshots and adsorption energy of the most stable adsorption configuration of thiolate form (MBT°) at low coverage (a) and surface structure of Cu₂O(111) film after adsorption (b) and before adsorption (bare surface) (c). E_{ads} value in brackets corresponds to the adsorption energy of MBT°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

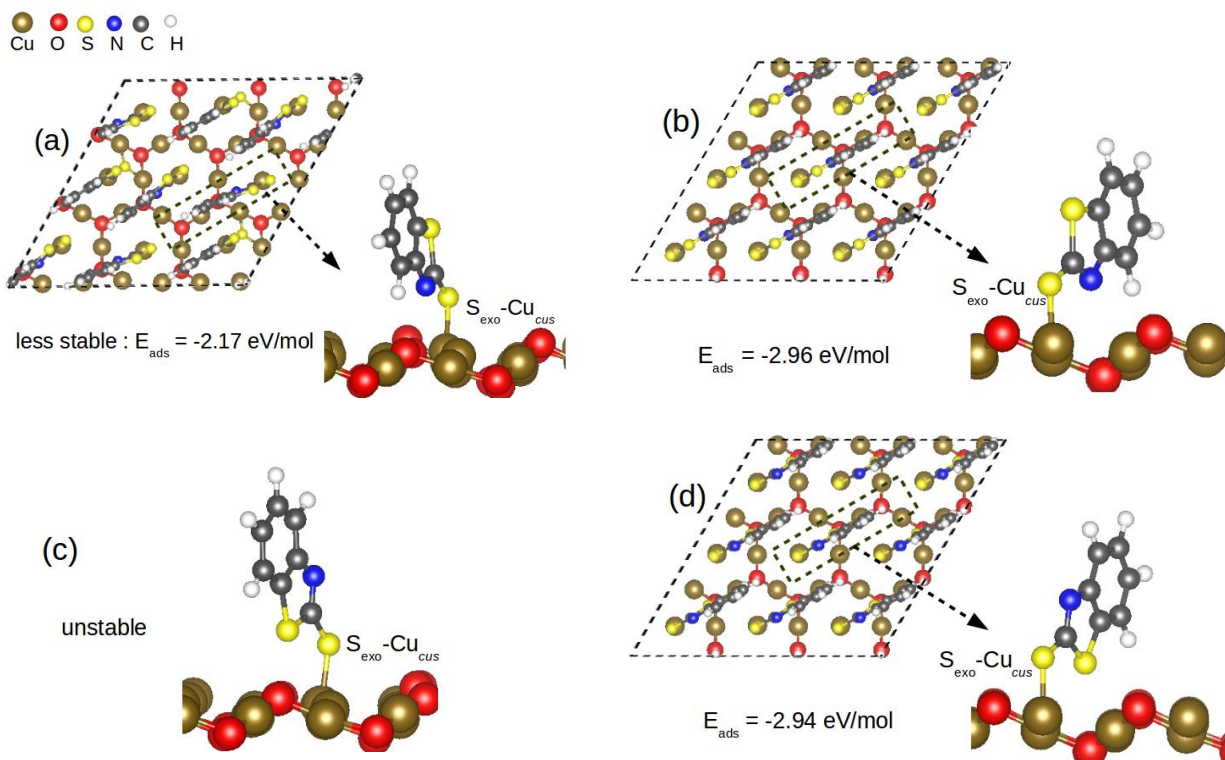


Figure 7: Snapshots and adsorption energies of different adsorption configurations of MBT^o form at full coverage and illustration of different adsorption modes. Top, adsorption through exocyclic sulfur and nitrogen atoms and orientation relative to the surface sites, (a): (S_{exo} - Cu_{cus} bond; N-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

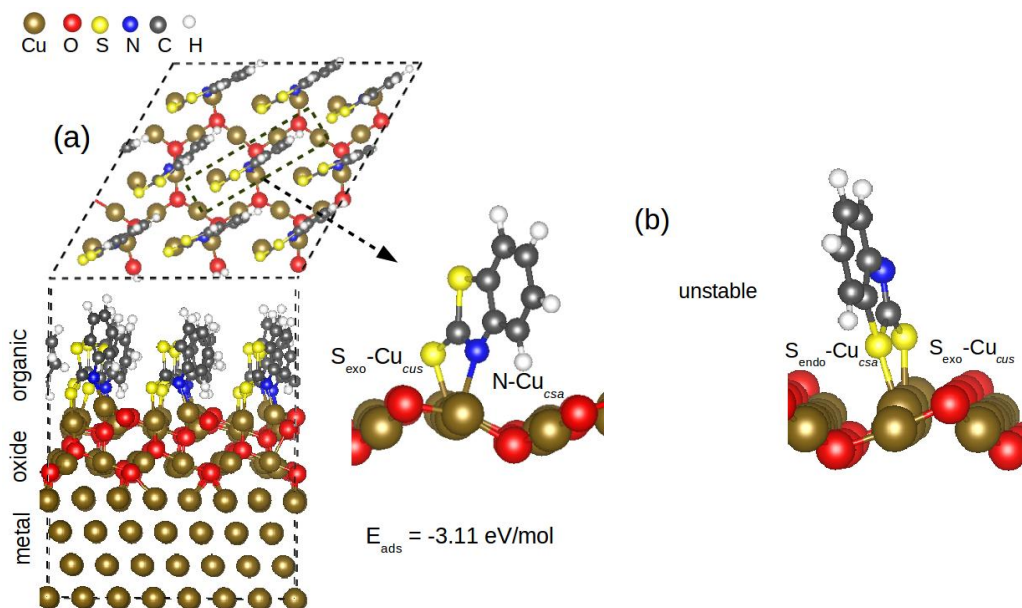


Figure 8: Snapshots and adsorption energy of different adsorption configurations of MBT° at full coverage and illustration of different adsorption modes. (a) adsorption through exocyclic sulfur and nitrogen atoms and orientation relative to the surface sites ($S_{\text{exo}}-\text{Cu}_{\text{cus}}$ bond;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

355 configurations are not further discussed below.

