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# Mo(VI) dithiocarbamate with no pre-existing Mo-S-Mo core as an active lubricant additive

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## Abstract (100 words)

MoDTC molecular additives reduce friction in boundary lubricated steel-steel contacts through formation of MoS<sub>2</sub> sheets. The chemical pathway from MoDTC to MoS<sub>2</sub> is investigated for optimizing MoS<sub>2</sub> formation. Our experiments show that a MoDTC molecule containing sulfur only in its thiocarbamate ligands forms MoS<sub>2</sub> sheets during friction, demonstrating that the presence of peripheral thiocarbamate ligands can be sufficient to provide the required sulfur source. This molecule is not only competitive with MoDTC containing sulfur in the core of the molecule but also more efficient at high contact pressures. Mechanistic investigations on the chemical transformation of MoDTC to MoS<sub>2</sub> reveal that thermal activation alone is not sufficient thus suggesting that pressure and/or shear are necessary for MoS<sub>2</sub> generation in this system.

## 22 1 Introduction

23 Energy saving has become a critical societal stake that stimulates drastic technological  
24 changes in the transportation and energy sectors [1]. In the field of tribology, reducing friction  
25 losses over extended durations is a key challenge. Several solutions have been developed, in  
26 particular Transition Metal Dichalcogenides (TMDs), like MoS<sub>2</sub>, have been known as efficient  
27 solid lubricants for more than fifty years [2–4]. MoS<sub>2</sub> is used in tribological contacts as coating  
28 but it can also be formed *in situ* through tribochemical reactions from molecular lubricant  
29 additives [5–10]. Among molecular lubricant additives effective under boundary lubrication for  
30 steel-steel contacts, the “all-in-one” types of molecules, that is the ones which provide the  
31 molybdenum and the sulfur atoms within a single molecule, are commonly used. Molybdenum  
32 DiThioCarbamates (MoDTC) are representative examples of these types of molecules (Figure  
33 1).

34 Even if the mechanism of action of MoDTC has been widely studied, [7–9,11–15] the  
35 understanding of the chemical pathway allowing the generation of MoS<sub>2</sub> sheets from the  
36 MoDTC molecule is still attracting substantial interest because of the potential insight in novel  
37 molecule design. Concerning the elementary steps of MoDTC decomposition, several  
38 approaches are found in literature. Initially, only the sulfur atoms present in the core of dimeric  
39 molecules, that is as bridging atoms across molybdenum two centers as in (R<sub>2</sub>NCS<sub>2</sub>) [Mo(O)(μ-  
40 S)<sub>2</sub>Mo(O)] (S<sub>2</sub>CNR<sub>2</sub>) were considered able to contribute to the formation of MoS<sub>2</sub> sheets [8,13].  
41 Later on, it was also proposed that the sulfur atoms from the thiocarbamate ligand, (R<sub>2</sub>NCS<sub>2</sub>)  
42 [Mo(O)(μ-S)<sub>2</sub>Mo(O)] (S<sub>2</sub>CNR<sub>2</sub>) could be involved in the generation of MoS<sub>2</sub> sheets, either by  
43 prior linkage isomerism, as in (R<sub>2</sub>NCOS) [Mo(S)(μ-S)<sub>2</sub>Mo(O)] (S<sub>2</sub>CNR<sub>2</sub>) [11,12] or by cleavage  
44 of carbon-sulfur bonds of the ligand, schematized as (R<sub>2</sub>NC) [(S<sub>2</sub>Mo(O)(μ-S)<sub>2</sub>Mo(O)S<sub>2</sub>)] (CNR<sub>2</sub>)  
45 [7,16]. All these approaches suggest that core [Mo<sub>n</sub>S<sub>m</sub>] fragments called MoS<sub>x</sub> intermediate  
46 products [7] are needed at some stage in generating well-organized MoS<sub>2</sub> lamellar sheets  
47 during friction.

48 In this work, the performance of a molecular precursor MoDTC **1**, containing only one  
49 molybdenum atom and no pre-formed core [Mo<sub>n</sub>S<sub>m</sub>], is compared with that of a well-established  
50 “all-in-one” MoDTC **2** molecule, which contains preformed [Mo(μ-S)<sub>2</sub>Mo] core classically used  
51 in engine lubrication. We show that the tribological properties of molecule MoDTC **1** are  
52 competitive with those of well-established MoDTC **2** and show better performances at high  
53 contact pressures.

54

## 55 2 Experimental methods

### 56 2.1 Lubricant additive synthesis

57 Two different MoDTC molecules were synthesized (Figure 1). MoDTC 1 has no pre-existing  
58 core  $[\text{Mo}-(\mu\text{-S})\text{-Mo}]$ , nor terminal sulfur atoms ( $\text{Mo}=\text{S}$ ) and is in oxidation state  $\text{Mo}(+\text{VI})$ .  
59 MoDTC 2 contains the  $[\text{Mo}(\mu\text{-S})_2\text{Mo}]$  sulphided core and is in oxidation state  $\text{Mo}(+\text{V})$ . Molecule  
60 MoDTC 2 is used here as a representative example of the classical molecules used in engine  
61 lubrication.

62 The lubricant composition is prepared in a beaker on a stirrer hot plate by adding a weight  
63 percentage of 0.3 w% of each molecule of MoDTC in the synthetic base oil PAO4 at a  
64 temperature of  $50^\circ\text{C}$ , whilst stirring for 30 min. Solutions were transparent after this mixing  
65 procedure showing the good solubility of the additives in base oil.

66 Note that the atomic concentration of Mo in lubricants containing MoDTC 1 or MoDTC 2 is in  
67 the same range since the contribution of Mo to the mass of MoDTC1 (23 wt%) is extremely  
68 close to that in MoDTC2 (21 wt%). Thus the difference in molybdenum atomic content in both  
69 lubricants is not significant enough to explain potential differences in tribological behaviors.  
70 The content of sulfur atoms is a bit larger in MoDTC 1 than in MoDTC 2. As both molecules  
71 don't have the same atomic S/Mo ratio (4 for MoDTC 1 and 3 for MoDTC 2), it is anyway not  
72 possible to have the exact same content of molybdenum and sulfur in each lubricant.

73

#### 74 • Synthesis method of MoDTC 1:

75 The complex was prepared according to literature [17]. Under air, ammonium molybdate  
76 tetrahydrate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}] \cdot 4 \text{H}_2\text{O}$  (3.20 g, 2.59 mmol) was dissolved in 25 mL of distilled  
77 water. 3.05 g (13.54 mmol) of sodium diethyldithiocarbamate trihydrate, dissolved in 10 mL of  
78 distilled water, were then slowly added over the course of 30 min under vigorous stirring, during  
79 which time the colour of the solution gradually turned from yellow to orange and then red with  
80 the formation of a precipitate. The red precipitate was isolated on a fritted glass connected to  
81 a vacuum Erlenmeyer flask then washed with distilled water (3x10 mL). After washing, the  
82 sample was dried under vacuum. Yield, 2.10 g (56 %). Anal. Calcd for  $\text{MoC}_{10}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_4$  (MW=  
83 424.48  $\text{g}\cdot\text{mol}^{-1}$ ): C 28.30, H 4.75, N 6.60; Found C 27.94, H 5.09, N 6.51%.

84

#### 85 • Synthesis method of MoDTC 2:

86 The complex was prepared according to the literature [17]. Ammonium molybdate tetrahydrate  
87  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}] \cdot 4 \text{H}_2\text{O}$  (4.22 g, 3.41 mmol) was dissolved in 20 mL of distilled water. 30 mL  
88 of dimethylformamide (DMF) were poured into the solution and stirred vigorously. Then 9 g of  
89 dioctylamine (37.27 mmol) and 30 mL of DMF were added at room temperature. The reaction

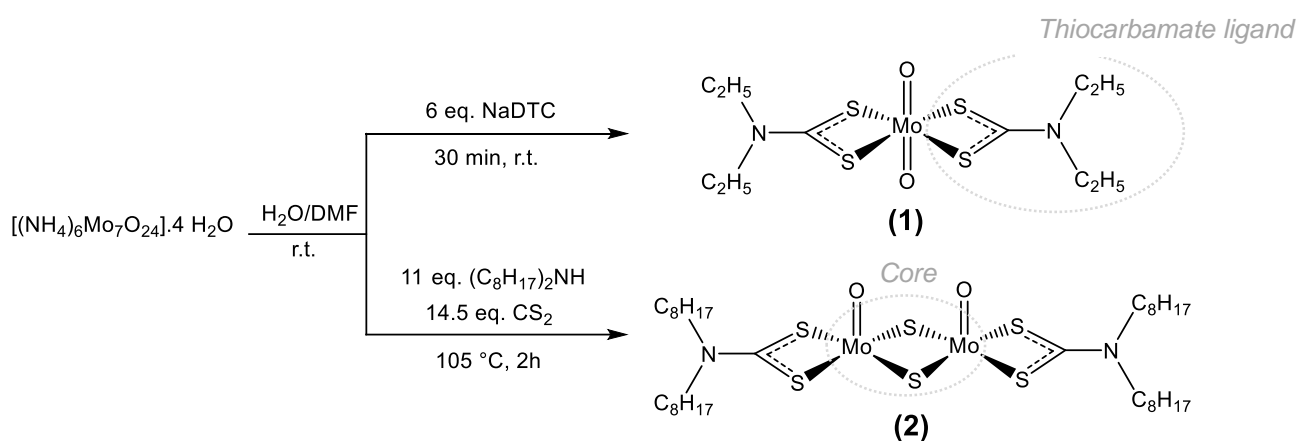
90 medium was cooled in an ice-water bath and finally, 3 mL of carbon disulphide CS<sub>2</sub> (49.65  
91 mmol) were added dropwise over a period of 15 min.

92 The addition of CS<sub>2</sub> resulted in a gradual colour change of the suspension from white to yellow,  
93 then orange and finally purple-red. The solution was then refluxed at 105°C under argon until  
94 the colour changed from purple-red to green. The resulting viscous residue was collected on  
95 a fritted glass connected to a vacuum Erlenmeyer flask, then washed with acetone (3x50 mL).  
96 After washing, a yellow precipitate appeared. After washing, the sample was dried under  
97 vacuum Yield, 1.10 g (10 %). Anal. Calcd for Mo<sub>2</sub>C<sub>34</sub>H<sub>68</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub> (MW = 921.19 g.mol<sup>-1</sup>): C  
98 44.33, H 7.44, N 3.04; Found C 41.13, H 7.10, N 3.78%.

99

100 The XPS characterizations of MoDTC **1** and MoDTC **2** are reported in supplementary  
101 information (SI 1) and corroborate the structures reported in Figure 1.

102



105 **Figure 1: Synthesis of the MoDTC derivatives 1 and 2 (only one linkage isomer**  
106 **represented).**

107

## 108 2.2 Friction experiments

109 Balls and flats counterfaces used for tribotests are both in steel AISI52100. The hardness is  
110 around 800 HV. The roughness of the flats and balls are respectively Ra = 12 ± 5 nm and Ra  
111 = 40 ± 1 nm. The base oil used is a PAO4. A reciprocating ball-on-flat tribometer [18] was used  
112 for tribotests. No external sulfur supply was added to the system. During the test, normal force  
113 (strain gage), tangential force (piezoelectric sensor and bi-blades) and temperature  
114 (thermocouple type K) were recorded.

