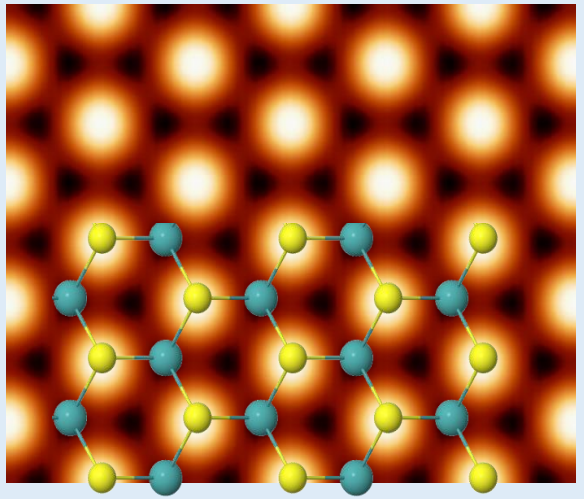
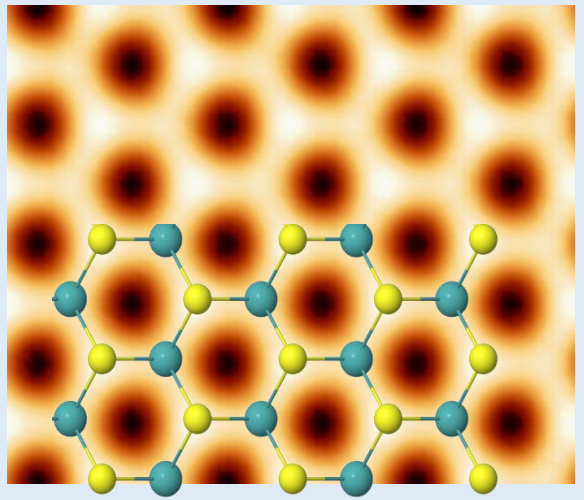
ugr Universidad de Granada

Graphene 2017
March 28-31
Barcelona (Spain)

Defects fingerprints in single layer MoS_2 by *ab initio*-based STM and AFM simulations

Blanca Biel
University of Granada
Biel@ugr.es





Acknowledgements

Collaborators:

Dr. Yannick Dappe

Dr. César González

Financial support:

Ramón y Cajal
Fellowship Program

Computational resources:

Outline

- Motivation
- Methodology
- STM simulations of point-like defects
- AFM simulations of point-like defects
- Work in progress

Motivation

ARTICLE

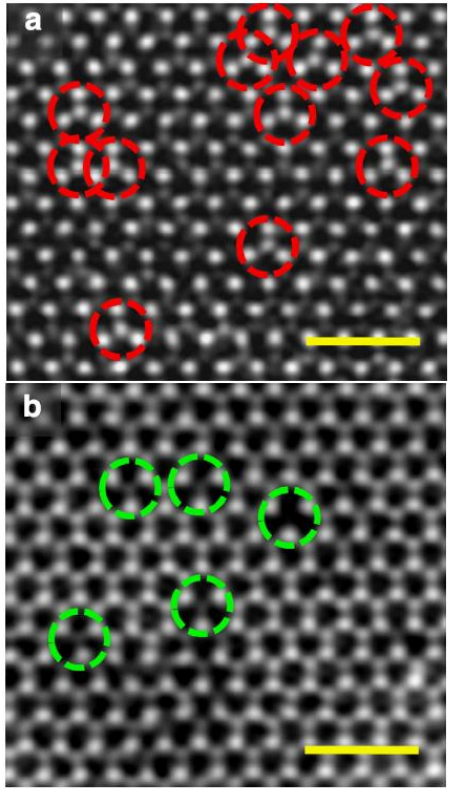
Received 31 Aug 2014 | Accepted 15 Jan 2015 | Published 19 Feb 2015

DOI: 10.1038/ncomms7293 OPEN

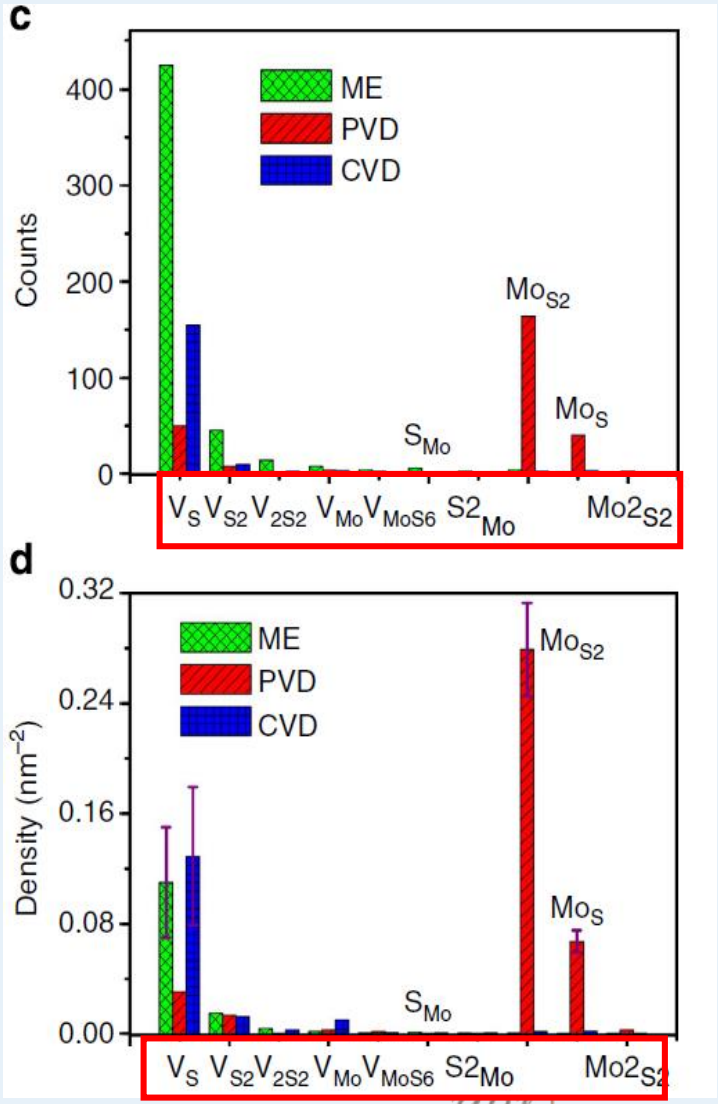
Exploring atomic defects in molybdenum disulphide monolayers

Jinhua Hong[1,*], Zhixin Hu[2,*], Matt Probert[3], Kun Li[4], Danhui Lv[1], Xinan Yang[5], Lin Gu[5], Nannan Mao[6,7], Qingliang Feng[6], Liming Xie[6], Jin Zhang[7], Dianzhong Wu[8], Zhiyong Zhang[8], Chuanhong Jin[1], Wei Ji[2,9], Xixiang Zhang[4], Jun Yuan[1,3] & Ze Zhang[1]

- Most common defects:
  - PVD: antisites → vacS+Mo, vacS2+Mo
  - ME, CVD: vacS, vacS2
  - But also: vacMo, vacMo+S, …
- Different impact on properties (tuning!)
  → **sample characterization**



STEM-ADF image



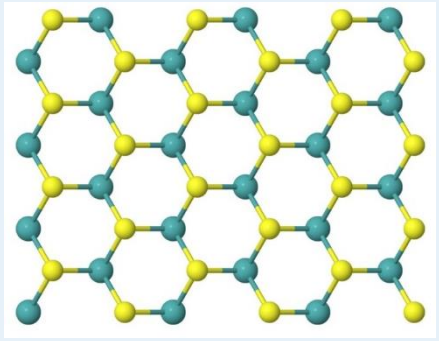
Universidad de Granada

Motivation

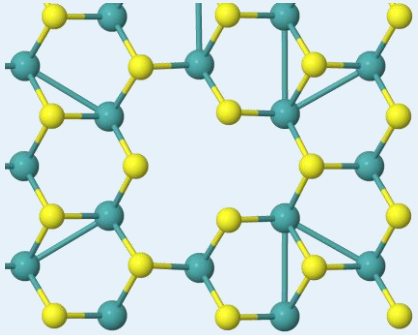
Open questions…

- Do the STM images change with voltage or distance?
- Are geometrical or electronic effects predominant?
- How strong is the influence of the AFM tip?
- Can we identify or at least discriminate between certain defects by force spectroscopy?
- Can we transfer atoms from tip to sample and *vice-versa*? (doping, manipulation, …)

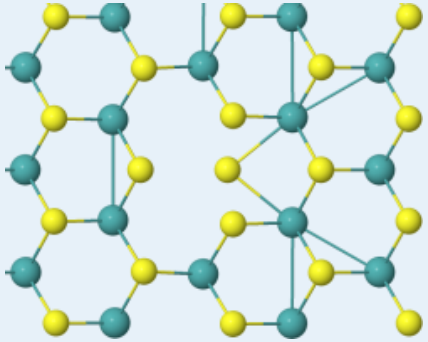
Motivation: selected defects



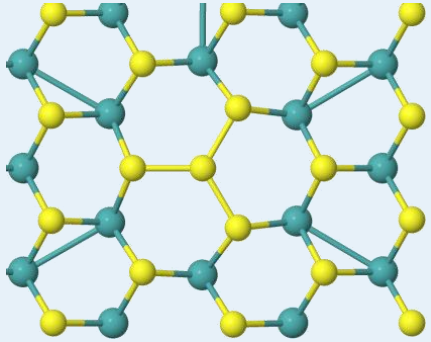
pristine



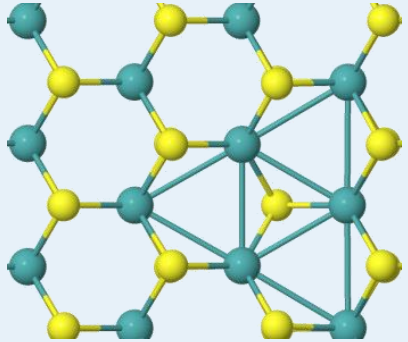
Mo vacancy



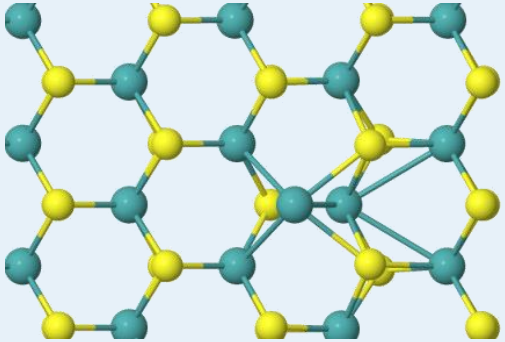
Mo vacancy+S



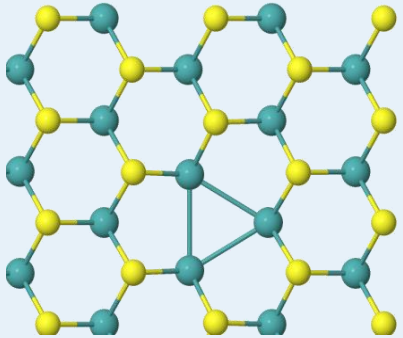
Mo vacancy+2S



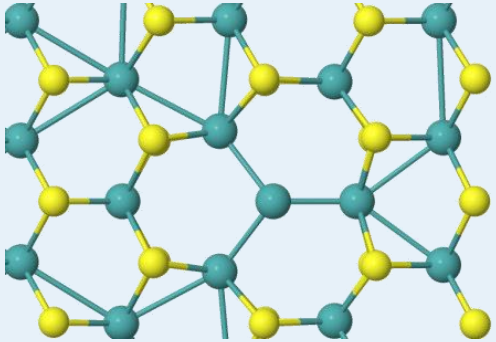
S vacancy



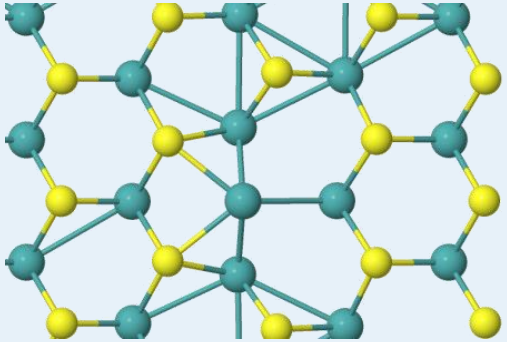
S vacancy+Mo



S di-vacancy



S di-vacancy+Mo



S di-vacancy+2Mo

Motivation: selected defects

Are all defects equivalent (in electronic terms)?

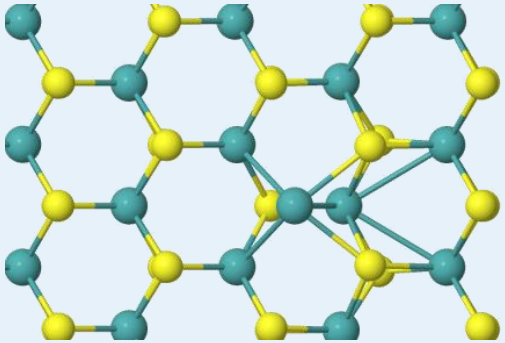
	Clean	V-Mo	V-Mo+S	V-Mo+S2	V-S	V-S+Mo	V-S2	V-S2+Mo	V-S2+Mo2
E_g(eV)	1.70	0.64	0.60	1.25*	1.0	no gap	0.80	no gap	no gap

Motivation: selected defects

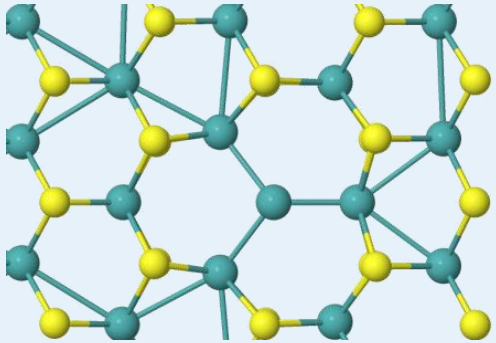
Are all defects equivalent?

