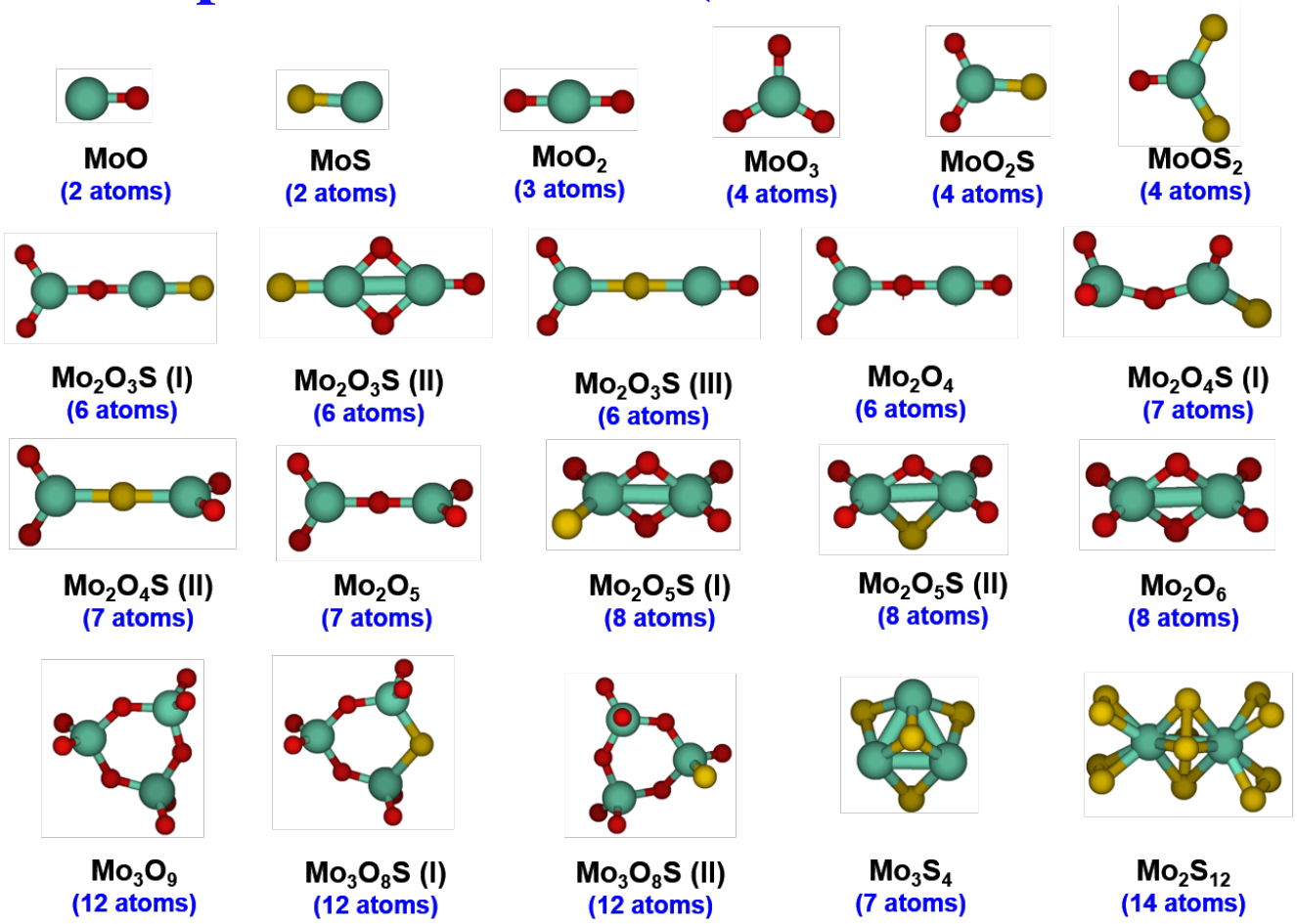
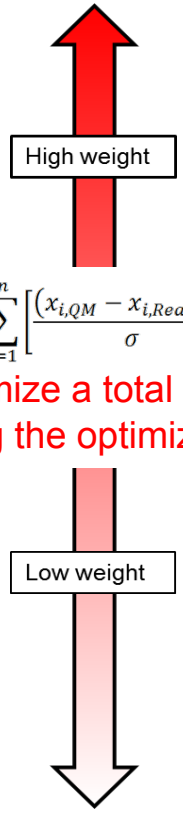
A training set for the ReaxFF force field optimization