115 Standard conditions of boundary lubrication were as follow: average sliding speed of 56 mm/s,  
116 temperature of 100°C and an initial Hertz maximum pressure of 1 GPa (Load of 17 N).

117 For other tests, the temperature was varied as well as load in order to vary the initial Hertz  
118 maximum contact pressure. The contact conditions are summed up in Table1.

<b>Contact conditions</b>	
Samples	Flat ball (R = 6.7 mm)
Load	4 N → 180 N
Speed	56 mm/s
Temperature	20°C, 100°C, 180°C
Stroke length	7 mm
Kinematic	Linear
Frequency	4 Hertz
Maximum Hertz pressure	0.62 GPa → 2.3 GPa
Number of cycles	18000
Immersion volume	80 µL

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**Table 1: Contact conditions of reciprocating ball-on-flat tribotests.**

121

122 Representative curves of the friction coefficient as the function of number of cycles are  
 123 reported. Steady state friction coefficient are calculated from the last 8000 cycles of each test.  
 124 As tests were repeated at least four times, average steady state friction coefficients and their  
 125 standard deviations were calculated from the values obtained from the different repeatability  
 126 tests.

127 After each test, wear scar diameters were measured by optical microscopy.

128

### 129 **2.3 Characterization of tribofilms**

130 All samples were cleaned with *n-heptane* for 10 min in ultrasonic bath before characterization  
 131 by XPS, Raman spectroscopy and FIB-TEM.

132 XPS analyses were carried out on a PHI 5000 Versaprobe II apparatus from ULVAC-PHI Inc.  
 133 A monochromatized AlK<sub>α</sub> source (1486.6 eV) was used with a spot size of 20 µm. A charge  
 134 neutralization system is used to limit charge effect. The remaining charge effect was corrected  
 135 fixing the C-C bond contribution of C1s peak at 284.8 eV. Spectra of Mo<sub>3d5/2</sub> and S<sub>2p</sub> regions  
 136 were obtained using a pass energy of 23.5 eV. All the peaks were fitted with CasaXPS software  
 137 using a Shirley background. Quantification was carried out using the transmission function of  
 138 the apparatus and angular distribution correction for a 45° angle. Sensitivity factors were  
 139 extracted from [19], they integrate cross section and escape depth correction.

140 Raman spectra were collected using a LabRam HR800 spectrometer from Horiba Scientific.  
 141 Two different laser wavelengths were used 785 nm (MoDTC 1) and 532 nm (MoDTC 2 and  
 142 tribofilms). Typical laser powers of 5 mW were used.

143 FIB sections were performed across tribofilms for TEM observations. A platinum layer was  
144 deposited as a protective layer on tribofilm before nanomachining with Ga<sup>+</sup> ions. Subsequent  
145 thinning was carried out to ensure that lamella is thin enough for TEM observations.

146 The TEM observations were carried out on JEOL2010F equipped with EDS and operating at  
147 an accelerating voltage of 200 kV.

148 Tribofilm compositions could slightly vary in terms of composition regarding position on the  
149 wear track. Because of reciprocating oscillatory motion, the contact conditions are most severe  
150 at the extremity of wear tracks, where the change of friction directions occurs. The Raman and  
151 XPS analyses were done close to these areas as the amount of MoS<sub>2</sub> was the most important.  
152 Then, some discrepancies in the results between XPS and Raman analyses could be related  
153 to the fact that the size of the analyzed area was slightly different for each technique (20 μm of  
154 diameter for XPS analyses and around 1 μm for Raman analyses) and to the fact that XPS  
155 spectroscopy is more surface sensitive than Raman.

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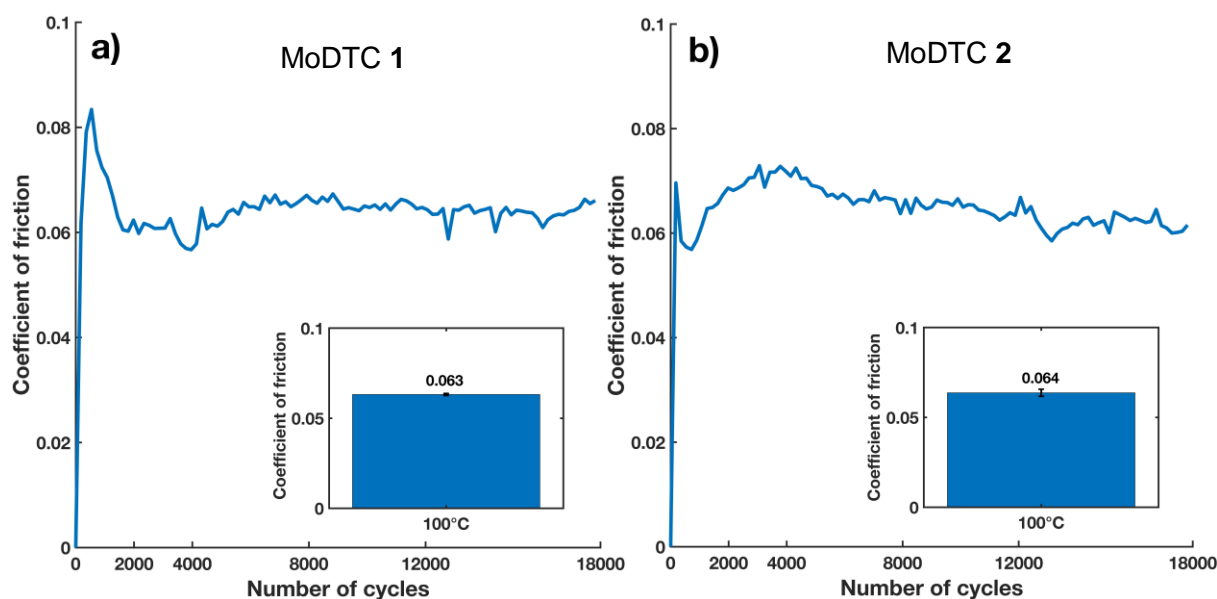
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### 159 3 Results

#### 160 3.1 Low friction with MoDTC (1) under standard boundary lubricated 161 conditions

##### 162 3.1.1 Friction results with MoDTC (1)

163 MoDTC 1 has been tested under our standard conditions of boundary lubrication ( $T = 100^{\circ}\text{C}$ ,  
164  $V = 56 \text{ mm/s}$ ,  $P_{\text{Hertzmax}} = 1 \text{ GPa}$ , 18 000 cycles). The evolution of the friction coefficient as  
165 function of the number of cycles is presented in Figure 2.a as well as statistical data processing  
166 from several measurements. The average steady state friction coefficient for MoDTC 1 is  $0.063$   
167  $\pm 0.001$  that is within the range obtained with the reference molecule MoDTC 2 (Figure 2.b -  
168  $\mu_{\text{MoDTC 2}} = 0.0644 \pm 0.009$ ). The values for the two molecules are statistically similar and in the  
169 expected range for the formation of  $\text{MoS}_2$  in a boundary lubricated contact [6,15]. It can be  
170 also noticed that MoDTC 1 requires longer induction time to reach the low friction steady state  
171 regime than MoDTC 2. No loss of friction reduction capabilities is observed over the full  
172 experiment (18000 cycles) for each molecule.



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174  
175 **Figure 2: Coefficient of friction at 100°C for a) molecule MoDTC 1 b) molecule MoDTC 2.**  
176 **The tests were performed at an initial maximum Hertz pressure of 1 GPa and an average**  
177 **sliding speed of 56 mm/s. Representative curves of the friction coefficient as the**  
178 **function of number of cycles are shown as well as average steady state friction**  
179 **coefficients calculated from several tests with the related standard deviation.**

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### 182 3.1.2 MoDTC 1 Tribofilm characterization

183 TEM tribofilm characterizations (Figure 3) confirm the presence of MoS<sub>2</sub> in the tribofilm (flat  
184 sample) obtained with MoDTC 1 in the absence of external sulfur supply. In TEM images of  
185 tribofilm obtained with MoDTC 1 in standard conditions, MoS<sub>2</sub> sheets are found at the top of  
186 the tribofilm of thickness between 30 and 40 nm. The presence of sheets is confirmed by EDS  
187 analyses with prominent molybdenum and sulfur peaks, and by interlayer distance around 0.6  
188 nm on HRTEM images, consistent with MoS<sub>2</sub> lamellar sheets observed in tribofilms [15].

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207 **Figure 3: a) and b) TEM images of FIB-cross section of tribofilm (flat) obtained with**  
208 **MoDTC 1 after 18 000 cycles of rubbing under standard contact conditions c) EDX**  
209 **spectrum recorded on the MoS<sub>2</sub> sheets area.**

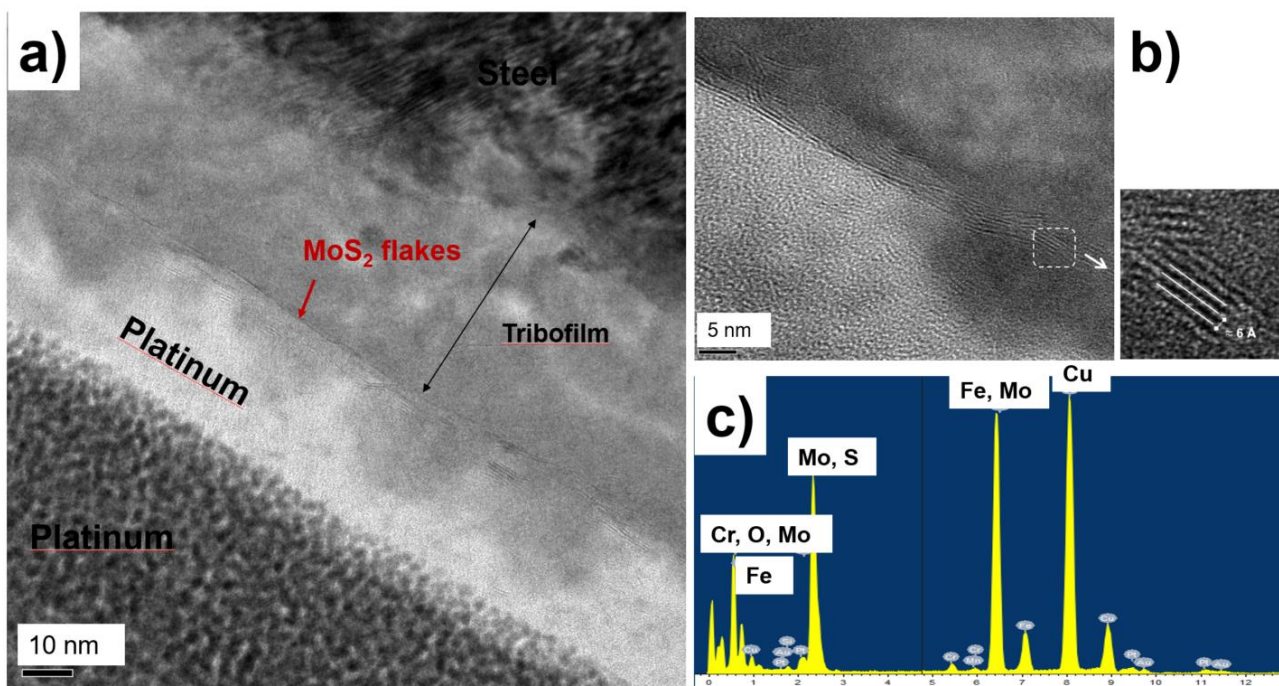
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215 The XPS analysis of the Mo<sub>3d</sub> and the S<sub>2p</sub> transitions carried out on the tribofilms obtained after  
216 18 000 cycles with MoDTC 1 at 100°C is reported in Figure 4; details of the fits can be found  
217 in Table 2.