	Clean	V-Mo	V-Mo+S	V-Mo+S2	V-S	V-S+Mo	V-S2	V-S2+Mo	V-S2+Mo2
E_g(eV)	1.70	0.64	0.60	1.25*	1.0	no gap	0.80	no gap	no gap

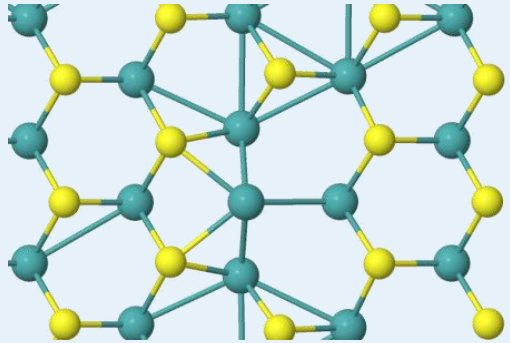
V-S+Mo



V-S2+Mo



V-S2+Mo2



Methodology

- **Fully *ab initio* DFT simulations**

- **STM**: combination of **DFT + Keldysh-NEGFs** formalism
  → **Fireball** (localized orbitals)

- **AFM**: **DFT** simulation of tip-sample interaction + **force extraction**
  → **VASP** (plane waves)

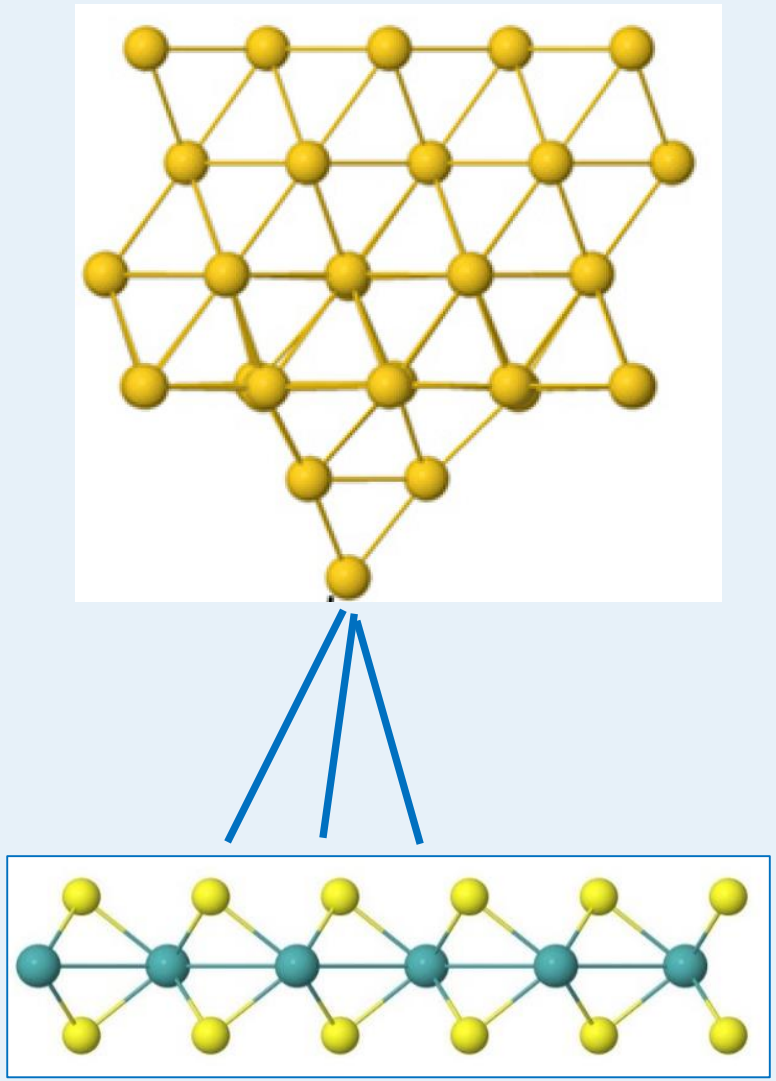
Scanning Tunneling Microscopy simulations

IOP Publishing Nanotechnology

Nanotechnology **27** (2016) 105702 (12pp) doi:10.1088/0957-4484/27/10/105702

Theoretical characterisation of point defects on a MoS_2 monolayer by scanning tunnelling microscopy

C González[1,2], B Biel[1] and Y J Dappe[2]



Theoretical STM model

- Keldysh-Green's functions formalism for STM images

- $H = H_{Tip} + H_{interaction} + H_{Sample}$ ⟸ DFT-LDA FIREBALL code

$$J = \frac{4\pi e}{\hbar} \int_{E_F}^{E_F + eV} Tr\left[T_{TS}\,\rho_{SS}(E)\,D^{R}_{SS}\,T_{ST}\,\rho_{TT}(E - eV)\,D^{A}_{TT}\right] dE$$

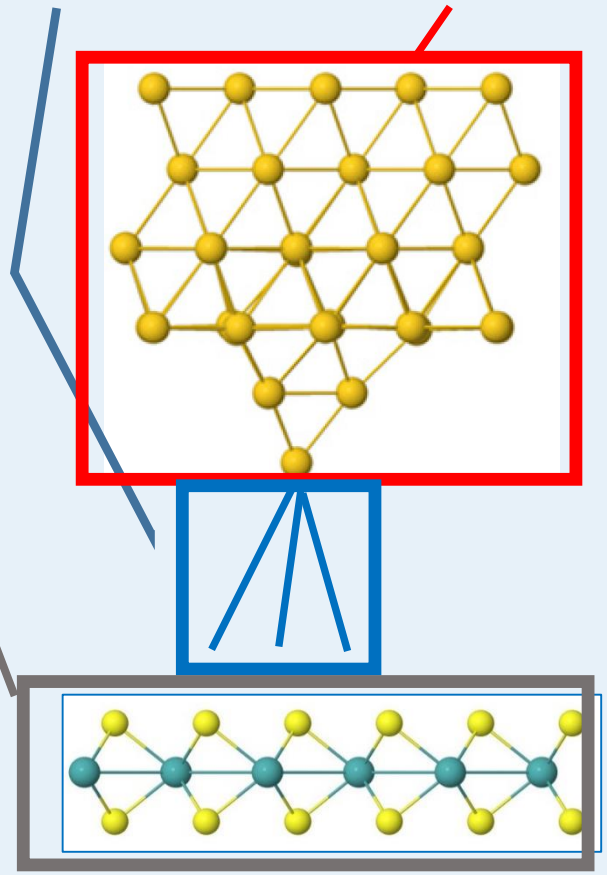
J. M. Blanco, F. Flores, and R. Pérez,
Prog. in Surf. Sci. **81**, 403 (2006)
P. Jelinek *et al.*, Phys. Rev. B 71 (2005) 235101

Theoretical STM model

$$J = \frac{4\pi e}{\hbar} \int_{E_F}^{E_F + eV} Tr\left[T_{TS}\,\rho_{SS}(E)\,D_{SS}^{R}\,T_{ST}\,\rho_{TT}(E - eV)\,D_{TT}^{A}\right] dE$$

$H = H_{Tip} + H_{interaction} + H_{sample}$

DFT-LDA FIREBALL code



Au(111) tip

MoS_2: 6x4 single layer

- J. M. Blanco, F. Flores, and R. Perez, Prog. in Surf. Sci. **81**, 403 (2006)
- P. Jelinek *et al.*, Phys. Rev. B 71 (2005) 235101

- Keldysh-Green's functions formalism

STM simulations

- **STM images:**

Determination of atom/defect position ➔ geometric effects should dominate (in principle)

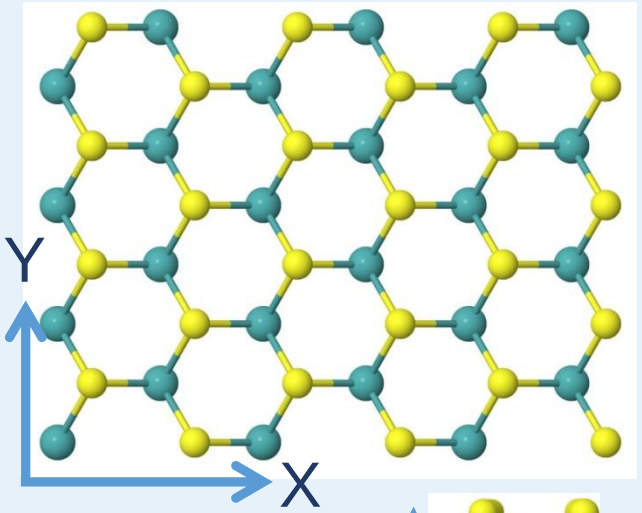
- **bright protrusión ←→ atom closer to tip**
- **dark holes ←→ atom far from tip**

- **BUT (some systems): actual interplay between geometrical and electronic effects**

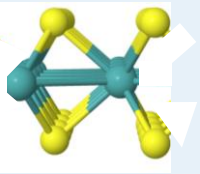
STM simulation of pristine MoS_2 monolayer

Pristine MoS_2 monolayer:

Top view

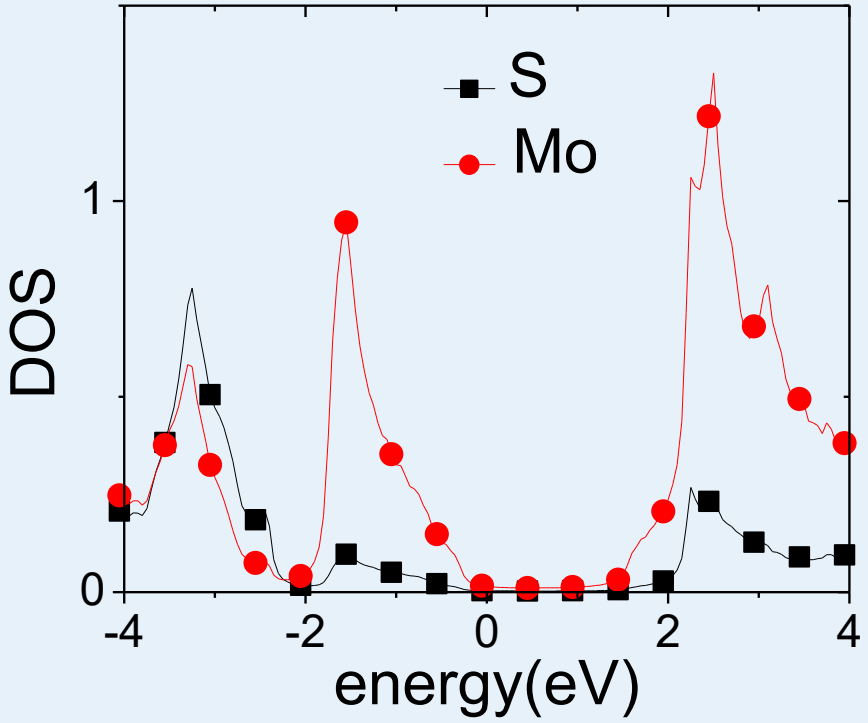


Lateral view 1.51 Å



S atoms

Mo atoms



S atoms 1.51 Å higher than Mo **BUT** Mo contribution to DOS larger than S's for empty states

predomination of geometry or electronic effects?

STM simulation of pristine MoS_2 monolayer

Clean monolayer:

(WSxM software)

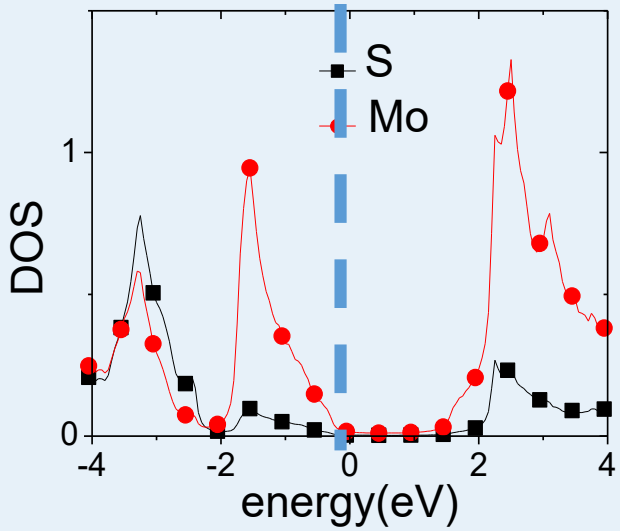
- Constant height mode
- 4.0 Å, **4.5 Å**, 5.0 Å
- No changes with distance
- Voltage range ~ -2V – 3.4V

STM simulation of pristine MoS_2 monolayer

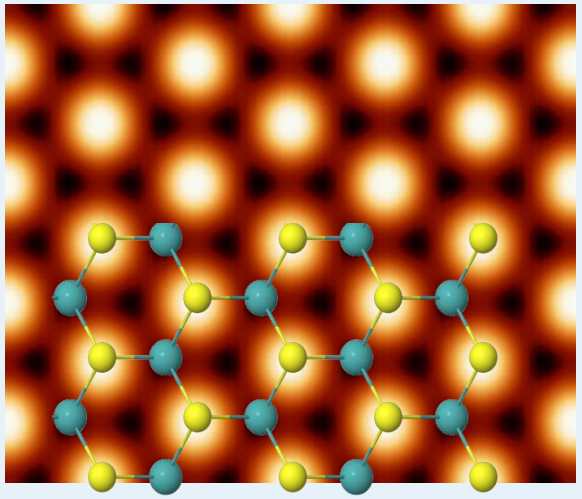
Clean monolayer:

(WSxM software)

- Constant height mode
- 4.0 Å, **4.5 Å**, 5.0 Å
- No changes with distance
- Voltage range ~ -2V – 3.4V



V = -0.1 (occupied states)



Triangular pattern

STM simulated images

S atoms

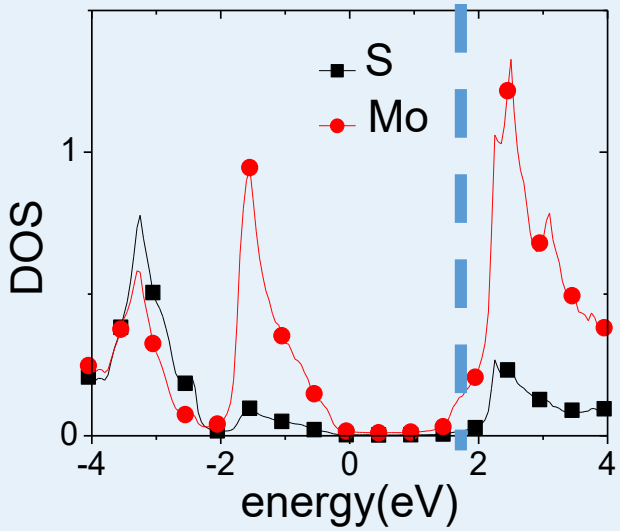
Mo atoms

STM simulation of pristine MoS_2 monolayer

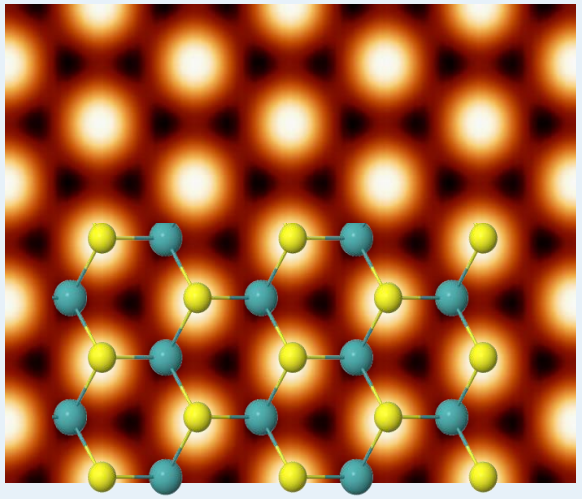
Clean monolayer:

(WSxM software)

- Constant height mode
- 4.0 Å, **4.5 Å**, 5.0 Å
- No alterations with distance
- Voltage range ~ -2V – 3.4V

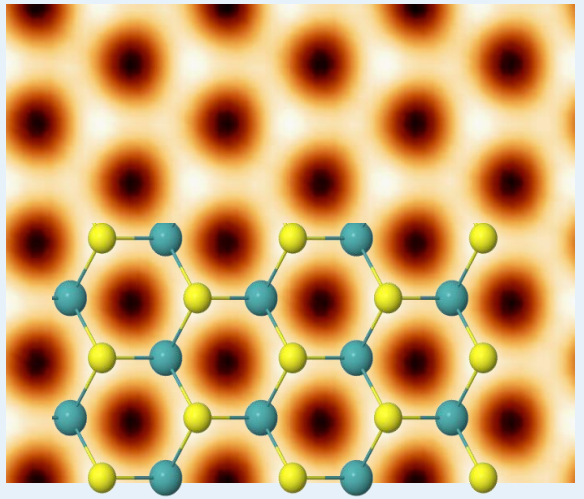


V = -0.1 (occupied states)



Triangular pattern

V = +1.9 (empty states)



Asymmetric hexagonal pattern

STM simulated images

S atoms

Mo atoms

Geometry effects

DOS compensation

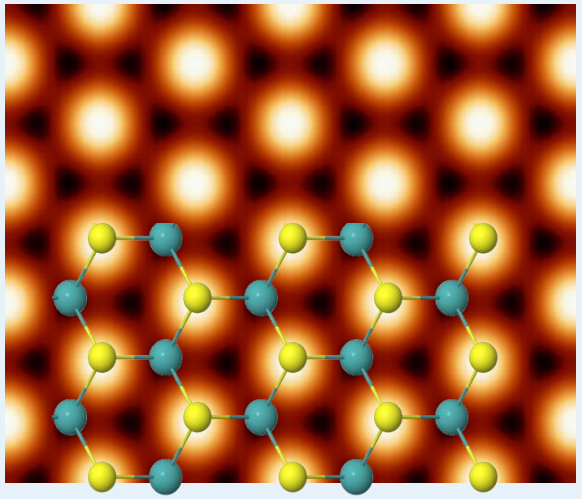
STM simulation of pristine MoS_2 monolayer

Clean monolayer:

(WSxM software)

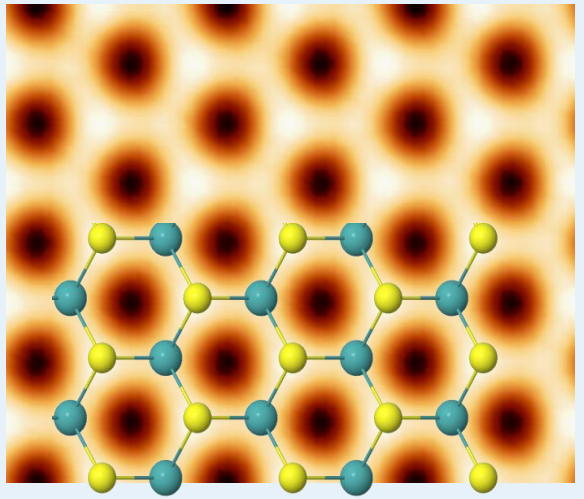
- Constant height mode
- 4.0 Å, **4.5 Å**, 5.0 Å
- No alterations with distance
- Voltage range ~ -2V – 3.4V

V = -0.1 (occupied states)



Triangular pattern

V = +1.9 (empty states)

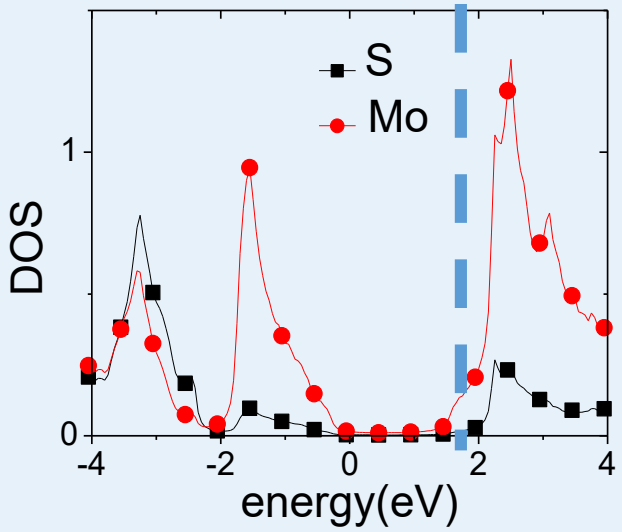


Asymmetric hexagonal pattern

STM simulated images

S atoms

Mo atoms



Geometry effects

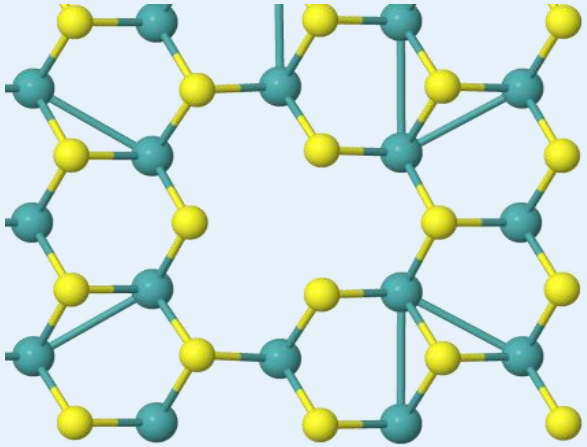
DOS compensation

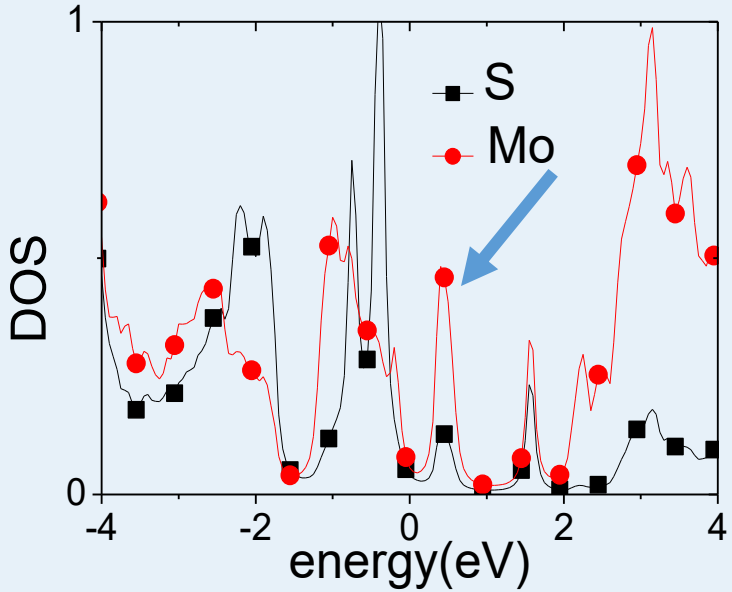
- Further voltage increase → triangular pattern
- Experimental confirmation?

ugr Universidad de Granada

STM simulation of atomic defects in MoS_2: Mo monovacancy

Mo monovacancy

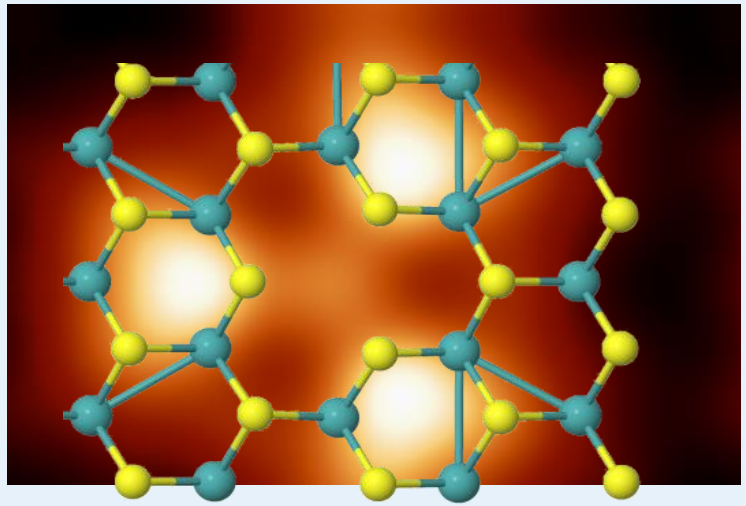


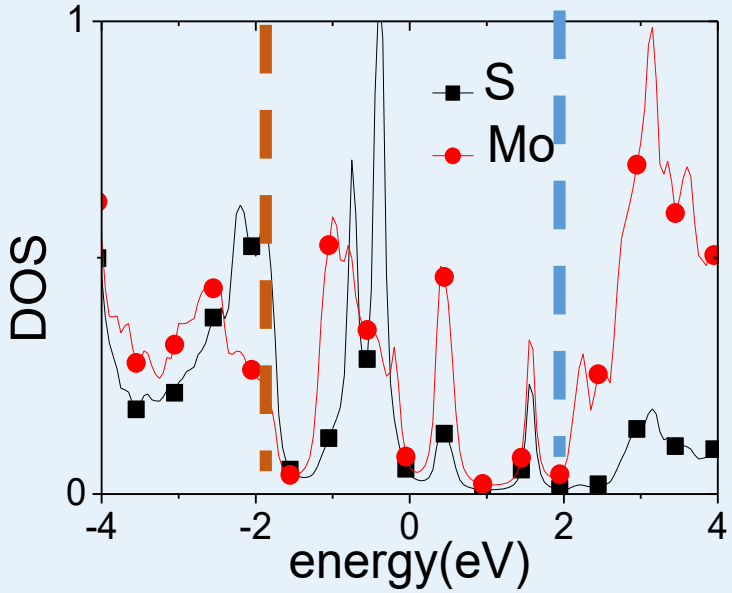


- Atoms displacements < 0.1 Å → dangling bonds in neighboring S and Mo atoms
- Strong modifications of the DOS → localised states associated with the unsaturated bonds in the midgap (*p* character)
- Decrease of gap size ~1 eV

STM simulation of atomic defects in MoS_2: Mo monovacancy

Mo monovacancy





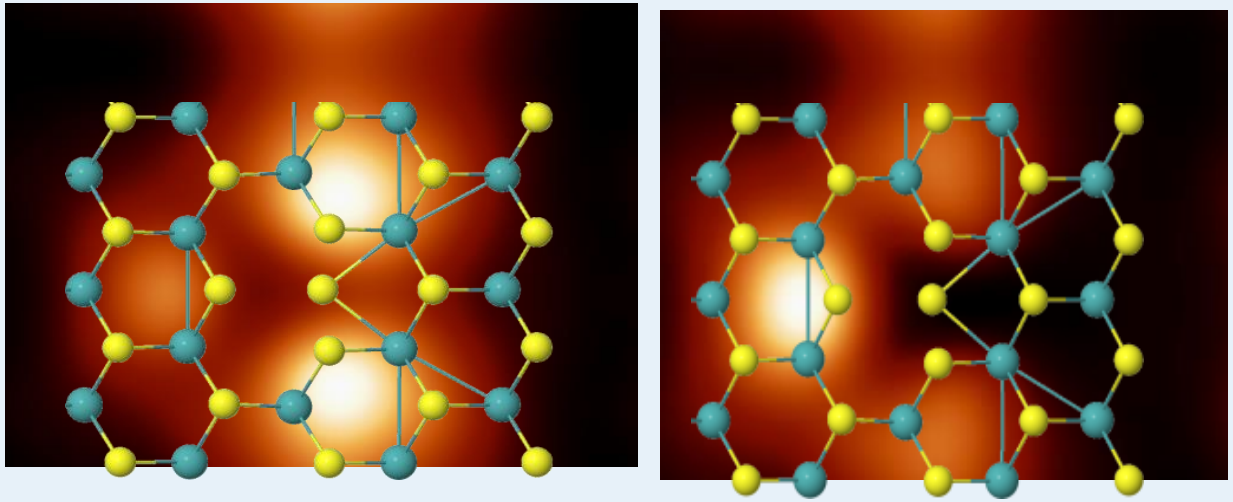
- **Images @ +1.9 V** (empty states) → three brilliant spots in the neighboring S atoms,
  not directly over the S
  (*p*-character of the S dangling bond → opposite direction to the original bond)

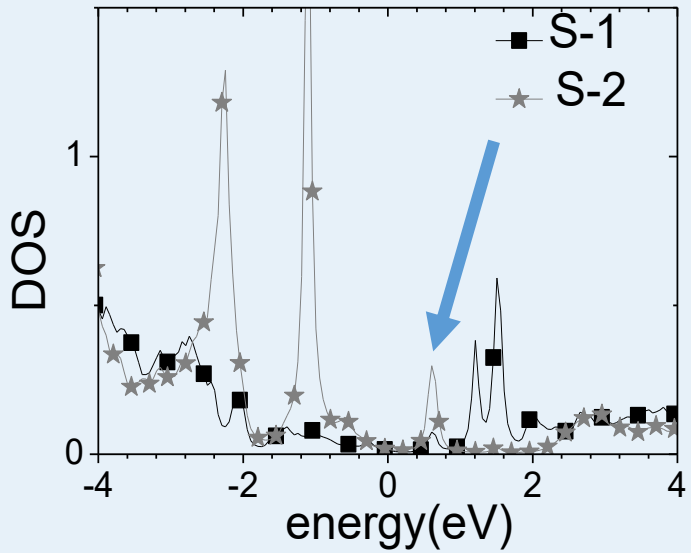
- **Images @ −1.9 V** (filled states) → dangling bond effect reduced ➔ **relocation over S atoms**

STM simulation of atomic defects in MoS_2: S antisite

Mo monovacancy with substitutional S

V= + 1.9 (high voltage) V= + 0.5 (low voltage)