356 At full coverage, MBT°, like MBTH, adsorbs in a perpendicular orientation.
 357 Interestingly, the adsorption via S_{exo} and N atoms or via S_{exo} and S_{endo}
 358 atoms, noted (b) and (d) in Fig.7, respectively, are iso-energetic. The ad-
 359 sorption energy is $-2.95 \pm 0.01 \text{ eV/mol}$ ($\varepsilon_{\text{norm}} = -1.55 \text{ J/m}^2$) and more stable
 360 by 0.25 eV/mol than for MBTH. This competitive adsorption is valid only
 361 in the presence of both species (thione and thiolate) in the same medium,
 362 as explained for low coverage case. MBT° binds only via S_{exo} atom to an
 363 unsaturated copper atom, with a bond length of 2.12 \AA . The distance from
 364 the S_{endo} and N atoms to the O_{dn} atom is 3.15 ± 0.03 and $4.48 \pm 0.03 \text{ \AA}$, re-
 365 spectively. These MBT° adsorbed configurations are oriented from Cu_{cus} to
 366 O_{dn} direction, whereas it is from Cu_{cus} to O_{up} direction for the most stable
 367 configuration of MBTH.

368 The most stable adsorbed configuration of MBT°, noted (a) in Fig.8, has
 369 an adsorption energy of -3.11 eV/mol ($\varepsilon_{\text{norm}} = -1.63 \text{ J/m}^2$). The normaliza-
 370 tion 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

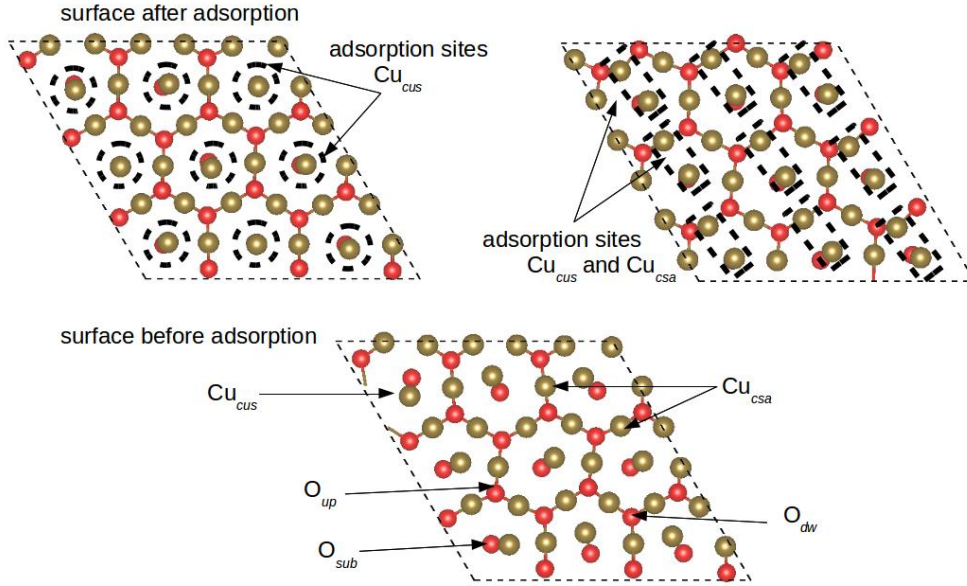


Figure 9: Surface structure after adsorption of MBT (top) compared to bare surface structure (bottom). Top left corresponds to all adsorption configurations of MBTH and MBT° with one covalent bond of the molecule to the Cu_{cus} atom (circled). Top right corresponds to the configuration in Fig8(a) with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

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 $+0.004 e/\text{\AA}^3$.

