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Effects of water vapour on 2-mercaptobenzothiazole corrosion inhibitor films deposited on copper

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Abstract

The effects of water on 2-mercaptobenzothiazole (2-MBT) film pre-formed on copper at low pressure and room temperature was investigated in situ by X-ray photoelectron spectroscopy. Upon exposure to water vapour at 5×10^{-6} mbar, the 2-MBT molecules not directly bonded to copper desorb, until only one monolayer remains adsorbed. Further exposure leads to cleavage of the bond between exocyclic sulphur and copper, whereas nitrogen remains bonded to copper. Dissociative adsorption of water is observed, without copper oxidation for exposure up to 3×10^6 L. This work brings new molecular scale insight into corrosion inhibition mechanisms in water-containing environments.

Keywords: A. 2-MBT, A. Copper, A.H₂O, C.Corrosion inhibition, B. XPS

1. Introduction

Given the extensive use of copper in industrial and civil sectors, its corrosion degradation plays a significant role in economics and safety, thus rising the importance of corrosion protection. The use of corrosion inhibitors is considered as one of the most effective ways to protect copper from corrosion. Their inhibition efficiency is directly related to their adsorption properties, which then depend on the nature of the copper surface and the

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structure of the inhibitors. Among the existing corrosion inhibitors, benzotriazole and its derivatives, notably 2-MBT, are the mostly used ones with high inhibition efficiency [1–8].

2-mercaptobenzothiazole (2-MBT, $C_6H_4(NH)SC=S$) is an organic compound showing wide application in a large spectrum of industries for the production of lubricant and additives, the sulphur vulcanization of rubber [9], the biological activities [10], and most importantly, the corrosion inhibition of metals and alloys [11–14]. More specifically, 2-MBT contains heteroatoms with high electron density, such as nitrogen and sulphur, which are considered as reactive sites for its adsorption on surfaces [7, 15–18].

In most phenomena, copper is exposed to water. So the understanding of the effect of water on the corrosion inhibition properties of 2-MBT on copper is the first step to further grasp its corrosion protection mechanisms in real conditions. Numerous studies have been performed to characterize the interaction between copper and 2-MBT in aqueous solution [8, 11, 19–22]. The molecule was found to coordinate with the copper substrate through sulphur and nitrogen atoms, leading to the formation of a protective barrier organic film on copper surface, thus preventing the metal from further degradation. However, for these studies carried out directly in liquid phase, it is difficult to control and follow each step of interaction between the inhibitor, copper and water. Moreover, surface contamination is a problem for ex situ analysis.

In this work, a surface science approach on a model system, innovative in the context of corrosion inhibition, was applied in order to gain detailed information on the interaction of water with the 2-MBT molecular layer formed on copper. More precisely, 2-MBT was deposited on copper in clean metallic state through sublimation at ultra-low pressure. This allows the formation of a chemically and structurally well characterized molecular layer. The sample was then exposed to water vapour at low pressure and room temperature, and the surface state was monitored in situ by X-ray photoelectron spectroscopy (XPS). This model approach enables a precise control of the interaction between the protective organic molecular layer and water. Although far from real conditions, the results allow us to understand in details the origin of the corrosion inhibition alterations that are essential to further understand the behaviour in real conditions.

2. Material and methods

2.1. Materials

A high purity (99.999 %) Cu(111) single-crystal was used. It was prepared clean in the metallic state under ultra-high vacuum (UHV) by repeated cycles of ion sputtering ($P_{\text{Ar}} = 5 \times 10^{-6}$ mbar, 600 V, 10 mA, 10 min) and annealing (600 °C, 10 min). The surface state was verified systematically until no contamination was detected by XPS, and a sharp (1×1) low energy electron diffraction pattern, indicative of a well-ordered surface termination, was observed.

The 2-MBT used was 99 % pure (Sigma-Aldrich). It is a yellow powder at room temperature. The powder was placed in a vacuum sealed glass tube which is connected to the preparation chamber of the UHV system for the *in situ* deposition of 2-MBT. The 2-MBT vapour pressure is about 10^{-9} mbar at room temperature.