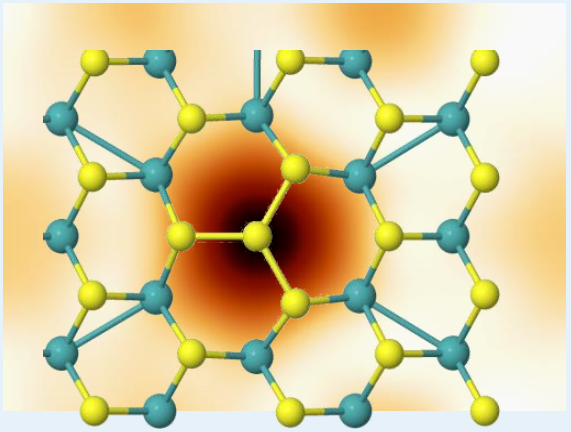


- Subs-S on same plane as Mo → lower contribution to current than other S
- Asymmetric position of subs-S → sharp peak in DOS of far S neighbor → **change of contrast**
- V = - 1 V → same contrast as for V = + 0.5 V

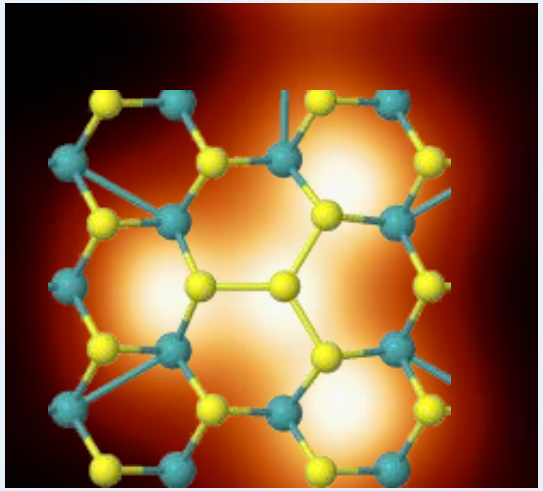
Strong dependence on applied voltage

STM simulation of atomic defects in MoS_2: 2-S antisite

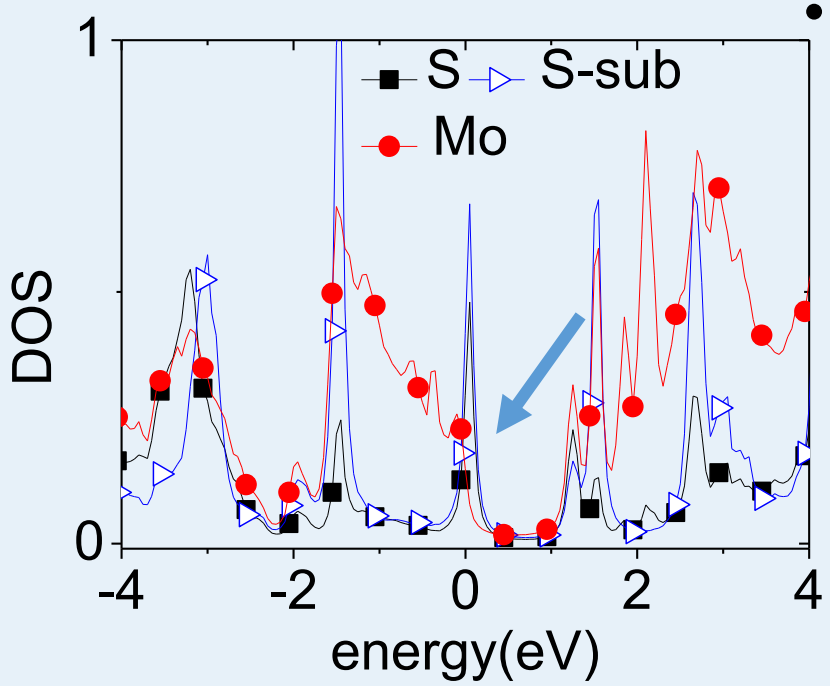
Mo monovacancy with 2 substitutional S



V= + 1.9



V= + 0.5



Dependence on applied voltage

- 2 subs-S no connected to Mo atoms but to S atoms:

→ S-subs atoms in a semioccupied state (sharp peak)

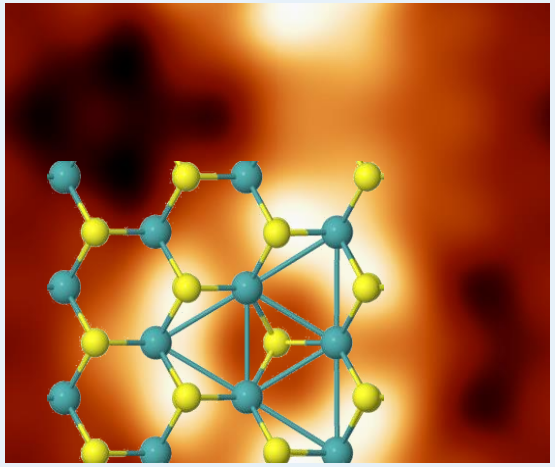
→ bright at low V

→ dark at high V, recovering pristine image

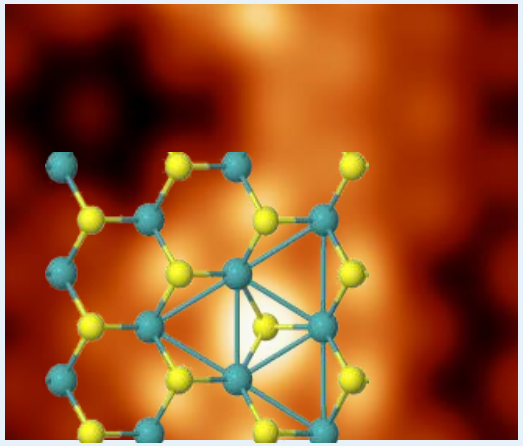
STM simulation of atomic defects in MoS_2: S mono- and di-vacancies

S monovacancy

V= + 1.9

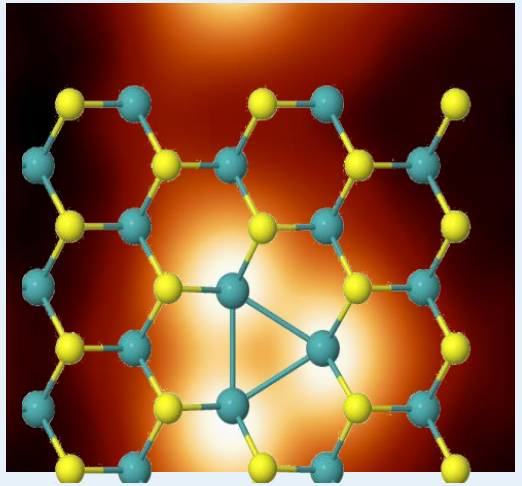


V= + 1

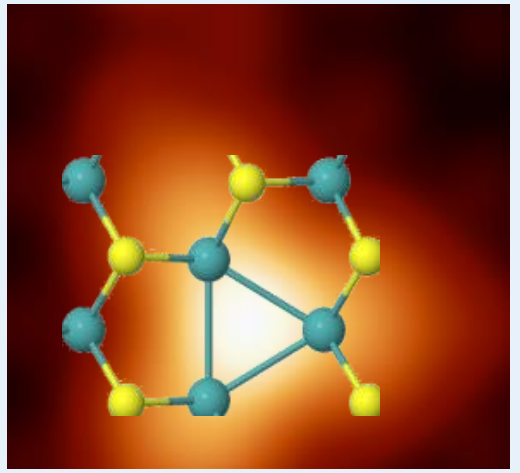


S divacancy

V= + 1.9



V= - 1.0

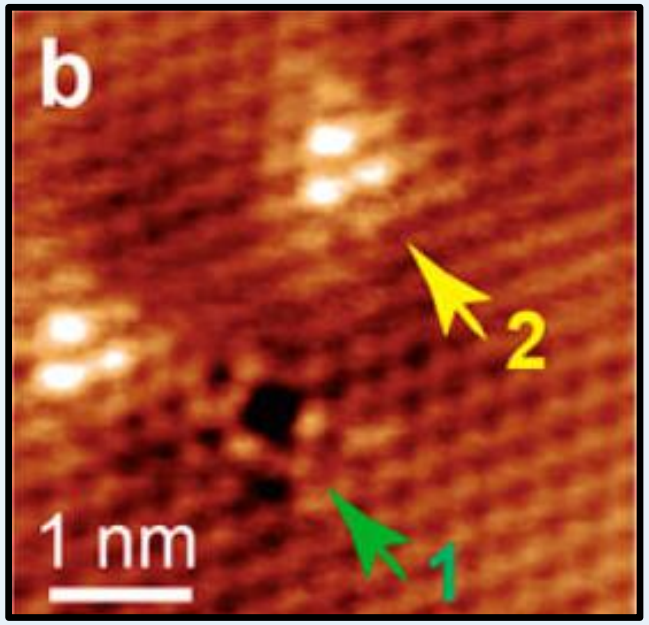


Dependence on applied voltage
→ contrast change
(dark hole or bright protrusión)

For **S or Mo vacancies** and
S substitutionals in the Mo vacancy

STM simulation of atomic defects in MoS_2: S mono- and di-vacancies

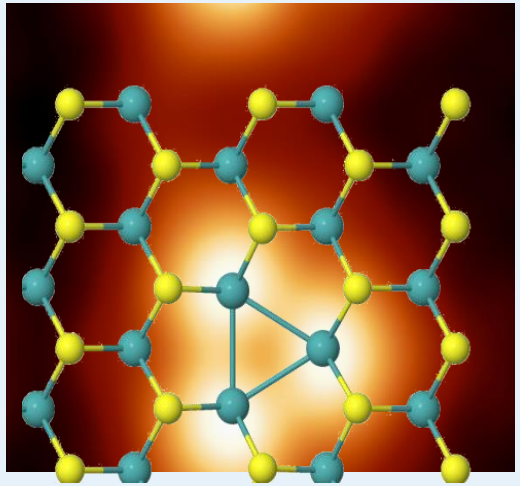
S divacancy - experiment



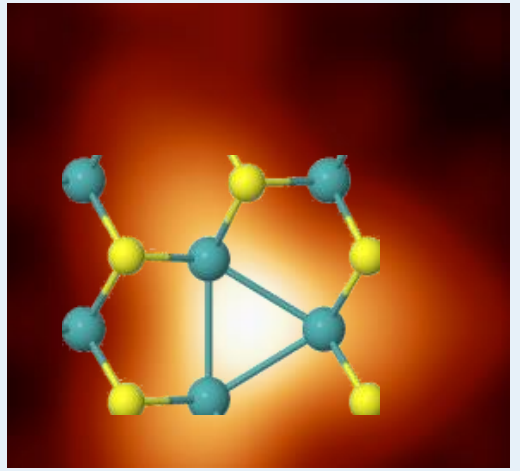
DOI: 10.1021/acs.jpcc.6b02073
J. Phys. Chem. C 2016, 120, 20798−20805

S divacancy – our simulation

V= + 1.9



V= - 1.0

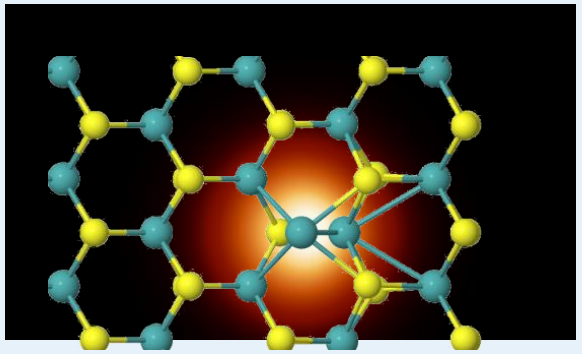


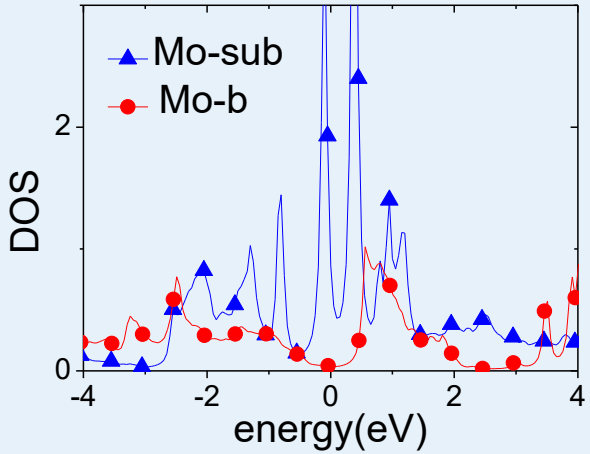
Experimental confirmation ?

STM simulation of atomic defects in MoS_2: Mo antisites

S monovacancy with substitutional Mo

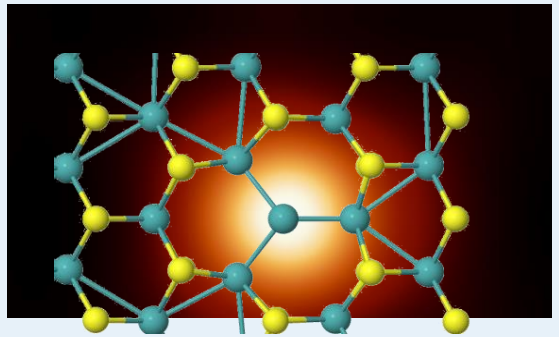
V= + 1.9

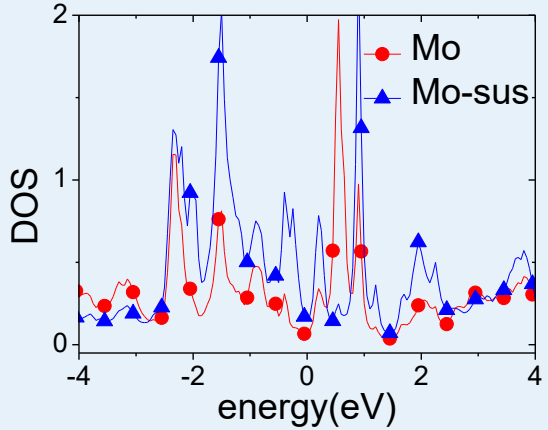




S divacancy with substitutional Mo

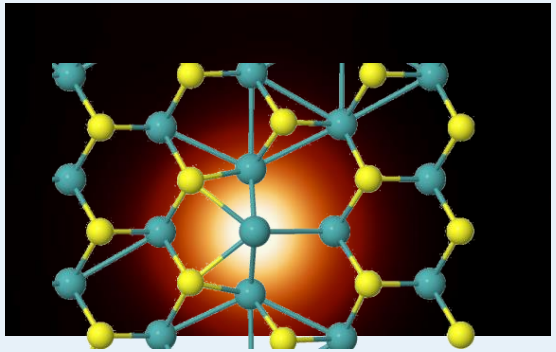
V= + 1.9

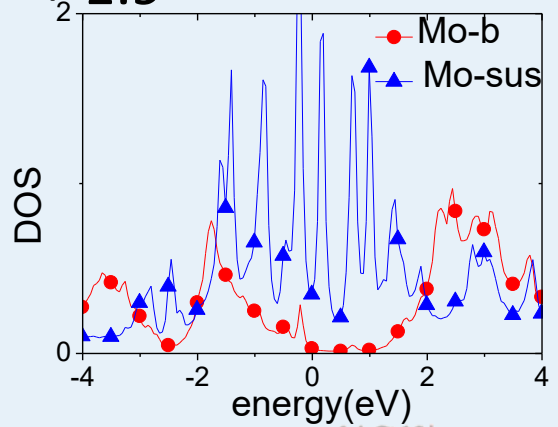




S divacancy with 2 substitutional Mo:

V= + 1.9





Bright protrusión
(regardless of voltaje)

One or two **Mo atoms in an empty S** site
("metallic" defects)

STM simulations: conclusions

- Do the STM images change with voltage or distance?
- Are geometrical or electronic effects predominant?

