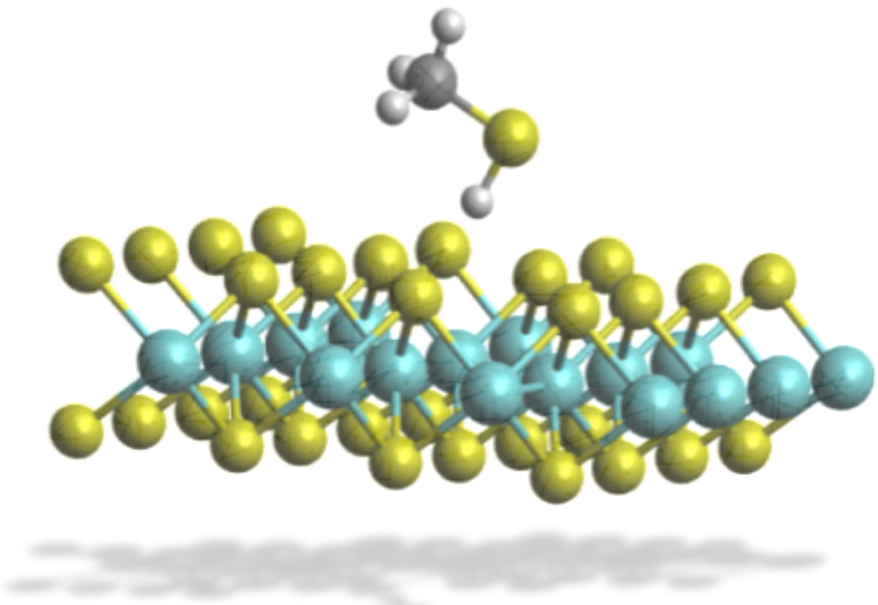
start

Defects in MoS_2 monolayers

repair, doping and functionalization



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DRESDEN concept
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WR WISSENSCHAFTSRAT

MoS_2 electronics - Early studies

1960-ies

R. Fivaz, E. Mooser

„Mobility of Charge Carriers in semiconducting layer structures“

Phys. Rev. **163** (1967) 743

•high purity

•mobilities MoS_2/$MoSe_2$ → 500 cm^2/Vs T ≤ 200 K

1980-ies

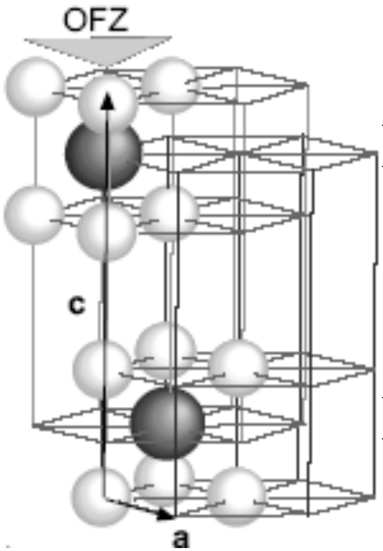
•Solar cells (Kautek, Gehrischer, Tributsch…)

•Heterojunctions (Bucher…)