2.2. Methods

The UHV system, equipped with preparation chambers for surface preparation, 2-MBT deposition and water vapour exposure, as well as an XPS spectrometer (Thermo Electron Corporation, ESCALAB 250) for chemical analysis, is pumped continuously to keep a base pressure below 10^{-10} mbar under normal conditions. A monochromatic Al K_{α} X-ray source (1486.6 eV) was used for the analysis. The binding energy was calibrated by referring to the Fermi level of the sample. Reference samples were used to calibrate the transmission of the analyser. The survey spectrum was recorded with a pass energy of 100 eV corresponding to an overall resolution of 1.8 eV, and the high resolution core level spectra were recorded with a pass energy of 20 eV corresponding to an overall resolution of 360 meV. The analysed photoelectrons were collected with a take-off angle of 90°, and the XPS spectra were analysed using the CasaXPS software (version 2.3.19) [23].

The clean Cu(111) surface was exposed to 2-MBT vapour at partial pressure of about 10^{-9} mbar at room temperature (RT). The sample and the 2-MBT powder were kept at RT during the entire deposition process, and the surface after exposure was characterized by XPS. The molecular exposure is expressed in langmuir ($1 \text{ L} = 10^{-6}$ torr s). The effect

of water on the pre-adsorbed molecular layer was studied by introducing water vapour progressively into the preparation chamber at partial pressure up to 5×10^{-6} mbar and RT until saturation.

The clean Cu(111) surface was exposed to water vapour under the same conditions as above until saturation, and the results were compared to those obtained on Cu(111) covered by the pre-deposited 2-MBT layer.

3. Results and discussion

Previously, we have studied the growth kinetics of 2-MBT on Cu(111) at ultra-low pressure and RT [2, 3]. A complete monolayer of thickness of about 0.2 nm was formed at low exposure, followed by the formation of multilayer of thickness of about 0.6 nm. In this work, the same conditions were applied to firstly grow 2-MBT layers on Cu(111). The sample was then exposed to water vapour at low pressure and RT, and the surface was characterized in situ by XPS.

3.1. 2-MBT multilayer exposed to water vapour

Fig. 1 shows the S 2p spectra obtained on the metallic Cu(111) surface covered by a 2-MBT multilayer before and after different exposures to water vapour at 5×10^{-6} mbar and RT. The S 2p spectra were decomposed using three spin-orbit doublets S 2p_{1/2} and S 2p_{3/2}, with a branching ratio of 0.51 and spin-orbit splitting of 1.18 eV [8, 24]. Before exposure to water vapour, an intense peak S₃ was observed, with the S 2p_{3/2} at a binding energy of 161.6 eV, corresponding to S bonded to copper, in atomic or intact molecular form [2, 3]. Two other components of equal intensity, S₁ (S 2p_{3/2} at 164.2 eV) and S₂ (S 2p_{3/2} at 162.6 eV), were observed, each representing 30 % of the total intensity of the S 2p spectrum. These two components were assigned to endocyclic and exocyclic sulphur in the molecule not bonded to copper, respectively [2, 3, 25]. This is in agreement with the formation of a 2-MBT multilayer as observed previously [2, 3], the molecules in the first monolayer being bonded to copper while those in the upper layer are not interacting directly with the copper substrate.

After exposure to water vapour, the intensities of S_1 and S_2 decreased gradually, as well as a decrease in the N 1s spectra, which could be explained by the desorption of the molecules in the multilayer not bonded to Cu. At the same time, the intensity of S_3 increased, which is explained by a reduced attenuation of the signal originating from molecules directly bonded to copper, due to the decrease of the 2-MBT layer thickness. Taking into account the signal attenuation, we calculated the thickness of the molecular layer at different water exposures. Since the intensity of oxygen was calculated to be only 10 % of that obtained on Cu(111) covered by two-dimensional oxide of characteristic “29” superstructure after exposing to oxygen under the same conditions [3, 26], and no evidence of copper oxide was observed on the Cu LMM spectra as discussed below, a homogeneous layer of 2-MBT was assumed while neglecting the presence of oxygen. Before exposure to water vapour, the thickness of the 2-MBT multilayer was calculated to be about 0.8 ± 0.1 nm, which is in good agreement with that obtained previously [3]. After exposure to water vapour, the thickness of the molecular layer decreased gradually, and was calculated to be 0.6 ± 0.1 nm for an exposure of 2.9×10^5 L, confirming the desorption of the 2-MBT molecule as suggested above. Given this desorption kinetics, in order to reach the monolayer (thickness of about 0.2 nm [3]), an exposure of more than 1×10^6 L is needed, which corresponds to at least 89 h of exposure at 5×10^{-6} mbar. This hypothesis will be confirmed as shown below. Since we are limited by the pressure of the water vapour in the UHV system as well as the deposition time to not deteriorate the UHV environment, slightly more than a monolayer was prepared directly on Cu(111) for further studies. The exact coverage is not crucial since the molecule in the multilayer will continue to desorb when exposed to water vapor.