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

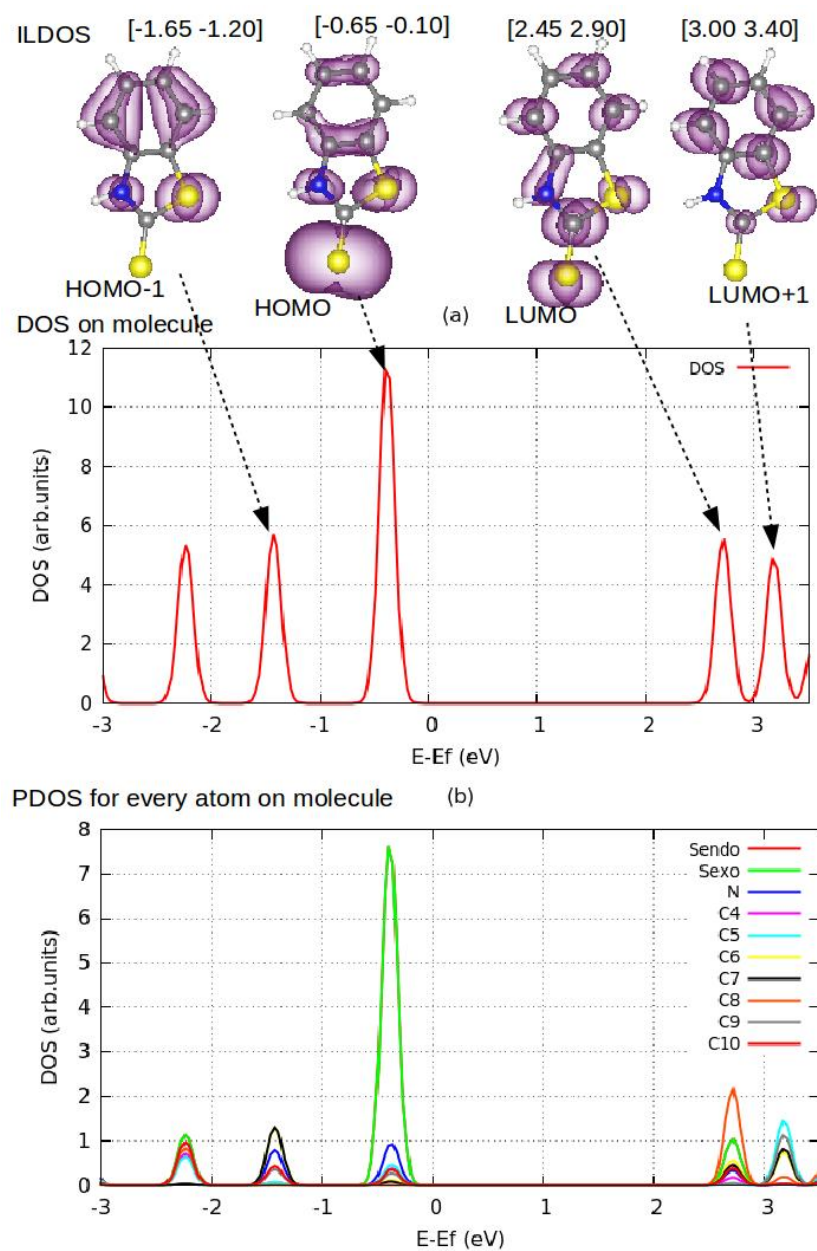


Figure 10: Electronic structure analysis of the isolated MBTH form of MBT: integral local density of states (ILDOS, top), density of states (DOS, middle) and projected density of states (PDOS, bottom).

462 *3.2.2. Adsorbed molecules at full coverage*

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

467
468 The comparison of the ILDOS and DOS projected on the molecules be-
469 fore and after adsorption, reveals drastic changes in the electronic structure
470 of the molecule, indicating a strong molecule-surface interaction. We observe
471 peak shifting, peak broadening, and the appearance of new peaks in the den-
472 sity of states after adsorption. Two peaks located below the Fermi energy
473 at -1.50 eV and -3.60 eV are dominated by the DOS of the exocyclic sulfur
474 atom. The ILDOS reveals that the peak at -1.50 eV is similar to the sulfur
475 contribution at HOMO before adsorption and that the peak at lower energy
476 (-3.60 eV) is associated to the sulfur-copper binding. It can be concluded
477 that the interaction via the exocyclic sulfur with the copper atom is very
478 strong and it is the only atom involved in the covalent binding of MBTH on
479 Cu(111)||Cu₂O(111) surface.

480
481 More details on the molecule-surface binding are provided by the charge
482 density difference analysis. Fig.12 show the charge density difference ($\Delta\rho(r)$),
483 plotted with an isosurface of ± 0.001 e/ \AA^3 for the most stable configuration
484 at full coverage of MBTH. For better visualization of the isosurface, we rep-
485 resented only one molecule on the surface in the same adsorption topology
486 as at full coverage.

487 $\Delta\rho(r)$ shows charge density accumulation between the exocyclic sulfur
488 atom and one unsaturated copper. In addition a charge density deficit is
489 observed on the S_{exo} and Cu_{cus} atoms, confirming again the formation of a
490 covalent bond between these atoms. We also observe charge density accu-
491 mulation on one unsaturated oxygen atom and charge density deficit on the
492 hydrogen of the NH group confirming the H-bonding NH...O.

493
494 The Bader charge analysis for MBTH form reveals an electron trans-
495 fer from the organic layer to the oxide. We calculated the values of 0.15
496 e/molecule at full coverage. The electrons were redistributed in the oxide,
497 whereas the electrons distribution after adsorption remains unchanged in
498 the metallic part of the slab substrate. The electrons redistribution on the