Layered Structure

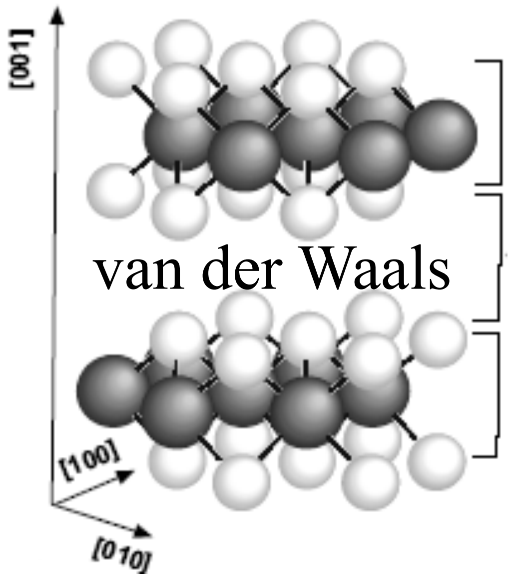
2H-MoS$_2$

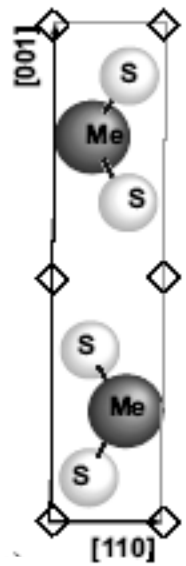
Space group: $D^{4}_{6h} - P6_3/mmc$



Sulfur
Molybdenum
Sulfur

Sulfur
Molybdenum
Sulfur

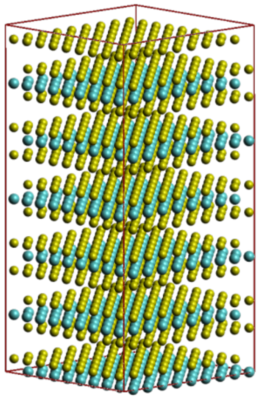




E_B (van der Waals) ≈ 0.06 eV/atom

E_B (van der Waals - Graphite) ≈ 0.01 eV/atom

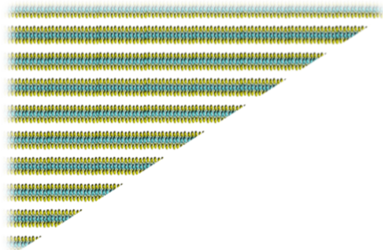
Layered Structure



bulk

indirect band gap

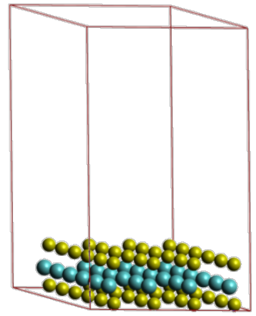
solid lubricant

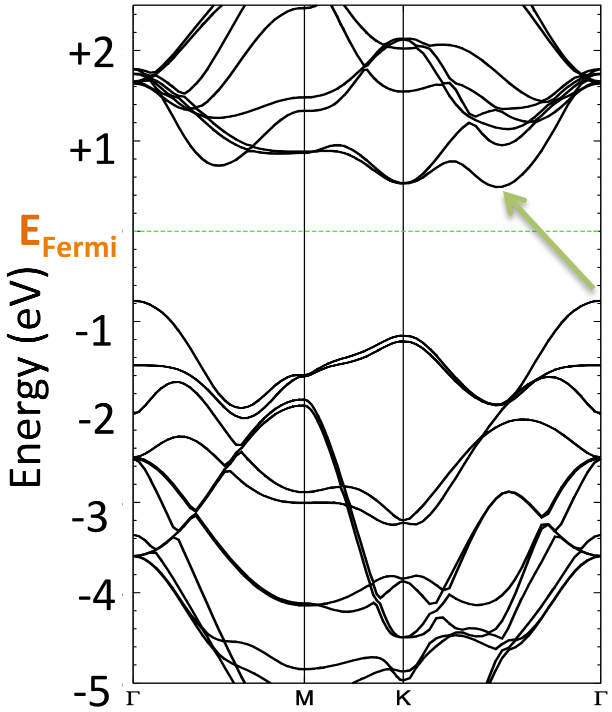


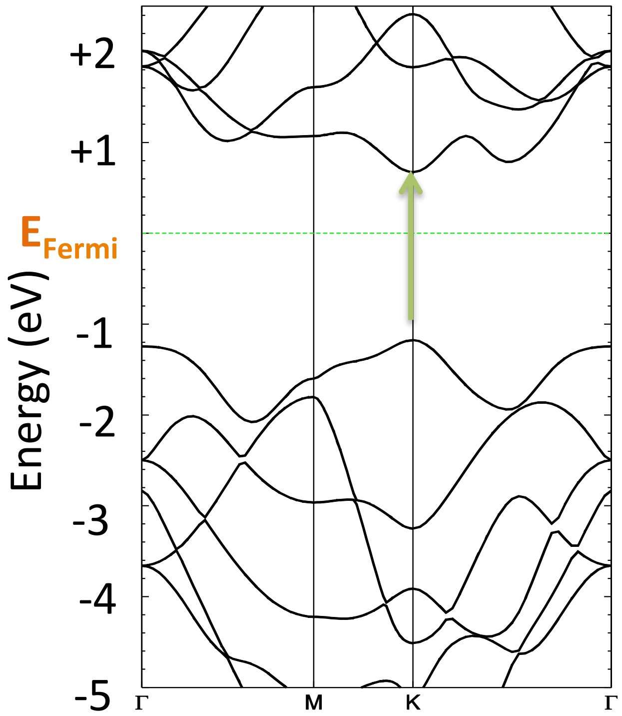
2D monolayer

direct band gap

nano- and optoelectronic devices

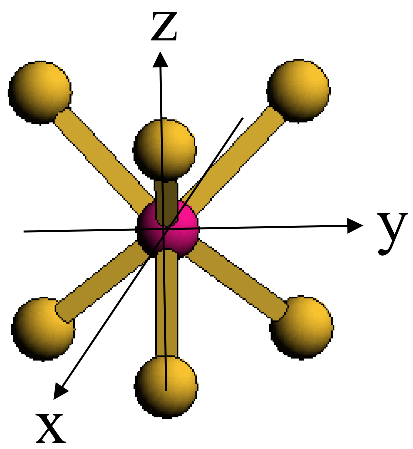




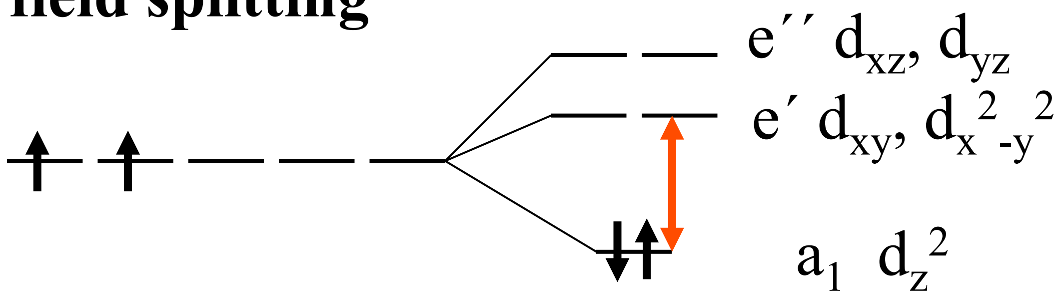


MoS_2: *formally* Mo^{4+} S^{2-} → MoS_6^{8-}

Trigonal prismatic
D_{3h}

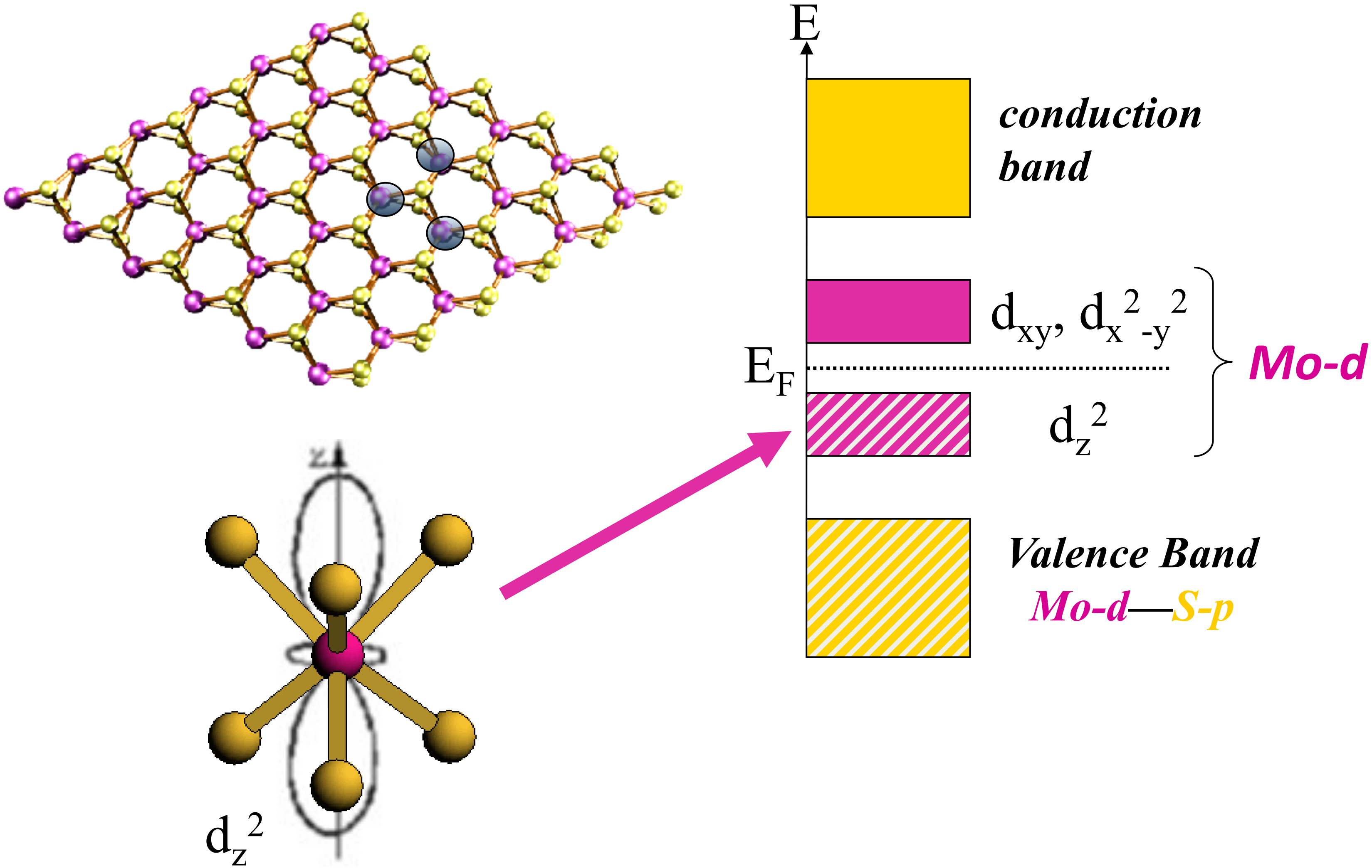


Ligand field splitting



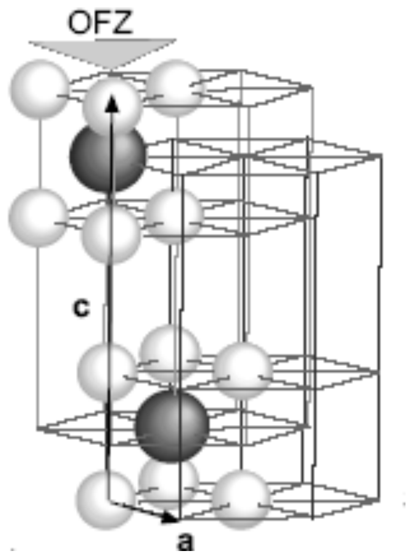
Cluster

Triple layer S-Mo-S



MoS_2 – Semiconductor

strong anisotropy in conductivity



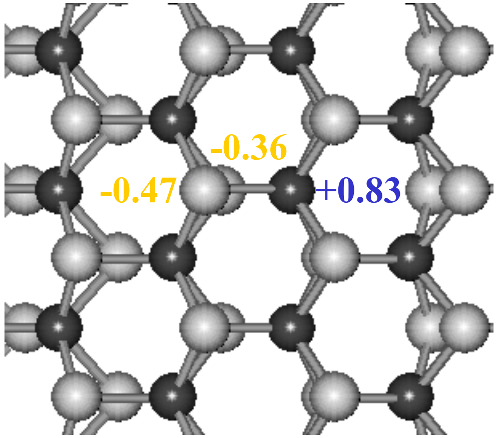
$\sigma_{\parallel} \sim 10^{-3}\, \sigma_{\perp}$

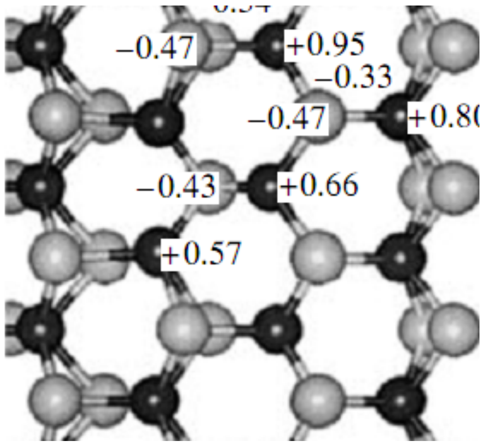
$\sigma_{\perp}$ ~ 0,6-7,9 S/cm

Charge carrier mobility: 2…500 cm^2/Vs

nominally „undoped“:n-MoS_2 ↔ sulfur defects

Electronic properties of MoS_2



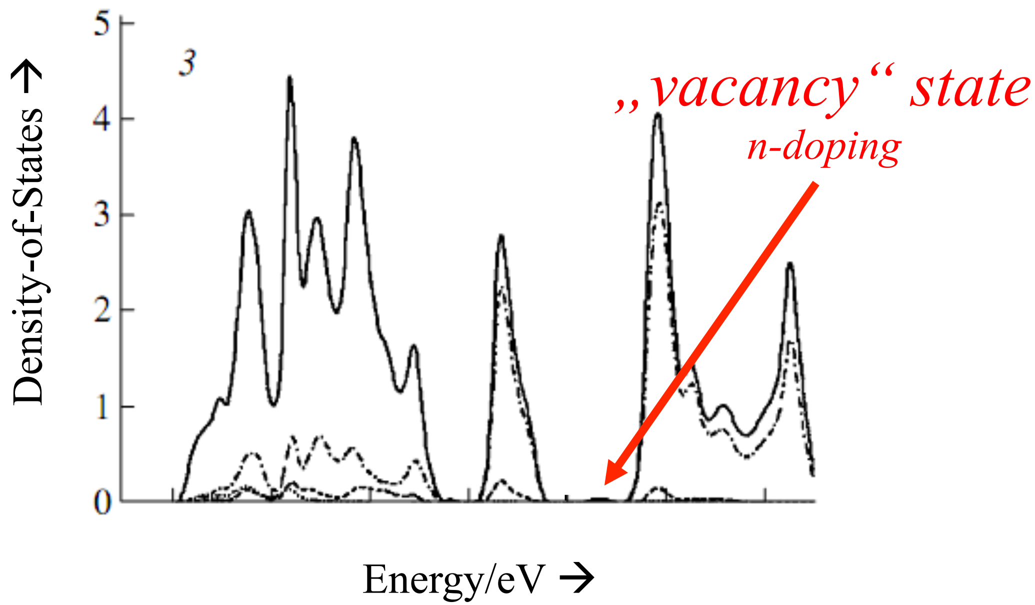


no defect

- S defect

Electronic properties of MoS_2

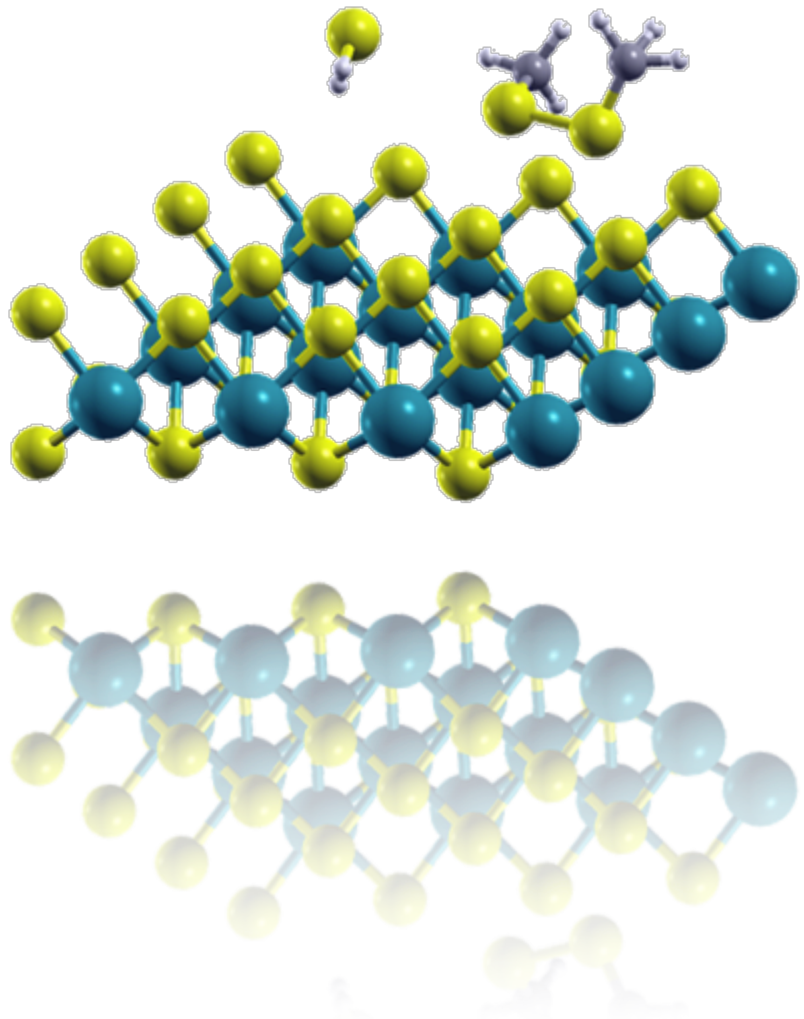
Density of States



- S defect

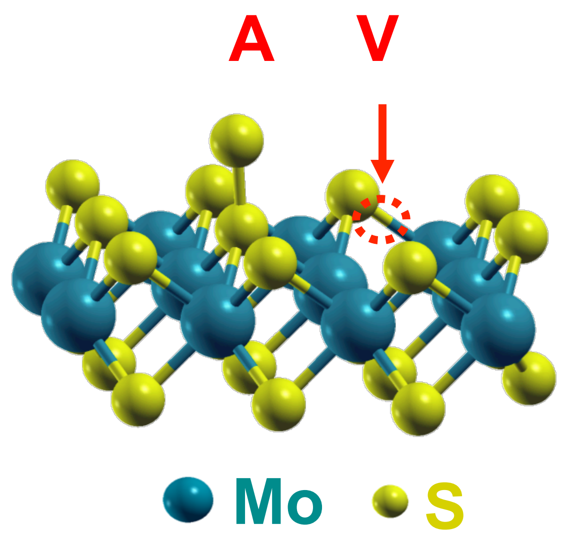
Repair and Functionalization of MoS_2 Monolayers via Thiols

- Reactions of Thiols on 2D MoS_2
    - Vacancy Repair
    - Adatom Repair
- Functionalization

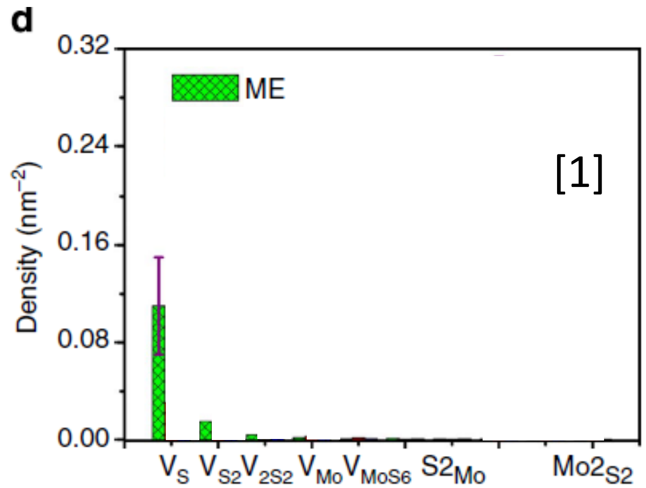


Defect states in MoS_2

- **Qualitatively most efficient** method (mechanical exfoliation, ME) **too expensive** for mass-production