218 Two main molybdenum contributions are found: one with a Mo<sub>3d5/2</sub> peak around 232.1 eV (Mo<sub>3d</sub>  
219 (C), pink) corresponding to a Mo(+VI) environment related to MoO<sub>3</sub> or FeMoO<sub>4</sub> [7,20,21] and  
220 another one with a Mo<sub>3d5/2</sub> peak around 229.0 eV (Mo<sub>3d</sub> (B), blue) attributed to a Mo(+IV)  
221 environment that could correspond to MoS<sub>2</sub> [6,20] or MoS<sub>3</sub> [22,23]. One minor Mo contribution  
222 is found at lower binding energy (228.2 eV, Mo<sub>3d</sub> (A), light blue). This Mo<sub>3d</sub> (A) contribution at  
223 low binding energy is related to a reduced molybdenum species. Such a contribution has been  
224 observed on sulfided molybdenum oxide thin films [21,22,24]. It has been proposed to be a  
225 defective Mo environment possibly formed in the present context by friction. The peaks near  
226 226 eV (yellow/brown) correspond to sulfur S<sub>2s</sub> contributions related to S<sub>2p</sub> contributions  
227 discussed in the following paragraph.

228 The S<sub>2p</sub> spectrum shows sulfide-type environment at binding energies near 161 eV. The shape  
229 and width of the sulfide part of the spectrum leads to the deconvolution of 3 separate  
230 contributions. The main S<sub>2p</sub> (B) contribution at 161.8 eV matches with S<sup>2-</sup> anion in MoS<sub>2</sub> or in  
231 MoS<sub>3</sub>. This contribution is consistent with the Mo<sub>3d</sub> results. A lower binding energy contribution  
232 around 161.0 eV S<sub>2p</sub> (A) would correspond to a more electron-rich sulfur. Such a contribution  
233 has been ascribed to sulfur depleted MoS<sub>2</sub> environments that could correspond to the reduced  
234 S<sub>2p</sub> (A) species films [21]. S<sub>2p</sub> (C) at around 163.1 eV matches either with FeS<sub>2</sub>, with  
235 thiomolybdate or (S<sub>2</sub>)<sup>2-</sup> in MoS<sub>3</sub> [22].

236 To summarize, XPS analyses performed at 100°C after tribotest under standard conditions in  
237 presence of MoDTC 1 suggest that MoS<sub>2</sub> is the main Mo based compound present at the top  
238 surface of the tribofilm. This is supported by quantification of sulfur (S<sub>2p</sub> (A) and (B)) over  
239 molybdenum (Mo (B)) species characteristic of MoS<sub>2</sub> yielding a S/Mo ratio close to 2. MoS<sub>3</sub>  
240 could be also considered as peak position of Mo<sub>3d</sub> (B), S<sub>2p</sub> (B) and S<sub>2p</sub> (C) are in agreement  
241 with [22], but in much lower amount compared to MoS<sub>2</sub> regarding the at% of S<sub>2p</sub>(C) peak  
242 (Figure 4 and Table 2).

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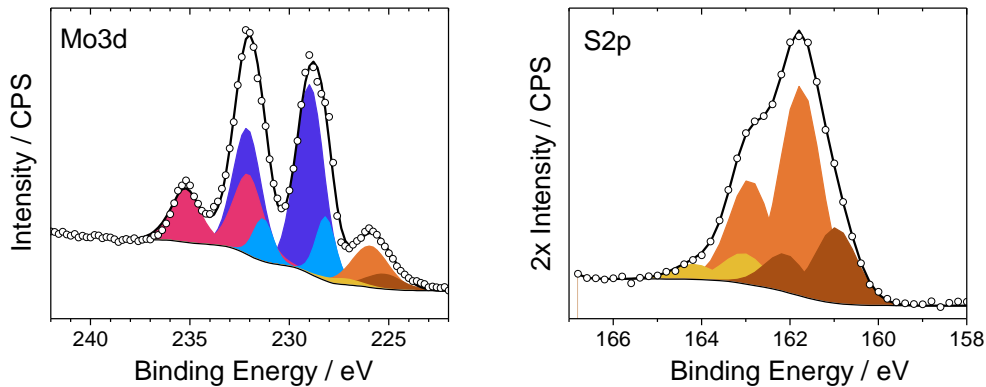
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Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at %)	Assignment
MoDTC 1	$Mo_{3d5/2 - 3/2}$				
	Mo <sub>3d</sub> - (A)	228.2 - 231.4	1.2	6.1	Reduced MoS <sub>2</sub>
	Mo <sub>3d</sub> - (B)	229.0 - 232.2	1.7	25.3	MoS <sub>2</sub> ou MoS <sub>3</sub>
	Mo <sub>3d</sub> - (C)	232.1 - 235.3	1.7	11.9	MoO <sub>3</sub> / FeMoO <sub>4</sub>
	$S_{2p3/2 - 1/2}$				
	S <sub>2p</sub> - (A)	161 - 162.1	1.1	13.6	S <sup>2-</sup> in reduced MoS <sub>2</sub>
	S <sub>2p</sub> - (B)	161.8 - 162.9	1.1	37.7	S <sup>2-</sup> in MoS <sub>2</sub> or in MoS <sub>3</sub>
	S <sub>2p</sub> - (C)	163.1 - 164.2	1.1	5.4	(S <sub>2</sub> ) <sup>2-</sup> in FeS <sub>2</sub> or thiomolybdate or MoS <sub>3</sub>

248

249 **Table 2: Peak fitting details related to Figure 4 e.i. XPS analyses of tribofilms obtained**  
 250 **with MoDTC 1 after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz**  
 251 **pressure of 1 GPa and an average sliding speed of 56 mm/s.**

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255 **Figure 4: XPS analyses (Mo3d) carried out of tribofilms (flats) obtained with MoDTC 1**  
 256 **after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz pressure of 1 GPa**  
 257 **and an average sliding speed of 56 mm/s.**

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260 The characteristic Raman analyses of the tribofilm obtained at 100°C under standard  
261 conditions with MoDTC 1 are presented in Figure 5. The two MoS<sub>2</sub> characteristic Raman shifts  
262  $E_{2g}^1$  and  $A_{1g}$  at 373 cm<sup>-1</sup> and 405 cm<sup>-1</sup>, respectively, are detected, in agreement with Raman  
263 analyses of MoDTC tribofilms [10,14,25]. The presence of amorphous MoS<sub>3</sub> compound [26]  
264 could explain the background shape near  $E_{2g}^1$  and  $A_{1g}$ . The presence of Fe(MoO<sub>4</sub>) is suggested  
265 by the presence of the Raman peak at 925 cm<sup>-1</sup> [7] and is consistent with the Mo (+VI) oxide  
266 contribution detected by XPS at 232.3 eV on Mo<sub>3d</sub> peak.

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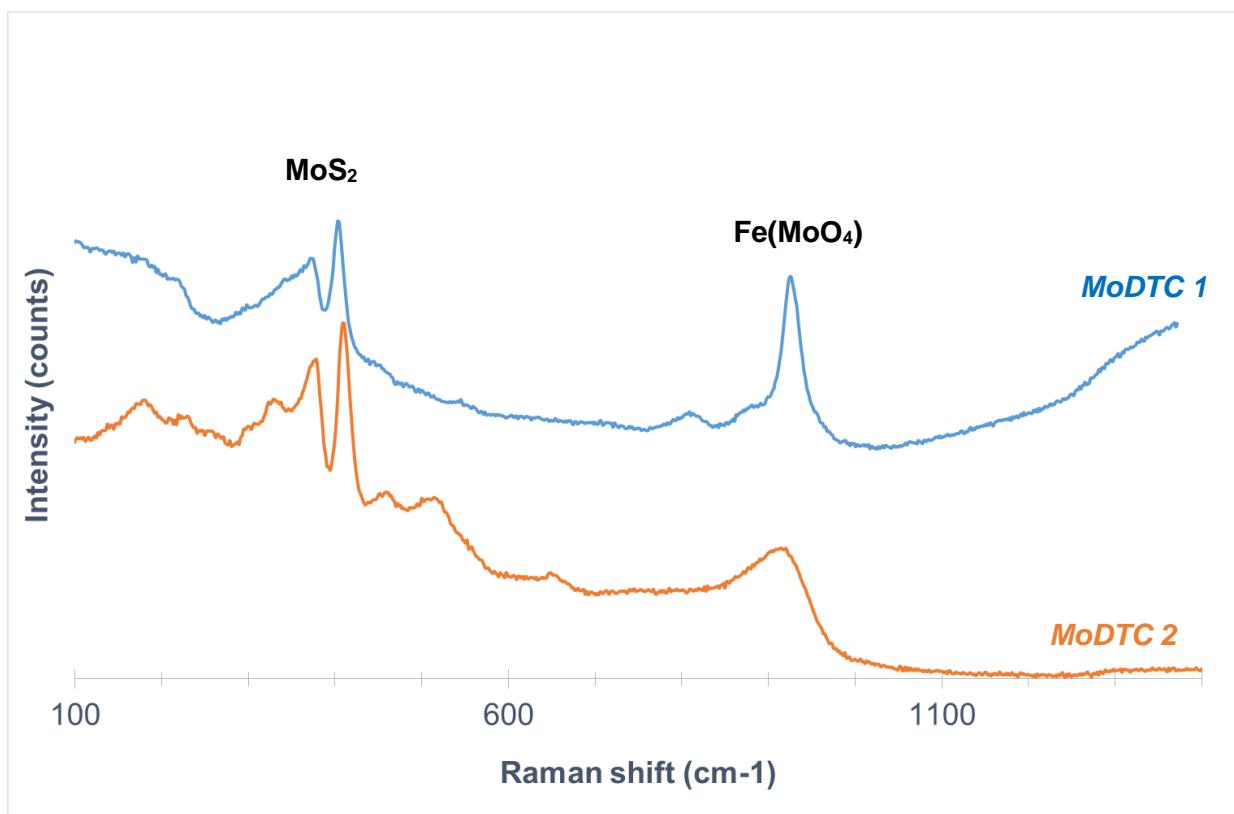
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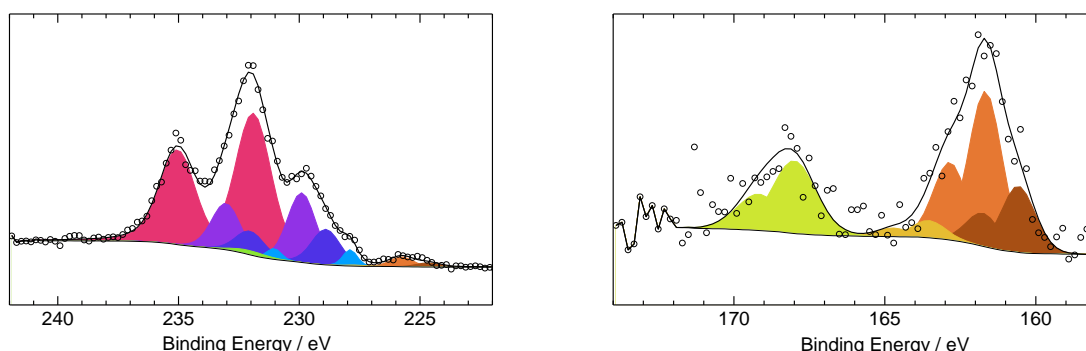
281 **Figure 5: Raman analyses on tribofilms (flats) obtained with MoDTC 1 and MoDTC 2**  
282 **after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz pressure of 1 GPa**  
283 **and an average sliding speed of 56 mm/s.**

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286 **3.1.3 MoDTC 2 Tribofilm characterization**

287 Raman (Figure 5) and XPS (Figure 6 and Table 3) characterizations were also performed on  
 288 tribofilm obtained with MoDTC 2 at 100°C and 1 GPa for comparison with MoDTC 1. Both  
 289 results show the presence of MoS<sub>2</sub> and FeMoO<sub>4</sub> for MoDTC 2 tribofilm, like for MoDTC 1. This  
 290 is in accordance with literature works since XPS analyses of tribofilm obtained with MoDTC  
 291 often propose the presence of two main contributions attributed to Mo+IV and Mo+VI [15,27].  
 292 The presence of molybdenum oxysulfide (purple contribution B' in Figure 6 and table 3) is also  
 293 detected for MoDTC 2 tribofilm by XPS and was previously suggested in literature [6,20].