3.2. 2-MBT monolayer exposed to water vapour

In this part, in order to confirm the previous hypothesis on the continuous desorption of water and then to study the effect of water on 2-MBT pre-deposited on Cu(111) in the monolayer range, the copper covered by slightly more than one 2-MBT monolayer was prepared by exposing the metallic substrate to 20 L of 2-MBT vapour and subsequently exposed to water vapour at 5×10^{-6} mbar and RT.

Fig. 2 shows the S 2p, N 1s, and O 1s spectra obtained on Cu(111) covered by slightly more than one monolayer of 2-MBT before and after different exposures to water vapour at 5×10^{-6} mbar and RT. Before exposure to water vapour, the S 2p spectrum is mainly composed of the S₃ component. Meanwhile, the two other components S₁ and S₂ are also observed with equal intensity, each representing 16 % of the total intensity of the S 2p spectrum. Due to the high surface sensitivity of XPS and the previous work on the growth of 2-MBT multilayer [3], this indicates the formation of slightly more than a monolayer of 2-MBT, with the molecules in the second layer not interacting directly with the copper substrate. The N 1s spectrum is composed of two components N₁ and N₂ at binding energies of 400.1 eV and 398.9 eV, corresponding to nitrogen bonded and not bonded to copper, respectively [3]. By assuming a homogeneous layer of 2-MBT, the molecular layer thickness was calculated to be about 0.3 nm. Compared to the thickness of one 2-MBT monolayer of about 0.2 nm [3], this confirms the adsorption of slightly more than one 2-MBT monolayer on copper.

After exposure to 456 L of water vapour, the intensities of S₁ and S₂ each decreased down to 10 % of the total intensity of the S 2p spectrum, and the intensity of S₃ increased by 21 %, with the full width at half maximum (FWHM) almost unchanged for each peak (0.9 ± 0.1 eV), suggesting the continuation of the desorption of the molecule in the second layer. As for the N 1s spectrum, the intensity of N₁ (N bonded to copper) increases by 45 %, and that of N₂ (N not bonded to copper) decreases by 54 %, confirming the desorption of 2-MBT molecules not bonded to copper. This confirms the hypothesis made at the end of the previous section.

At higher exposure, up to 2.1×10^6 L, as the organic layer continues to be exposed to water vapour, the non-bonded molecules continue to desorb (decrease of S₁ and S₂). However, a new component designated, S₄, appeared in the S 2p spectrum, with the S 2p_{3/2} at a binding energy of 162.8 eV, accompanied by a decrease in the intensity of S₃, indicating a change in the sulphur environment. The FWHM of S₁, S₂ and S₃ are varying less than 13 %. The evolution of the S₃ and S₄ components after different exposures to water vapour was analysed in detail, and the results are shown in Fig. 3. The total area of the S 2p core level

peaks were normalized by the transmission of analyser, the photoionization cross section and the inelastic mean free path. The normalized area is proportional to the density of sulphur atoms. The component S₄ appears from an exposure of 6×10^5 L. Then its intensity increases with increasing exposure, while that of S₃ decreases accordingly so that the sum of S₃ and S₄ remained unchanged. We can thus conclude that there is a transformation of the S 2p spectra from S₃ to S₄. The binding energy of S₄ is shifted only by 0.3 eV compared to that of S₂ (exocyclic sulphur not bonded to copper), suggesting a breakdown of the bond between exocyclic sulphur and copper in the monolayer, which could be explained by the catalytic effect of metallic copper, as also observed previously [27]. Meanwhile, the intensity of N₁ component decreases, accompanied with the presence of a new component designated, N₃, at binding energy of 399.9 eV, which is shifted only by 0.2 eV compared to that of N₁ (nitrogen bonded to copper). This suggests that nitrogen remains bonded to copper, and the shift in binding energy could also be explained by the cleavage of the bond between sulphur and copper in 2-MBT as suggested above. Since the total intensity of sulphur and nitrogen remained unchanged, there is no further desorption of the molecule in the monolayer. The FWHM of N₁ increase by 50 % compared to that obtained before exposure to water, which could be explained by the change in the structure of the layer as disorder may appear and induce slightly different configurations associated with slightly different chemical shifts resulting in the broadening of the peak.