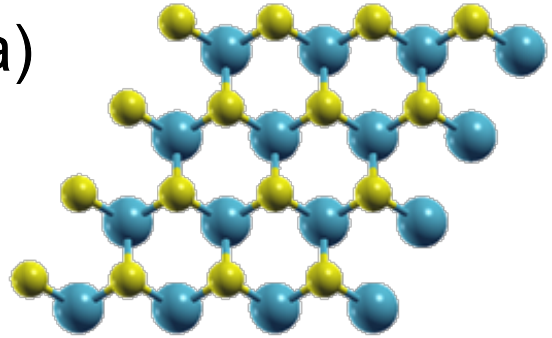
- **Quantitatively most efficient** method (Physical/Chemical Vapor Deposition, PVD/CVD) still includes **too many defects** for a mass-distribution



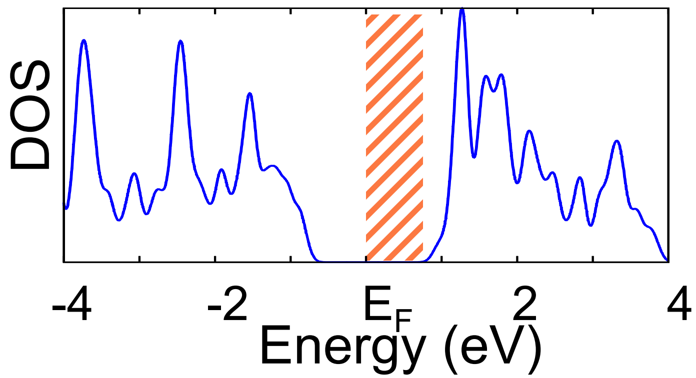
[1] Hong et al, *Nature communications* 6 (2015)

Defect states in MoS_2

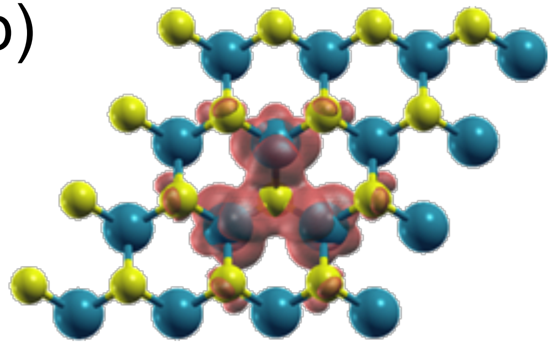
(a)



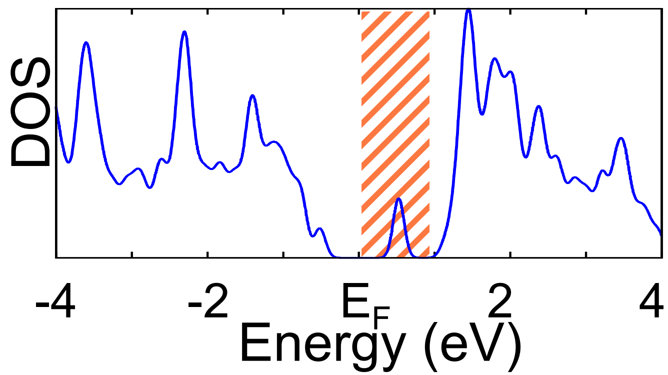
ideal MoS_2



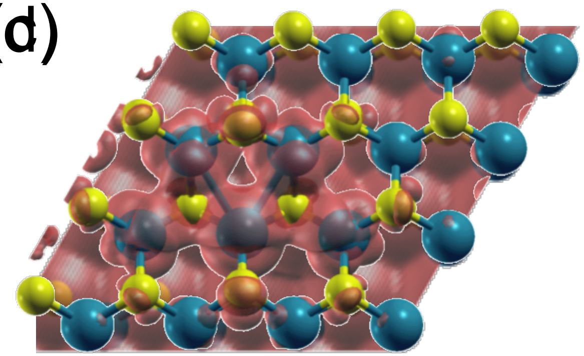
(b)



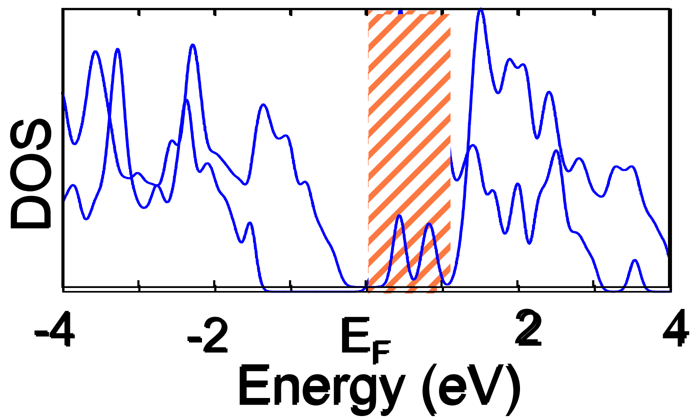
Monovacancy
→ **defect state**



(d)

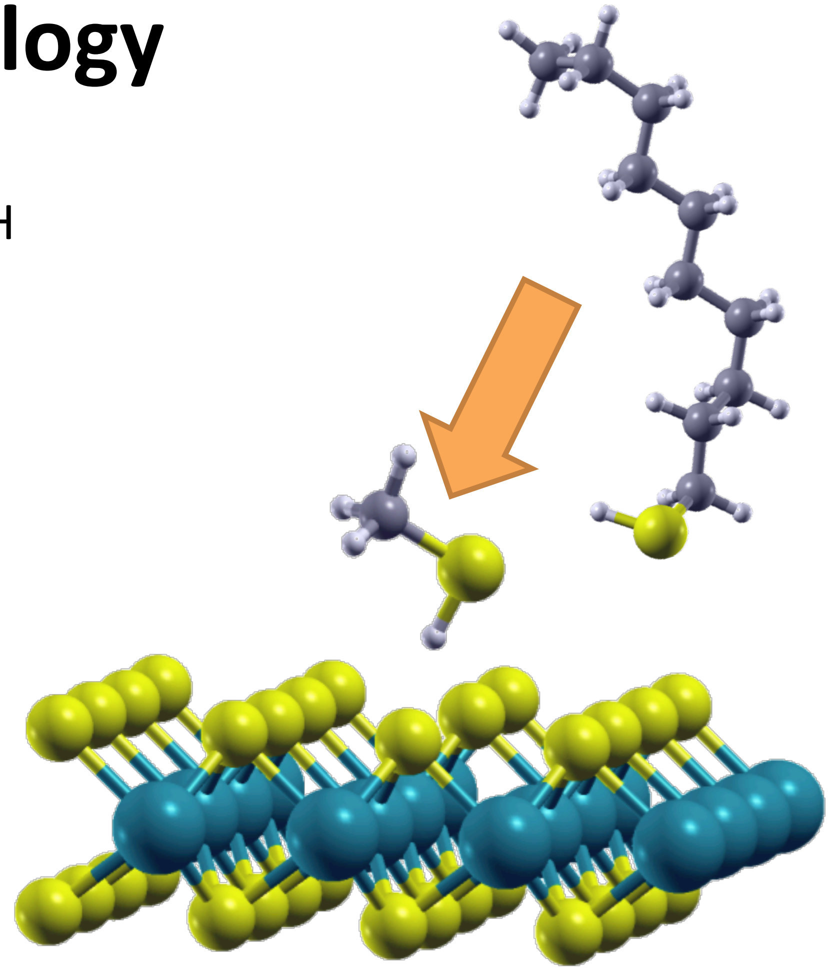


Divacancy
Sulfur adatom
⇒ **defect states**
left shift



Reactions of Thiols on 2D MoS_2

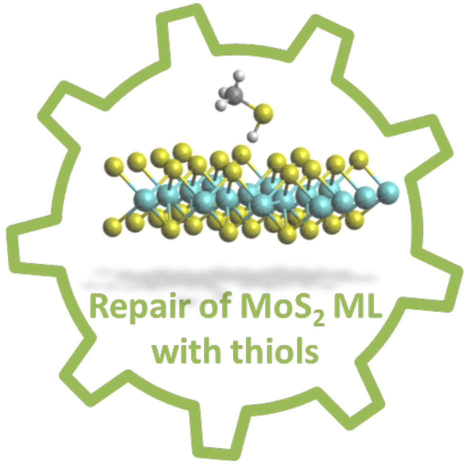
Methology

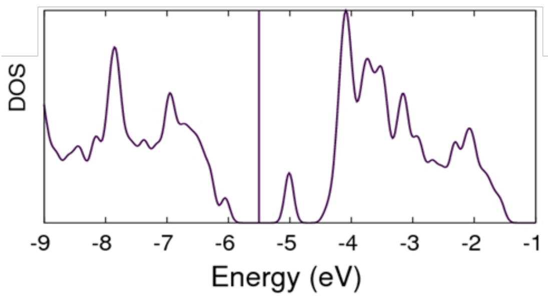


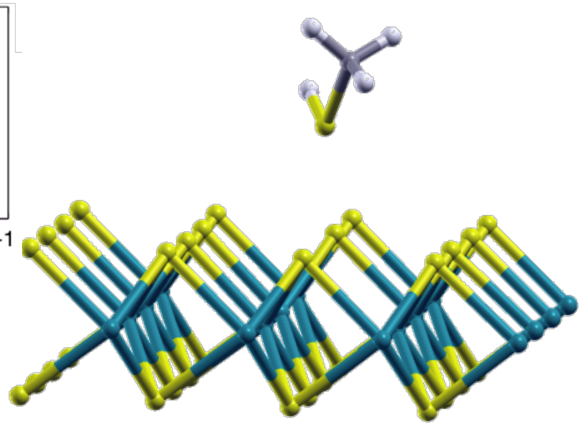
- Thiols exemplarily represented by CH_3SH
- MoS_2 consists of a 4x4x1 super cell
- 15 Å vacuum above MoS_2 monolayer

- **Computational details:**
  - Siesta (version 3.1)
  - functional: PBE
  - basis: DZP
  - 4x4x1 *k*-points

Sulfur vacancy defect (SV)

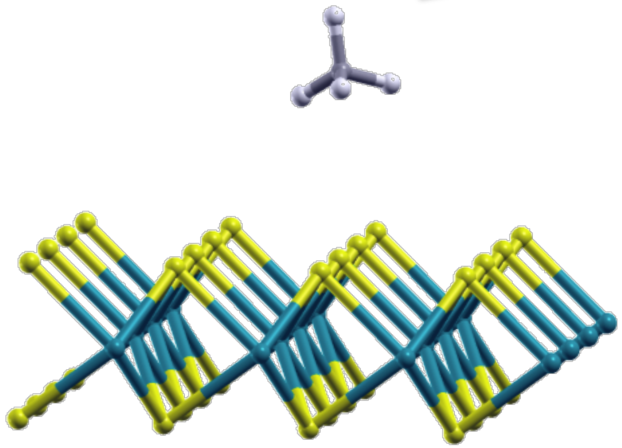


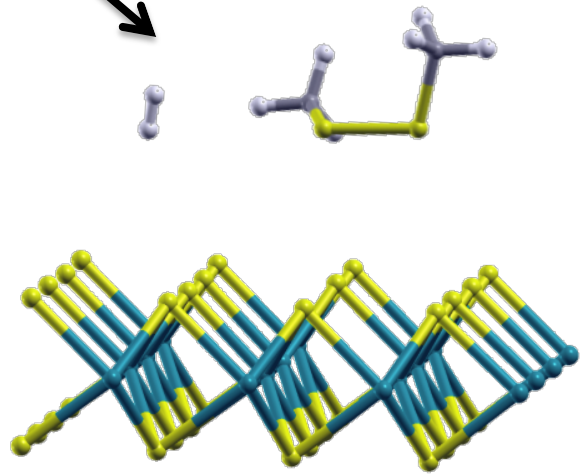




SV defect repair
[1]

Disulfide formation
[2]