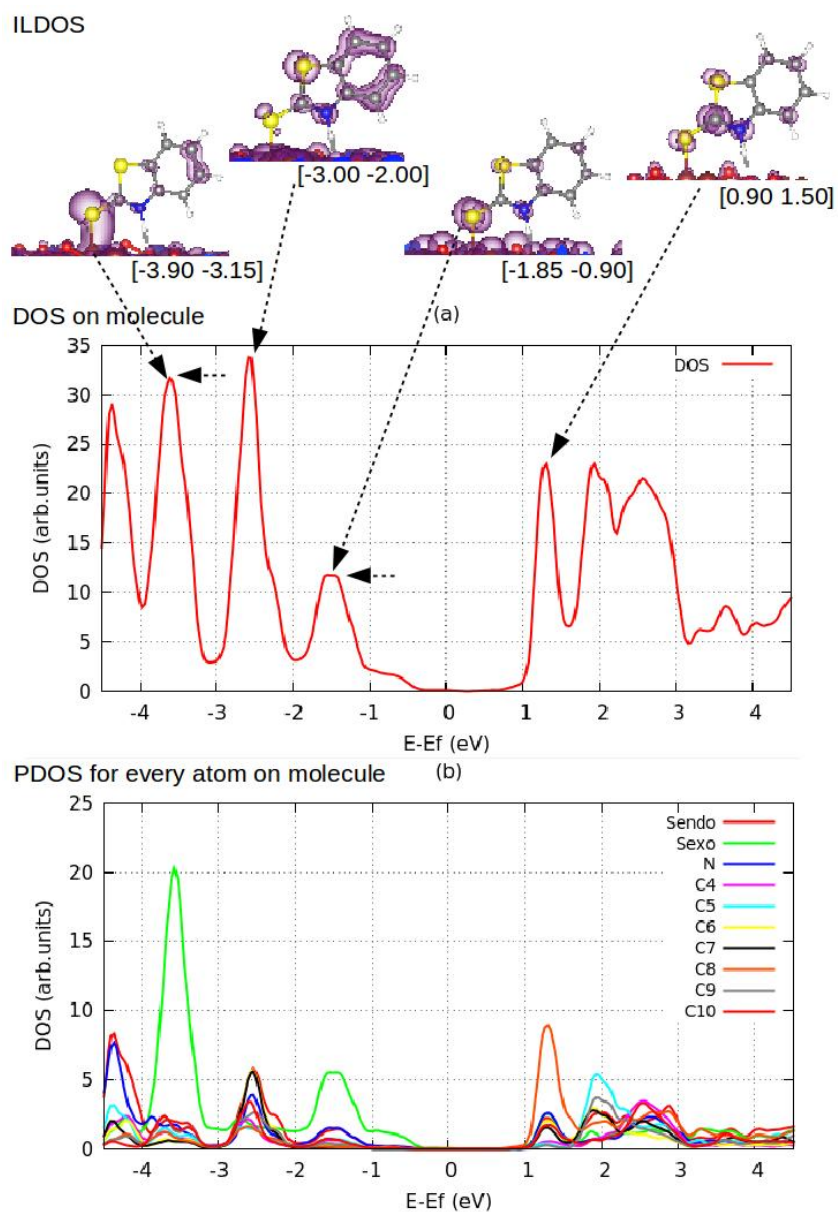


Figure 11: Electronic properties of adsorbed MBTH at full coverage: visualisation of integral local density of states (ILDOS, top), projected density of states on the molecules (PDOS, middle) and projected density of states for every atom of the molecule (PDOS, bottom).

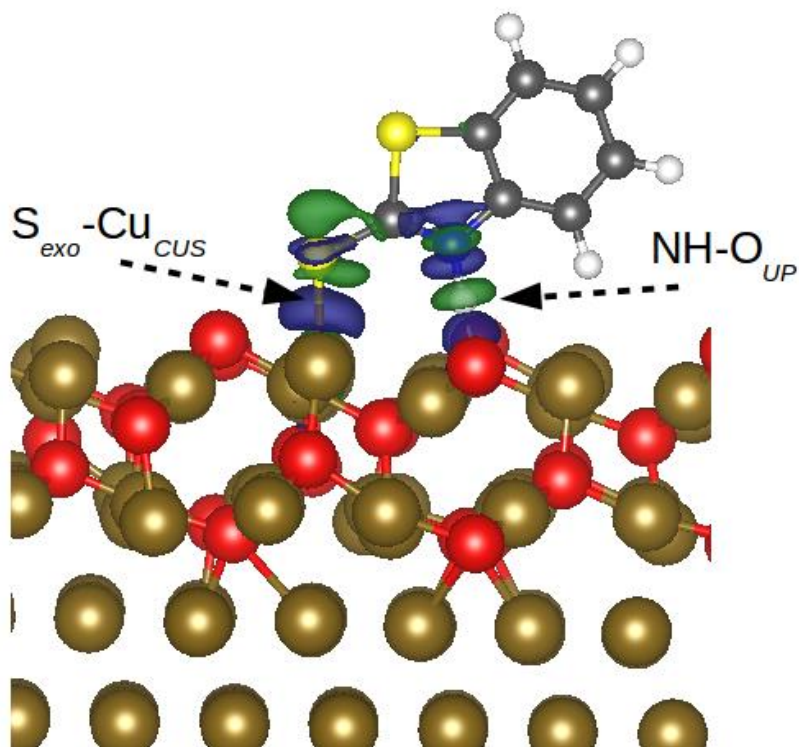


Figure 12: Charge density difference analysis for most stable full coverage adsorbed configuration of MBTH. Blue and green color correspond to accumulation and deficit of charge density, respectively

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^\ominus) 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-

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

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

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

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

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

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

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

544 Acknowledgments

545 This project has received funding from the European Research Council
546 (ERC) under the European Union’s Horizon 2020 research and innovation

547 program (ERC Advanced Grant No. 741123, Corrosion Initiation Mecha-
548 nisms at the Nanometric and Atomic Scales : CIMNAS).