As for the O 1s spectra, there is no increase in the O 1s intensity for exposure up to 456 L of water vapour on Cu(111) with pre-adsorbed 2-MBT at RT. When increasing the exposure to 2.1×10^6 L, a small peak of oxygen was observed, with the presence of two components O₁ and O₂, at binding energies of 532.6 eV and 531.4 eV, respectively. The component O₁ may be assigned to molecular H₂O, and the component O₂ could be explained by the adsorption of OH groups, possibly due to the dissociative adsorption of water [28–31]. No significant change was observed in the Cu LMM spectra upon exposure to water vapour as shown in Fig. 4, indicating no copper oxide formation. The O 1s spectra obtained on Cu(111) exposed to water vapour or to gaseous oxygen at RT until saturation are also shown for comparison. When exposing the clean Cu(111) to water vapour, the two components O₁

and O_2 were slightly shifted to a lower binding energy (0.4 eV), which could be explained by the influence of the absence of pre-adsorbed 2-MBT molecules, and no formation of copper oxide was observed in the Cu LMM spectrum (Fig. 4). Finally, when exposing metallic Cu(111) to oxygen at 5×10^{-6} mbar and RT, the two components were shifted by 1.3 eV to lower binding energy, confirming the difference in the nature of the oxygen. The FWHM of O_1 and O_2 are varying less than 16 %. The new component O_3 at binding energy of 529.7 eV is usually attributed to the formation of bulk oxide [30, 32]. Moreover, the decrease of the intensities of peaks 1 and 2 at lower binding energies (characteristic for metallic copper) in the Cu LMM spectrum compared to those of peaks 3 and 4 at higher binding energies (characteristic for copper oxide) indicates the formation of copper oxide, confirming the oxidation of copper when exposing to oxygen.

Finally, the intensity of oxygen was measured and compared to that obtained on metallic Cu(111) exposed to water vapour under the same conditions, and the results are shown in Fig. 5. The area of the O 1s spectra were normalized relatively to the background. On metallic Cu(111) without 2-MBT, the normalized O 1s peak area increases rapidly with increasing exposure, confirming the dissociative adsorption of water on the Cu(111) surface when exposed to water vapour. A decrease in the O 1s growth rate was then observed, and a saturation regime was reached after an exposure of about 10^4 L, which gave a normalized peak area of about 0.5. On Cu(111) covered by 0.3 nm of 2-MBT, the normalized O 1s area increased much slower, and remains below 0.2 after an exposure of 3.4×10^6 L. On Cu(111) covered by a 2D oxide after exposing to oxygen under the same conditions [3], a rapid increase in the oxygen intensity was observed until reaching the saturation regime at an exposure of only 600 L, with the normalized O 1s peak area equal to 1. So the amount of oxygen observed on copper with and without 2-MBT after exposure to water vapour only represents 20 % and 50 % compare to a complete 2D oxide layer, respectively. The absence of oxide signal in the Cu LMM spectra shows that water adsorption is partially dissociative without leading to copper oxide formation in these room temperature exposure conditions, in contrast with the dissociative adsorption of oxygen that leads to the surface oxidation of copper. This result confirms that atomic oxygen, and thus the dissociation of hydroxyl

groups, is required for the surface oxidation of copper. In the presence of pre-adsorbed 2-MBT, water dissociative adsorption is considerably slow down while altering the bonding of the inhibitor with the copper surface.

4. Conclusions

In this work, the effects of water on corrosion inhibition films of 2-MBT pre-formed on metallic copper was investigated. In order to allow a precise control of the interaction mechanisms, a surface science approach on a model system was employed, with exposure to water vapour in gaseous phase at low pressure and RT of Cu(111) single crystal surface pre-covered by a well-characterized 2-MBT layer, and in situ surface chemical analysis by XPS.

When exposing to water vapour, a desorption of 2-MBT molecules in the multilayer (not directly bonded to copper) was observed, indicating that even extremely low amount of water already have a significant effect on the inhibitor layer. This desorption of 2-MBT continues until only a monolayer remains on the surface. Further exposure to water vapour led to the cleavage of the bond between exocyclic sulphur and copper in the monolayer, whereas nitrogen remains bonded to the copper surface. Dissociative adsorption of water is observed, without desorption of 2-MBT. No copper oxide formation was observed, and water uptake was markedly slow down by the pre-adsorbed organic layer.