?

- **No dependence on distance**
- **Possible change of contrast** in the **pristine** monolayer

- **Defects → dependence on voltage/type of defect**

  - Vacancies and S substitutionals in the Mo vacancy
    → imaged as **large protrusions or dark holes**, depending on the applied voltage

  - One or two Mo atoms in an empty S site (**'metallic defects'**)
    → **bright protrusion** independently of the applied bias

C. González, BB, Y. Dappe, Nanotechnology 27 (10), 105702

Atomic Force Microscopy simulations

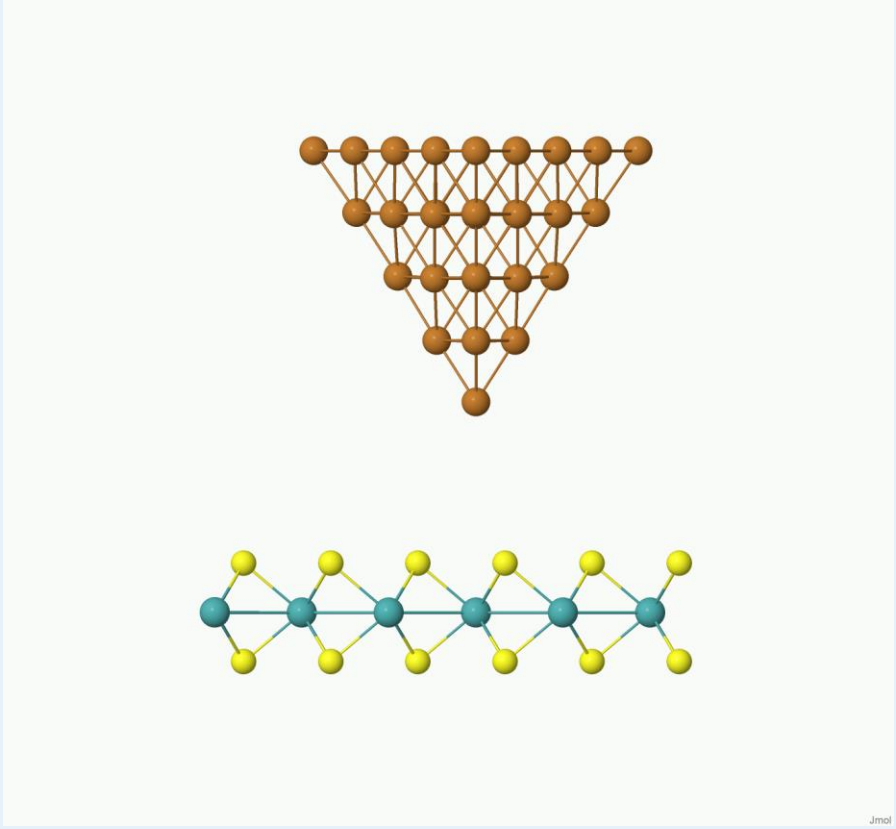
THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Reactivity Enhancement and Fingerprints of Point Defects on a MoS_2 Monolayer Assessed by *ab Initio* Atomic Force Microscopy

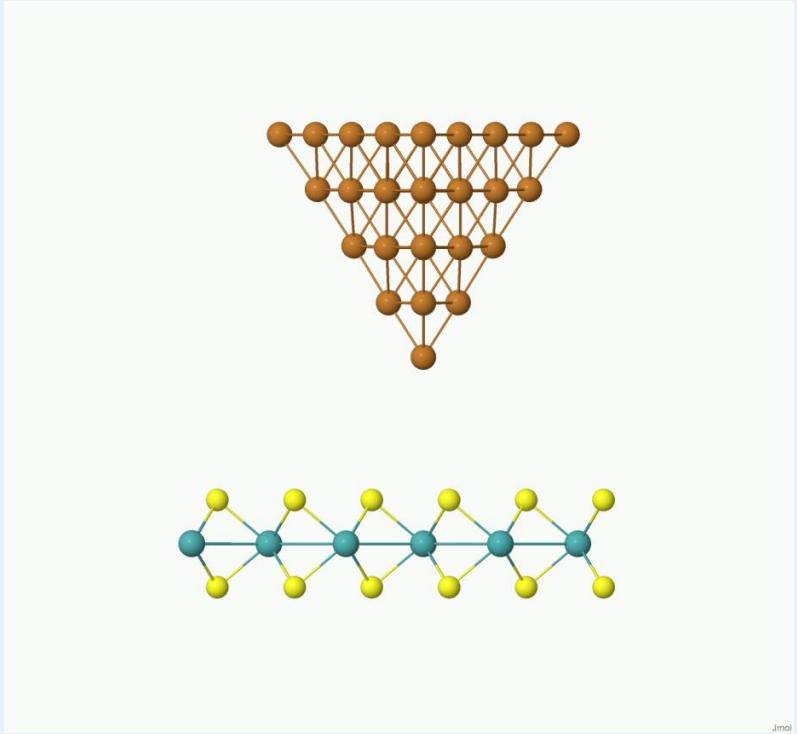
C. González,*[,†,‡] Y. J. Dappe,[‡] and B. Biel[†]



Theoretical AFM model

DFT calculations: VASP code

- Initial distance: 5 Å
- Steps of 0.25 Å
- Relaxation of whole system in each step
- Range: 2 Å - 5 Å
- Non-contact AFM (FM-AFM)



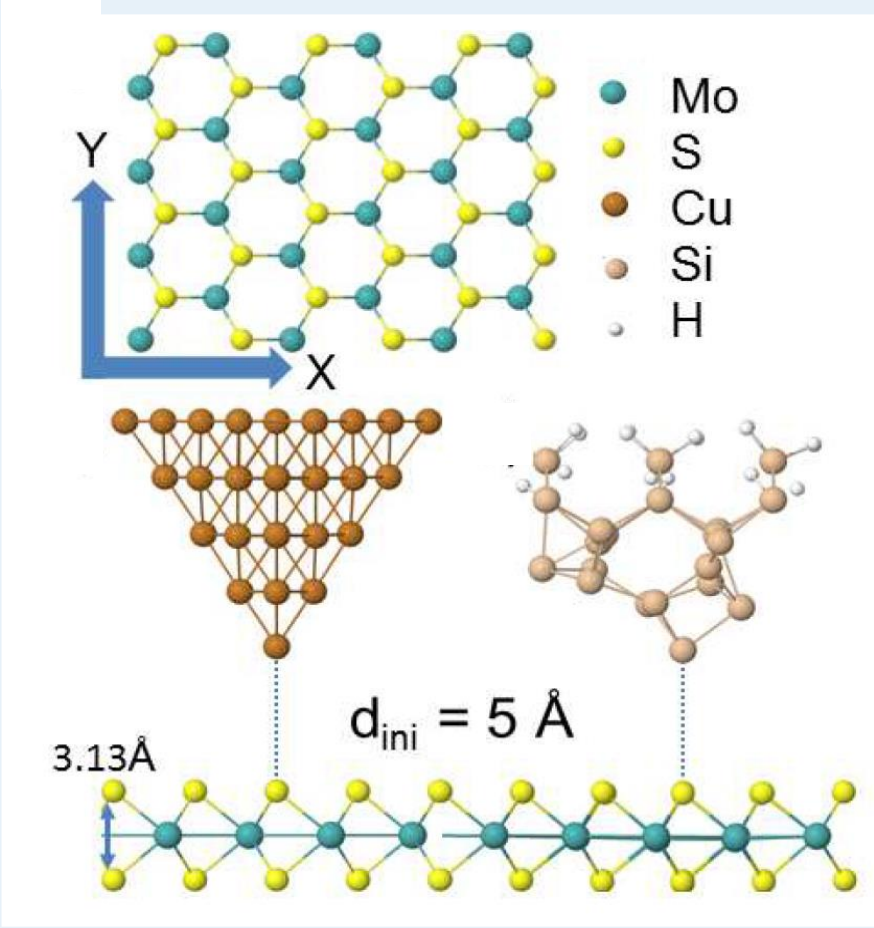
$$\Delta f = \frac{f_0}{2\pi k A_0} \int_0^{2\pi} F_{TS}\left[d + A_0 + A_0 \cos\varphi\right] \cos\varphi \, d\varphi$$

R. García and R. Pérez Surf. Sci. Rep. 47 (2002) 197

Theoretical AFM model

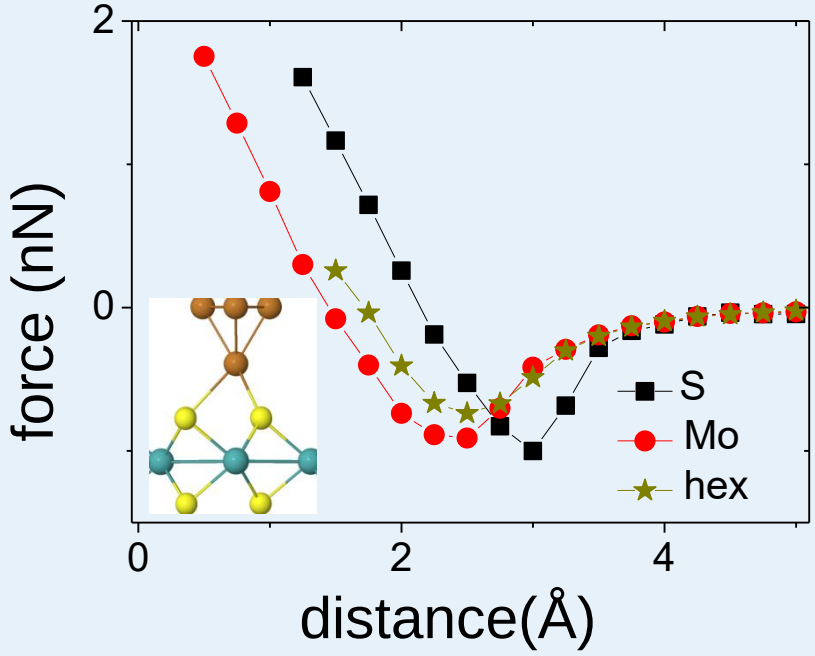
DFT calculations: VASP code

- Two tips:
  - Cu (very reactive)
  - Si (less reactive)
- Analysis of tip-sample force interaction curves
  - Most attractive point ➔ force minimum value
  - Type of interaction ➔ tip-sample distance at minimum force
- Comparison of force curves → discrimination between defects?



AFM simulations of pristine MoS_2 monolayer

Cu tip



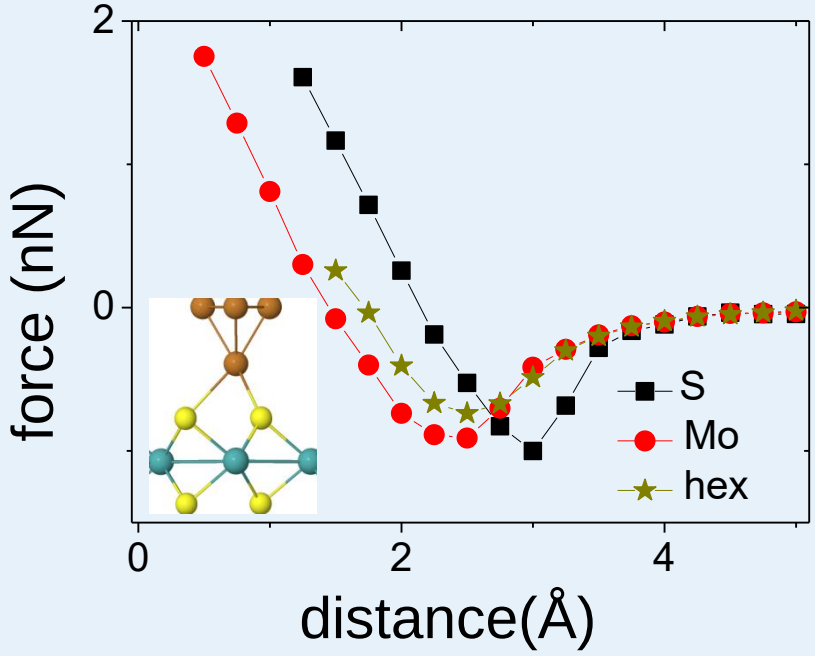
- Most attractive point for the Cu tip: over a S atom
  - Mo more visible than S at ~ 2.5 Å

(due to interaction with neighboring S atoms!)

