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SUPPORTING INFORMATION

The structural parameters of MoS$_2$ on SiO$_2$H are show in the second column of Tab. S1. S$_1$ is the sulphur top layer and S$_2$ is the sulphur bottom layer. The structural parameters of the halogenation of MoS$_2$ without defects are shown in the third and fourth columns. In the third column the average F-F and F-S1 distances are 3.17±0.74 Å and 1.74±0.09 Å, respectively. The F$_2$ bond length is 1.34 Å (see Ref. [S1]) which is much shorter than observed here. Additionally, in the SF$_4$ the S-F bond length is 1.60 Å in equatorial position and 1.69 Å in axial position. In SF$_6$, it is 1.60 Å and in SF$_5$Cl it is 1.62 Å. In spite of the F-S$_1$ distance being greater than expected, based on structure parameters, our results seem to indicate that there is chemical bond between F and S$_1$ atoms, as reported by Cao et al. with bond length of the 1.75 Å [S2]. The greater bond length could be a result of the interaction of S with Mo atoms.

Tab. S1. Structural Parameters of MoS$_2$ on SiO$_2$H with and without halogens.

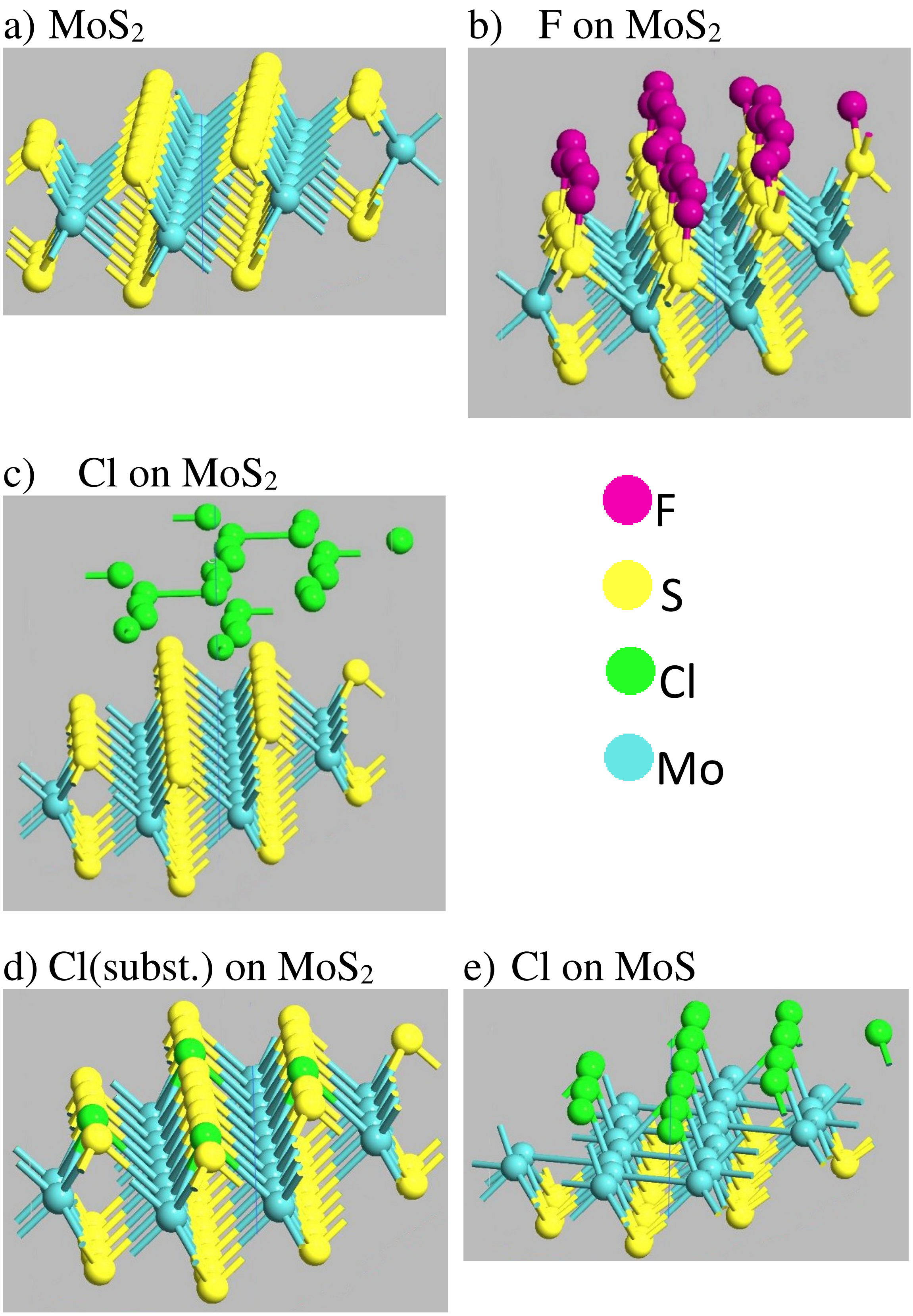
	Distances (Å)				
	MoS$_2$	F on MoS$_2$	Cl on		
			MoS$_2$	MoS$_2$ with a single S vacancy	MoS$_2$ without S$_1$* atoms
X-X		3.17±0.74	2.05±0.00	4.59	3.04±0.05
X-S$_1$*		1.74±0.09	3.91±0.18		
S$_1^*$-Mo	2.41±0.01	2.42±0.03	2.39±0.01	2.41±0.01 (2.49±0.01**)	2.49±0.02**
Mo-Mo	3.13±0.00	3.09±0.08	3.00±0.01	2.94±0.00	2.65±0.11
Mo-S$_2$*	2.41±0.01	2.39±0.01	2.39±0.01	2.40±0.01	2.38±0.03
S$_2^*$-O	3.47±0.04	3.50±0.21	3.33±0.08	3.28±0.07	3.42±0.14

