

## Supplementary material

### SI 1: XPS characterizations of pure MoDTC 1 and MoDTC 2

XPS analyses were fitted as follow:

- Carbon C (red): the three contributions correspond to the three chemically different carbon environment of the carbamate ligands: carboxylates,  $[\text{CH}_3(\text{C}_n\text{H}_{2n})]_2\text{NCO}_2$ , methylene carbons,  $[\text{CH}_3(\underline{\text{C}}_n\text{H}_{2n})]_2\text{NCO}_2$  and terminal carbons  $[\underline{\text{C}}\text{H}_3(\text{C}_n\text{H}_{2n})]_2\text{NCO}_2$  ( $n=1$  in MoDTC 1,  $n=7$  in MoDTC 2); Small CC and CO compounds contaminations could also be considered regarding C/Mo and O/Mo ratio as both elements are found in slight excess.
- Nitrogen N (orange);
- Molybdenum (purple); The dark purple peak corresponds to Mo(+VI) environment (main contribution in MoDTC 1) and the light purple peak correspond to Mo(+V) environment (main contribution in MoDTC 2). A small Mo(+V) contributions is found in MoDTC 1 (contamination). The small Mo(+VI) contributions in MoDTC 2 could correspond to surface oxidation of the molecule which is not detected by elemental analysis presented in §2 since it was obtained by a less surface sensitive technique.
- Oxygen (green): the main contribution (dark green) correspond to the oxygen within the molecule. The two other contributions are related to small CO compounds contaminations.
- Sulfur (light blue).

Ratio X/Mo: semi-quantification was performed by XPS. From at% obtained for each considered elements ( $X = \text{C}, \text{N}, \text{O}$  or  $\text{S}$ ), ratio X/Mo were calculated (ratio obtained by XPS semi-quantification) and compared to the one obtained from the chemical formula (Theoretical ratio calculated from chemical formula).

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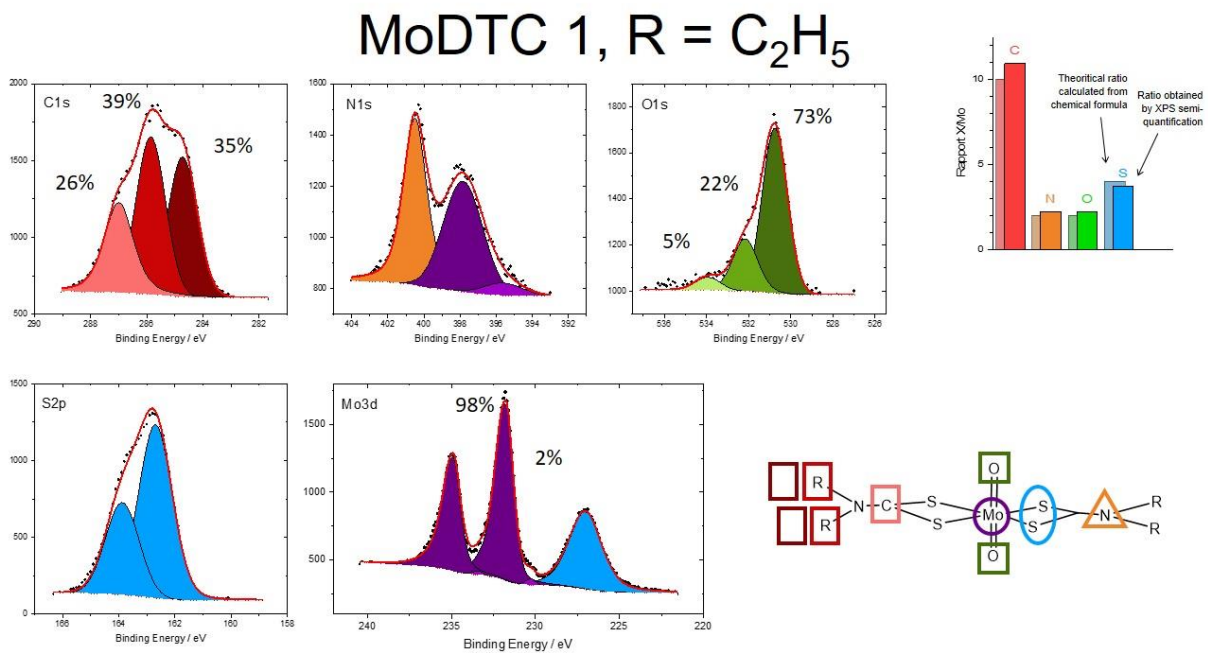
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44 **Figure SI 1-1: XPS characterization of MoDTC 1**