294

295 **Figure 6: XPS analyses (Mo3d) carried out of tribofilms (flats) obtained with MoDTC 2**  
 296 **after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz pressure of 1 GPa**  
 297 **and an average sliding speed of 56 mm/s.**

Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at%)	S (at%) /Mo (at%) ratio	Assignment
MoDTC 2	<b>Mo<sub>3d5/2 - 3/2</sub></b>				0.5	
	Mo <sub>3d</sub> - (A)	227.9- 231.0	0.7	1.7		Reduced MoS <sub>2</sub>
	Mo <sub>3d</sub> - (B)	228.9 - 232.0	1.4	7.4		MoS <sub>2</sub> or MoS <sub>3</sub>
	Mo <sub>3d</sub> - (B')	229.9- 233.0	1.4	14.6		MoO <sub>x</sub> S <sub>y</sub>
	Mo <sub>3d</sub> - (C)	231.9 – 235.0	1.8	42.0		MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b>S<sub>2p3/2 - 1/2</sub></b>					
	S <sub>2p</sub> - (A)	160.6 – 161.8	1.3	6.7		S <sup>2-</sup> in reduced MoS <sub>2</sub>
	S <sub>2p</sub> - (B)	161.7 - 162.9	1.3	15.8		S <sup>2-</sup> in MoS <sub>2</sub> or in MoS <sub>3</sub>
	S <sub>2p</sub> - (C)	163.6 - 164.9	1.3	1.9		(S <sub>2</sub> ) <sup>2-</sup> in FeS <sub>2</sub> , thiomolybdate MoO <sub>x</sub> S <sub>y</sub> or MoS <sub>3</sub>
	S <sub>2p</sub> - (E)	168.0 – 169.2	1.3	10		Sulfate

298 **Table 3: Peak fitting details related to Figure 6 e.i. XPS analyses of tribofilms obtained**  
 299 **with MoDTC 2 after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz**  
 300 **pressure of 1 GPa and an average sliding speed of 56 mm/s.**

301

302

## 303 3.2 Effect of temperature

### 304 3.2.1 Friction and wear results

305 The friction performances of molecules MoDTC **1** and MoDTC **2** have been studied at three  
306 different temperatures ( $T = 20^{\circ}\text{C}$ ,  $100^{\circ}\text{C}$  and  $180^{\circ}\text{C}$  at  $V = 56 \text{ mm/s}$ ,  $P_{\text{Hertzmax}} = 1 \text{ GPa}$ , Figure  
307 7).

308 The optimal tested temperature for both molecules is  $100^{\circ}\text{C}$  as a durable and low friction  
309 regime is achieved in both cases (cf §3.1.1).

310 At  $20^{\circ}\text{C}$ , MoDTC **2** performs only marginally worse than at  $100^{\circ}\text{C}$ , while MoDTC **1** significantly  
311 underperforms ( $\mu = 0.074$  vs  $0.099$ , respectively). Considering the overall monotonous  
312 decrease of the friction coefficients over the whole experiment (Total number of cycles = 18  
313 000) for both molecular lubricants, it might be possible that neither system has reached steady  
314 state by the end of the experiment. Given the more pronounced decrease of the friction  
315 coefficient (both in terms of starting absolute value and in terms of overall drop) for MoDTC **1**  
316 than for MoDTC **2**, the induction process seems more pronounced for MoDTC **1** than for  
317 MoDTC **2**.

318 At  $180^{\circ}\text{C}$ , the loss of friction reduction capabilities is observed after a few thousand cycles for  
319 both MoDTC **1** and MoDTC **2** and very high friction coefficient are observed for most of the  
320 experiment, leading to high (apparent) steady state coefficients.

321 The wear behaviors obtained with the two molecules over the three temperatures appear to  
322 follow the same trend as the apparent steady state coefficients described above (cf Figure 8).  
323 The lowest wear is found at  $100^{\circ}\text{C}$  for both molecules MoDTC **1** and MoDTC **2**, with MoDTC  
324 **1** still marginally outperforming MoDTC **2** (width of the wear =  $180 \mu\text{m}$  vs.  $222 \mu\text{m}$ ,  
325 respectively). Both wear (MoDTC **1** and MoDTC **2** at  $100^{\circ}\text{C}$ ) are just slightly superior to Hertz  
326 diameter (red line) which represent the size of the contact before friction without any wear. The  
327 loss in performance at  $20^{\circ}\text{C}$  is more noticeable for MoDTC **1** than for MoDTC **2** (width of the  
328 wear =  $558 \mu\text{m}$  vs.  $299 \mu\text{m}$ , respectively). The poorest performances are observed at  $180^{\circ}\text{C}$   
329 for both lubricants (width of the wear =  $620 \mu\text{m}$  for MoDTC **1** and  $650 \mu\text{m}$  for MoDTC **2**).

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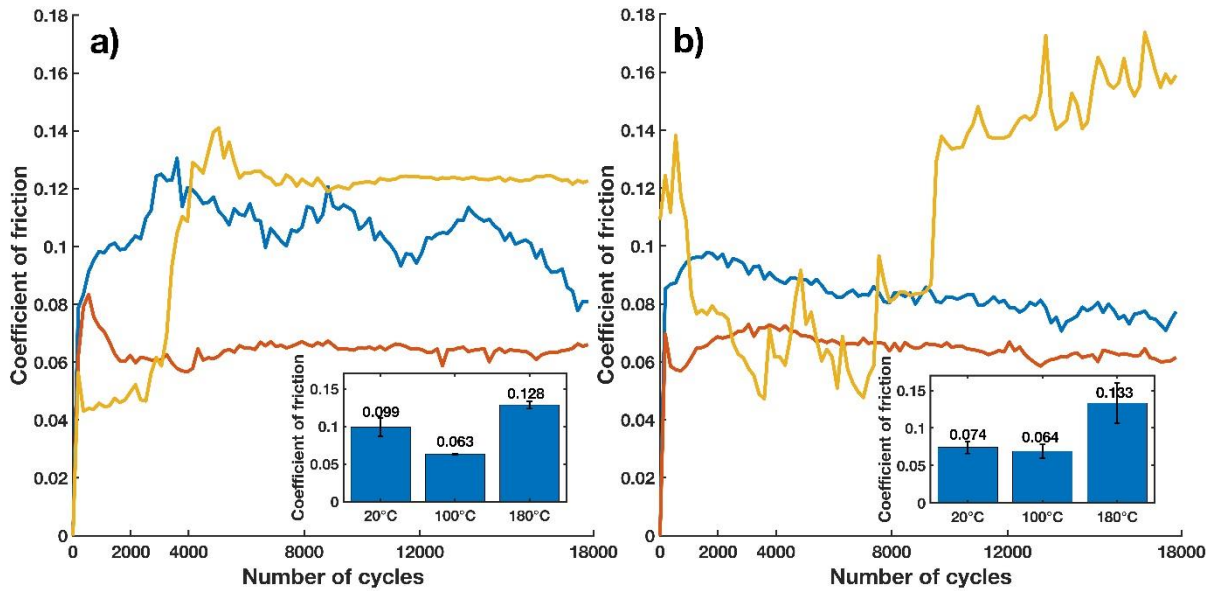
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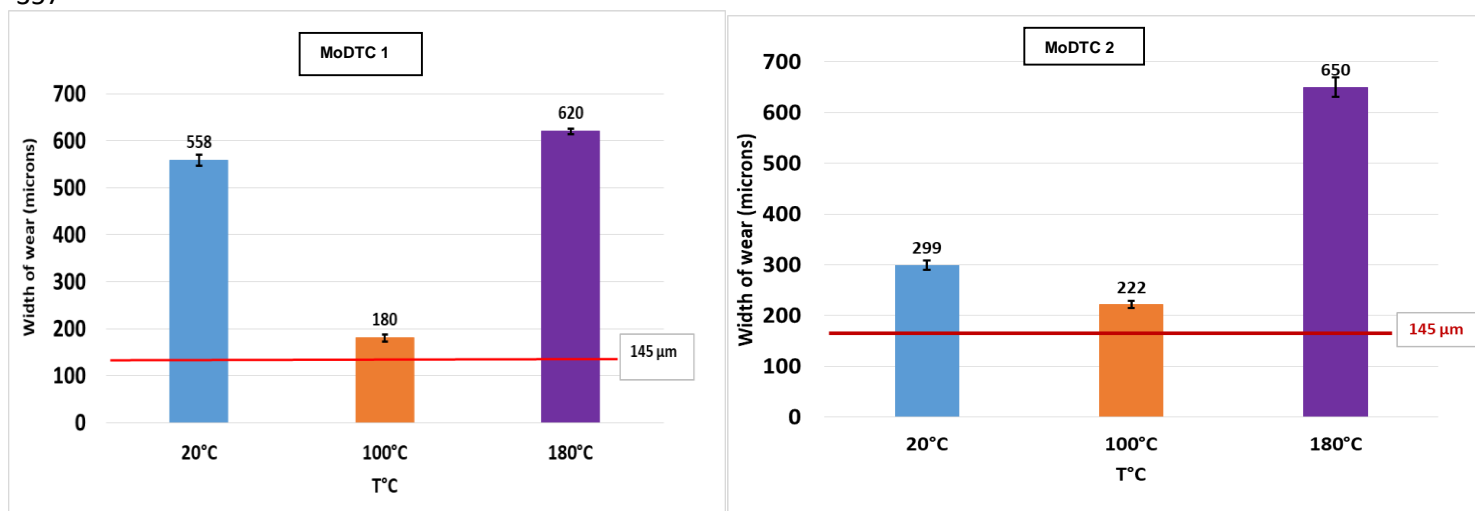
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**Figure 7: Coefficient of friction at 20°C (blue), 100°C (orange) and 180°C (yellow) for a) molecule MoDTC 1 b) molecule MoDTC 2. The tests were performed at an initial maximum Hertz pressure of 1 GPa and an average sliding speed of 56 mm/s. Representative curves of the friction coefficient as the function of number of cycles are shown as well as average steady state friction coefficients calculated from several tests with the related standard deviation.**

356

357



365 **Figure 8: Width of ball wear obtained at 20°C, 100°C and 180°C for a) molecule MoDTC**  
366 **1 b) molecule MoDTC 2. The tests were performed at an initial maximum Hertz pressure**  
367 **of 1 GPa and an average sliding speed of 56 mm/s. The red line represents the Hertz**  
368 **diameter (size of the contact before friction).**

369

### 370 3.2.2 Tribofilm characterizations with MoDTC 1 at 20°C, 100°C and 180°C (XPS and 371 Raman)

372 The XPS analyses of the Mo<sub>3d</sub> and the S<sub>2p</sub> transitions carried out on the tribofilms obtained  
373 with MoDTC 1 at different temperatures after 18 000 cycles are reported in Figure 9; details of  
374 the fits can be found in Table 4.