*S$_1$ and S$_2$ correspond to S atoms in the top and bottom layer, respectively.
** Cl-Mo.

In the case of Cl on MoS_2, a different behavior is exhibited. In the fourth column, the average Cl-Cl and Cl-S_1 distances are 2.05±0.00 Å and 3.91±0.18 Å, respectively. According to Ref. S1, the Cl_2 bond length is 1.99 Å, while in the SF_5Cl molecule the S-Cl distance is 2.11 Å. Thus, our results point to the formation of a Cl_2 bond and a weak interaction between Cl and MoS_2. The comparison of the average Mo-Mo distances from the second to fourth columns shows a weak influence of halogenation. However, when we compare deviations, the fluorinated system has the largest one. It seems that F bonding to S is strong enough to modify the MoS_2 atomic structure. Cl also influences the Mo-Mo distance. Nevertheless, the deviation is almost the same of the pristine sample, characterizing a weak interaction of the unbound type.

Cl inserted substitutionally to one S_1 atom in the MoS_2 structure resulted in a 6 % shorter Mo-Mo distance in comparison with the pristine sample. Nevertheless, this modification does not prominently perturb the MoS_2 structure. The other distances are similar to those of the pristine sample. Chlorination of a sample without S_1 atoms was also investigated. Results are shown in the last column in Tab. S1. The Cl-Mo distance obtained is the same (2.49±0.02 Å) to that observed with substitutional Cl, indicating Cl bonded to Mo. Moreover, the Mo-Mo distance of this system presents the shortest average and the largest deviation, in accordance with the etching effect observed experimentally.

Structural parameters were obtained from MoS_2 layers without the underlying SiO_2 substrate. Images of the resulting structures are shown in Fig. S1, where the disorder induced by halogenation is clearly observed in the case of i) MoS_2 following F exposure and of ii) MoS after chlorination.



a) MoS_2

b) F on MoS_2

c) Cl on MoS_2

d) Cl(subst.) on MoS_2

e) Cl on MoS

Figure S1. Optimized structures of a) a freestanding MoS_2 layer and the same structure following b) fluorination, and c) to e) chlorination.

Results of spin-polarized total density of states (TDOSs) calculations of the freestanding MoS_2 layers are shown in Fig. S2. Besides the structural modifications induced by halogenation, a clear modification of the electronic structure of these samples are evidenced. Comparing Fermi levels, a slight shift to the valence band is observed while comparing Cl adsorbed on MoS_2 with that of pristine MoS_2, indicating p-type doping. On the other hand, Cl substitutionally inserted in MoS_2 act as a n-type dopant, shifting the Fermi level towards the conduction band.