➔ contrast change between Mo and S with distance

AFM simulations of pristine MoS_2 monolayer

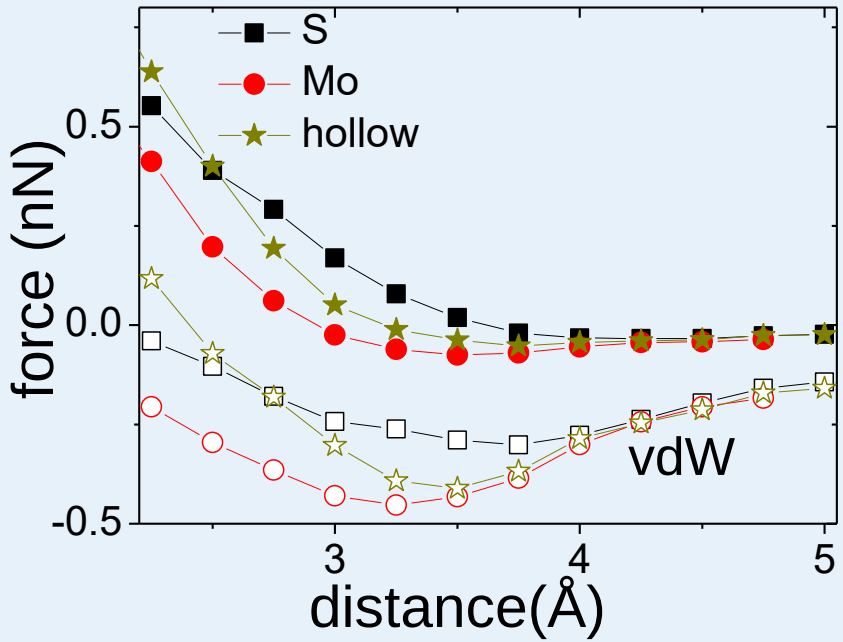
Cu tip



- Most attractive point for the Cu tip: over a S atom
  - Mo more visible than S at ~ 2.5 Å
    (due to interaction with neighboring S atoms!)

➔ contrast change between Mo and S with distance

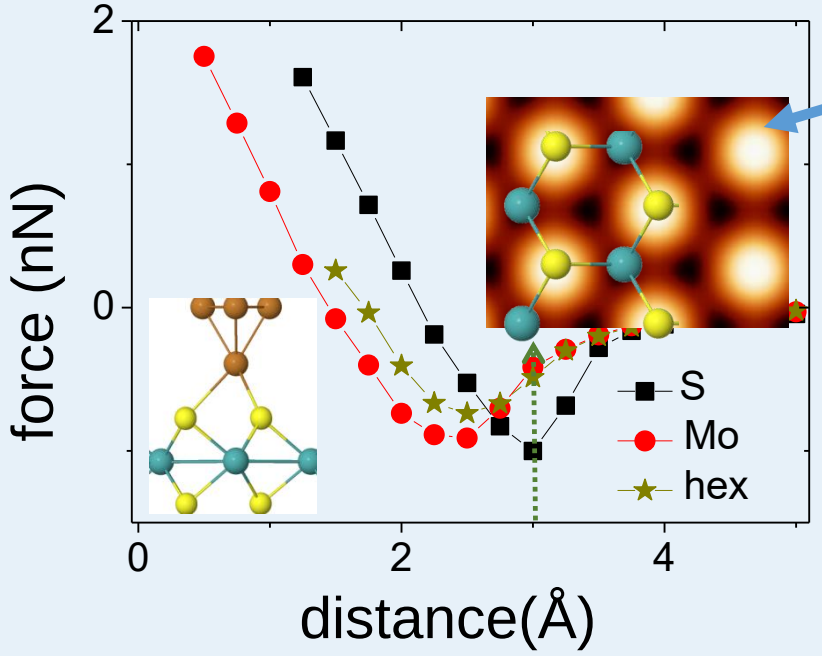
Si tip



- Most attractive point for the Si tip: over a Mo atom
- Need to introduce vdW interaction to get attractive forces
- **No contrast change expected**

AFM simulations of pristine MoS_2 monolayer

Cu tip

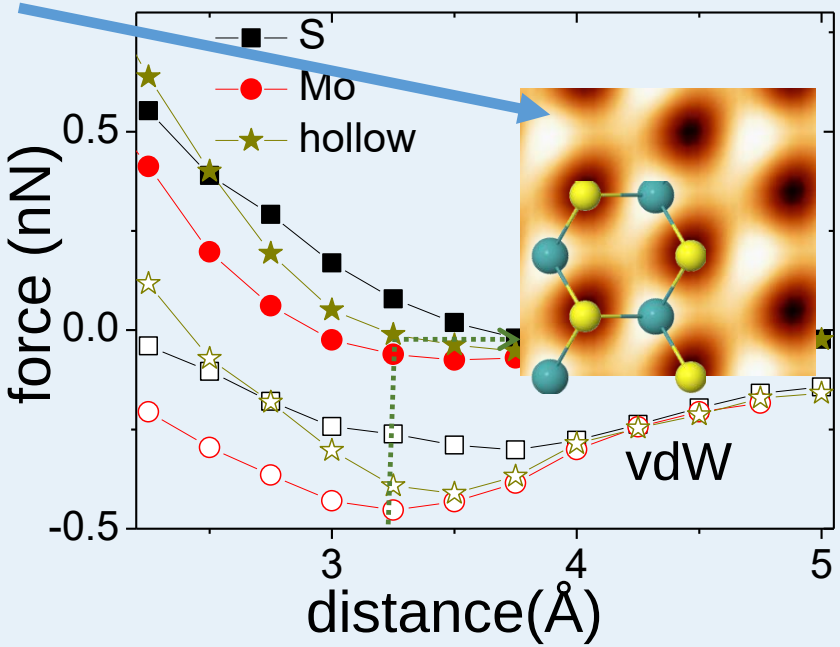


Expected nc-AFM images obtained at 3 Å

Hexagonal pattern (asymmetric)

Triangular pattern

Si tip



- Most attractive point for the Cu tip: over a S atom
  - Mo more visible than S at ~ 2.5 Å
    (due to interaction with neighboring S atoms!)

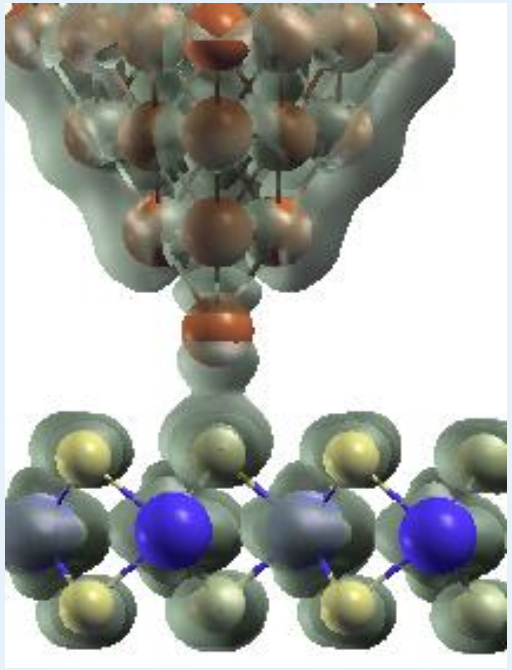
➔ contrast change between Mo and S with distance

- Most attractive point for the Si tip: over a Mo atom
- Need to introduce vdW interaction to get attractive forces
- **No contrast change expected**

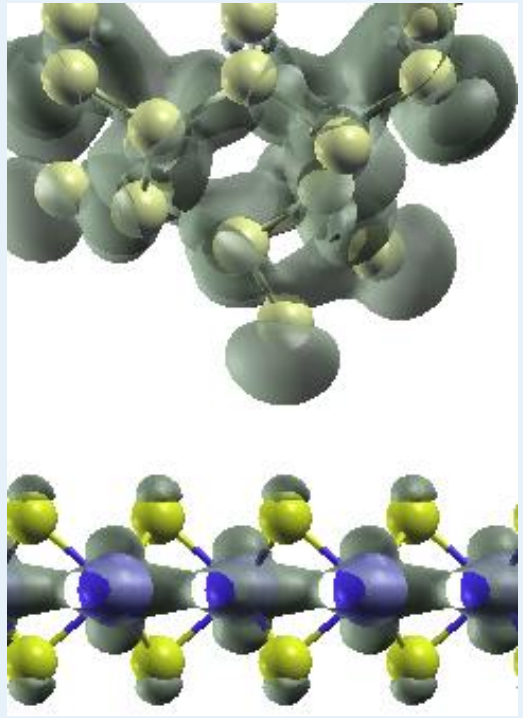
AFM simulations of pristine MoS_2 monolayer

- **Tip interaction** → analysis of charge density:
  - Bond between Cu tip and S atom
  - No bond between Si tip and S atom

→ **Cu tip more reactive**



Most attractive point for a Cu tip approaching a S atom

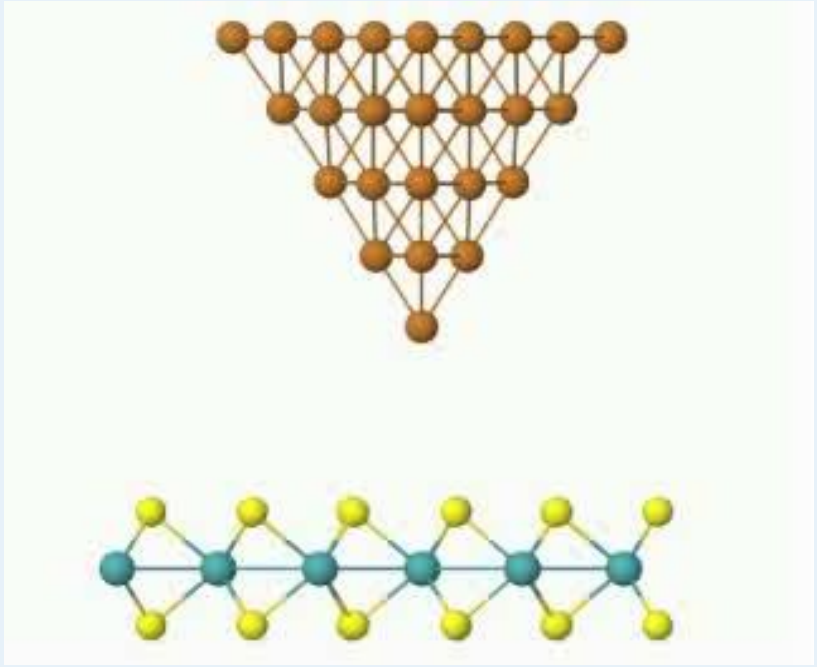


Most attractive point for a Si tip approaching a S atom

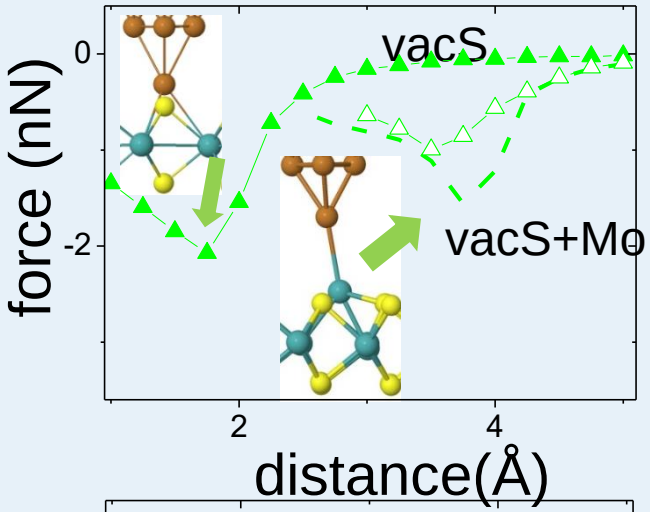
AFM simulations of atomic defects in MoS_2

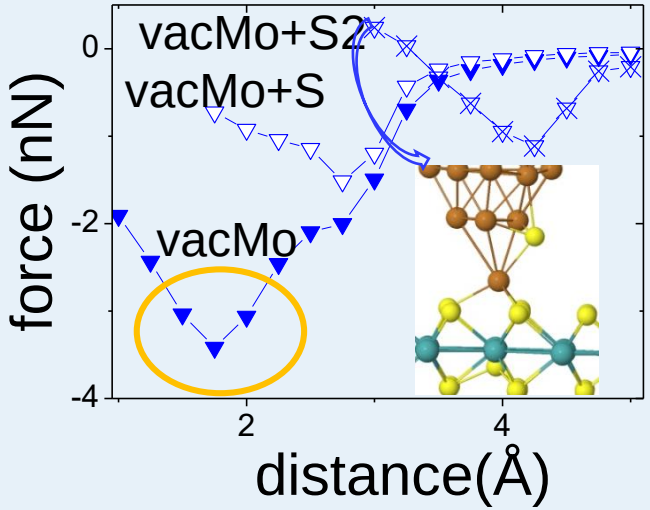
Cu tip:

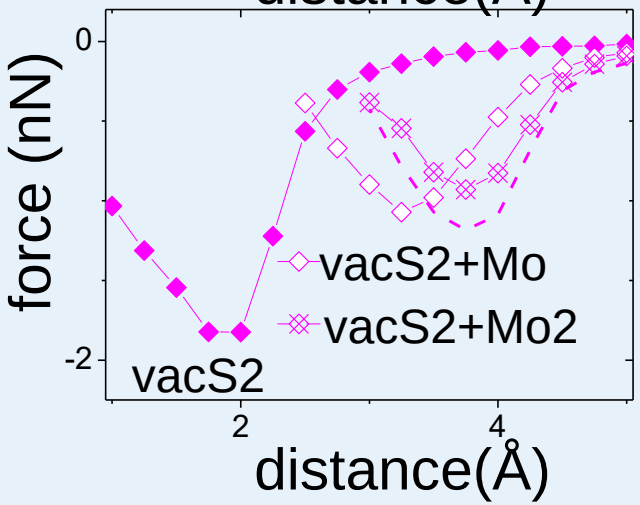
- Most attractive force → over a **Mo vacancy**

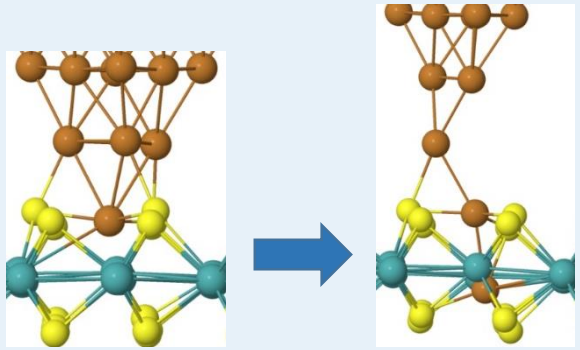


- Capture of apex atoms
- Transfer of atoms from sample to tip









AFM simulations of atomic defects in MoS_2

Cu tip:

tipCu	F_m(nN)	d_m(Å)	Δh_{Cu}(Å)	$\Delta h_{Mo/S}$(Å)	$\Delta Chg_{Cu}(e)$
vacMo	-3.42	1.75	-0.90	-	-0.55
vacS	-2.07	1.75	-0.63	-	-0.34
vacS2	-1.85	1.75	-0.63	-	-0.33
Mo	-0.88	2.50	-0.20	+0.18	-0.11
vacMo+S	-1.56	2.75	-0.33	+0.09	-0.33
vacS2+Mo	-1.07	3.00	-0.15	+1.30	-0.39
S	-1.00	3.00	-0.25	+0.38	-0.12
vacS+Mo	-1.01(-1.51)	3.50(3.75)	-0.22	+0.46	-0.39
vacS2+Mo2	-0.93(-1.18)	3.75(3.75)	-0.26	+0.34	-0.28
vacMo+S2	-1.11	4.25	-0.29	+0.27	-0.23