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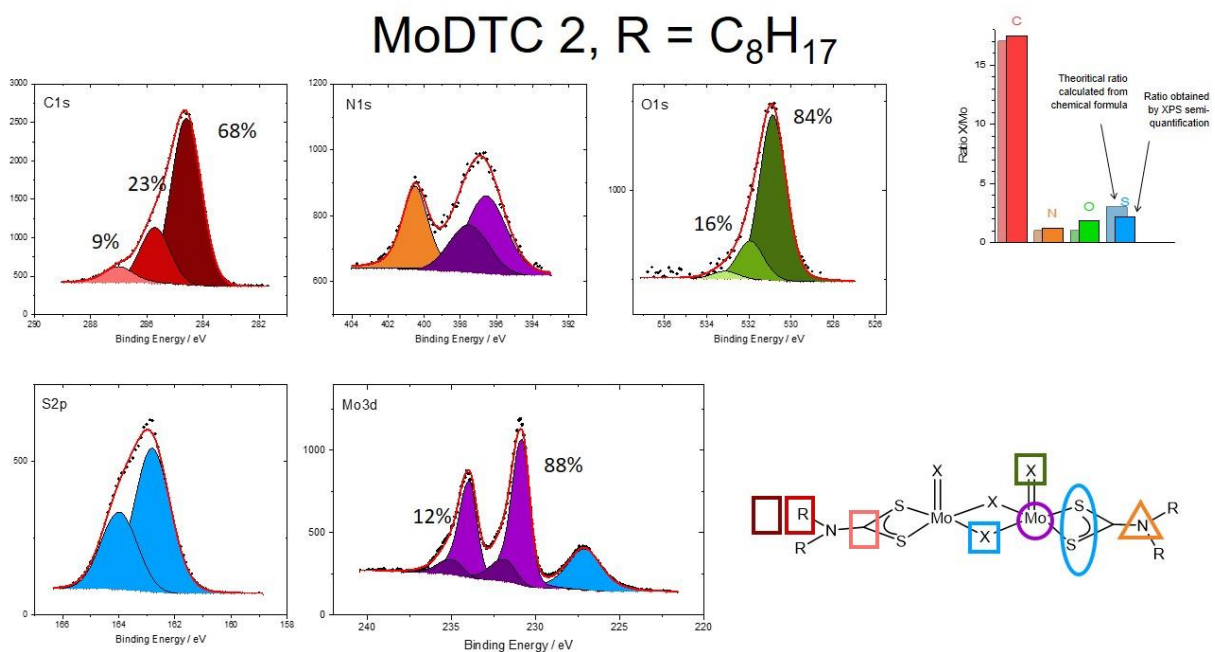
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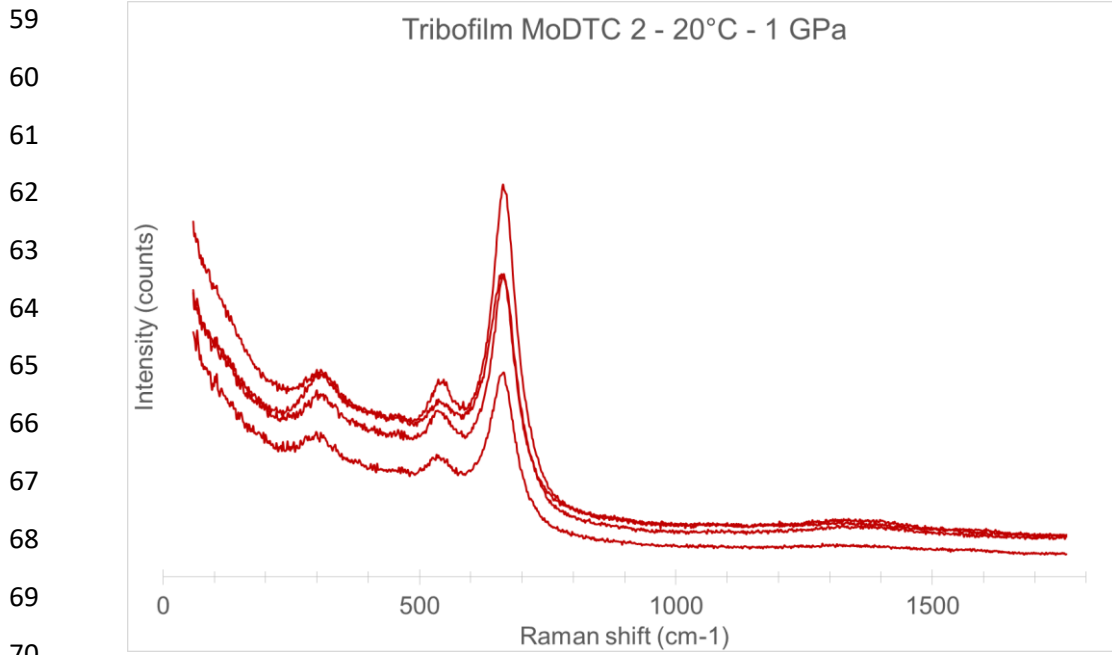
56 **Figure SI 1-2: XPS characterization of MoDTC 1**