549 **References**

- 550 [1] I. Milošev, Contemporary modes of corrosion protection and function-
551 alization of materials, *Acta Chim. Slov.* 66 (2019) 511–533.
- 552 [2] S. Gangopadhyay, P. A. Mahanwar, Recent developments in the volatile
553 corrosion inhibitor (VCI) coatings for metal: A review, *J. Coat. Technol.*
554 *Res.* 15 (2018) 789–807.
- 555 [3] P. B. Raja, M. G. Sethuraman, Natural products as corrosion inhibitor
556 for metals in corrosive media - A review,, *Mater. Lett.* 62 (2008) 113–
557 116.
- 558 [4] R. L. Twite, G. P. Bierwagen, Review of alternatives to chromate for
559 corrosion protection of aluminum aerospace alloys, *Prog. Org. Coat.* 33
560 (1998) 91–100.
- 561 [5] M. Kendig, S. Jeanjaquet, R. Addison, J. Waldrop, Role of hexavalent
562 chromium in the inhibition of corrosion of aluminum alloys, *Surf. and*
563 *Coat. Techn.* 140 (2001) 58–66.
- 564 [6] J. Sinko, Challenges of chromate inhibitor pigments replacement in
565 organic coatings, *Prog. Org. Coat.* 42 (2001) 267–282.
- 566 [7] Y. Qiang, S. Zhang, S. Yan, X. Zou, S. Chen, Three indazole derivatives
567 as corrosion inhibitors of copper in a neutral chloride solution, *Corros.*
568 *Sci.* 126 (2017) 295–304.
- 569 [8] J. Li, C. W. Du, Z. Y. Liu, X. G. Li, M. Liu, Inhibition film formed by
570 2-mercaptobenzothiazole on copper surface and its degradation mech-
571 anism in sodium chloride solution, *Int. J. Electrochem. Sci.* 11 (2016)
572 10690–10705.
- 573 [9] Z. Tao, W. He, S. Wang, G. Zhou, Electrochemical study of cyprocona-
574 zole as a novel corrosion inhibitor for copper in acidic solution, *Ind.*
575 *Eng. Chem. Res.* 52 (2013) 17891–17899.

- 576 [10] H. Tian, W. Li, K. Cao, B. Hou, Potent inhibition of copper corrosion in
577 neutral chloride media by novel non-toxic thiadiazole derivatives, *Corros. Sci.* 73 (2013) 281–291.
578
- 579 [11] M. Finšgar, 2-mercaptobenzimidazole as a copper corrosion inhibitor:
580 Part II. surface analysis using X-ray photoelectron spectroscopy, *Corros. Sci.* 72 (2013) 90–98.
581
- 582 [12] Y. S. Tan, M. P. Srinivasan, S. O. Pehkonen, S. Y. M. Chooi, Effects
583 of ring substituents on the protective properties of self-assembled benzenethiols on copper, *Corros. Sci.* 48 (2006) 840–862.
584
- 585 [13] R. Subramanian, V. Lakshminarayanan, Effect of adsorption of some
586 azoles on copper passivation in alkaline, *Corros. Sci.* 44 (2002) 535–554.
- 587 [14] J. D. G. Xue, X. Y. Huang, J. Zhang, The formation of an effective
588 anti-corrosion film on copper surfaces from 2-mercaptobenzimidazole solution, *J. Electroanal. Chem. Interfacial Electrochem.* 310 (1991) 139–
589 148.
590
- 591 [15] D. Chadwick, T. Hashemi, Electron spectroscopy of corrosion in-
592 hibitors: Surface films formed by 2-mercaptobenzothiazole and 2-
593 mercaptobenzimidazole on copper, *Surf. Sci.* 89 (1979) 649–659.
- 594 [16] M. Ohsawa, W. Suetaka, Spectro-electrochemical studies of the corro-
595 sion inhibition of copper by 2-mercaptobenzothiazole, *Corros. Sci.* 19
596 (1979) 709–722.
- 597 [17] J. C. Marconato, L. O. Bulho, A spectroelectrochemical study of the in-
598 hibition of the electrode process on copper by 2- mercaptobenzothiazole
599 in ethanolic solutions, *Electrochim. Acta* 43 (1998) 771–780.
- 600 [18] J. A. Ramírez-Cano, L. Veleza, R. M. Souto, B. M. Fernández-Pérez,
601 SECM study of the pH distribution over Cu samples treated with 2-
602 mercaptobenzothiazole in NaCl solution, *Electrochem. commun.* 78
603 (2017) 60–63.
- 604 [19] M. Finšgar, D. K. Merl, An electrochemical, long-term immersion, and
605 XPS study of 2-mercaptobenzothiazole as a copper corrosion inhibitor
606 in chloride solution, *Corros. Sci.* 83 (2014) 164–175.