375 The fit explanation of the tribofilm obtained at 100°C is detailed in § 3.1.2.

376 For the tribofilm at 20°C, only one Mo environment is found around 232.1 eV (Mo<sub>3d</sub> (C), pink)  
377 corresponding to a Mo(+VI) environment related to MoO<sub>3</sub> or FeMoO<sub>4</sub>. Significant amount of  
378 SO<sub>x</sub> species is found but no evidence of MoS<sub>2</sub> is detected.

379 For the tribofilm at 180°C, two Mo environments are found. The main one with a Mo<sub>3d5/2</sub> peak  
380 around 232.1 eV (Mo<sub>3d</sub> (C), pink) corresponds to a Mo(+VI) environment related to MoO<sub>3</sub> or  
381 FeMoO<sub>4</sub>. The Mo<sub>3d</sub> (B') contribution (229.9 eV, purple) at binding energy higher than MoS<sub>2</sub> but  
382 lower than a typical Mo(+VI) signal could correspond to oxysulfide species MoO<sub>x</sub>S<sub>y</sub> [6,20]. SO<sub>x</sub>  
383 species are also detected.

384



Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at%)	Assignment
MoDTC 1 20°C	<b>MO<sub>3d5/2</sub> - 3/2</b>				
	Mo <sub>3d</sub> - (C)	232.2 - 235.4	1.3	54.0	MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b>S<sub>2p3/2</sub> - 1/2</b>				
	S <sub>2p</sub> - (B)	162.1 - 163.2	1.7	8.3	(S <sub>2</sub> ) <sup>2-</sup> in FeS <sub>2</sub> or Fe thiomolybdate
	S <sub>2p</sub> - (D)	166.4 - 167.5	1.5	12.4	SO <sub>3</sub> species
	S <sub>2p</sub> - (E)	168.3 - 169.4	1.5	25.3	Sulfate
MoDTC 1 100°C	<b>MO<sub>3d5/2</sub> - 3/2</b>				
	Mo <sub>3d</sub> - (A)	228.2 - 231.4	1.2	6.1	Reduced MoS <sub>2</sub>
	Mo <sub>3d</sub> - (B)	229.0 - 232.2	1.7	25.3	MoS <sub>2</sub> ou MoS <sub>3</sub>
	Mo <sub>3d</sub> - (C)	232.1 - 235.3	1.7	11.9	MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b>S<sub>2p3/2</sub> - 1/2</b>				
	S <sub>2p</sub> - (A)	161 - 162.1	1.1	13.6	S <sup>2-</sup> in reduced MoS <sub>2</sub>
	S <sub>2p</sub> - (B)	161.8 - 162.9	1.1	37.7	S <sup>2-</sup> in MoS <sub>2</sub> or in MoS <sub>3</sub>
	S <sub>2p</sub> - (C)	163.1 - 164.2	1.1	5.4	(S <sub>2</sub> ) <sup>2-</sup> in FeS <sub>2</sub> or thiomolybdate or MoS <sub>3</sub>
MoDTC 1 180°C	<b>MO<sub>3d5/2</sub> - 3/2</b>				
	Mo <sub>3d</sub> - (B')	229.9 - 233.0	1.9	26.2	MoO <sub>x</sub> S <sub>y</sub>
	Mo <sub>3d</sub> - (C)	232.0 - 235.1	1.3	46.2	MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b>S<sub>2p3/2</sub> - 1/2</b>				
	S <sub>2p</sub> - (B)	163.0 - 164.1	1.7	9.0	(S <sub>2</sub> ) <sup>2-</sup> in FeS <sub>2</sub> or thiomolybdate
	S <sub>2p</sub> - (E)	168.3 - 169.4	1.7	18.6	Sulfate

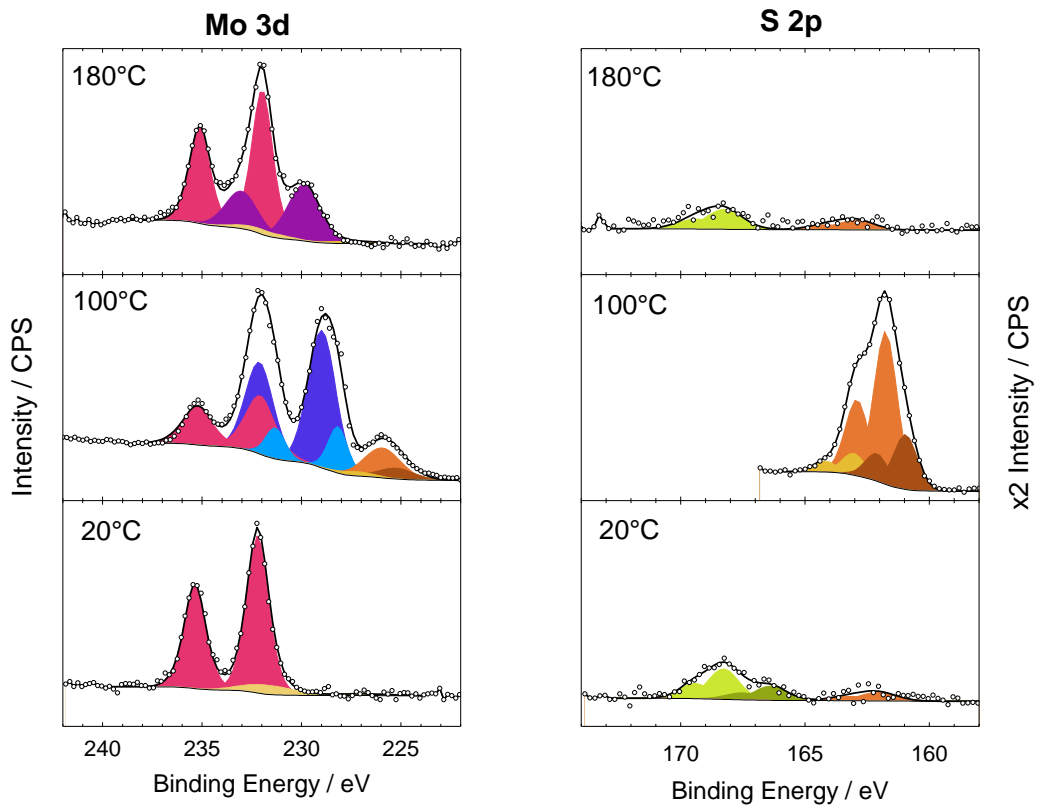
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387 **Table 4: Peak fitting details related to Figure 9 e.i. XPS analyses of tribofilms obtained**  
388 **with MoDTC 1 after 18 000 cycles of rubbing at 20°C, 100°C and 180°C at an initial**  
389 **maximum Hertz pressure of 1 GPa and an average sliding speed of 56 mm/s**

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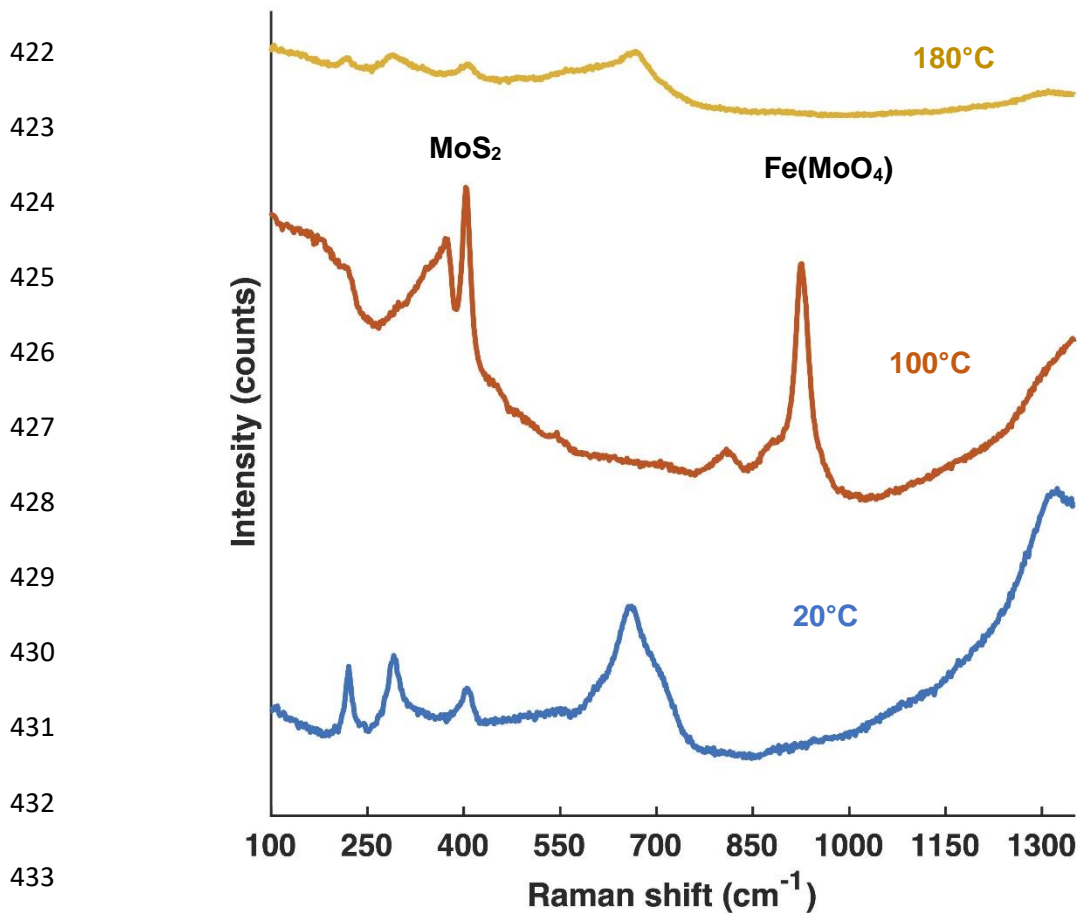
404 **Figure 9: XPS analyses (Mo3d) carried out of tribofilms (flats) obtained with MoDTC 1**  
405 **after 18 000 cycles of rubbing at 20°C, 100°C and 180°C at an initial maximum Hertz**  
406 **pressure of 1 GPa and an average sliding speed of 56 mm/s (see text for further details).**

407

408 The Raman analyses of the MoDTC 1 tribofilms obtained at 20°C, 100°C and 180°C are  
409 presented in Figure 10.

410 At 20°C, the observed peaks are mostly related to iron oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ), like at 180°C  
411 [28] and molybdenum based species like  $\text{MoO}_3$  are poorly detected [29]. Atomic ratio Mo/Fe  
412 calculated from XPS data ( $\text{Mo/Fe}_{20^\circ\text{C}} = 0.5$  -  $\text{Mo/Fe}_{100^\circ\text{C}} = 2.9$  -  $\text{Mo/Fe}_{180^\circ\text{C}} = 0.9$ ) suggests that  
413 the amount of molybdenum compared to iron in tribofilms is much smaller at 20°C and 180°C  
414 than at 100°C. As Raman technic is much less surface sensitive than XPS, it could explain  
415 why such molybdenum-based compounds are poorly detected by Raman technics at 20°C and  
416 180°C.