56 **Figure SI 1-2: XPS characterization of MoDTC 1**

57 **SI 2: Raman and XPS characterizations of tribofilm with MoDTC 2**

58 *Temperature effect: Raman Analyses*



71 **Figure SI 2-1: Raman analyses carried out on several points of the tribofilm obtained**  
72 **after reciprocating steel-steel tribotest lubricated with PAO4 + 0.3 w% MoDTC 2 at 20°C**  
73 **and 1 GPa of contact pressure.**

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79 *Temperature effect: XPS Analyses*

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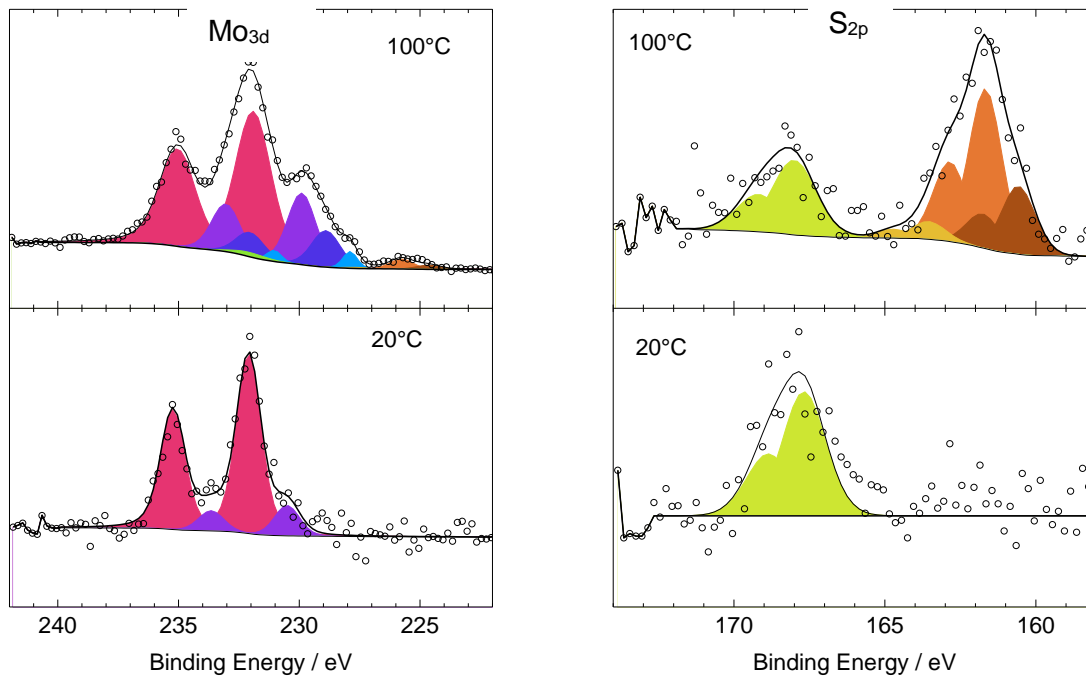
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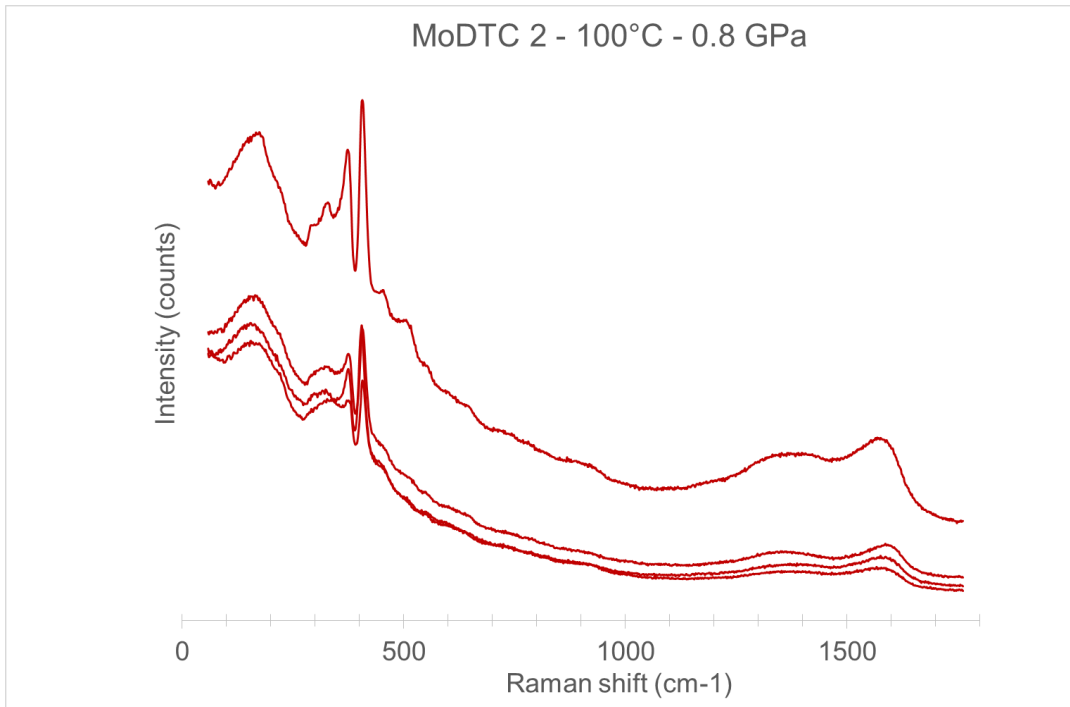