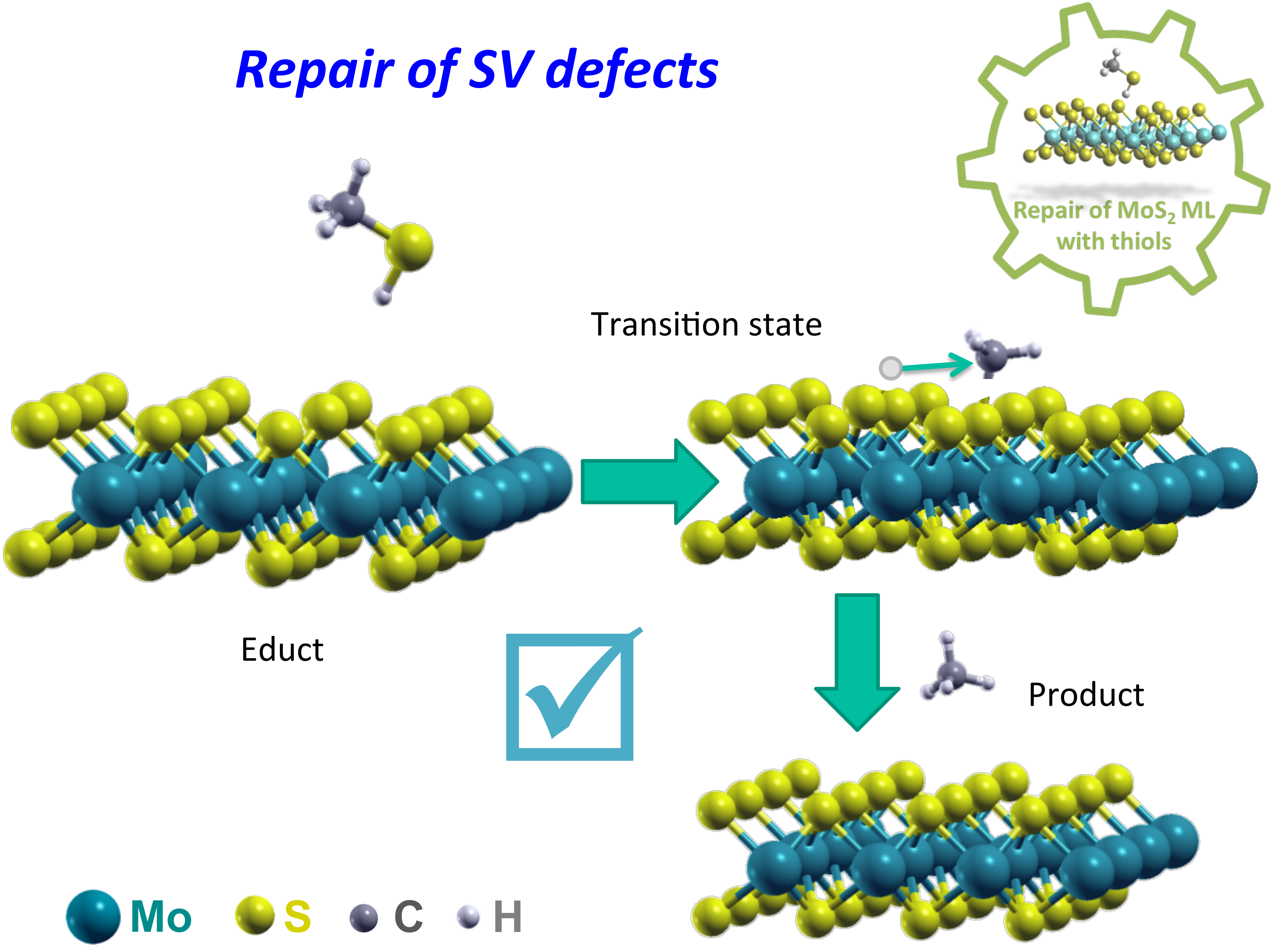




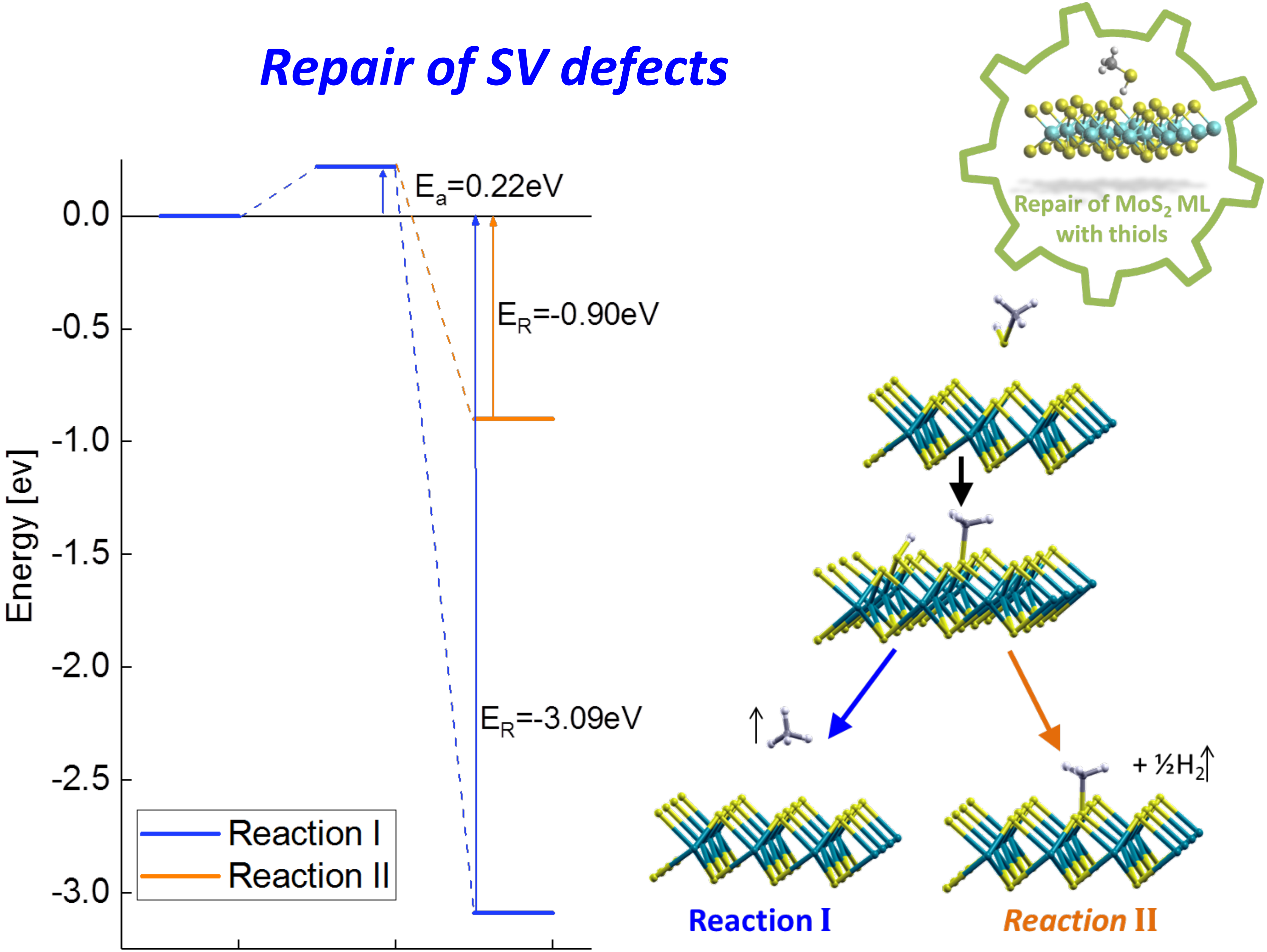
[1] Bertolazzi et al. *Advanced Materials* 29 (2017)

[2] Chen et al. *Ang. Chem. Int. Ed.* 55 (2016)