417 At 100°C, the two  $\text{MoS}_2$  characteristic peaks  $E_{2g}^1$  and  $A_{2g}$  at  $373\text{ cm}^{-1}$  and  $405\text{ cm}^{-1}$ ,  
418 respectively are detected. The presence of amorphous  $\text{MoS}_3$  compound could explain the  
419 background shape near  $E_{2g}^1$  and  $A_{2g}$ . The presence of  $\text{Fe}(\text{MoO}_4)$  at 100°C is suggested by the  
420 presence of the Raman peak at  $925\text{ cm}^{-1}$  and is consistent with the Mo (+VI) oxide contribution  
421 detected by XPS at 232.3 eV on Mo3d peak.



434 **Figure 10: Raman analyses on tribofilms (flats) obtained with MoDTC 1 after 18 000**  
 435 **cycles of rubbing at 20°C, 100°C and 180°C at an initial maximum Hertz pressure of 1**  
 436 **GPa and an average sliding speed of 56 mm/s.**

### 437 3.2.3 Tribofilm characterizations with MoDTC 2

438 XPS and Raman analyses of tribofilms obtained with MoDTC 2 at 20°C are reported in Figures  
 439 SI 2-1 and SI 2-2 for comparison. Like for tribofilm obtained with MoDTC 1 at 20°C, Mo+VI  
 440 contribution is mostly detected by XPS on Mo3d peak as well as sulfate on S2p peak. The  
 441 composition of the tribofilm dominated by molybdenum oxide at temperatures around 20°C-  
 442 30°C was already observed in literature for such type of MoDTC [15,27].

443 The comparison of tribofilm composition of MoDTC 1 and MoDTC 2 at 100°C was presented  
 444 in §3.1.3. As found in literature [15,27], the Mo+IV contribution (MoS<sub>2</sub>) increases in tribofilms  
 445 obtained at higher temperatures, up to 80°C-100°C. Rai *et al.* [14] and Komaba *et al.* [15] have  
 446 also suggested that such temperatures have an effect on the structural organization of the  
 447 MoS<sub>2</sub> layers.

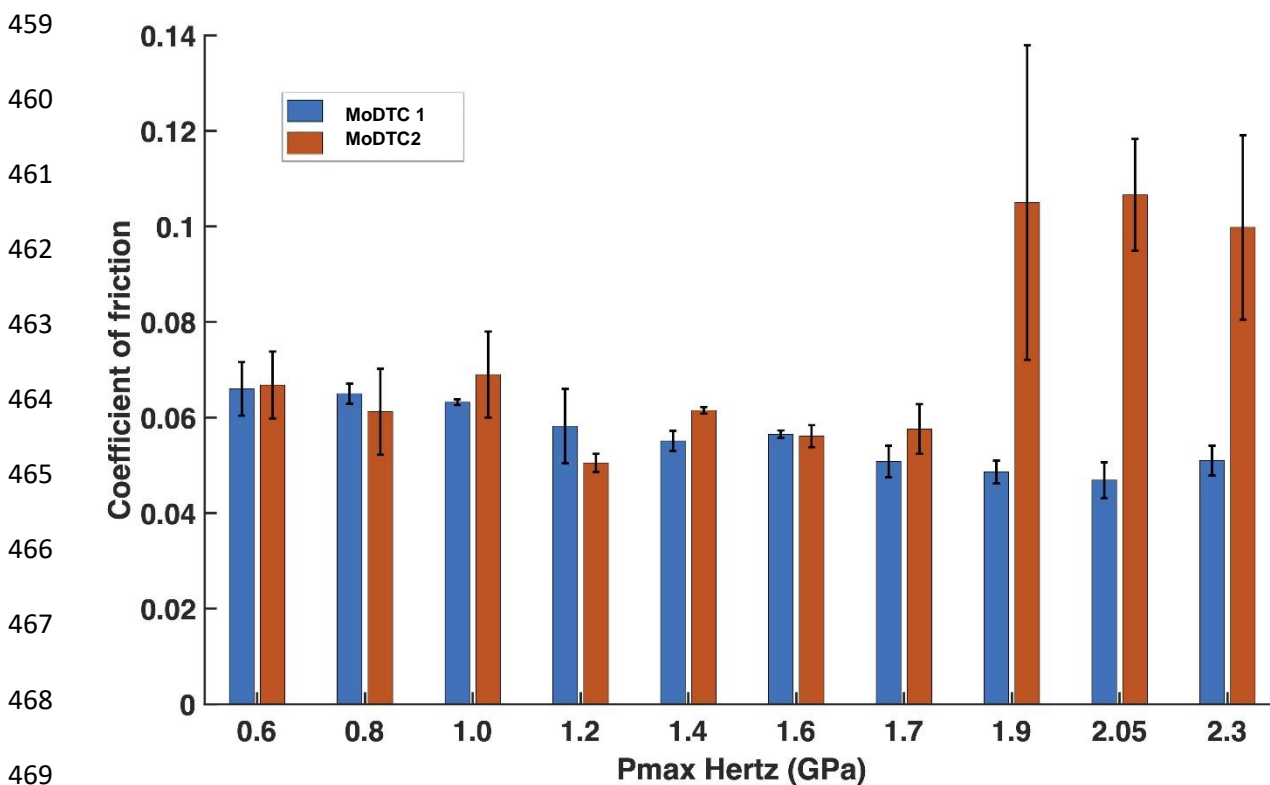
448 For temperatures higher than 100°C, only few data are found in literature [27].

### 449 3.3 Effect of contact pressure

#### 450 3.3.1 Friction results

451 Friction results obtained at 100°C for the two molecules MoDTC 1 and MoTDC 2 at different  
452 initial maximum Hertz pressures (from 0.6 to 2.3 GPa) are reported in Figure 11 ( $V = 56$  mm/s.  
453  $T = 100^\circ\text{C}$ , 18 000 cycles). Average steady state friction coefficients obtained from repeated  
454 tests and observed standard deviations are reported.

455 At low contact pressures, the friction behavior at the steady state is similar for the two  
456 molecules within standard deviations. Above an initial maximum Hertz contact pressure of 1.9  
457 GPa, significant differences in friction behavior appear between the two molecules: MoDTC 1  
458 still achieves a low friction regime whereas MoDTC 2 does not.



470

471

472 **Figure 11: Average steady state friction coefficient for different Initial Hertz maximum**  
473 **contact pressures for molecule MoDTC 1 and molecule MoDTC 2. The tests were**  
474 **performed at a temperature of 100°C and an average sliding speed of 56 mm/s. Average**  
475 **steady state friction coefficients are calculated from several tests with the related**  
476 **standard deviation.**

477

478

### 479 3.3.2 Tribofilms characterization

480 The XPS and Raman characterizations performed on tribofilms obtained with MoDTC 1 at  
481 different contact pressures are shown respectively in Figure 12/Table 5 and Figure 13.

482 The interpretation of the XPS data follows the results presented in §3.1.2. For all tested contact  
483 pressures, beside the main contributions ( $\text{Mo}_{3d}$  (B), blue) attributed to  $\text{MoS}_2$  or  $\text{MoS}_3$ , Mo (+VI)  
484 oxide contributions attributed to  $\text{Fe}(\text{MoO}_4)$  is also found in significant amount (namely,  $\text{Mo}_{3d}$   
485 (C), pink and  $925\text{ cm}^{-1}$  Raman peak). At high contact pressures,  $\text{Mo}_{3d}$  (B) is the main  
486 contribution, and  $\text{Mo}_{3d}$  (C) dominates at low contact pressure (0.8 GPa). The low binding  
487 energy  $\text{Mo}_{3d}$  (A) contribution is detected mainly at low contact pressures (0.8 GPa and 1 GPa)  
488 and would correspond to defective  $\text{MoS}_2$ . No oxysulfide-type molybdenum is evidenced  
489 (binding energies expected between  $\text{Mo}_{3d}$  (B) and  $\text{Mo}_{3d}$  (C)) [6,20,22].

490 Concerning the  $\text{S}_{2p}$  spectra, two main characteristic sulfur environments are found with no  
491 clear dependence on contact pressure: a sulfide-type environment at low binding energies  
492 ( $\text{S}_{2p_{3/2}} < 164\text{ eV}$ ) and a  $\text{SO}_x$  type environment at higher binding energies ( $\text{S}_{2p_{3/2}} > 166\text{ eV}$ )  
493 characteristic of oxidized sulfur.

494 In Raman spectra, different components,  $\text{MoS}_2$ ,  $\text{Fe}(\text{MoO}_4)$ , amorphous  $\text{MoS}_3$  and  
495 carbonaceous matrix [30] are identified. It is difficult to further interpret the observed  
496 differences as they may be related to the localization of the analyzed area within the  
497 heterogeneous wear track, rather than to systematic dependence on contact pressure.

