Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Oxo-sulfido molybdenum and tungsten fluorides with M-O and M-S multiple bonds

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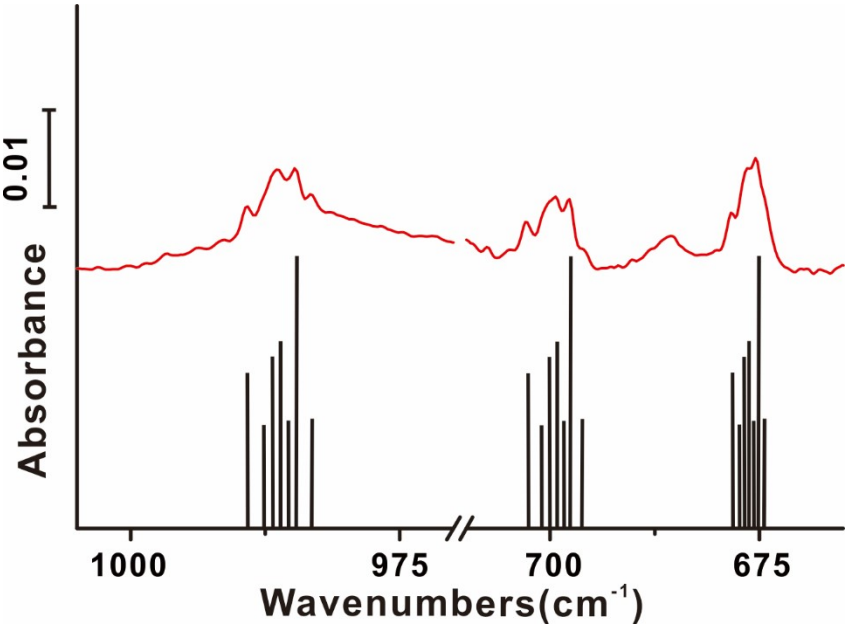


**Fig. S1** Infrared spectrum with expanded wavenumber scale (taken from Figure 3c) for the molybdenum product absorptions and line spectrum showing the natural abundance of Mo isotopes ($^{92}$Mo, $^{94}$Mo, $^{95}$Mo, $^{96}$Mo, $^{97}$Mo, $^{98}$Mo, and $^{100}$Mo).

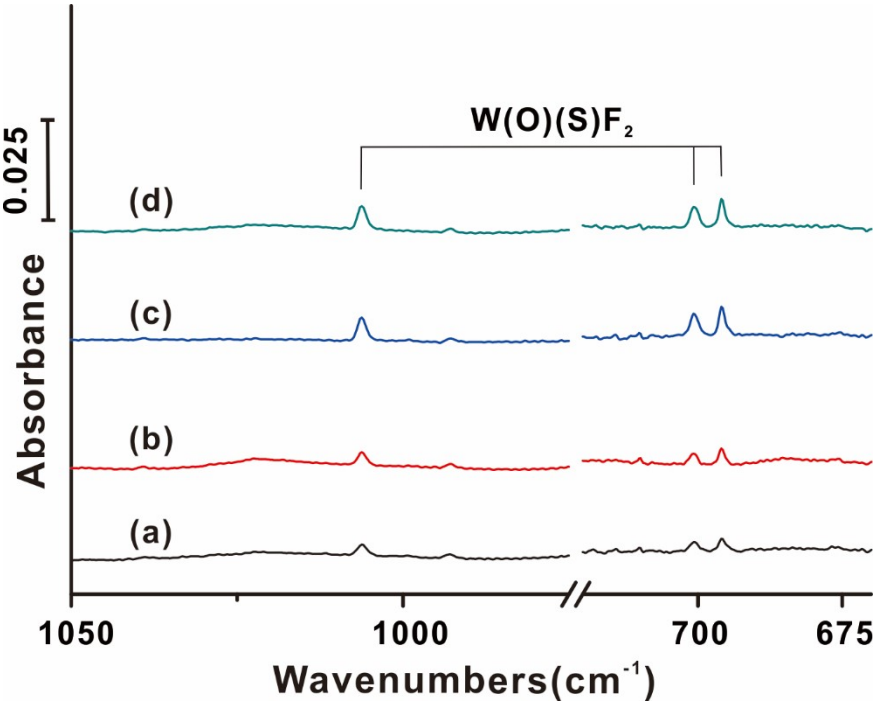


**Fig. S2** Infrared spectra in the product regions from the reactions of laser-ablated tungsten atoms and 0.5% $SOF_2$ in excess neon at 4 K. (a) after deposition for 30 min; (b) after annealing to 6 K; (c) after $\lambda > 220$ nm irradiation; (d) after annealing to 8 K.