- **Non-periodic clusters (Mo/O/S interactions)**





$$\text{Error} = \sum_{i=1}^{n}\left[\frac{(x_{i,QM} - x_{i,ReaxFF})}{\sigma}\right]^2$$

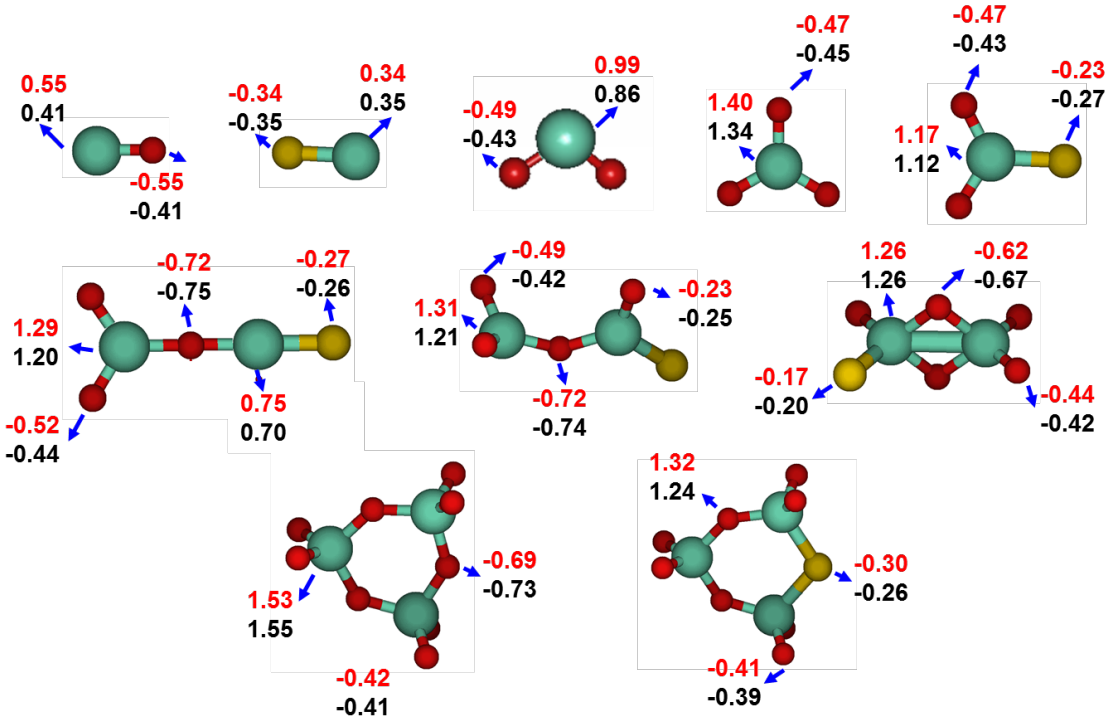
Minimize a total error during the optimization