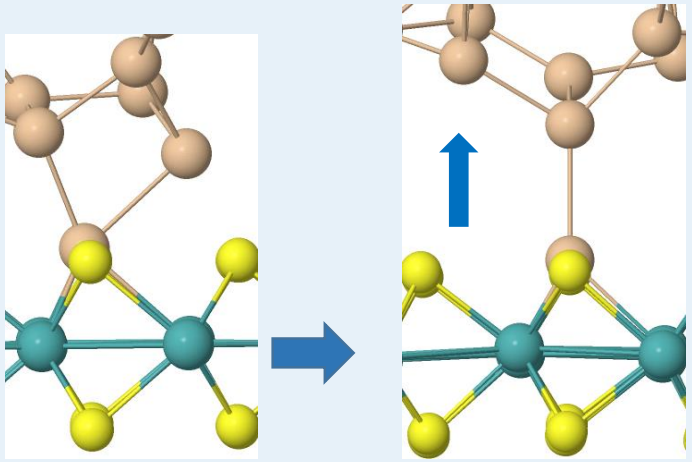
The monolayer is more semiconducting than the metallic tip
➔ significant charge transfer takes place from the tip to the substrate

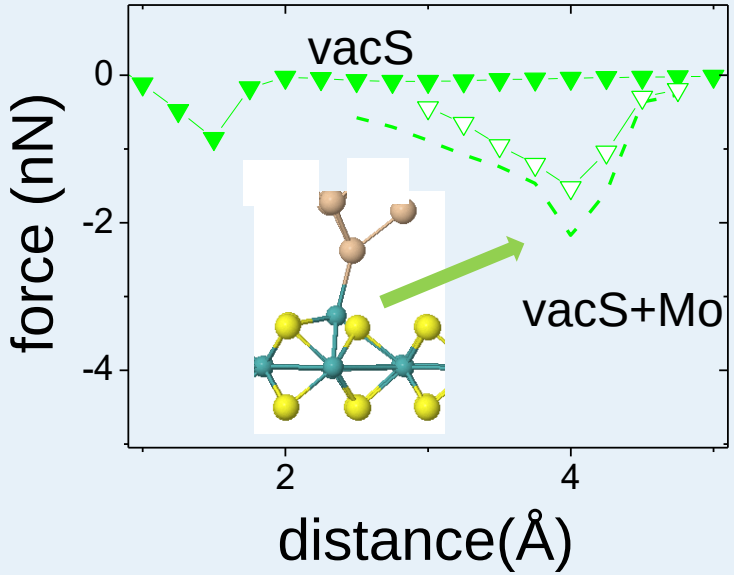
AFM simulations of atomic defects in MoS_2

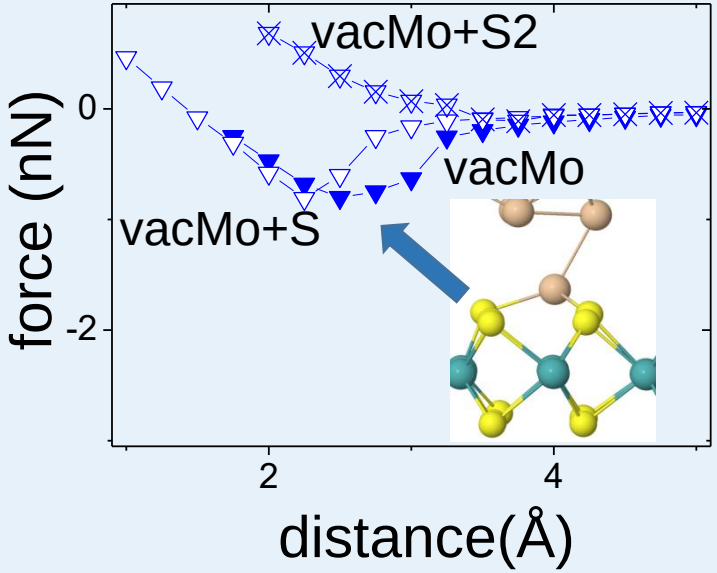
Si tip:

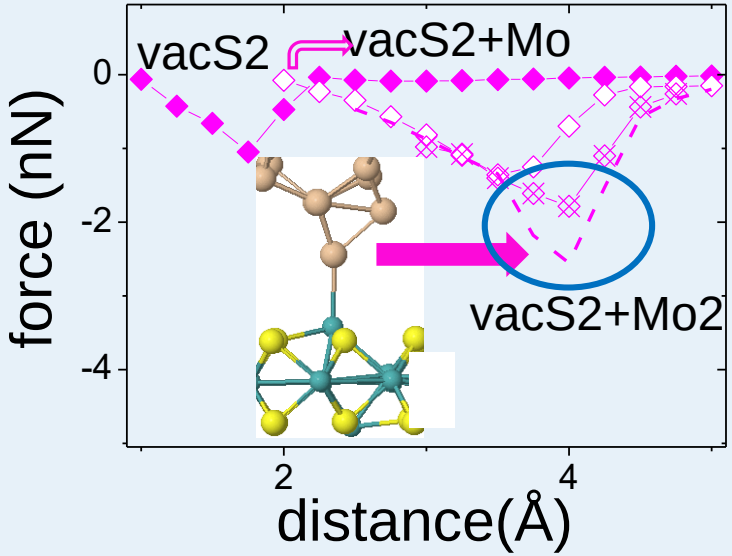
- Most attractive force
  → over a **2S+2Mo vacancy**

- **Capture of a S atom** in the S2-subs case









AFM simulations of atomic defects in MoS_2

Si tip:

tipSi	F_m(nN)	d_m(Å)	Δh_{Si}(Å)	$\Delta h_{Mo/S}$(Å)	$\Delta Chg_{Si}(e)$
vacS2+Mo2	-1.80(-2.55)	4.00	-0.60	+0.60	+0.49
vacS+Mo	-1.55(-2.17)	4.00	-0.60	+0.49	+0.39
S	-0.03	4.00	-0.00	+0.00	+0.03
vacMo+S2	-0.11	3.75	-0.01	-0.00	+0.14
vacS2+Mo	-1.36	3.50	-0.25	+1.32	+0.20
Mo	-0.07	3.50	-0.01	+0.00	+0.06
vacMo	-0.80	2.50	-1.20	-	+0.68
vacMo+S	-0.81	2.25	-0.78	-0.28	+0.47
vacS2	-1.05	1.75	-1.03	-	+0.48
vacS	-0.86	1.50	-1.03	-	+0.46

The monolayer is more metallic than the **semiconducting tip**

➔ significant charge transfer takes place from the substrate to the tip

How to interpret the information?

tipCu	F_m(nN)	d_m(Å)
vacMo	-3.42	1.75
vacS	-2.07	1.75
vacS2	-1.85	1.75
Mo	-0.88	2.50
vacMo+S	-1.56	2.75
vacS2+Mo	-1.07	3.00
S	-1.00	3.00
vacS+Mo	-1.01(-1.51)	3.50(3.75)
vacS2+Mo2	-0.93(-1.18)	3.75(3.75)
vacMo+S2	-1.11	4.25

tipSi	F_m(nN)	d_m(Å)
vacS2+Mo2	-1.80(-2.55)	4.00
vacS+Mo	-1.55(-2.17)	4.00
S	-0.03	4.00
vacMo+S2	-0.11	3.75
vacS2+Mo	-1.36	3.50
Mo	-0.07	3.50
vacMo	-0.80	2.50
vacMo+S	-0.81	2.25
vacS2	-1.05	1.75
vacS	-0.86	1.50

- **@ 3 Å : pristine S**
  BUT: vacMo force ~2nN @ 3 Å ➔ competing with 'pristine' S !

➡ **Need to check for force curve**

- Metallic defects at long distances

- **S network deduced** from:
  - vacS position at short distances
  - vacS+Mo, vacS2+Mo2 at large distances

AFM simulations: conclusions

- How strong is the influence of the AFM tip?
- Can we identify or at least discriminate between certain defects by force spectroscopy?
- Can we transfer atoms from tip to sample and *vice-versa*? (doping, manipulation, …)

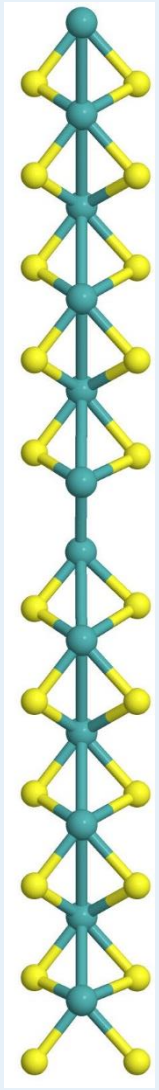
?

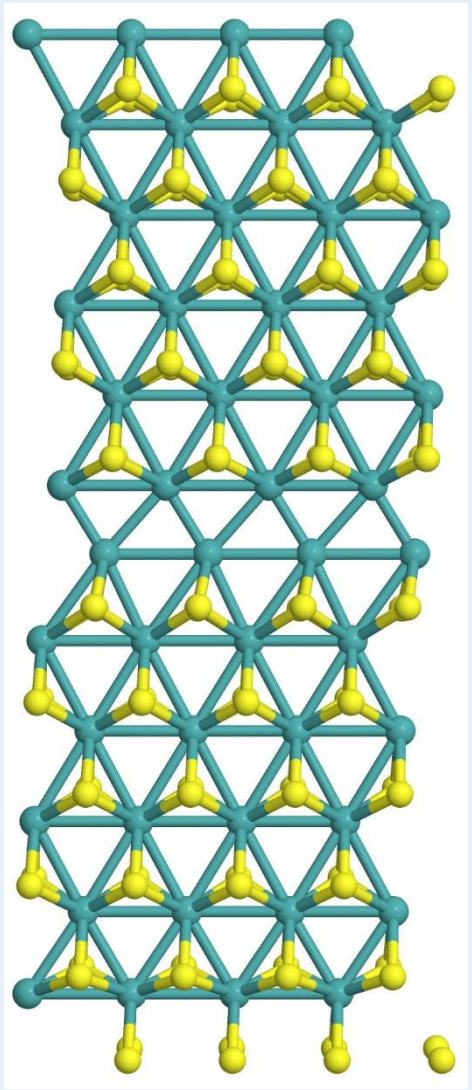
- Characterization of all **features** (S and Mo atoms, their vacancies and the corresponding antisites) by force minimum and tip-sample distance
- Great reactivity **enhancement** in the MoS_2 monolayer in the presence of defects
  ➔**metal-semiconductor junction between the tip and the MoS_2 substrate**
- Atoms transference from/to tip-sample ➔ tool to **locally modify the electronic environment**

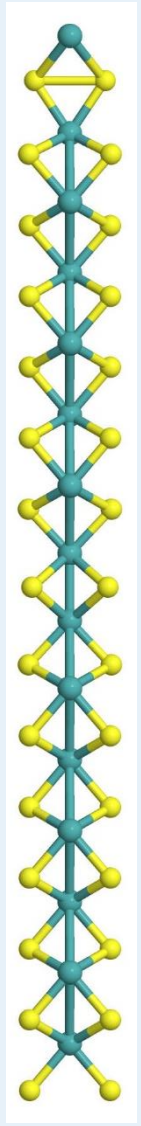
C. González, Y. Dappe, BB, J. Phys. Chem. C 120 (30), 17115-1712

Work in progress: extended defects (grain boundaries -GBs)

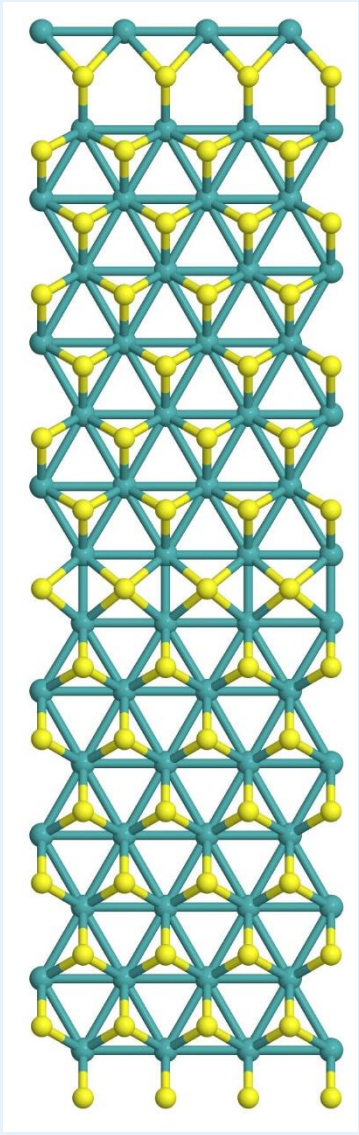
GB1 (mirror)