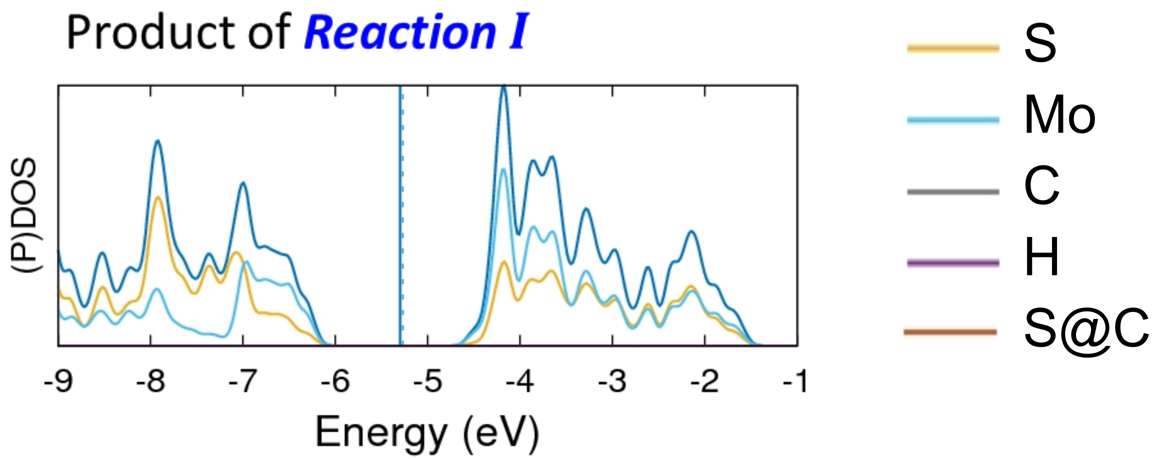
Repair of SV defects

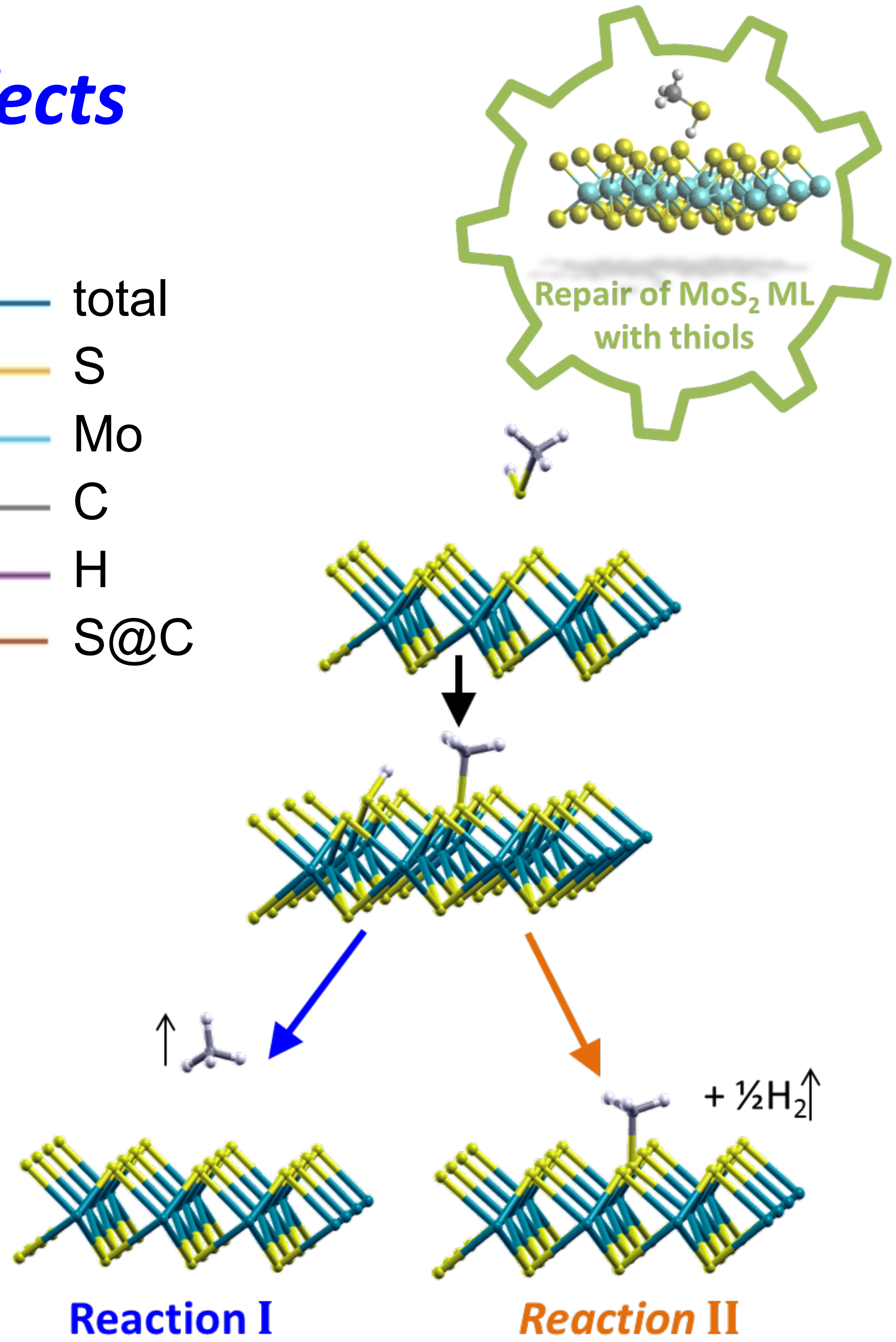


Repair of SV defects

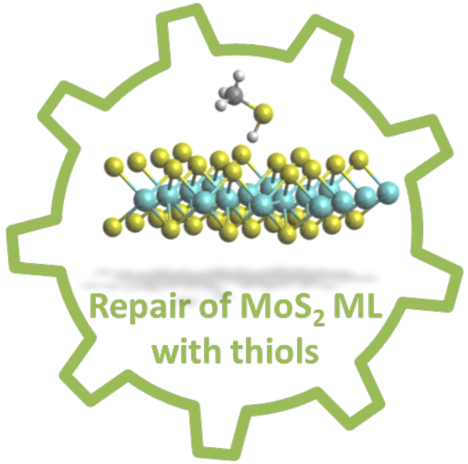


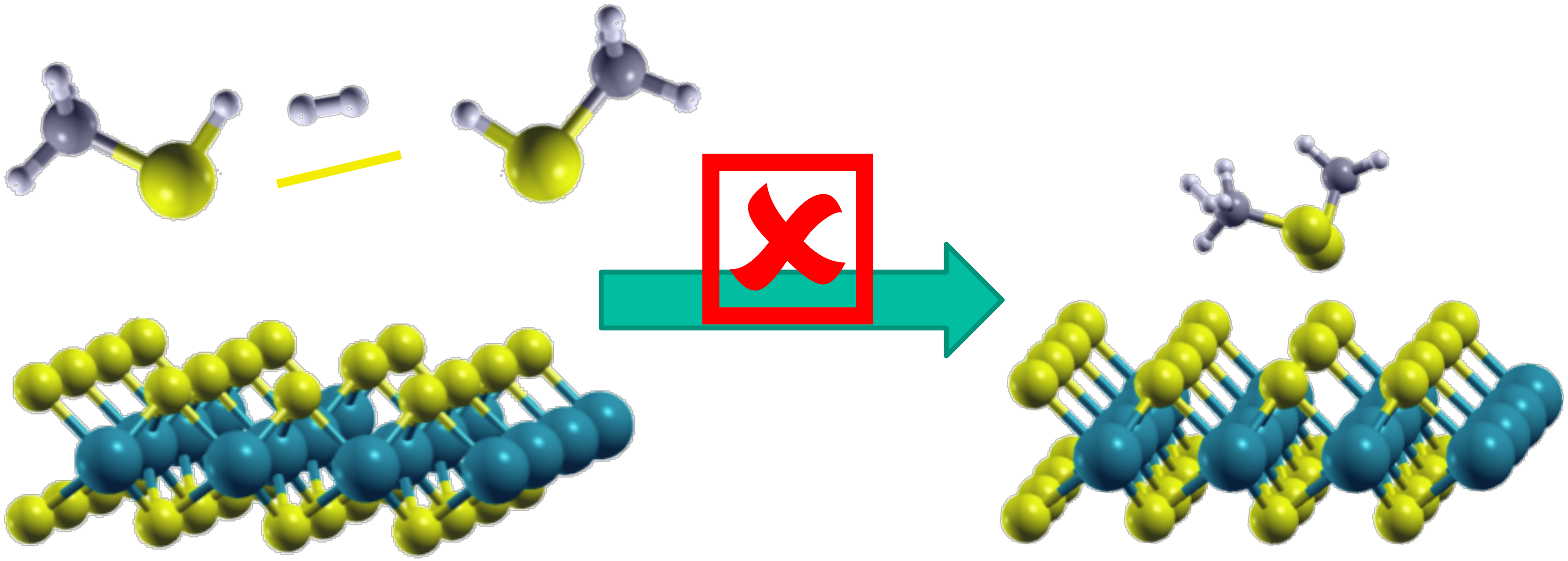
Repair of SV defects



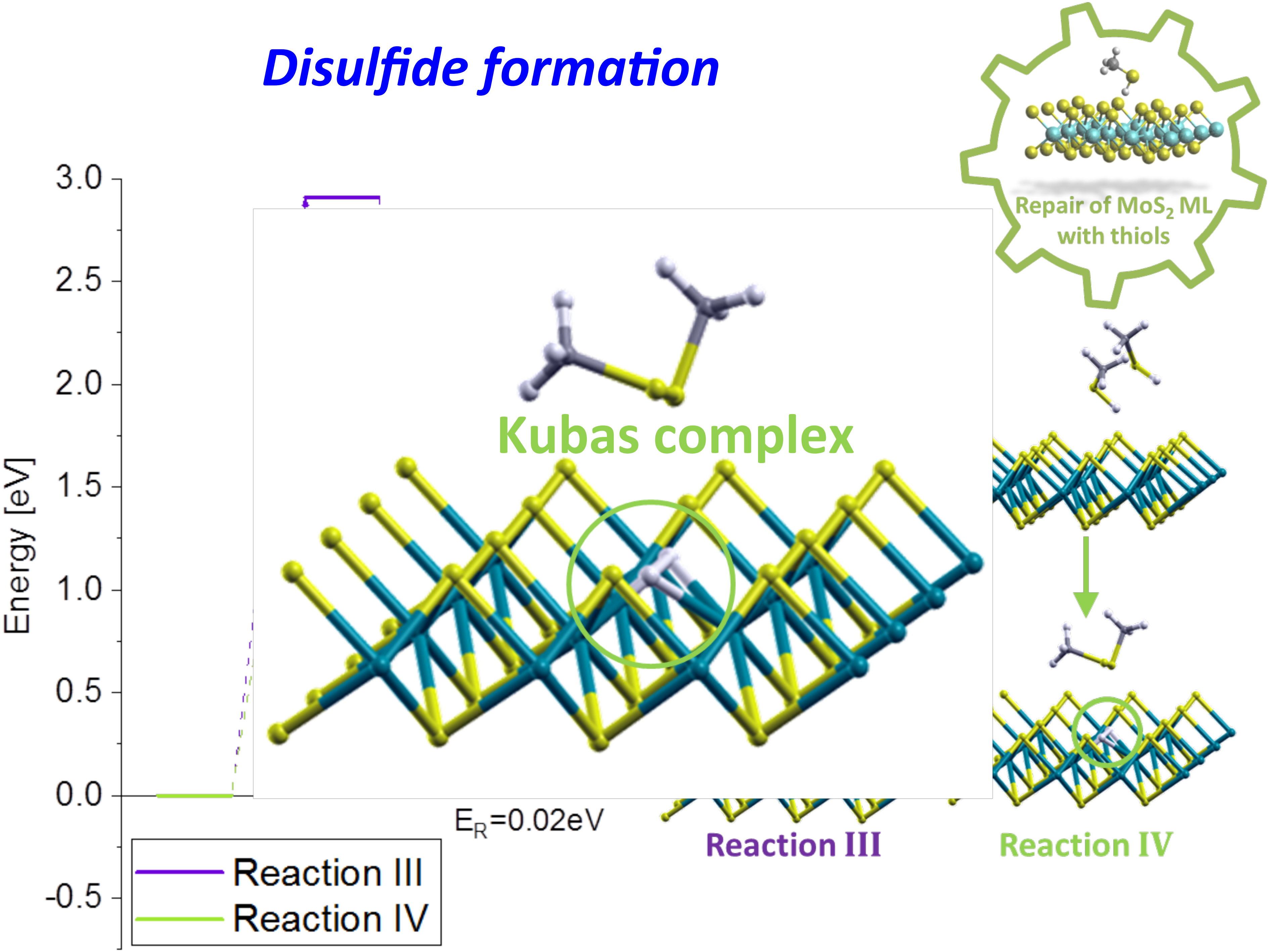


Disulfide formation

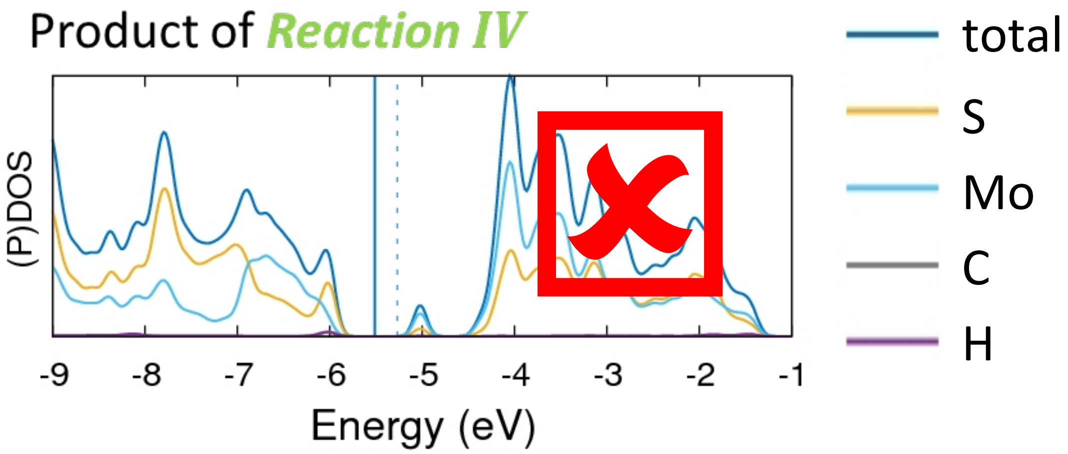