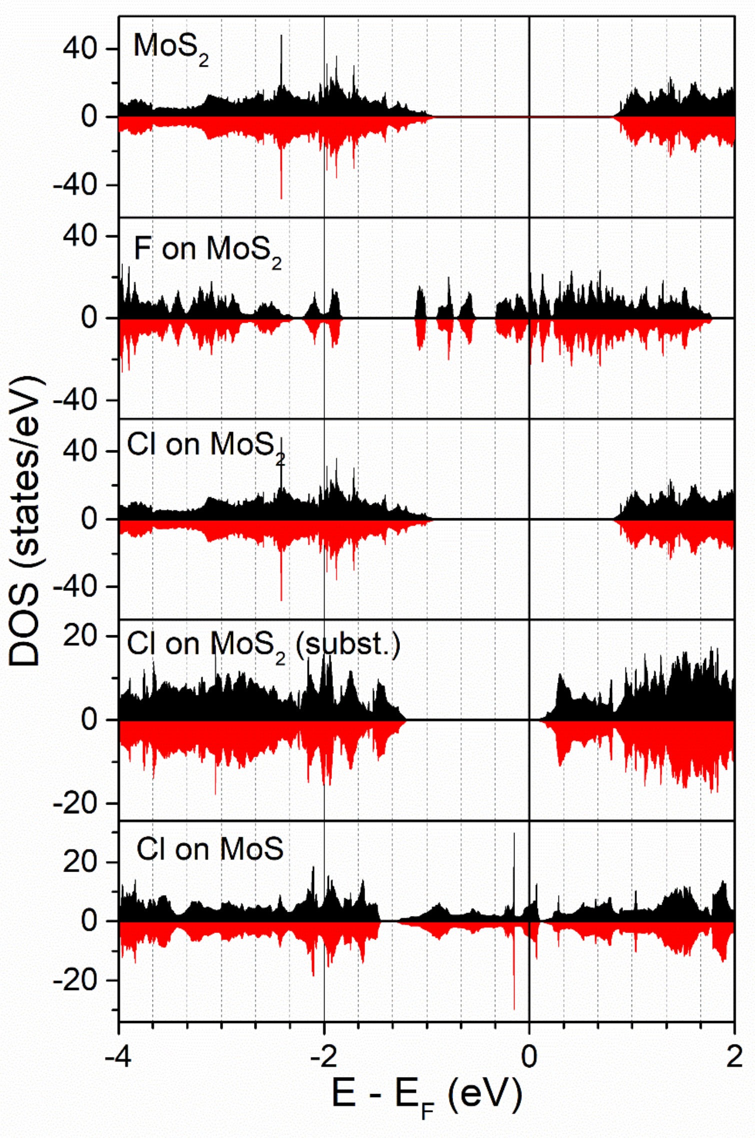


Figure S2. TDOS of optimized freestanding structures. The positive and negative DOS denote the spin-up and spin-down states, respectively.

The binding energies of the optimized structures are listed in Tab. S2, evidencing their stabilities. They were calculated by

$$BE = E_{structure} - \sum_{atom} nE_{atom} \tag{1}$$

where $E_{structure}$ refers to the total all-electron energy of the MoS$_y$-X structure, E_{atom} is the total all-electron energy of an element in the structure, and n is the number of atoms of an element in the structure.

Tab. S2. Binding energies of freestanding MoS$_2$ with and without halogens.

	Binding energy (eV)
MoS$_2$	-130,7854257
F on MoS$_2$	-147,5509111
Cl on MoS$_2$	-141,8021227
Cl on MoS$_2$ (subst..)	-126,8630254
Cl on MoS	-115,2335414

High-resolution XPS spectra of bulk MoS$_2$ were obtained using synchrotron radiation of 350 eV. Mo 3d and S 2p regions are shown in Fig. S1(a) before and S1(b) after 20 min photochemical chlorination. Mo 3d lines at 229.8 eV and 233.0 eV are characteristic of MoS$_2$. A doublet with chemical displacement of -0.8 eV due to substoichiometric MoS$_{x<2}$ is present. After chlorination, a strong signal with chemical displacement of +0.6 eV is observed for both regions. Mo 3d lines at 230.3 eV and 233.5 eV are characteristic of MoCl$_3$, evidencing Cl incorporation. Fig 1 (c) shows the Cl 2p region after chlorination. Since synchrotron based XPS is very surface-sensitive, there is a great contribution to the signal of Cl incorporated into carbon residues on the sample surface. Nevertheless, a doublet due to Cl bonding with Mo (Cl $2p_{3/2}$ at 199.4 eV) is observed.