Cyan: Mo atoms; Red: O atoms; Yellow: S atoms

Results: the ReaxFF force field optimization

- **Non-periodic clusters' point charges**

ReaxFF: Red, top number
Mulliken Charges (Qchem): Black, bottom number

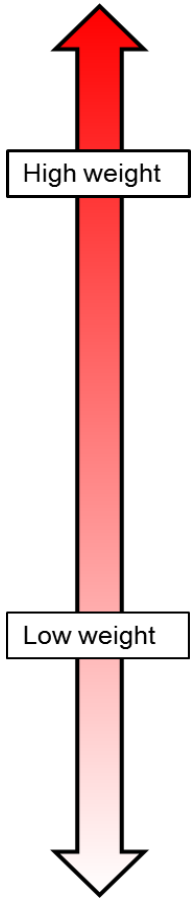


Cyan: Mo atoms; Red: O atoms; Yellow: S atoms

Results: the ReaxFF force field optimization

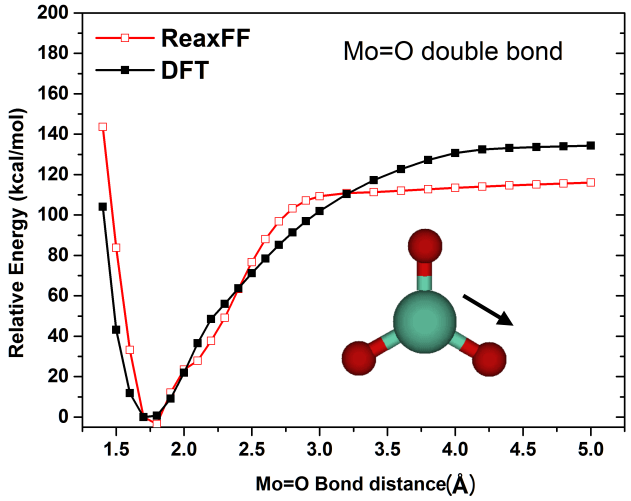
- **Non-periodic clusters' cohesive energies**

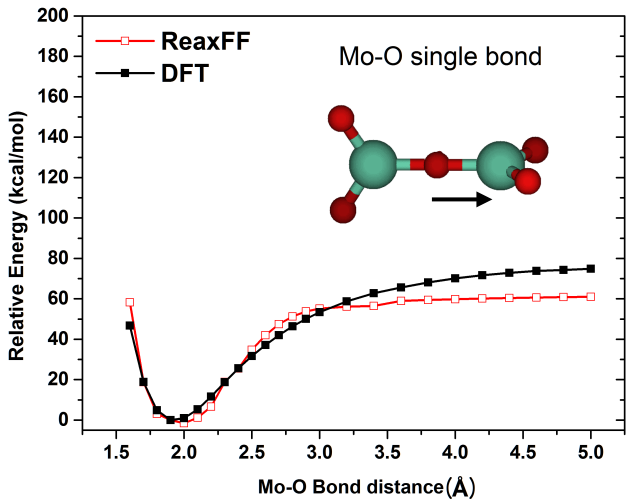
Cluster	ReaxFF (kcal/mol)	DFT (kcal/mol)	Diff. (%)
MoO	-146.73	-143.85	2.00
MoS	-105.17	-106.98	1.69
MoO_2	-295.11	-291.17	1.35
MoS_2	-202.83	-205.23	1.17
MoO_3	-425.38	-427.56	0.51
MoS_3	-292.25	-292.17	0.03
MoO_2S	-382.88	-381.65	0.32
$MoOS_2$	-339.14	-336.63	0.75
Mo_2O_4	-650.25	-635.48	2.32
Mo_2O_5	-789.12	-798.21	1.14
Mo_2O_6	-936.16	-976.83	4.16
Mo_2O_3S (I)	-615.29	-590.70	4.16
Mo_2O_3S (II)	-632.06	-606.06	4.29
Mo_2O_3S (III)	-604.12	-576.63	4.77
Mo_2O_4S (I)	-750.68	-754.59	0.52
Mo_2O_4S (II)	-738.96	-738.27	0.09
Mo_2O_5S (I)	-894.66	-927.29	3.52
Mo_2O_5S (II)	-894.51	-933.49	4.18
Mo_3O_9	-1426.47	-1506.24	5.30
Mo_3O_8S (I)	-1372.46	-1451.26	5.43
Mo_3O_8S (II)	-1380.86	-1459.14	5.36
Mo_3S_4	-646.38	-611.83	5.65