94 **Figure SI 2-2: XPS analyses carried out on tribofilms obtained after reciprocating steel-**  
 95 **steel tribotest lubricated with PAO4 + 0.3 w% MoDTC 2 at 20°C and 100°C and 1 GPa of**  
 96 **contact pressure.**

Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at%)	S (at%) / Mo (at%) ratio	Assignment
MoDTC 2 20°C	<i>Mo<sub>3d5/2 - 3/2</sub></i>				1.2	
	Mo <sub>3d</sub> - (B')	230.5 - 233.7	1.2	6		MoO <sub>x</sub> S <sub>y</sub>
	Mo <sub>3d</sub> - (C)	232.1 - 235.2	1.2	38.7		MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<i>S<sub>2p3/2 - 1/2</sub></i>					
	S <sub>2p</sub> - (E)	167.7- 168.9	1.7	55.3		sulfate
MoDTC 2 100°C	<i>Mo<sub>3d5/2 - 3/2</sub></i>				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>
	<i>S<sub>2p3/2 - 1/2</sub></i>					
	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

97 **Table SI-2-1: Peak fitting details related to Figure SI 2-2.**

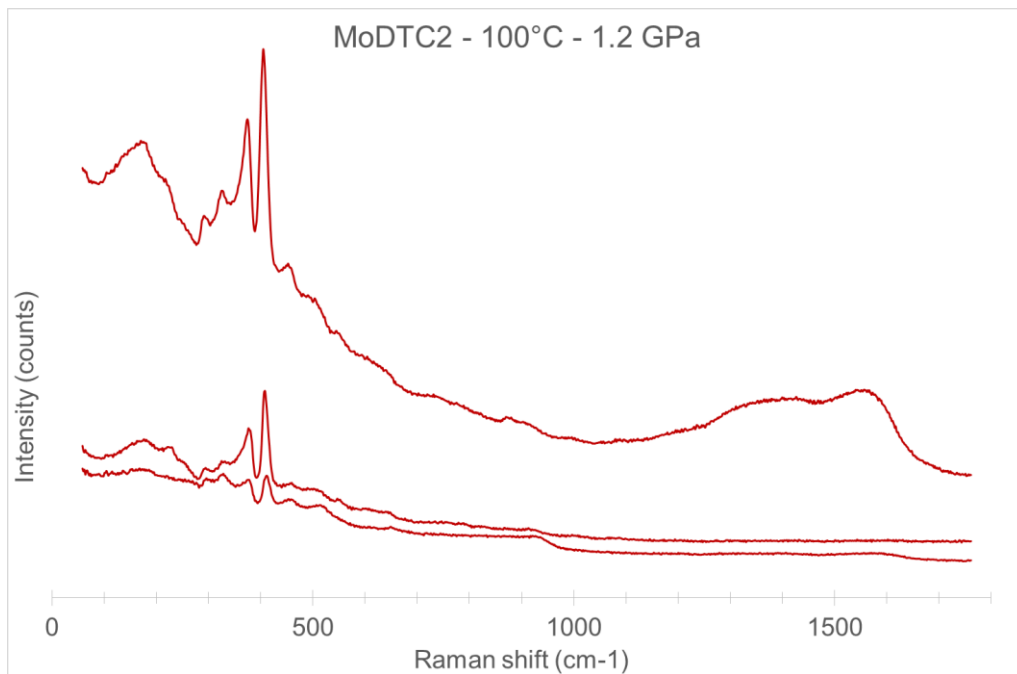