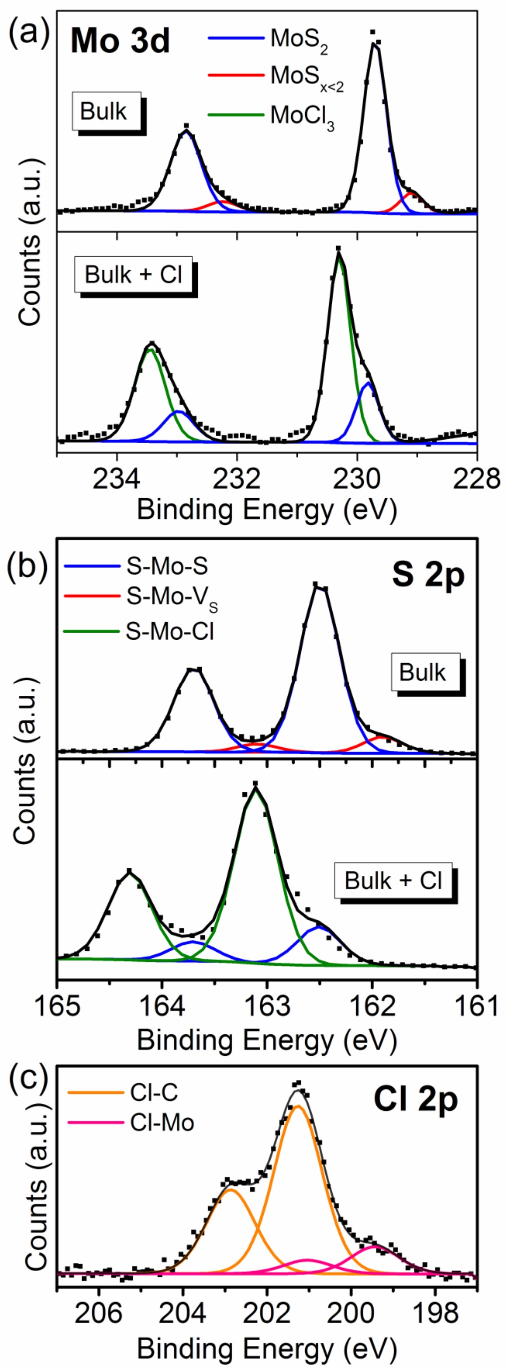


Figure S3. High resolution XPS spectra of (a) Mo 3d and (b) S 2p regions, before and after chlorination of bulk MoS_2. V_s stands for S vacancy. (c) Cl 2p region after chlorination. a.u. stands for arbitrary units.

In order to confirm the assignment of the Mo 3d components, XPS measurements using Al-Kα radiation were obtained after sputtering MoS_2 and following sample exposure to atmospheric air for 1 week (Fig S2). Though some degree of oxidation takes place, there are no Mo lines at 230.3 and 233.5 eV, attributed in this work to Mo bonded to Cl. Moreover, the doublet corresponding to substoichiometric MoS_2 is still present.

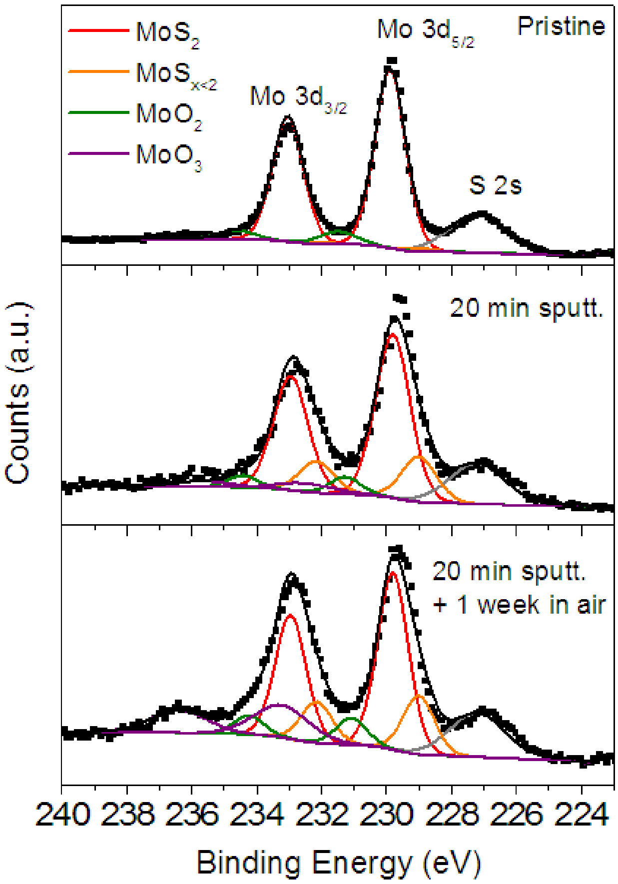


Figure S4. Mo 3d regions of XPS spectra of pristine MoS_2 monolayer, following 20 min sputtering with Ar^+ ions of 1 keV, and the same sample following exposure to atmospheric air for 1 week. a.u. stands for arbitrary units.

REFERENCES

(S1) Segala, M.; Takahata, Y.; Chong, D. P. Density functional theory calculation of 2p core-electron binding energies of Si, P, S, Cl, and Ar in gas-phase molecules. *J. Electron Spectrosc. Relat. Phenom.* 2006, *151*, 9–13.

(S2) Li, H.; Huang, M.; Cao, G. Stability, bonding and electronic structures of halogenated MoS_2 monolayer: A first-principles study. *Physica E* 2017, *91*, 8–14.