- 607 [20] L. P. Kazansky, I. A. Selyaninov, Y. I. Kuznetsov, Adsorption of
608 2-mercaptobenzothiazole on copper surface from phosphate solutions,
609 Appl. Surf. Sci. 258 (2012) 6807–6813.
- 610 [21] R. Woods, G. A. Hope, K. Watling, A SERS spectroelectrochemical
611 investigation of the interaction of 2-mercaptobenzothiazole with copper,
612 silver and gold surfaces, J. Appl. Electrochem. 30 (2000) 1209–1222.
- 613 [22] T. Shahrabi, H. Tavakholi, M. G. Hosseini, Corrosion inhibition of
614 copper in sulphuric acid by some nitrogen heterocyclic compounds, Anti-
615 Corrosion Methods and Materials 54 (2007) 308–313.
- 616 [23] D. He, F. Chen, J. Chen, S. Yao, W. Wei, Real-time bulk acoustic wave
617 studies of the inhibition behavior of mercaptobenzothiazole on copper,
618 Thin Solid Films 352 (1999) 234–238.
- 619 [24] Q. Bao, D. Zhang, Y. Wan, 2-mercaptobenzothiazole doped
620 chitosan/11-alkanethiolate acid composite coating: Dual function for
621 copper protection, Appl. Surf. Sci. 257 (2011) 10529–10534.
- 622 [25] Y.-H. Chen, A. Erbe, The multiple roles of an organic corrosion inhibitor
623 on copper investigated by a combination of electrochemistry-coupled
624 optical in situ spectroscopies, Corros. Sci. 145 (2018) 232–238.
- 625 [26] X. Wu, F. Wiame, V. Maurice, P. Marcus, Adsorption and thermal
626 stability of 2-mercaptobenzothiazole corrosion inhibitor on metallic and
627 pre-oxidized Cu(111) model surfaces, Applied Surface Science 508 (2020)
628 145132.
- 629 [27] X. Wu, F. Wiame, V. Maurice, P. Marcus, 2-mercaptobenzothiazole
630 corrosion inhibitor deposited at ultra-low pressure on
631 model copper surfaces, Corrosion science (2020). URL:
632 <https://doi.org/10.1016/j.corsci.2020.108464>.
- 633 [28] P. J. Denissen, S. J. Garcia, Reducing subjectivity in EIS interpretation
634 of corrosion and corrosion inhibition processes by in-situ optical analysis,
635 Electrochim. Acta 293 (2019) 514–524.
- 636 [29] K. Khanari, M. Finšgar, The corrosion inhibition of AA6082 aluminium
637 alloy by certain azoles in chloride solution: Electrochemistry and surface
638 analysis, Coating 9 (2019) 380.

- 639 [30] M. A. Zadeh, J. Tedim, M. Zheludkevich, S. van der Zwaag, S. J. Garcia,
640 Synergetic active corrosion protection of AA2024-T3 by 2D- anionic and
641 3D-cationic nanocontainers loaded with Ce and mercaptobenzothiazole,
642 *Corros. Sci.* 135 (2018) 35–45.
- 643 [31] P. Visser, H. Terryn, J. M. C. Mol, On the importance of irreversibility of
644 corrosion inhibitors for active coating protection of AA2024-T3, *Corros.*
645 *Sci.* 140 (2018) 272–285.
- 646 [32] A. C. Balaskas, T. Hashimoto, M. Curioni, G. E. Thompson,
647 Two-shell structured PMAA@CeO₂ nanocontainers loaded with 2-
648 mercaptobenzothiazole for corrosion protection of damaged epoxy
649 coated AA2024-T3, *Nanoscale* 9 (2017) 5499.
- 650 [33] F. Maia, K. A. Yasakau, J. Carneiro, S. Kallip, J. Tedim, T. Henriques,
651 A. Cabral, J. Venâncio, M. L. Zheludkevich, M. G. S. Ferreira, Corrosion
652 protection of AA2024 by sol-gel coatings modified with MBT-loaded
653 polyurea microcapsules, *Chem. Eng. J.* 283 (2016) 1108–1117.
- 654 [34] E. Roussi, A. Tsetsekou, A. Skarmoutsou, C. A. Charitidis, A. Karantonis,
655 Anticorrosion and nanomechanical performance of hybrid organo-
656 silicate coatings integrating corrosion inhibitors, *Surf. Coat. Techn.* 232
657 (2013) 131–141.
- 658 [35] H. Cen, J. Cao, Z. Chen, X. Guo, 2-mercaptobenzothiazole as a corrosion
659 inhibitor for carbon steel in supercritical CO₂-H₂O condition, *Appl.*
660 *Surf. Sci.* 476 (2019) 422–434.
- 661 [36] Z. Mirzakhazadeh, A. Kosari, M. H. Moayed, R. Naderi, P. Taheri,
662 J. M. C. Mol, Enhanced corrosion protection of mild steel
663 by the synergetic effect of zinc aluminum polyphosphate and 2-
664 mercaptobenzimidazole inhibitors incorporated in epoxy-polyamide
665 coatings, *Corros. Sci.* 138 (2018) 372–379.
- 666 [37] I. A. Kartsonakis, S. G. Stanciu, A. A. Matei, R. Hristu, A. Karantonis,
667 C. A. Charitidis, A comparative study of corrosion inhibitors on hot-dip
668 galvanized steel, *Corros. Sci.* 112 (2016) 289–307.
- 669 [38] K. Rahmani, R. Jadidian, S. Haghtalab, Evaluation of inhibitors and
670 biocides on the corrosion, scaling and biofouling control of carbon steel