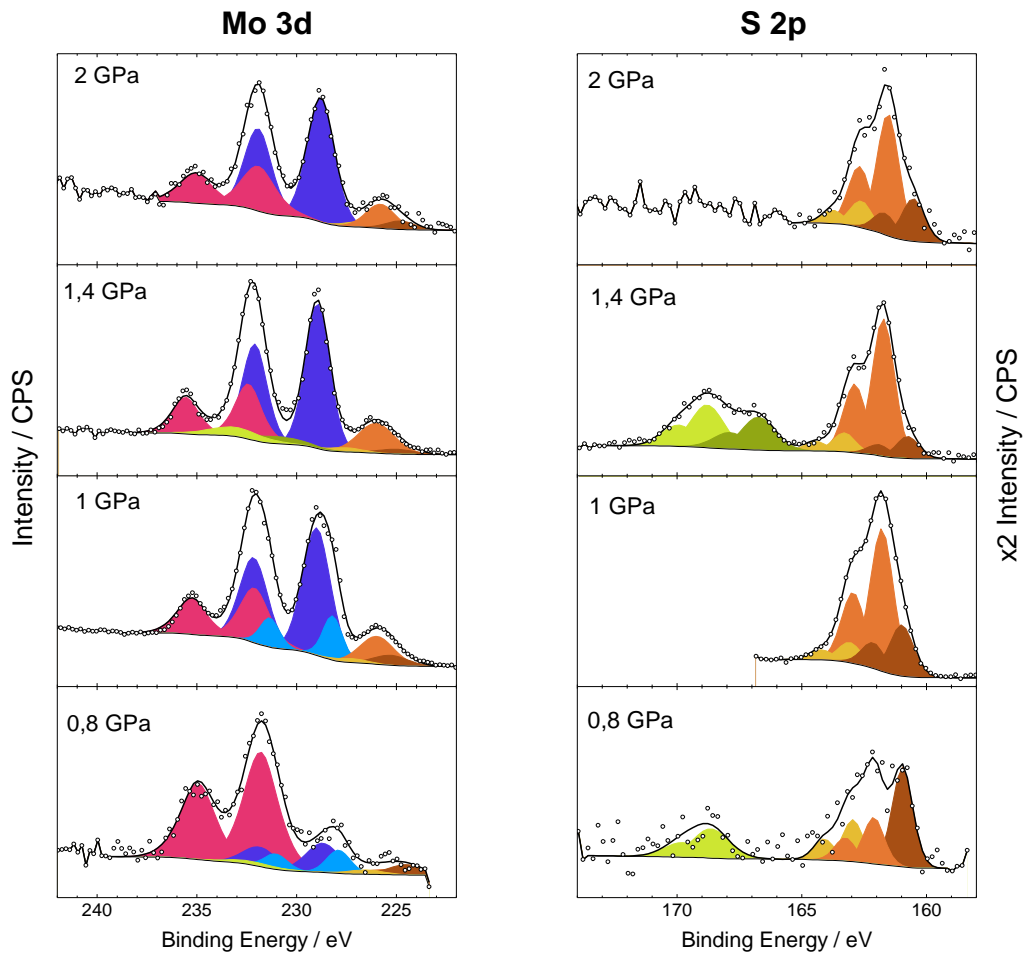
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Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at%)	S (at%) /Mo (at%) ratio	Assignment
MoDTC 1 0.8 GPa	<b>Mo<sub>3d5/2</sub> - 3/2</b>				1.6	
	Mo <sub>3d</sub> - (A)	227.9 - 231.1	1.4	3.7		Reduced MoS <sub>2</sub>
	Mo <sub>3d</sub> - (B)	228.7 - 231.9	2.0	6.7		MoS <sub>2</sub> or MoS <sub>3</sub>
	Mo <sub>3d</sub> - (C)	231.8 - 235.0	2.0	28.2		MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b>S<sub>2p3/2</sub> - 1/2</b>					
	S <sub>2p</sub> - (A)	161.0 - 162.1	1.0	25.6		S <sup>2-</sup> in reduced MoS <sub>2</sub>
	S <sub>2p</sub> - (B)	162.1 - 163.3	1.0	11.9		S <sup>2-</sup> in MoS <sub>2</sub> or in MoS <sub>3</sub>
	S <sub>2p</sub> - (C)	163.0 - 164.1	1.0	10.8		(S <sub>2</sub> ) <sup>2-</sup> in FeS <sub>2</sub> or thiomolybdate or MoS <sub>3</sub>
S <sub>2p</sub> - (E)	168.6 - 169.8	1.7	13.1	Sulfate		
MoDTC 1 1 GPa	<b>Mo<sub>3d5/2</sub> - 3/2</b>				1.3	
	Mo <sub>3d</sub> - (A)	228.2 - 231.4	1.2	6.1		Reduced MoS <sub>2</sub>
	Mo <sub>3d</sub> - (B)	229.0 - 232.2	1.7	25.3		MoS <sub>2</sub> or MoS <sub>3</sub>
	Mo <sub>3d</sub> - (C)	232.1 - 235.3	1.7	11.9		MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b>S<sub>2p3/2</sub> - 1/2</b>					
	S <sub>2p</sub> - (A)	161 - 162.1	1.1	13.6		S <sup>2-</sup> in reduced MoS <sub>2</sub>
	S <sub>2p</sub> - (B)	161.8 - 162.9	1.1	37.7		S <sup>2-</sup> in MoS <sub>2</sub> or in MoS <sub>3</sub>
	S <sub>2p</sub> - (C)	163.1 - 164.2	1.1	5.4		(S <sub>2</sub> ) <sup>2-</sup> in FeS <sub>2</sub> or thiomolybdate or MoS <sub>3</sub>
MoDTC 1 1.4 GPa	<b>Mo<sub>3d5/2</sub> - 3/2</b>				2.3	
	Mo <sub>3d</sub> - (B)	229.0 - 231.1	1.4	21.2		MoS <sub>2</sub> or MoS <sub>3</sub>
	Mo <sub>3d</sub> - (C)	232.4 - 235.6	1.6	9.1		MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b>S<sub>2p3/2</sub> - 1/2</b>					
	S <sub>2p</sub> - (A)	160.8 - 161.9	1.1	5.3		S <sup>2-</sup> in reduced MoS <sub>2</sub>
	S <sub>2p</sub> - (B)	161.7 - 162.9	1.1	33.0		S <sup>2-</sup> in MoS <sub>2</sub> or in MoS <sub>3</sub>
	S <sub>2p</sub> - (C)	163.3 - 164.4	1.1	4.6		(S <sub>2</sub> ) <sup>2-</sup> in FeS <sub>2</sub> or thiomolybdate or MoS <sub>3</sub>
	S <sub>2p</sub> - (D)	166.7 - 167.9	1.6	11.7		SO <sub>3</sub> species
S <sub>2p</sub> - (E)	168.8 - 170.0	1.6	15.1	Sulfate		
MoDTC 1 2 GPa	<b>Mo<sub>3d5/2</sub> - 3/2</b>				1.55	
	Mo <sub>3d</sub> - (B)	228.8 - 231.9	1.6	26.5		MoS <sub>2</sub> or MoS <sub>3</sub>
	Mo <sub>3d</sub> - (C)	231.9 - 235.1	2.0	12.6		MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b>S<sub>2p3/2</sub> - 1/2</b>					
	S <sub>2p</sub> - (A)	160.5 - 161.7	1.1	13.6		S <sup>2-</sup> in reduced MoS <sub>2</sub>
	S <sub>2p</sub> - (B)	161.5 - 162.7	1.1	38.8		S <sup>2-</sup> in MoS <sub>2</sub> or in MoS <sub>3</sub>
S <sub>2p</sub> - (C)	162.6 - 163.8	1.1	8.5	(S <sub>2</sub> ) <sup>2-</sup> in FeS <sub>2</sub> or thiomolybdate or MoS <sub>3</sub>		

500

501 **Table 5: Peak fitting details related to Figure 12 e.i. XPS analyses of tribofilms obtained**  
502 **with MoDTC 1 after 18 000 cycles of rubbing at 100°C at an initial maximum Hertz**  
503 **pressure of 0.8 GPa, 1 GPa, 1.4 GPa, 2 GPa and an average sliding speed of 56 mm/s**

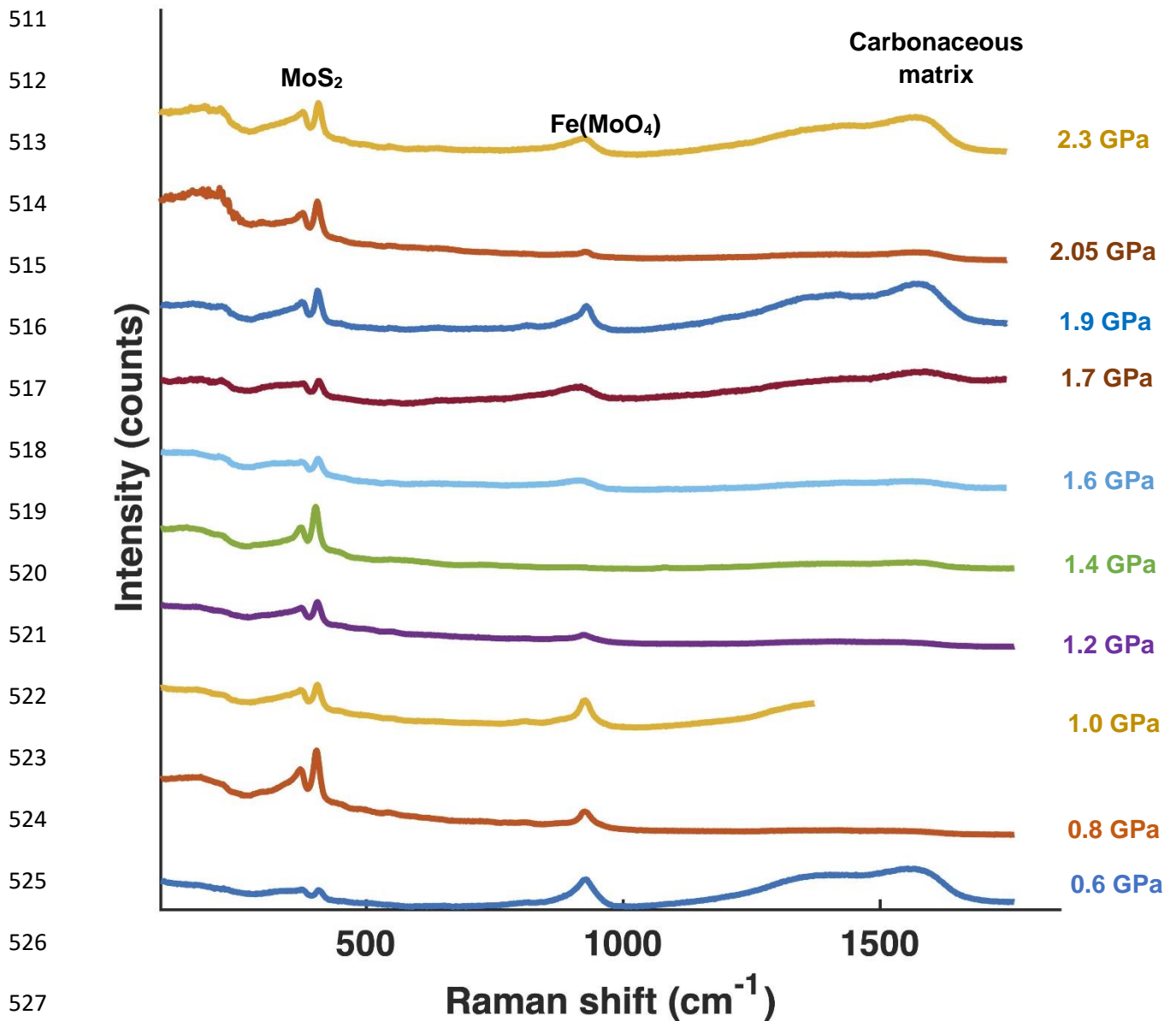
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507 **Figure 12: XPS analyses (Mo3d peak) carried out of tribofilms (flats) obtained with**  
 508 **MoDTC 1 at various initial maximum Hertz pressure after 18 000 cycles of rubbing at**  
 509 **100°C and an average sliding speed of 56 mm/s.**

510



528 **Figure 13: Raman analyses on tribofilms (flats) obtained with MoDTC 1 after 18 000**  
 529 **cycles of rubbing at different initial maximum Hertz pressure, at 100°C and at an average**  
 530 **sliding speed of 56 mm/s.**

531 XPS and Raman analyses of tribofilms obtained with MoDTC 2 at 0.8 GPa and 1.2 GPa are  
 532 reported in Figures SI 2-3, SI 2-4 and SI 2-5 for comparison with MoDTC 1. Like for tribofilms  
 533 obtained with MoDTC 1, MoS<sub>2</sub> is mainly detected by Raman and XPS. The low binding energy  
 534 Mo<sub>3d</sub> (A) contribution detected by XPS and that would correspond to defective MoS<sub>2</sub> analyses  
 535 is also mainly detected at low contact pressures (0.8 GPa) like for MoDTC 1. The peak at 925  
 536 cm<sup>-1</sup> on Raman spectra attributed to Fe(MoO<sub>4</sub>) seems more significant in case of MoDTC 1  
 537 than for MoDTC 2.