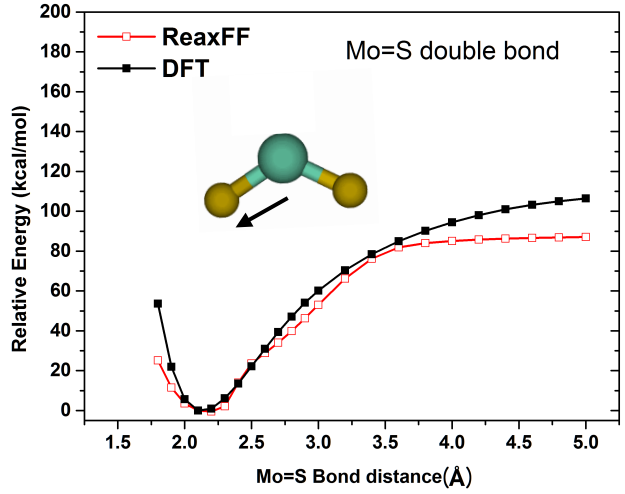


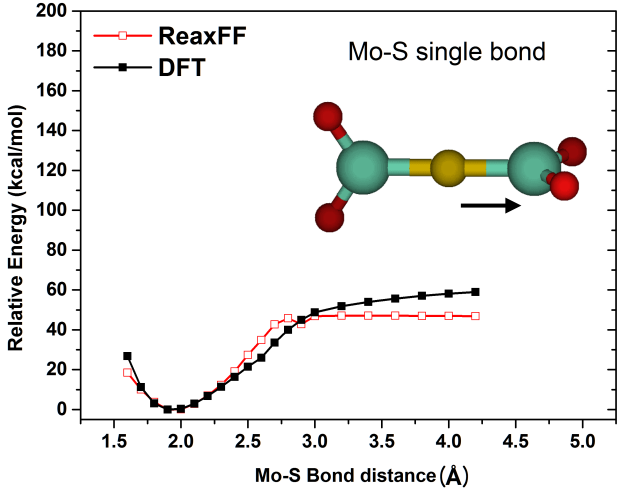
Results: the ReaxFF force field optimization