Although far from real conditions, this study provides an effective approach to investigate in details the interaction mechanisms between water, organic inhibitor molecules and copper, which is of great importance for the understanding of the mechanisms governing the corrosion inhibition efficiency of organic inhibitors in real conditions.

5. Acknowledgments

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6. Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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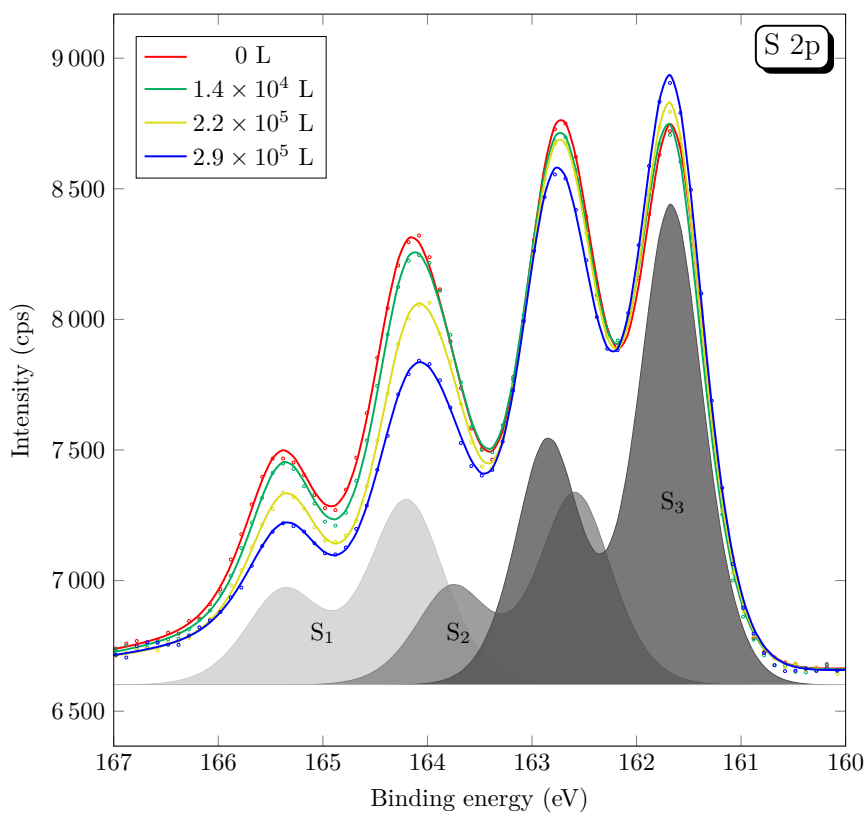


Figure 1: XPS spectra of the S 2p core level of a 2-MBT multilayer on Cu(111) before and after different exposures to water vapour at 5×10^{-6} mbar and RT. The decomposition of the S 2p spectrum after 2.9×10^5 L exposure to water vapour is shown.