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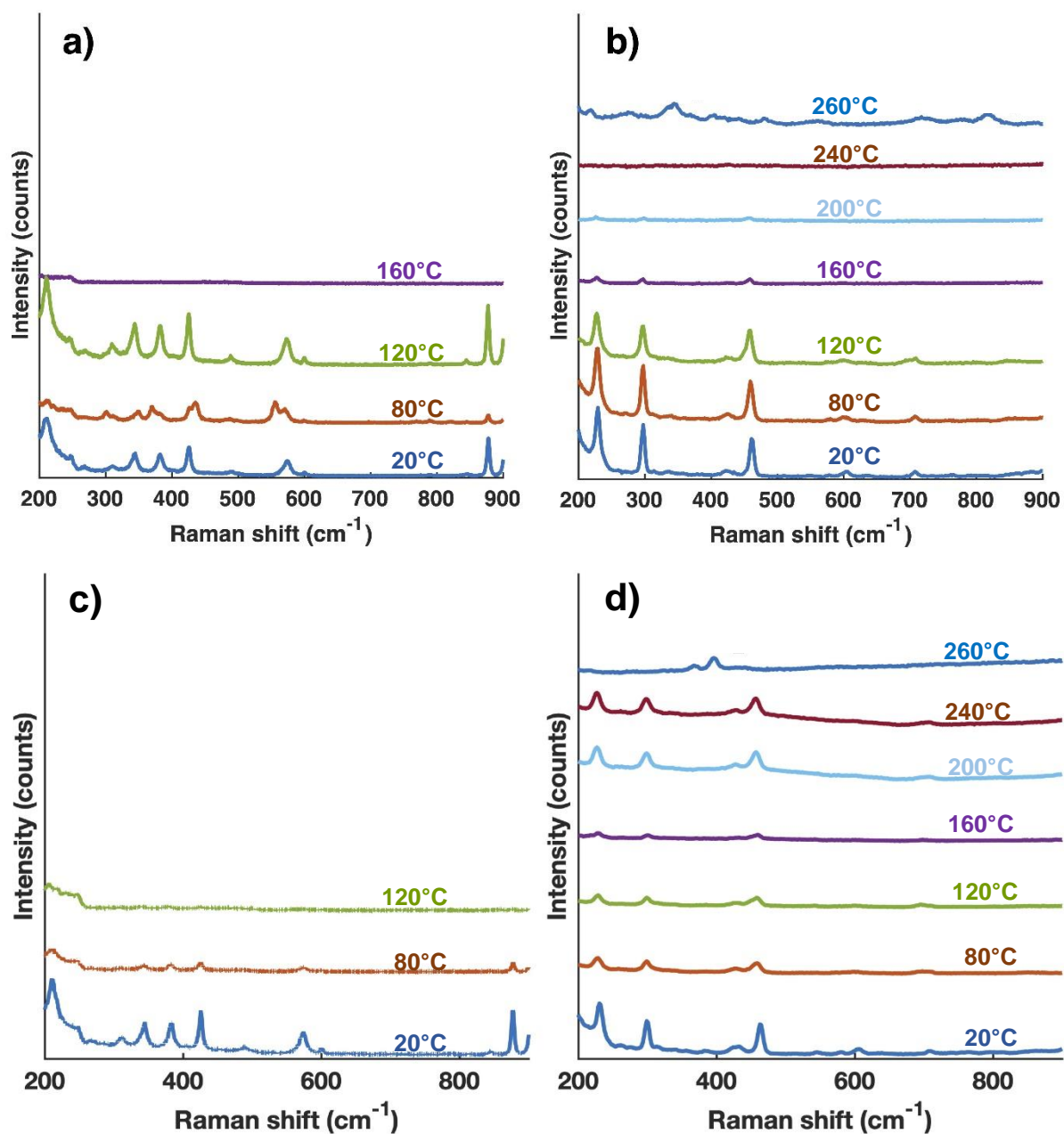


### 539 **3.4 Effect of temperature without contact pressure and shear**

540 To test if the decomposition of both MoDTC molecules toward MoS<sub>2</sub> can be thermally induced  
541 (with no other concurrent reagent), we performed Raman analyses after thermal degradation  
542 for both molecules at different temperatures in air and under argon atmosphere (Figure 14) in  
543 the absence of steel material. At high temperature (160°C for open air tests and 120°C for  
544 argon atmosphere tests), the molecule MoDTC **1** is decomposed but no MoS<sub>2</sub> formation is  
545 observed. In contrast, Raman spectra obtained from 260°C both in air and Ar atmosphere with  
546 MoDTC **2** exhibits Raman peaks around 400 cm<sup>-1</sup>. This is not compatible with MoO<sub>3</sub> and MoO<sub>2</sub>  
547 [31] but that could be related to Mo-S vibrations. The  $E_{2g}^1$  and  $A_{1g}$  peaks are found at slightly  
548 lower positions than standard MoS<sub>2</sub> analyzed at ambient temperature, but this may be due the  
549 temperature dependence of the peak position with temperature [32] or to the fact that it is more  
550 a MoS<sub>x</sub> compound rather than MoS<sub>2</sub> [33]. The decomposition in MoS<sub>2</sub> of MoDTC closed to  
551 MoDTC **2** structure by thermal degradation was already found in literature [34].

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**Figure 14: Raman analyses performed on pure additives in different atmosphere and at different temperatures: a) MoDTC 1 in air (laser wavelength 784 nm) and b) MoDTC 2 in air (laser wavelength 532 nm) c) MoDTC 1 under argon atmosphere (laser wavelength 784 nm) and d) MoDTC 2 under argon atmosphere (laser wavelength 532 nm).**

## 572 4 Discussion

573 The achievement of low friction coefficients (0.05 to 0.07) under boundary lubrication in steel-  
574 steel contact was observed for both molecules MoDTC **1** and MoDTC **2**, and is concurrent with  
575 the formation of MoS<sub>2</sub>. The originalities of MoDTC **1** are to outperform MoDTC **2** at high contact  
576 pressures, and to allow MoS<sub>2</sub> formation without a preformed dimeric core in the molecule,  
577 external sulfur supply, and with a high starting oxidation number (Mo(+VI)). Such distinctive  
578 chemical properties open mechanistic questions on how such MoDTC molecules can lead to  
579 the formation of MoS<sub>2</sub>.

580 Concerning the oxidation state of molybdenum atom within the molecule, systems with a  
581 Mo(+VI) molybdate core have been described but they need to be blended with other additives  
582 to form MoS<sub>2</sub> sheets [26]. Among the potential reductive sources, the organic oil or the organic  
583 ligands could play a chemical reducing role, but the formation of iron-molybdate involving both  
584 iron coming from the steel surface and molybdenum from the additive supports the idea of an  
585 active role of steel in these phenomena. This is further corroborated by the fact that MoS<sub>2</sub> is  
586 not observed upon thermal heating of MoDTC powder in the absence of steel (results §3.4)  
587 and by the fact that molybdate is the main detected phase under less severe conditions at low  
588 contact pressure (Figures 12 and 13). Therefore, it can be suggested that the steel-steel  
589 contact lubricated with oil environment is reducing enough to reduce Mo(+VI) in MoDTC **1** into  
590 Mo(+IV), in the absence of other additives.

591 The two MoDTC molecules display a very different response during thermal degradation.  
592 Additive MoDTC **2** seems to degrade into MoS<sub>x</sub> compounds in both air and argon atmospheres  
593 near 260°C. This is in agreement with reported mechanism on thermal degradation of such  
594 molecules containing the [Mo(μ-S)<sub>2</sub>Mo] sulphided core as MoDTC **2** [34]. Conversely, as  
595 shown on Figures 14, MoS<sub>2</sub> is not formed from MoDTC **1** during thermal degradation. This  
596 suggests a strong role of mechanical stresses and a chemical role of iron. Consistently, we  
597 have evidenced the formation of MoS<sub>2</sub> from MoDTC **1** only in wear tracks of tribotests (Figures  
598 3 and 4). As shown above, mechanical stresses for MoDTC **2** action does not seem necessary  
599 for forming MoS<sub>2</sub>, as it seems to form in thermal degradation experiments, but they may  
600 positively add to thermal degradation and/or chemical role of steel surface.

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602 To summarize, MoDTC **1** is an interesting molecular additive to reduce friction in boundary  
603 lubricated steel-steel contacts. This efficient molecule achieves high performance up to high  
604 contact pressures by accessing mechanistic pathways that could be distinct from those of  
605 classical molecules such as MoDTC **2** or molybdate [26]. We ruled out the formation of MoS<sub>2</sub>  
606 by a mechanism based solely on the thermal degradation of MoDTC **1**. The absence of core

607 sulfur in molecule MoDTC **1** also rules out (at least in the initial stages) the chemical  
608 degradation mechanism proposed by Grossiord *et al.* [8] where only sulfur atoms present in  
609 the core of the molecule contribute to the MoS<sub>2</sub> generation. The necessary involvement of the  
610 sulfur atoms in the ligands of MoDTC **1** remains compatible with at least two proposed  
611 mechanisms: the formation of a Linkage Isomer - MoDTC [11,12], or the cleavage of carbon-  
612 sulfur bonds of the ligand [7,16]. Then, MoS<sub>x</sub> intermediate products seems needed before  
613 generating well-organized MoS<sub>2</sub> lamellar sheets during friction as it was proposed previously  
614 [7,26].

615

## 616 **5 Conclusion**

617 In this work, the tribological properties and factors influencing the formation of MoS<sub>2</sub> from  
618 {[MoO<sub>2</sub>](S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>} (MoDTC **1**) and {[Mo<sub>2</sub>(S/O)<sub>4</sub>](S<sub>2</sub>CNOc<sub>2</sub>)<sub>2</sub>} (MoDTC **2**) were investigated.  
619 Unexpectedly, MoDTC **1**, comprising Mo(+VI) and containing sulfur atoms only in its  
620 thiocarbamate ligands, is able to form MoS<sub>2</sub> sheets in lubricated steel/steel contacts under  
621 boundary lubrication conditions. This experimental study therefore demonstrates that, contrary  
622 to what was classically assumed, the presence of peripheral thiocarbamate ligands can be  
623 sufficient to provide the required sulfur source in these “all-in-one” types of molecules. This  
624 molecule is not only competitive with “classical” MoDTC used in engine lubrication, containing  
625 sulfur in the core of the molecule, but is even more powerful at high contact pressures.

626 On the mechanistic point of view, this work confirms that the chemical pathway from MoDTC  
627 to MoS<sub>2</sub> is not only thermal. Pressure and shear take an important role in the tribochemical  
628 reactions route leading to the formation of MoS<sub>2</sub>. A substantial contribution of the surface, as  
629 mentioned in the discussion section, remains an important parameter to consider as well.

630 Those results give insights in molecule design and lubricant formulation to improve MoS<sub>2</sub>  
631 sheets generation from several types of contact conditions

632

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