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101 **Figure SI 2-3: Raman analyses carried out on several points of the tribofilm obtained**  
102 **after reciprocating steel-steel tribotest lubricated with PAO4 + 0.3 w% MoDTC 2 at 100°C**  
103 **and 0.8 GPa of contact pressure.**

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117 **Figure SI 2-4: Raman analyses carried out on several points of the tribofilm obtained**  
118 **after reciprocating steel-steel tribotest lubricated with PAO4 + 0.3 w% MoDTC 2 at 100°C**  
119 **and 1.2 GPa of contact pressure.**

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121 *Contact pressure effect : XPS analyses*

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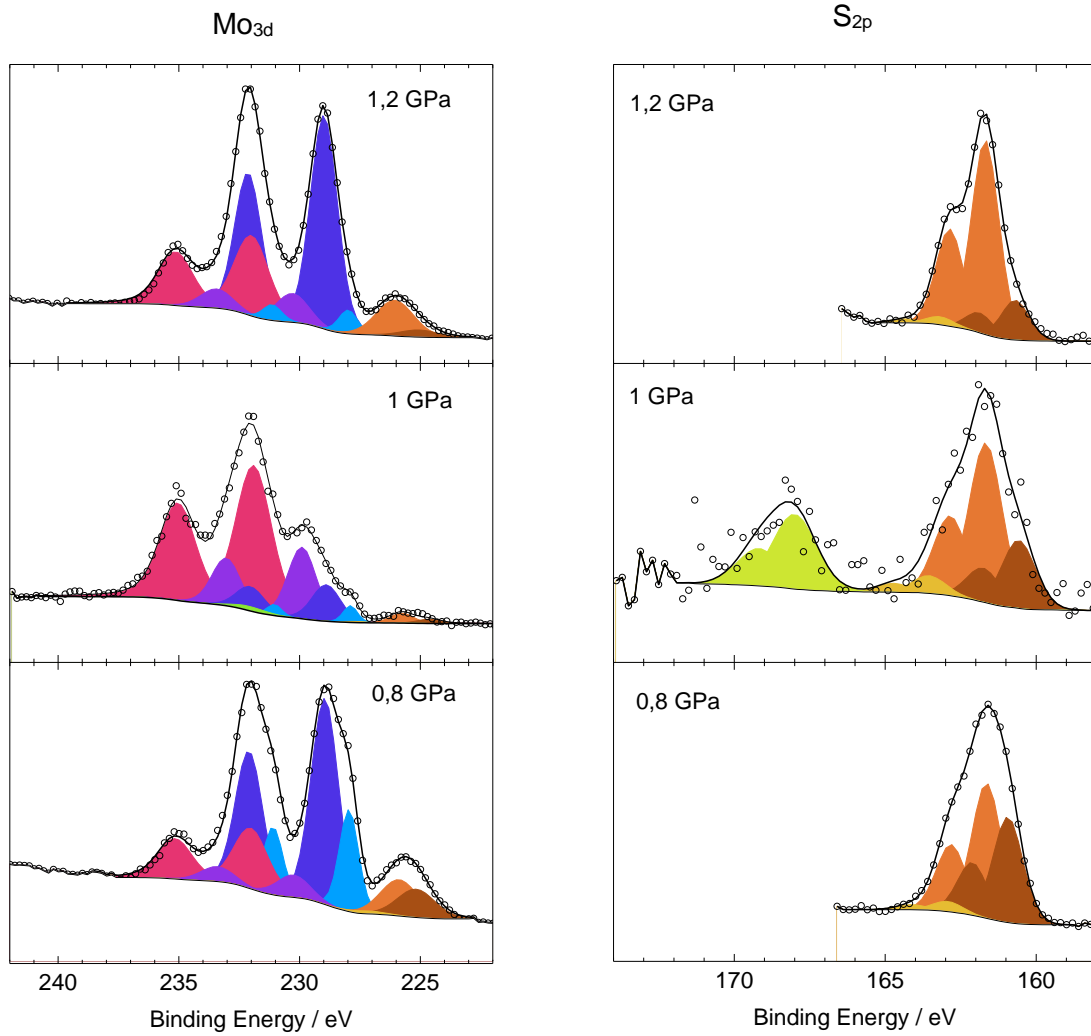
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137 **Figure SI 2-5: XPS analyses carried out on tribofilms obtained after reciprocating steel-**  
138 **steel tribotest lubricated with PAO4 + 0.3 w% MoDTC 2 at 100°C and 0.8 GPa, 1 GPa and**  
139 **1.2 GPa of contact pressure:**