- 671 and copper–nickel alloys in a power plant cooling water system, *Desali-*
672 *nation* 393 (2016) 174–185.
- 673 [39] M. Gholami, I. Danaee, M. H. Maddahy, M. RashvandAvei, Corre-
674 lated ab initio and electroanalytical study on inhibition behavior of 2-
675 mercaptobenzothiazole and its thiole thione tautomerism effect for the
676 corrosion of steel (API 5L X52) in sulphuric acid solution, *Ind. Eng.*
677 *Chem. Res.* 52 (2013) 14875–14889.
- 678 [40] J. Zhang, Q. Zhang, H. Ren, W. Zhao, H. Zhang, Inhibition performance
679 of 2-mercaptobenzothiazole derivatives in CO₂ saturated solution and its
680 adsorption behavior at Fe surface, *Appl. Surf. Sci.* 253 (2017) 7416–7422.
- 681 [41] L. P. Kazansky, Y. E. Pronin, I. A. Arkhipushkin, XPS study of ad-
682 sorption of 2-mercaptobenzothiazole on a brass surface, *Corros. Sci.* 89
683 (2014) 21–29.
- 684 [42] K. Ramji, D. R. Cairns, S. Rajeswari, Synergistic inhibition effect of 2-
685 mercaptobenzothiazole and Tween-80 on the corrosion of brass in NaCl
686 solution, *Appl. Surf. Sci.* 254 (2008) 4483–4493.
- 687 [43] X. Xing, X. Xu, J. Wang, W. Hu, Preparation, release and anticorro-
688 sion behavior of a multi-corrosion inhibitors-halloysite nanocomposite,
689 *Chem. Phys. Lett.* 718 (2019) 69–73.
- 690 [44] Y. Li, S. Zhang, Q. Ding, D. Feng, B. Qin, L. Hu, The corrosion and
691 lubrication properties of 2-mercaptobenzothiazole functionalized ionic
692 liquids for bronze, *Tribology International* 114 (2017) 121–131.
- 693 [45] D. Liu, E. Han, Y. Song, D. Shan, Enhancing the self-healing prop-
694 erty by adding the synergetic corrosion inhibitors of Na₃PO₄ and 2-
695 mercaptobenzothiazole into the coating of Mg alloy, *Electrochim. Acta*
696 323 (2019) 134796.
- 697 [46] Z.-H. Xie, S. Shan, Nanocontainers-enhanced self-healing Ni coating for
698 corrosion protection of Mg alloy, *J. Mater. Sci.* 53 (2018) 3744–3755.
- 699 [47] H. Yang, Y. Sun, J. Ji, W. Song, X. Zhu, Y. Yao, Z. Zhang, 2-
700 mercaptobenzothiazole monolayers on zinc and silver surfaces for an-
701 t anticorrosion, *Corros. Sci.* 50 (2008) 3160–3167.

- 702 [48] V. Grekulović, M. R. Vujasinović, A. Mitovski, Electrochemical be-
703 havior of AgCu50 in alkaline media in the presence of chlorides and 2-
704 mercaptobenzothiazole, *J. Min. Metall. Sect. B-Metall* 53 (2017) 349–
705 356.
- 706 [49] B. Cui, T. Chen, D. Wang, L.-J. Wan, In situ STM evidence for the
707 adsorption geometry of threen-heteroaromatic thiols on Au(111), *Lang-*
708 *muir* 27 (2011) 7614–7619.
- 709 [50] R. K. Shervedani, M. K. Babadi, Application of 2-
710 mercaptobenzothiazole self-assembled monolayer on polycrystalline
711 gold electrode as a nanosensor for determination of Ag(I), *Talanta* 69
712 (2006) 741–746.
- 713 [51] S. Bharathi, V. Yegnaraman, G. P. Rao, Potential-dependent “open-
714 ing” and “closing” of self-assembled 2-mercaptobenzthiazole on gold
715 substrates, *Langmuir* 9 (1993) 1614–1617.
- 716 [52] H. Parham, N. Pourreza, F. Marahel, Resonance rayleigh scatter-
717 ing method for determination of 2-mercaptobenzothiazole using gold
718 nanoparticles probe, *Spectrochim. Acta A* 151 (2015) 308–314.
- 719 [53] Z. Zhang, Q. Wang, X. Wang, L. Gao, The influence of crystal faces
720 on corrosion behavior of copper surface: First-principle and experiment
721 study, *Appl. Surf. Sci.* 396 (2017) 746–753.
- 722 [54] E. Vernack, D. Costa, P. Tingaut, P. Marcus, Theoretical studies of
723 2-mercaptobenzothiazole and 2-mercaptobenzimidazole as corrosion in-
724 hibitors for copper, submitted (2019).
- 725 [55] E. Protopopoff, P. Marcus, Potential–pH diagrams for hydroxyl and
726 hydrogen adsorbed on a copper surface, *Electrochim. Acta* 51 (2005)
727 408–417.
- 728 [56] A. Gharachorlou, M. D. Detwiler, X.-K. Gu, L. Mayr, B. Klötzer,
729 J. Greeley, R. G. Reifenberger, W. N. Delgass, F. H. Ribeiro, D. Y.
730 Zemlyanov, Trimethylaluminum and oxygen atomic layer deposition on
731 hydroxyl-free Cu(111), *ACS Appl. Mater. Interfaces* 7 (2015) 16428–
732 16439.