- **Non-periodic clusters' bond dissociation energies**



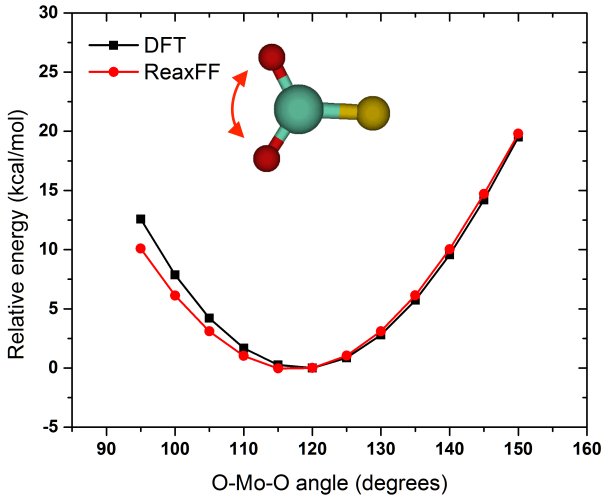


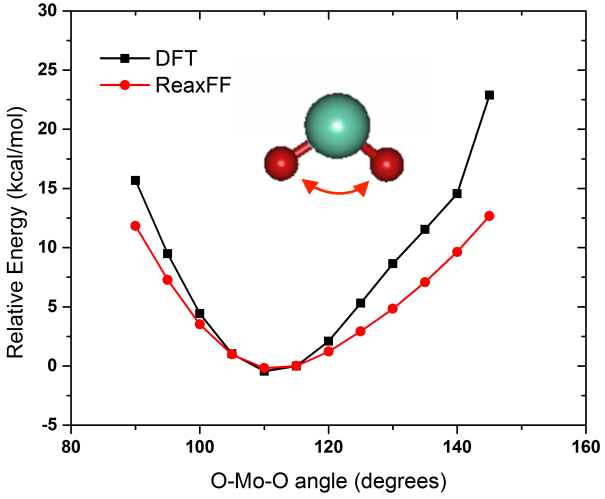


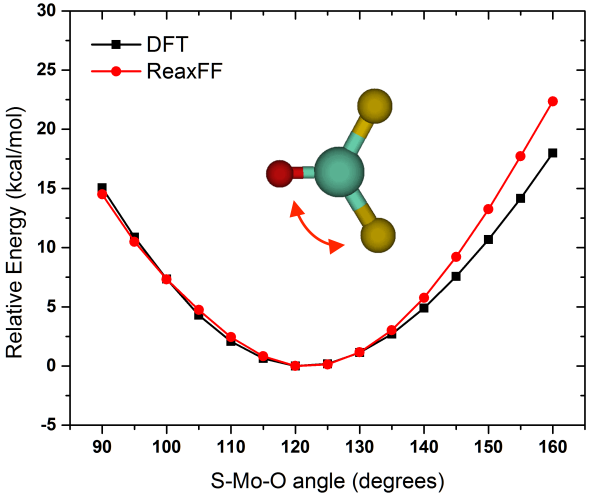


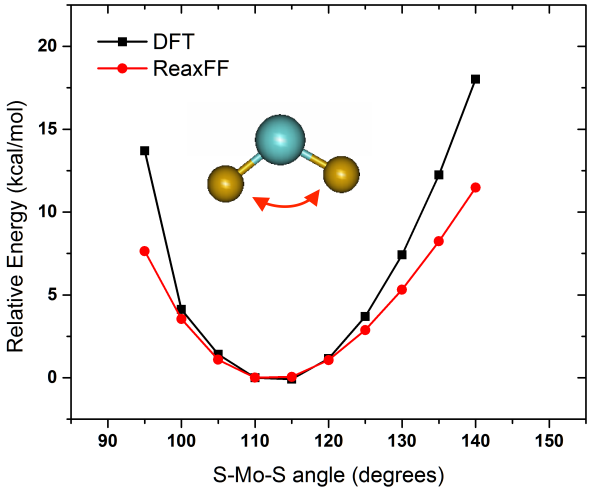
Results: the ReaxFF force field optimization