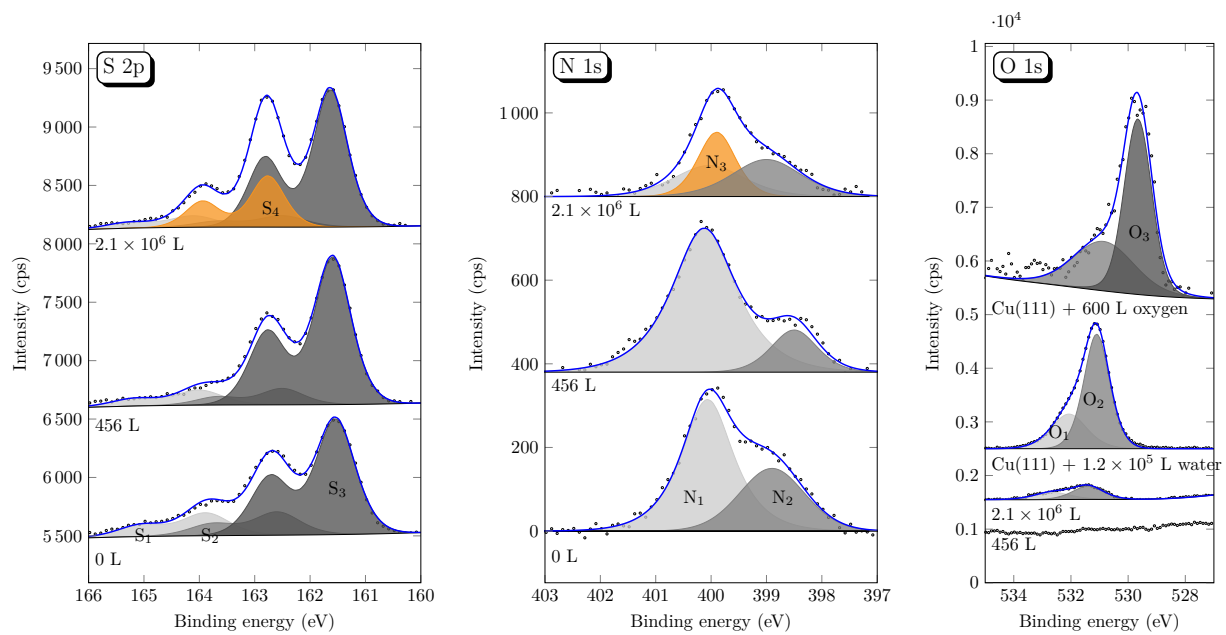


Figure 2: XPS spectra of the S 2p, N 1s, and O 1s core levels obtained on metallic Cu(111) covered by 0.3 nm of 2-MBT layer before and after different exposures to water vapour at 5×10^{-6} mbar and RT. The O 1s spectra obtained on metallic Cu(111) after exposure to water vapour (1.2×10^5 L) and to oxygen (600 L) under the same conditions until saturation are shown for comparison.

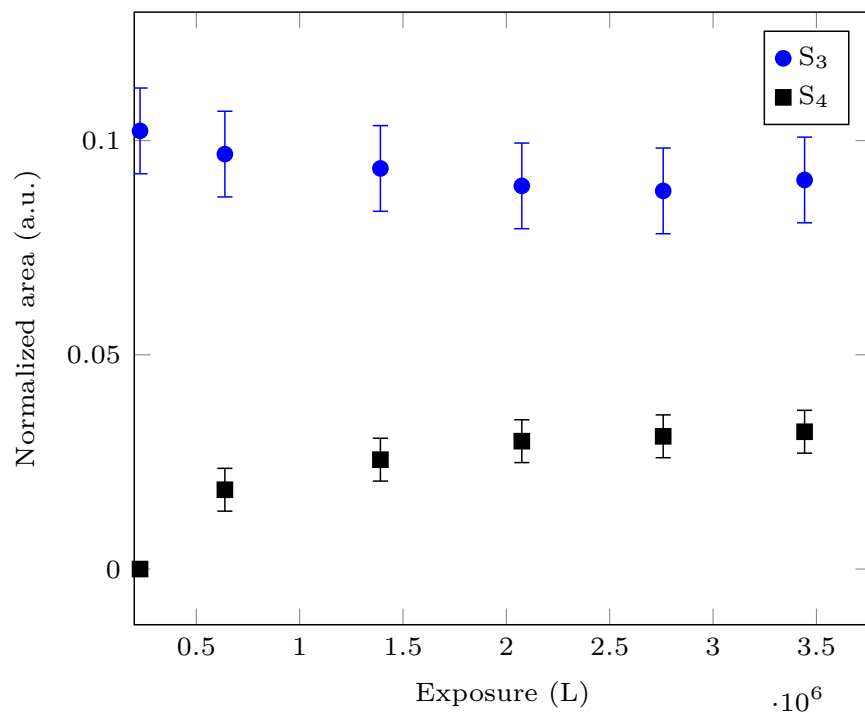


Figure 3: Evolution of S_3 and S_4 with exposure to water vapour at 5×10^{-6} mbar and RT.