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Sample Id.	Element/Transition	Peak energy (eV)	FWHM (eV)	Atomic concentration (at%)	S (at%) /Mo (at%) ratio)	Assignment
MoDTC 2 0.8 GPa	<b><i>Mo<sub>3d5/2 - 3/2</sub></i></b>				1.5	
	Mo <sub>3d</sub> - (A)	228.0 - 231.1	0.9	7.3		Reduced MoS <sub>2</sub>
	Mo <sub>3d</sub> - (B)	229.0 - 232.1	1.4	21.0		MoS <sub>2</sub> or MoS <sub>3</sub>
	Mo <sub>3d</sub> - (B')	230.3 - 233.4	1.6	2.7		MoO <sub>x</sub> S <sub>y</sub>
	Mo <sub>3d</sub> - (C)	232.0 - 235.2	1.7	8.5		MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b><i>S<sub>2p3/2 - 1/2</sub></i></b>					
	S <sub>2p</sub> - (A)	160.9 - 162.1	1.2	25.4		S <sup>2-</sup> in reduced MoS <sub>2</sub>
	S <sub>2p</sub> - (B)	161.6 - 162.8	1.2	32.6		S <sup>2-</sup> in MoS <sub>2</sub> or in MoS <sub>3</sub>
	S <sub>2p</sub> - (C)	162.9- 164.1	1.2	2.5		(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>
MoDTC 2 1 GPa	<b><i>Mo<sub>3d5/2 - 3/2</sub></i></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><i>S<sub>2p3/2 - 1/2</sub></i></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		
MoDTC 2 1.2 GPa	<b><i>Mo<sub>3d5/2 - 3/2</sub></i></b>				1.0	
	Mo <sub>3d</sub> - (A)	228.0- 231.1	0.9	2.2		Reduced MoS <sub>2</sub>
	Mo <sub>3d</sub> - (B)	229.0 - 232.1	1.3	28.9		MoS <sub>2</sub> or MoS <sub>3</sub>
	Mo <sub>3d</sub> - (B')	230.3- 233.4	1.6	4.7		MoO <sub>x</sub> S <sub>y</sub>
	Mo <sub>3d</sub> - (C)	232.0 - 235.1	1.7	15.4		MoO <sub>3</sub> / FeMoO <sub>4</sub>
	<b><i>S<sub>2p3/2 - 1/2</sub></i></b>					
	S <sub>2p</sub> - (A)	160.7 - 161.9	1.1	8.0		S <sup>2-</sup> in reduced MoS <sub>2</sub>
	S <sub>2p</sub> - (B)	161.7 - 162.9	1.1	39.2		S <sup>2-</sup> in MoS <sub>2</sub> or in MoS <sub>3</sub>
	S <sub>2p</sub> - (C)	163.2 - 164.4	1.1	1.6		(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>

144 **Table SI-2-2: Peak fitting details related to Figure SI 2-5.**

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