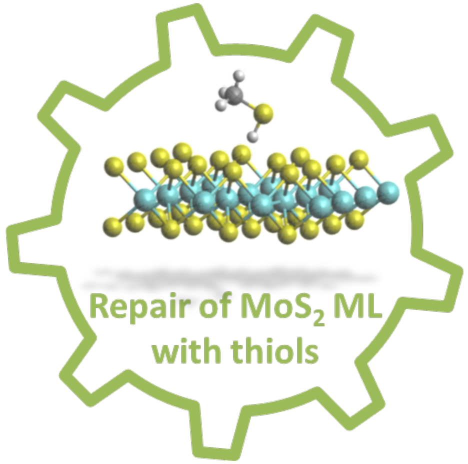


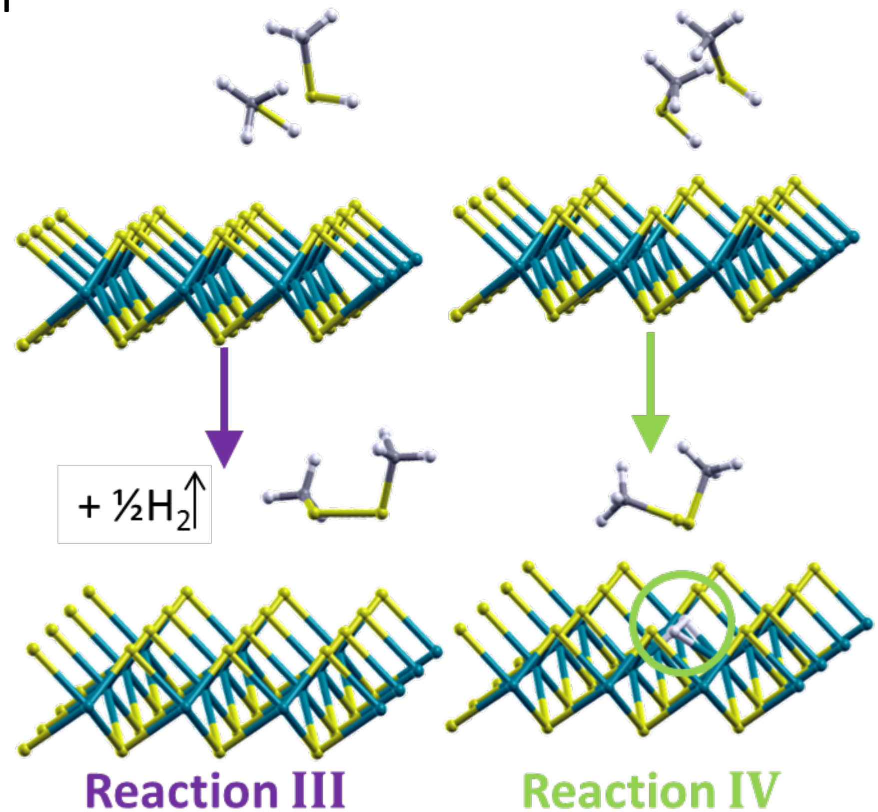
Disulfide formation



Disulfide formation



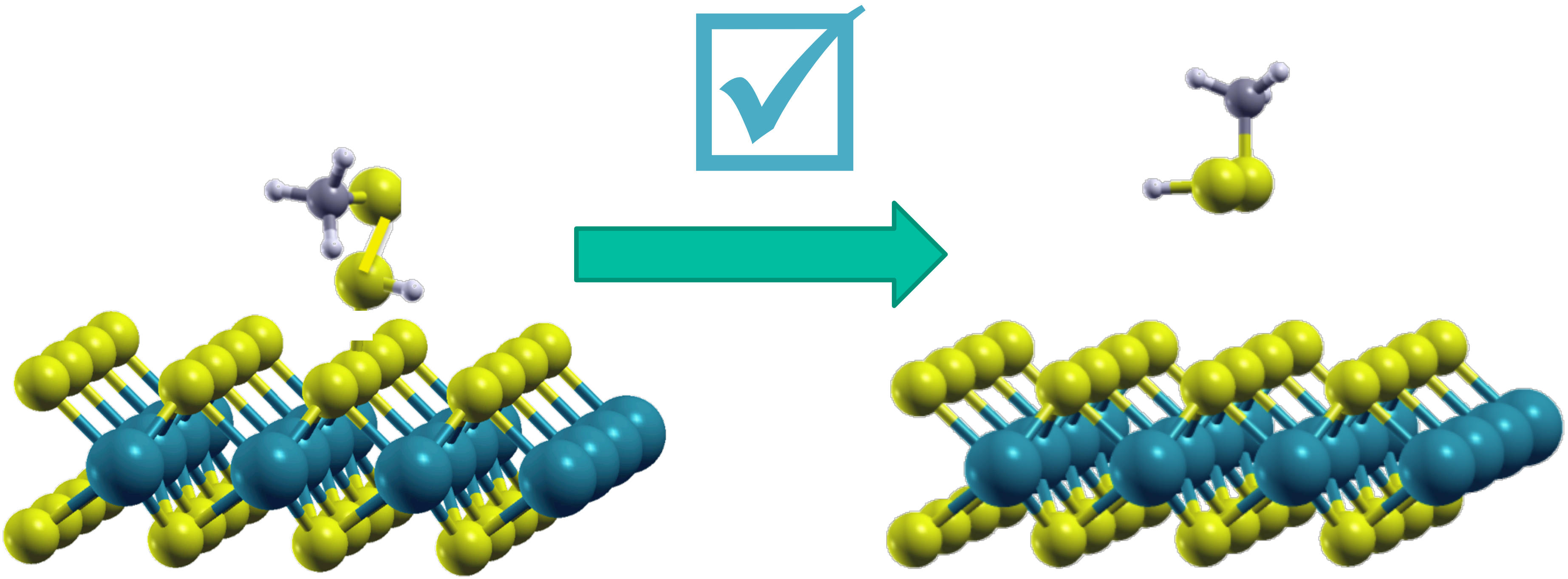




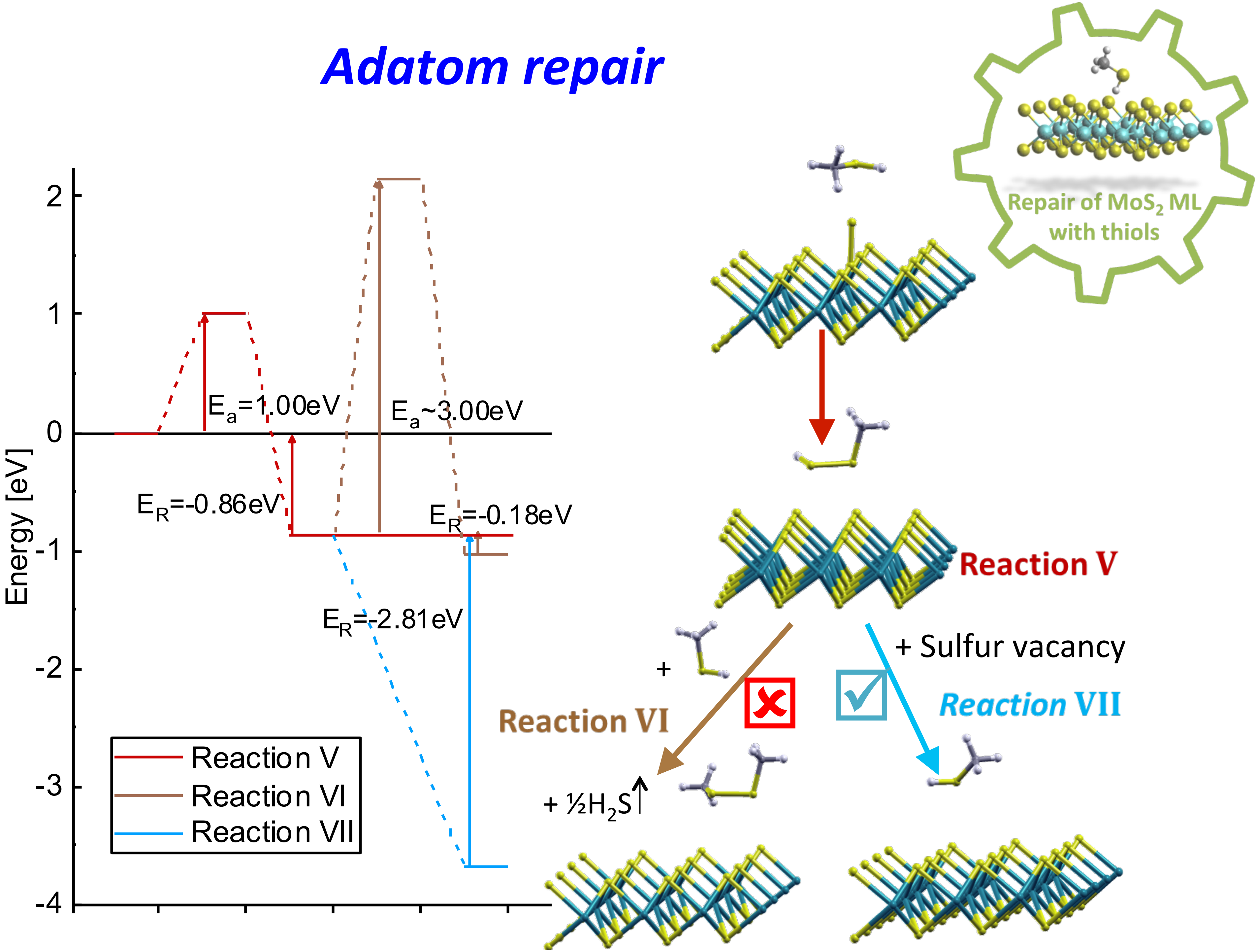
Adatom repair

Repair of MoS_2 ML with thiols

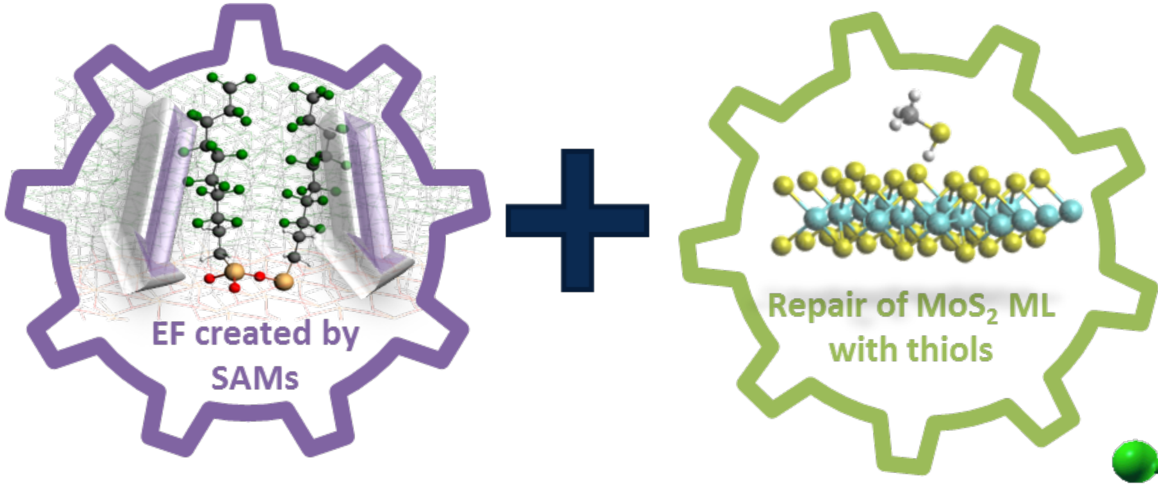
Condition for disulfide formation?