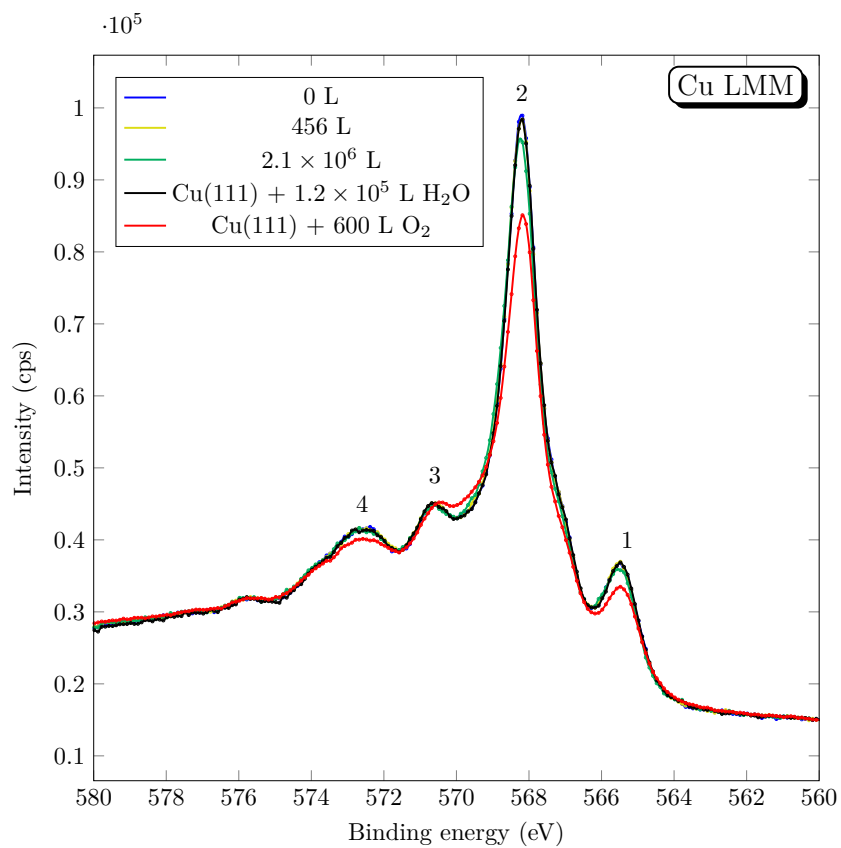


Figure 4: Cu LMM spectra obtained on metallic Cu(111) covered by 0.3 nm of 2-MBT layer before and after different exposures to water vapour at 5×10^{-6} mbar and RT. The Cu LMM spectra obtained on metallic Cu(111) after exposure to water vapour (1.2×10^5 L) and to oxygen (600 L) under the same conditions until saturation are shown for comparison.

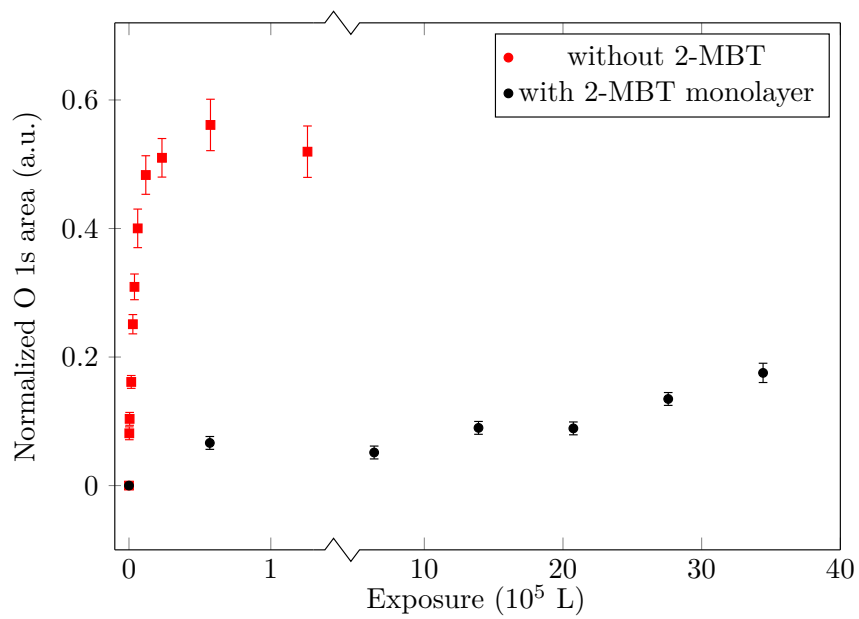


Figure 5: Oxidation kinetics of Cu(111) with and without 2-MBT monolayer exposed to water vapour at 5×10^{-6} mbar and RT.