- **Non-periodic clusters' angle distortion energies**





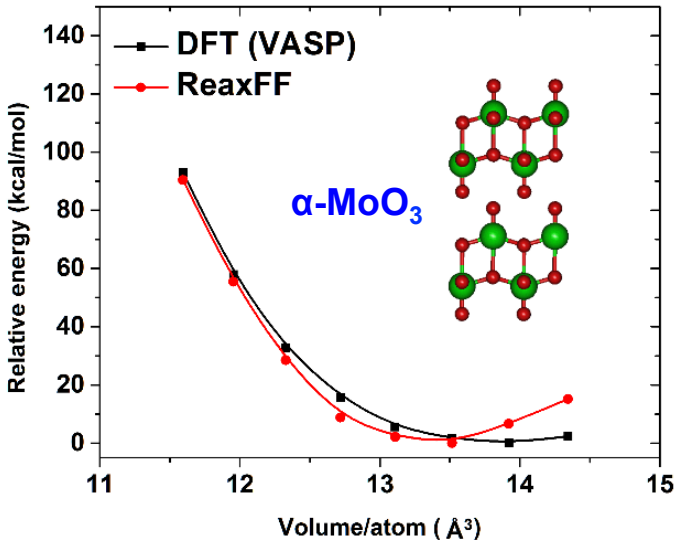




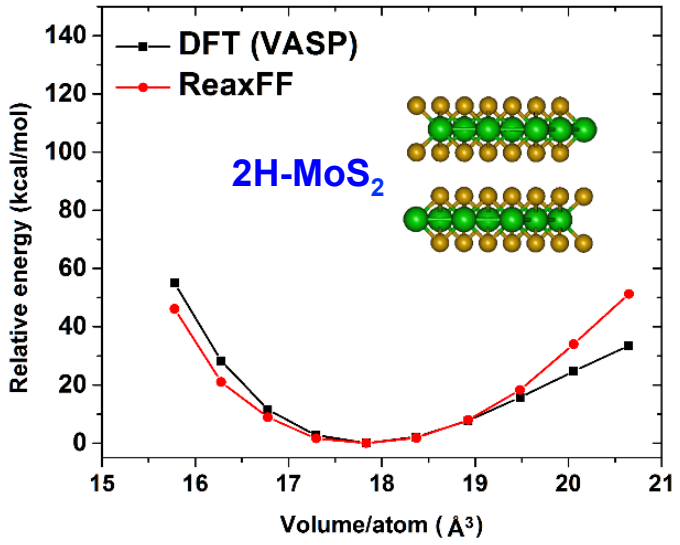
Results: the ReaxFF force field optimization

- **Equations of state for MoO_3/MoS_2 crystal structures**

(a)



(b)



Cohesive energies (per atom)	ReaxFF (kcal/mol)	DFT (kcal/mol)
α-MoO_3	-128.15	-124.12
2H-MoS_2	-117.67	-123.36
3R-MoS_2	-117.65	-123.35
1T-MoS_2	-116.92	-119.14

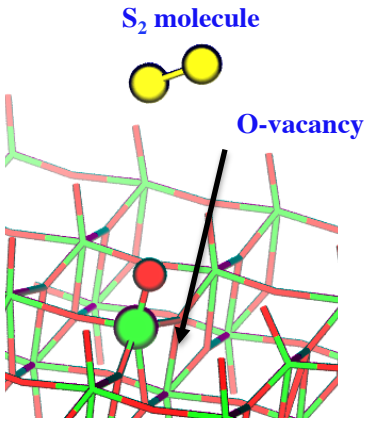
Results: the ReaxFF force field optimization

- **ReaxFF reactive force field validation**

  We need a ReaxFF reactive force field for CVD chemistry

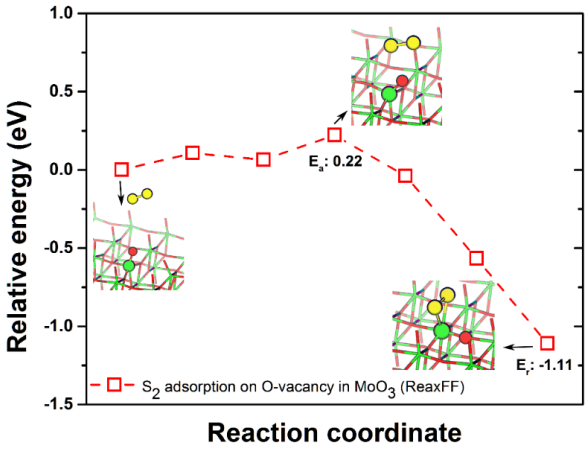
❑ **Reaction profiles for S_2 adsorption on an O-vacancy MoO_3 surface calculated by DFT-nudged elastic band (NEB) methods**

	Methods			
	DFT	DFT + *U*	Spin polarized DFT	Spin polarized DFT + *U*
Reaction barrier (eV)	0.20	0.38	0.22	0.52
Reaction energy (eV)	-1.43	-0.80	-1.07	-0.59



Note. DFT + *U*: additional on-site Coulomb interactions between localized *d*-electrons

❑ **ReaxFF-NEB**



Our ReaxFF force field can reasonably describe interactions between S_2 gas and MoO_3 surface