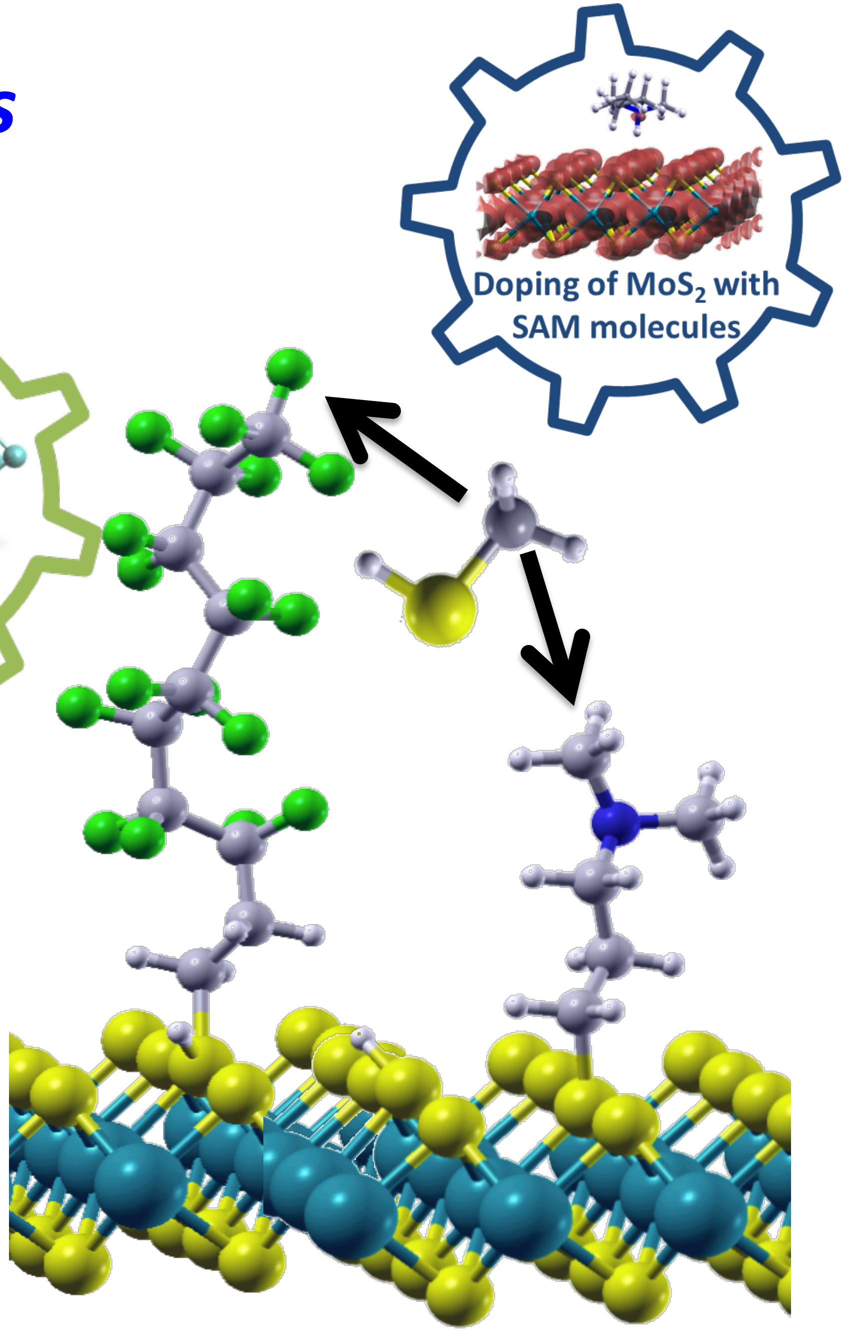


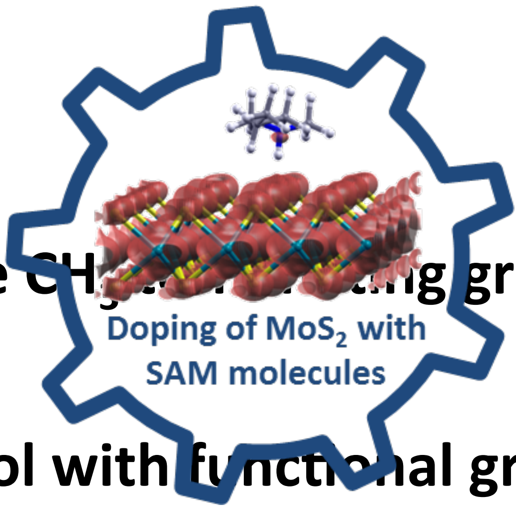
Adatom repair



Doping with thiols



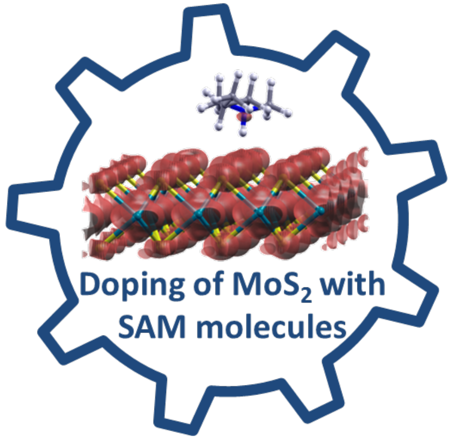




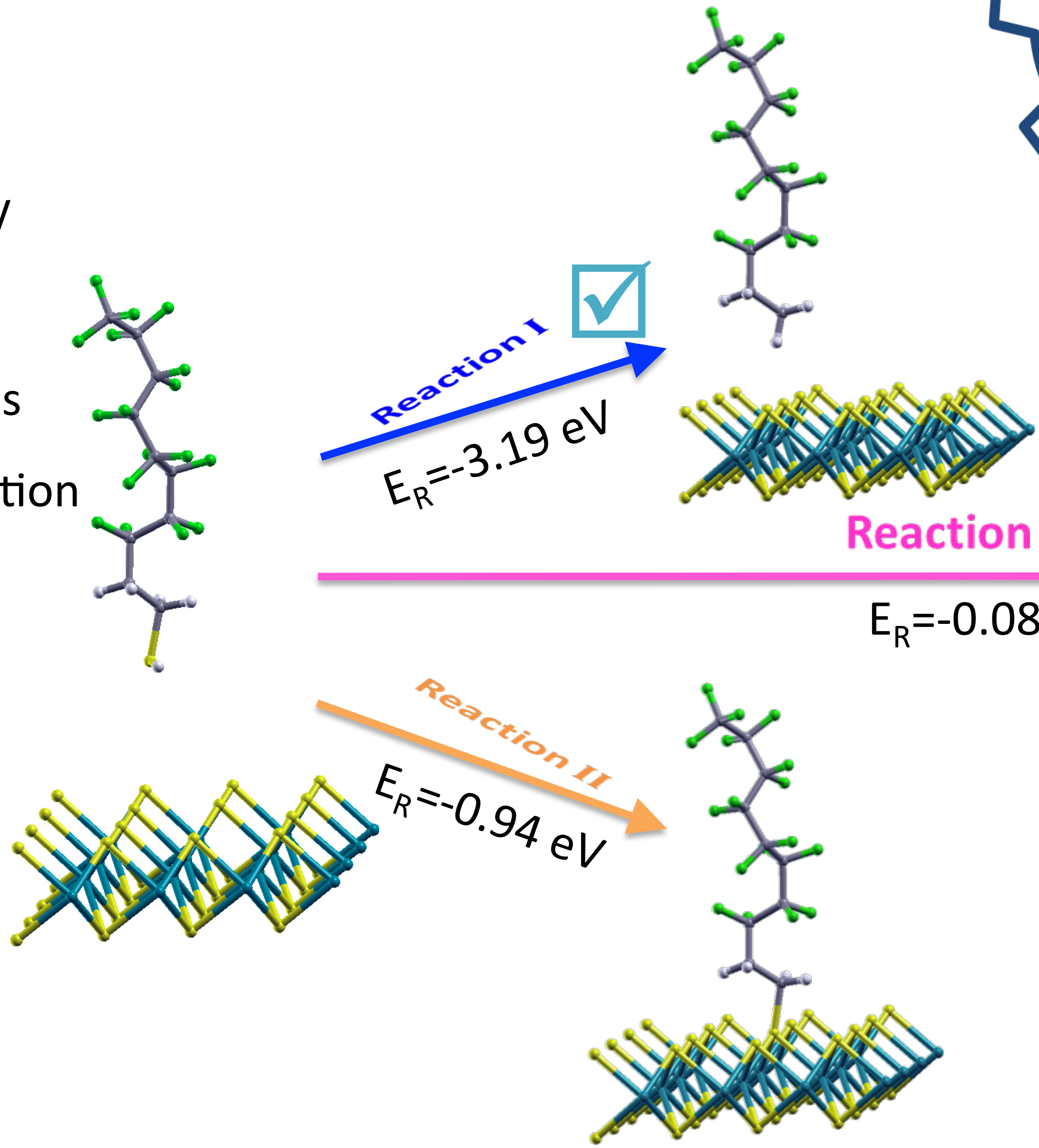
→ replace CH_3 terminating group

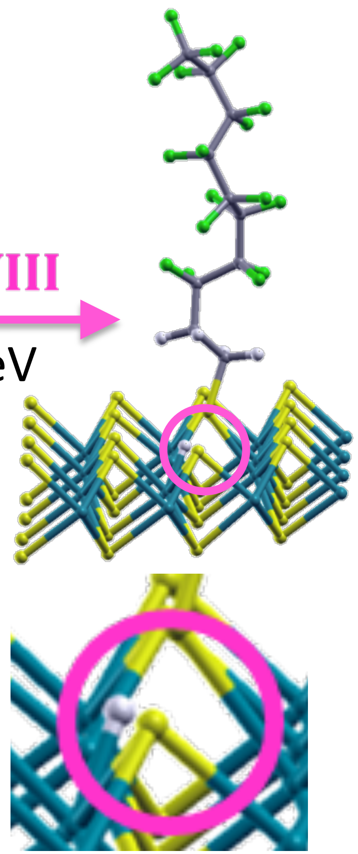
of the thiol with functional groups

p-doping with thiols



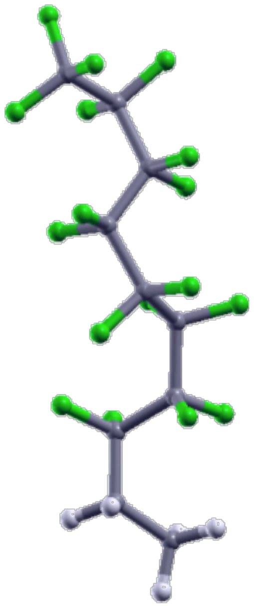
- 3 possibilities
- **reaction 1** ≡ SV repair and physisorption is dominant reaction