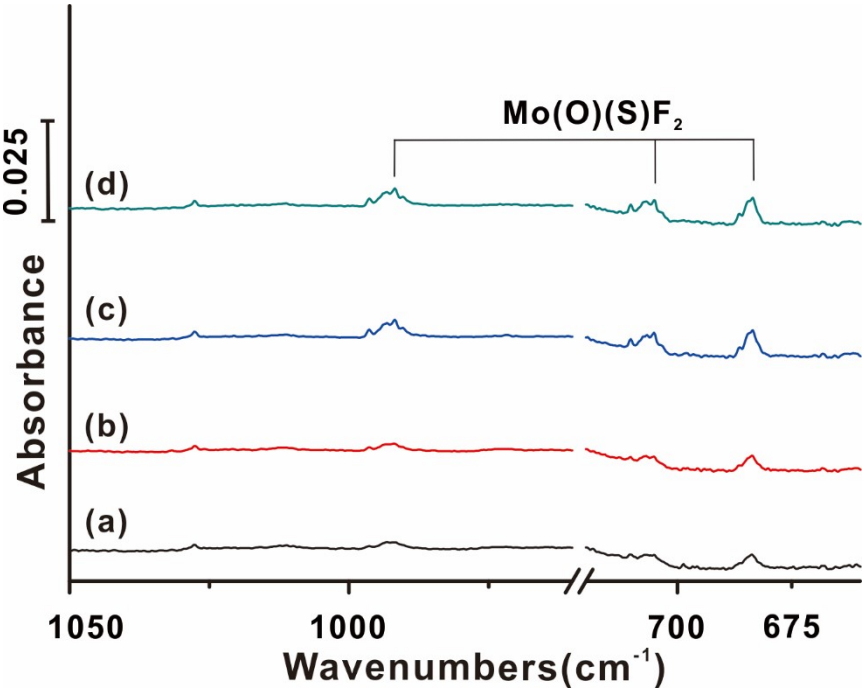


**Fig. S3** Infrared spectra in the product regions from the reactions of laser-ablated molybdenum atoms and 0.5% $SOF_2$ in excess neon at 4 K. (a) after deposition for 30 min; (b) after annealing to 6 K; (c) after $\lambda > 220$ nm irradiation; (d) after annealing to 8 K.