- 733 [57] J.-H. Park, J.-H. Lee, A. Soon, Organics on oxidic metal surfaces: a
734 first-principles DFT study of PMDA and ODA fragments on the pristine
735 and mildly oxidized surfaces of Cu(111), *Phys. Chem. Chem. Phys.* 18
736 (2016) 21893.
- 737 [58] D. Gustinčič, A. Kokalj, DFT study of azole corrosion inhibitors
738 on Cu₂O model of oxidized copper surfaces: I. Molecule–surface and
739 Cl–surface bonding, *Metals* 8 (2018) 310.
- 740 [59] D. Gustinčič, A. Kokalj, DFT study of azole corrosion inhibitors on
741 Cu₂O model of oxidized copper surfaces: II. Lateral interactions and
742 thermodynamic stability, *Metals* 8 (2018) 311.
- 743 [60] A. Kokalj, D. Gustinčič, M. Poberžnik, M. Lozinšek, New insights into
744 adsorption bonding of imidazole: A viable C2–H bond cleavage on cop-
745 per surfaces, *Appl. Surf. Sci.* 479 (2019) 463–468.
- 746 [61] G. Sun, J. Kürti, P. Rajczy, M. Kertesz, J. Hafner, G. Kresse, Perform-
747 ance of the vienna ab initio simulation package (VASP) in chemical
748 applications, *J. Mol. Struct. THEOCHEM* 624 (2003) 37–45.
- 749 [62] G. Kresse, J. Hafner, *Phys. Rev. B* 47 (1993) 558.
- 750 [63] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calcula-
751 tions for metals and semiconductors using a plane-wave basis set, *Com-
752 put. Mater. Sci* 6 (1996) 15–50.
- 753 [64] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-
754 energy calculations using a plane-wave basis set, *Phys. Rev. B* 54 (1996)
755 11169–11186.
- 756 [65] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector
757 augmented-wave method, *Phys. Rev. B* 59 (1999) 1758–1775.
- 758 [66] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* 50
759 (1994).
- 760 [67] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson,
761 D. J. Singh, C. Fiolhais, Atoms , molecules , solids , and surfaces:
762 Applications of the generalized gradient approximation for exchange and
763 correlation, *Phys. Rev. B* 46 (1992).

- 764 [68] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approxima-
765 tion made simple, *Phys. Rev. Lett.* 77 (1996).
- 766 [69] M. Methfessel, A. T. Paxton, High-precision sampling for Brillouin-zone
767 integration in metals, *Phys. Rev. B* 40 (1989).
- 768 [70] H. J. Monkhorst, J. D. Pack, Special points for Brillouin-zone integra-
769 tions, *Phys. Rev. B* 13 (1976).
- 770 [71] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, B. I. Lundqvist,
771 Van der Waals density functional for general geometries, *Phys. Rev.*
772 *Lett.* 92 (2004) 246401.
- 773 [72] J. Klimeš, D. R. Bowler, A. Michaelides, Chemical accuracy for the van
774 der Waals density functional, *J. Phys.: Condens.* 22 (2010) 022201.
- 775 [73] J. Klimeš, D. R. Bowler, A. Michaelides, Van der Waals density func-
776 tionals applied to solids, *Phys. Rev. B* 83 (2011) 195131.
- 777 [74] J. Klimeš, A. Michaelides, Perspective: Advances and challenges in
778 treating van der Waals dispersion forces in density functional theory, *J.*
779 *Chem. Phys.* 137 (2012) 120901.
- 780 [75] V. Maurice, H.-H. Strehlowa, P. Marcus, In situ STM study of the initial
781 stages of oxidation of Cu(111) in aqueous solution, *Surf. Sci.* 458 (2000)
782 185–194.
- 783 [76] J. Kunze, V. Maurice, L. H. Klein, H.-H. Strehlowa, P. Marcus, In situ
784 scanning tunneling microscopy study of the anodic oxidation of Cu(111)
785 in 0.1 M NaOH, *J. Phys. Chem. B* 105 (2001) 4263–4269.
- 786 [77] J. Kunze, V. Maurice, L. H. Klein, H.-H. Strehlowa, P. Marcus, In
787 situ STM study of the effect of chlorides on the initial stages of anodic
788 oxidation of Cu(111) in alkaline solutions, *Electrochim. Acta* 48 (2003)
789 1157–1167.
- 790 [78] J. Kunze, V. Maurice, L. H. Klein, H.-H. Strehlowa, P. Marcus, In situ
791 STM study of the duplex passive films formed on Cu(111) and Cu(001)
792 in 0.1 M NaOH, *Corros. Sci.* 46 (2004) 245–264.
- 793 [79] P. Marcus, V. Maurice, Atomic level characterization in corrosion stud-
794 ies, *Phil. Trans. R. Soc. A* 375 (2016) 20160414.

- 795 [80] H. P. Koch, Absorption spectra and structure of organic sulphur com-
796 pounds., *J. Chem. Soc. Part III* (1949) 401–108.
- 797 [81] J. P. Chesick, J. Donohue, The molecular and crystal structure of 2-
798 mercaptobenzothiazole, *Acta Cryst. B* 27 (1971) 1441–1444.
- 799 [82] A. K. Rai, R. Singh, K. N. Singh, V. B. Singh, FTIR, raman spectra and
800 ab initio calculations of 2-mercaptobenzothiazole, *Spectrochim. Acta A*
801 63 (2006) 483–490.
- 802 [83] T. A. Mohamed, A. M. Mustafa, W. M. Zoghaib, M. S. Affi, R. S.
803 Farag, Y. Badr, Reinvestigation of benzothiazoline-2-thione and 2-
804 mercaptobenzothiazole tautomers: Conformational stability, barriers to
805 internal rotation and DFT calculations, *J. Mol. Struct.: THEOCHEM*
806 868 (2008) 27–36.
- 807 [84] W. Tang, E. Sanville, G. Henkelman, A grid-based bader analysis algo-
808 rithm without lattice bias, *J. Phys.: Condens. Matter* 21 (2009) 084204.