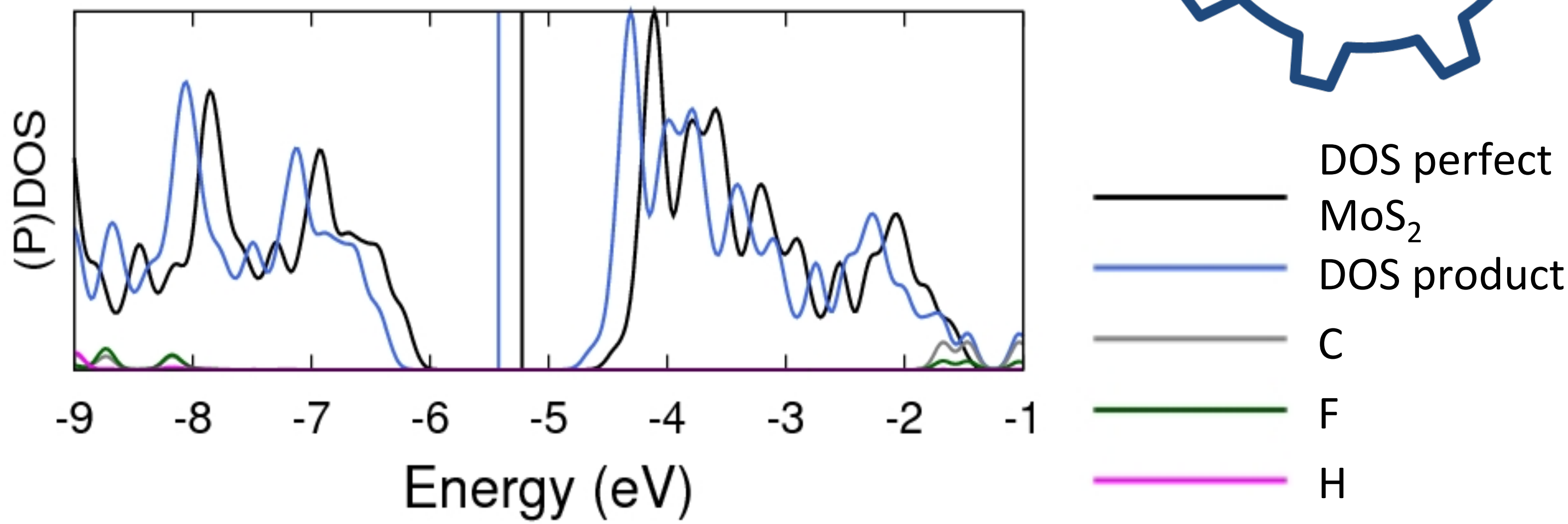


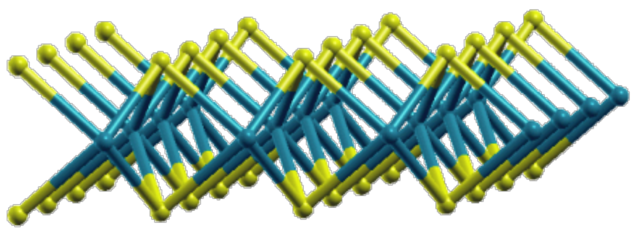


p-doping with thiols

Doping of MoS_2 with SAM molecules

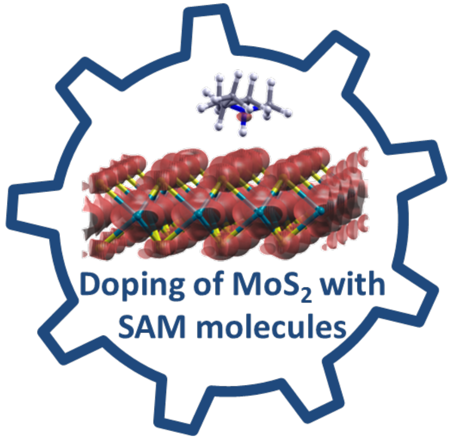






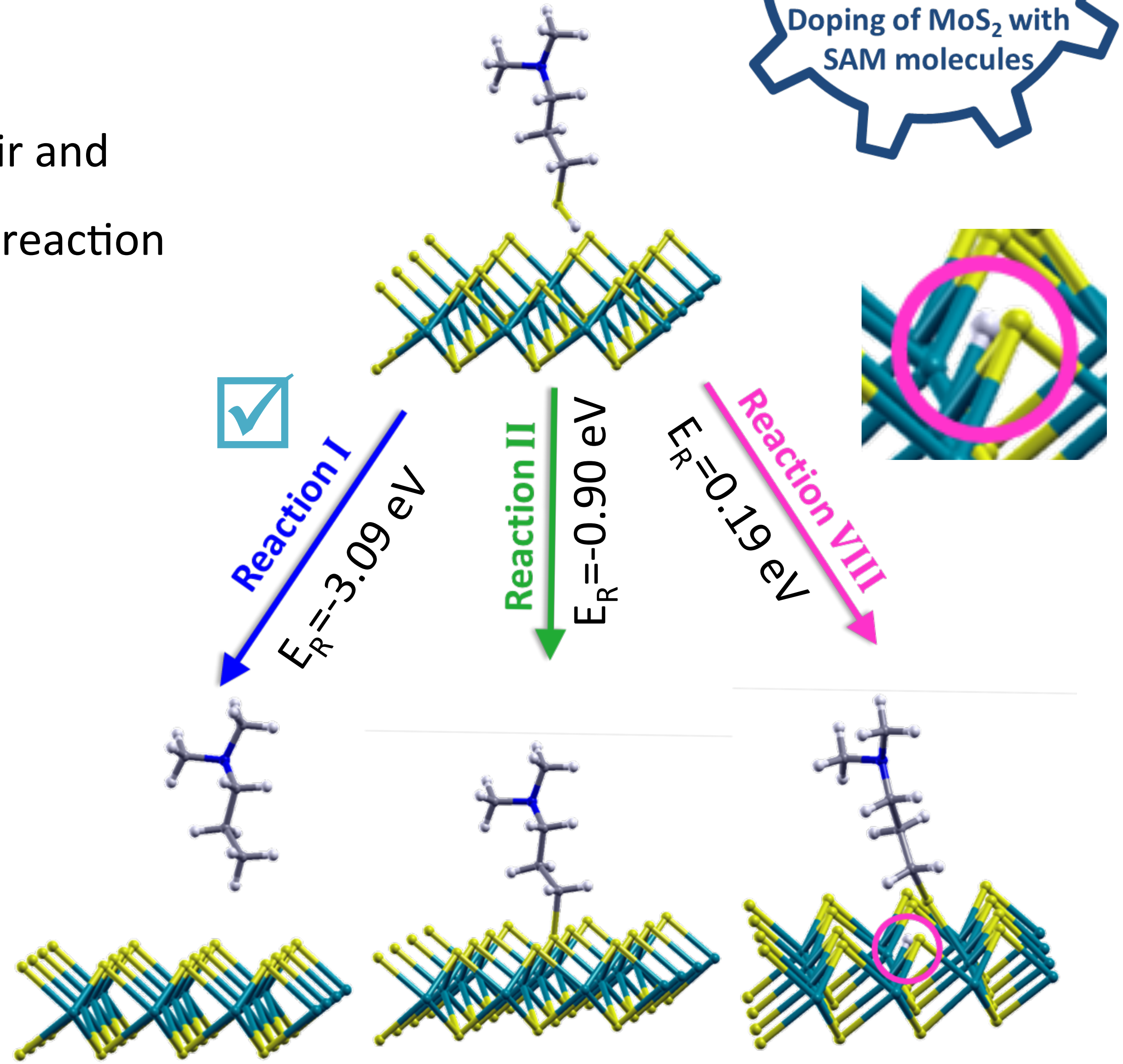
p-type doping

n-doping with thiols

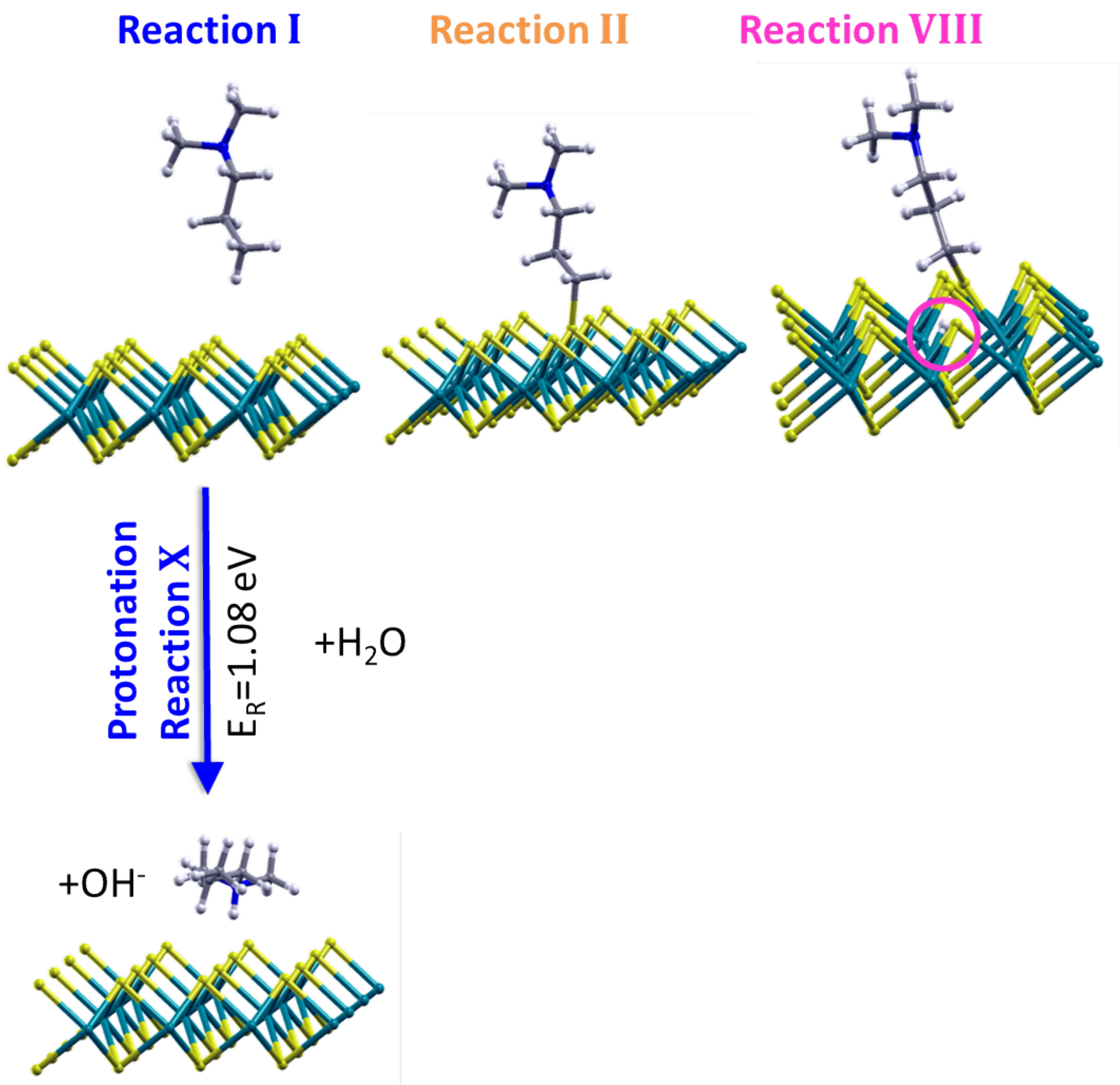


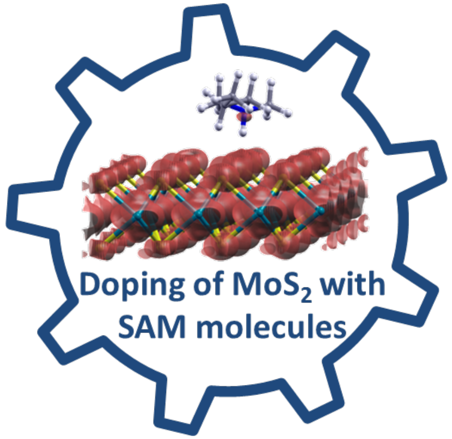
- 3 possibilities
- again **reaction 1** ≡ SV repair and physisorption is dominant reaction

Protonation?

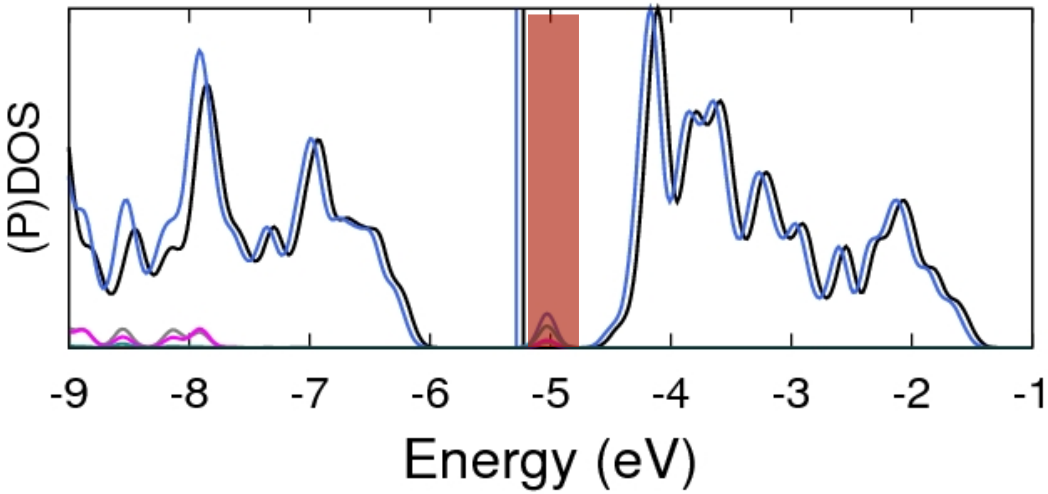


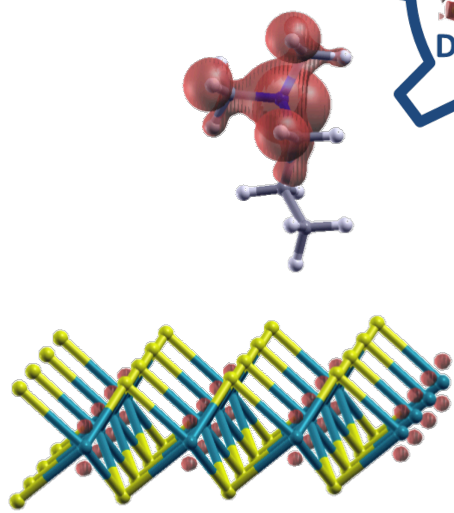
n-doping with thiols

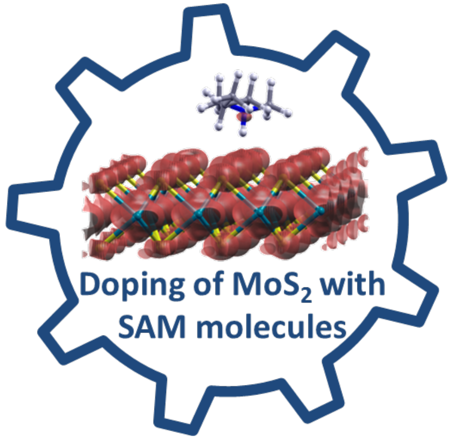




n-doping with thiols







n-type doping

Conclusions

- **thiols** are powerful **healing agents** for several defects in MoS_2 monolayers

  → charge transport limiting defects can be quickly and efficiently healed
  → use of MoS_2 monolayers that were prepared by fast and cheap methods - such as CVD

- "functional" **thiols** for **doping** MoS_2 monolayers

Challenges - Outlook

- Understanding/Tuning Schottky barrier
- Influence of edge properties
- p- and n-type doping (Nb; Re)
- Doping level <-> mobility!
- Gate control
- „Atomistic“ device simulations

➢ **New devices:**

- Nanotube based devices – no edge effects!
- CD waves, superconductivity (NbS_2, TaS_2)

Thanks

Anja Förster (Dresden)

Sibylle Gemming (Dresden)

David Tomanek (E. Lansing)

Financial Support

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DRESDEN concept

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