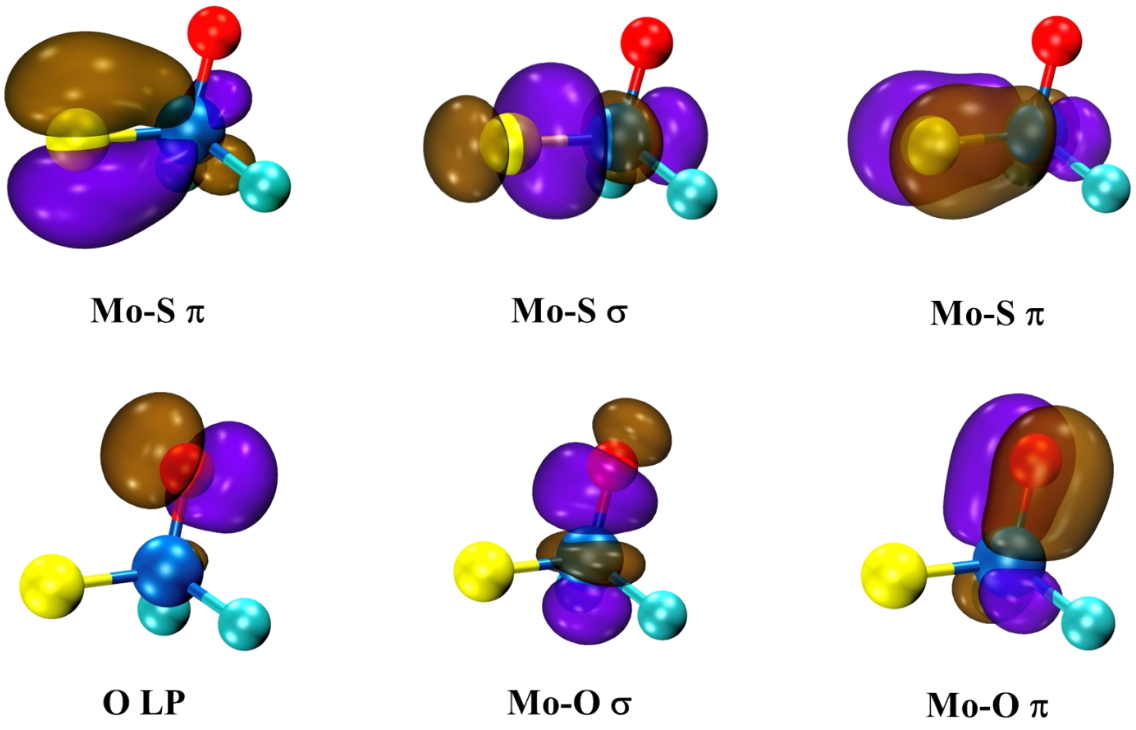


**Fig. S4** Natural bond orbitals showing the Mo–S and Mo-O interactions of $Mo(O)(S)F_2$.

**Table S1.** Experimental infrared absorptions ($cm^{-1}$) of $M(O)(S)F_2$ (M = Mo, W) in neon matrixes.

| | M−O str. | antisym. F-M-F str. | sym. F-M-F str. |
|---|---|---|---|
| $W(O)(S)F_2$ | 1006.2 | 700.7 | 695.9 |
| $Mo(O)(S)F_2$ | 996.3 ($^{92}Mo$)<br>993.7 ($^{94\text{-}97}Mo$)<br>991.8 ($^{98}Mo$)<br>990.3 ($^{100}Mo$) | 710.2 ($^{92}Mo$)<br>707.0 ($^{94\text{-}97}Mo$)<br>705.0 ($^{98}Mo$)<br>703.4 ($^{100}Mo$) | 686.5 ($^{92}Mo$)<br>684.6 ($^{94\text{-}97}Mo$)<br>683.5 ($^{98}Mo$)<br>682.3 ($^{100}Mo$) |

**Table S2.** Calculated frequencies ($cm^{-1}$) and infrared intensities (km/mol) of $M(O)(S)F_2$ (M = Mo, W) and its isotopomers at the B3LYP level.

| | $^{32}S$, $^{16}O$ | | $^{32}S$, $^{18}O$ | | $^{34}S$, $^{16}O$ | |
|---|---|---|---|---|---|---|
| | frequency | intensity | frequency | intensity | frequency | intensity |
| $W(O)(S)F_2$ | 1012.3 | 137 | 959.2 | 124 | 1012.2 | 137 |
| | 690.2 | 117 | 690.2 | 117 | 690.2 | 117 |
| | 683.7 | 107 | 683.6 | 107 | 683.6 | 107 |
| | 554.9 | 45 | 554.8 | 45 | 541.2 | 43 |
| | 283.0 | 2 | 271.5 | 2 | 281.7 | 2 |
| | 258.7 | 7 | 249.6 | 6 | 258.7 | 7 |
| | 202.6 | 2 | 202.3 | 2 | 201.4 | 2 |
| | 186.3 | 1 | 186.2 | 1 | 184.2 | 1 |
| | 183.5 | 5 | 183.5 | 5 | 183.4 | 5 |
| $^{98}Mo(O)(S)F_2$ | 1019.9 | 156 | 970.3 | 143 | 1019.9 | 156 |
| | 707.2 | 142 | 707.1 | 142 | 707.2 | 142 |
| | 683.7 | 140 | 683.4 | 140 | 683.5 | 139 |
| | 576.0 | 37 | 575.8 | 37 | 563.8 | 37 |
| | 290.6 | 1 | 279.6 | 1 | 289.0 | 1 |
| | 257.4 | 7 | 248.8 | 6 | 257.4 | 7 |
| | 211.9 | 3 | 211.2 | 3 | 210.9 | 3 |
| | 187.8 | 1 | 187.8 | 1 | 185.8 | 1 |
| | 183.2 | 5 | 183.1 | 5 | 182.8 | 5 |

**Cartesian coordinates for the singlet $W(O)(S)F_2$ and $Mo(O)(S)F_2$ complexes obtained at the B3LYP/6-311+G(3df)/SDD level of theory**

$W(O)(S)F_2$

| | | | |
|---|---|---|---|
| W | -0.0355352086 | -0.2266011894 | 0 |
| F | 0.7461756398 | -0.8937504508 | 1.5646419406 |
| F | 0.7461756398 | -0.8937504508 | -1.5646419406 |
| S | 0.1287063683 | 1.9043645901 | 0 |
| O | -1.7022845493 | -0.6092214389 | 0 |

$Mo(O)(S)F_2$

| | | | |
|---|---|---|---|
| Mo | -0.0426034009 | -0.2242348094 | 0.0000000005 |
| F | 0.7476262834 | -0.8917907124 | 1.552668546 |
| F | 0.7476262834 | -0.8917907193 | -1.552668542 |
| S | 0.1210040979 | 1.8844513912 | -0.0000000042 |
| O | -1.6904153737 | -0.595594097 | 0.0000000013 |