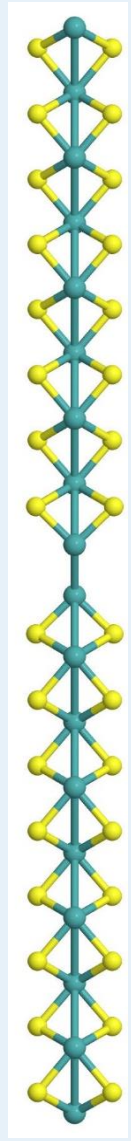




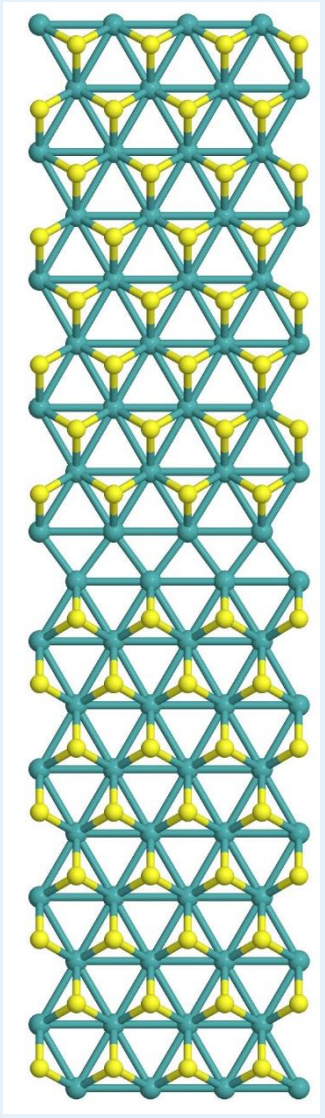


GB2



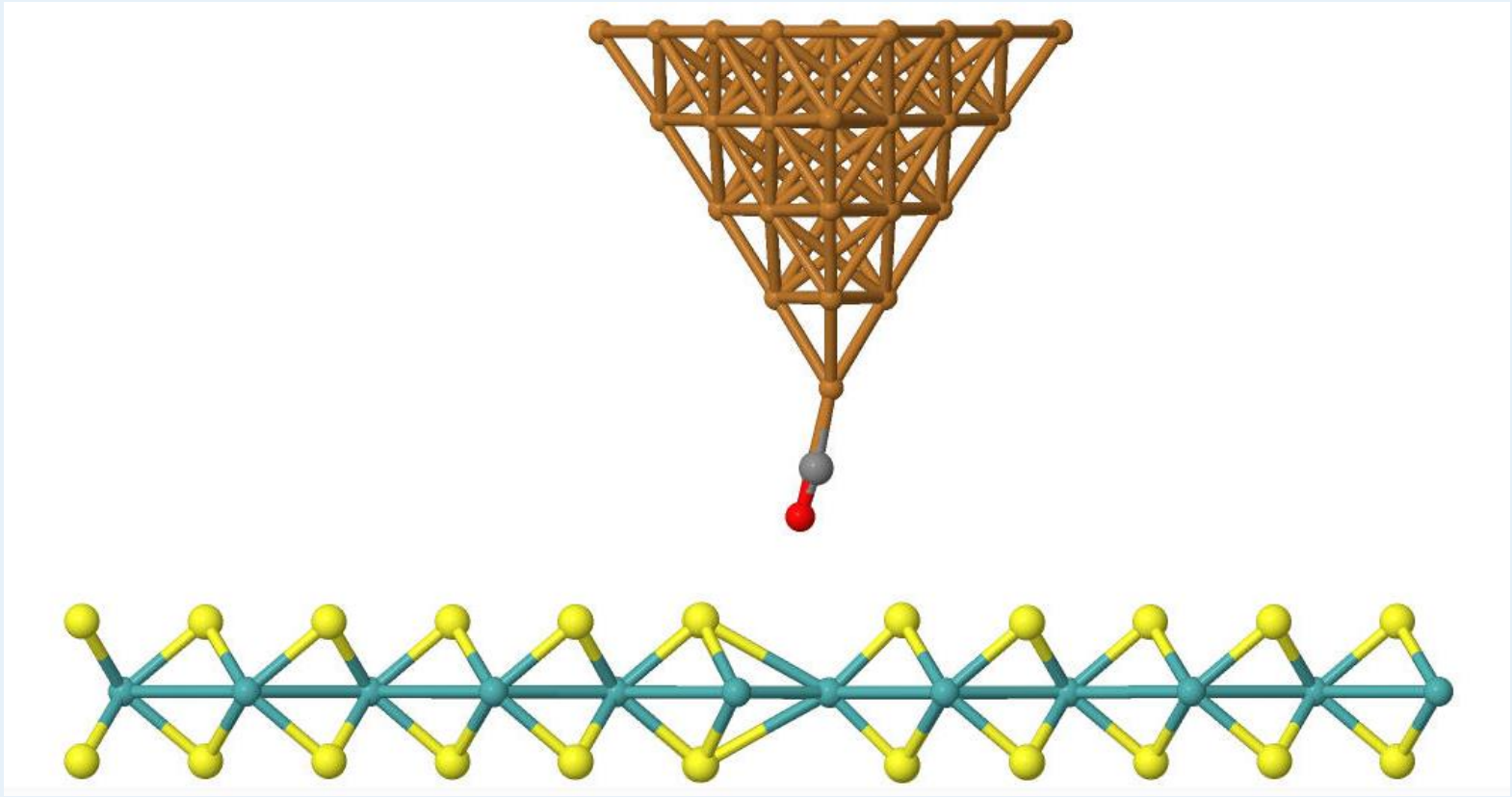


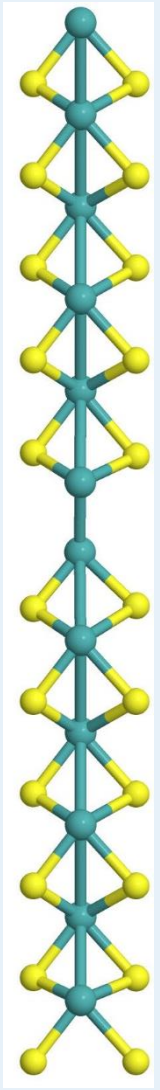
GB3

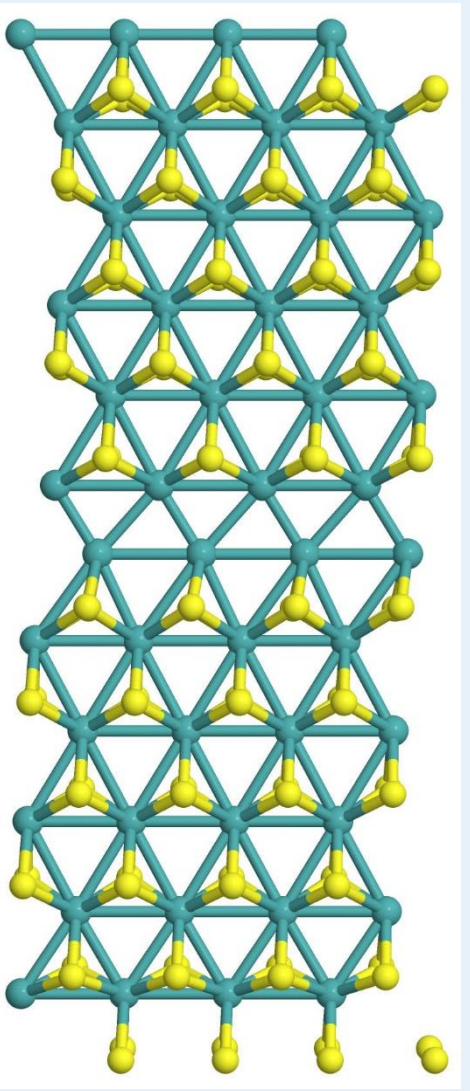


Work in progress: extended defects (grain boundaries -GBs)

CO tip on GB1

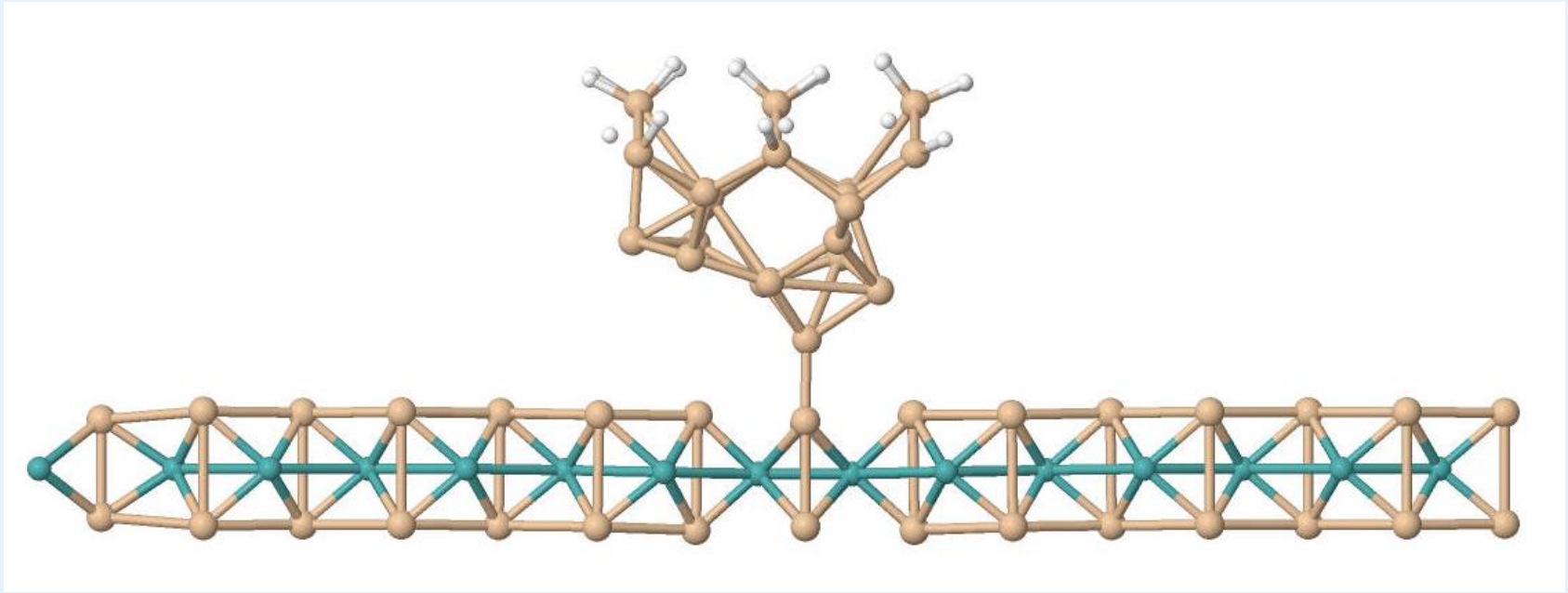


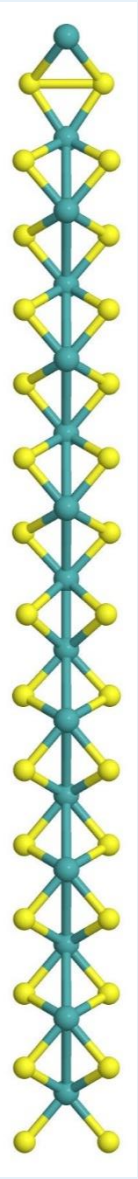


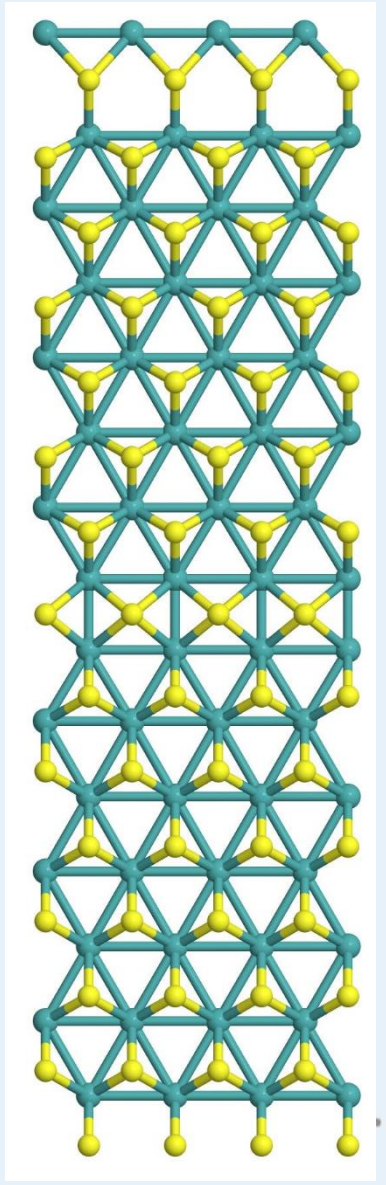


Work in progress: extended defects (grain boundaries -GBs)

Si tip on GB2



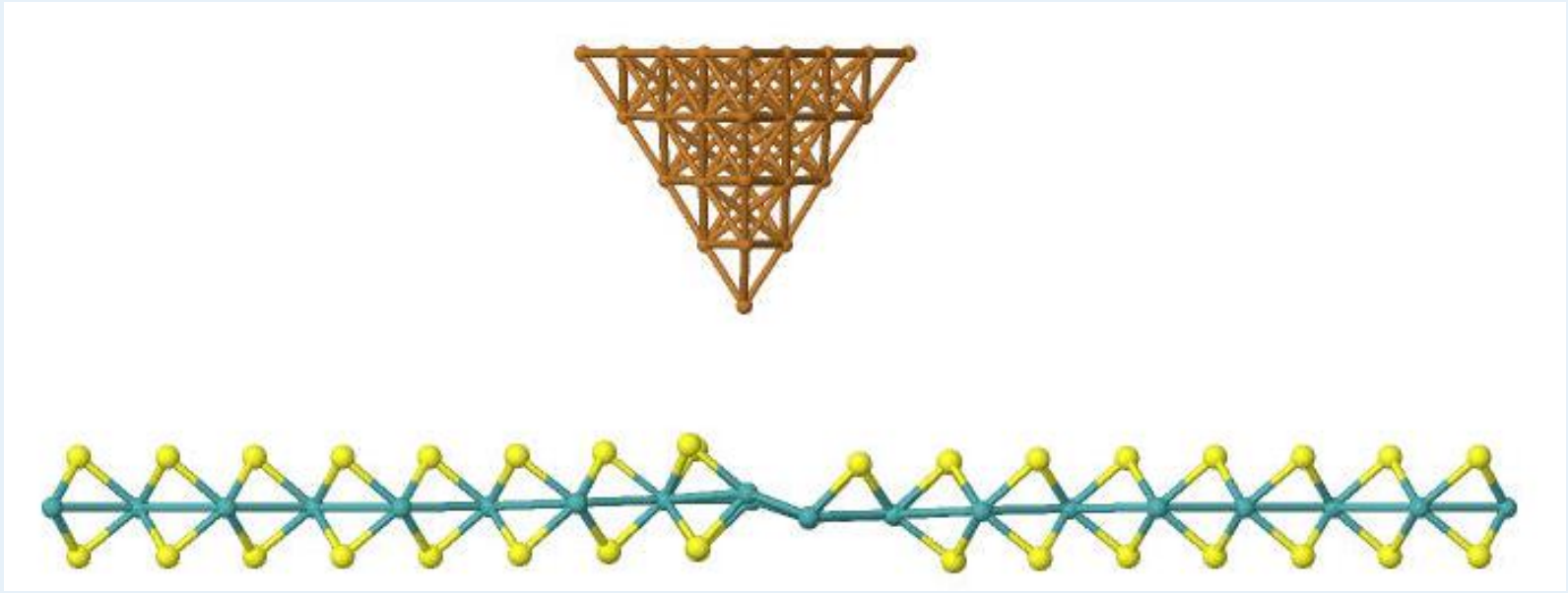


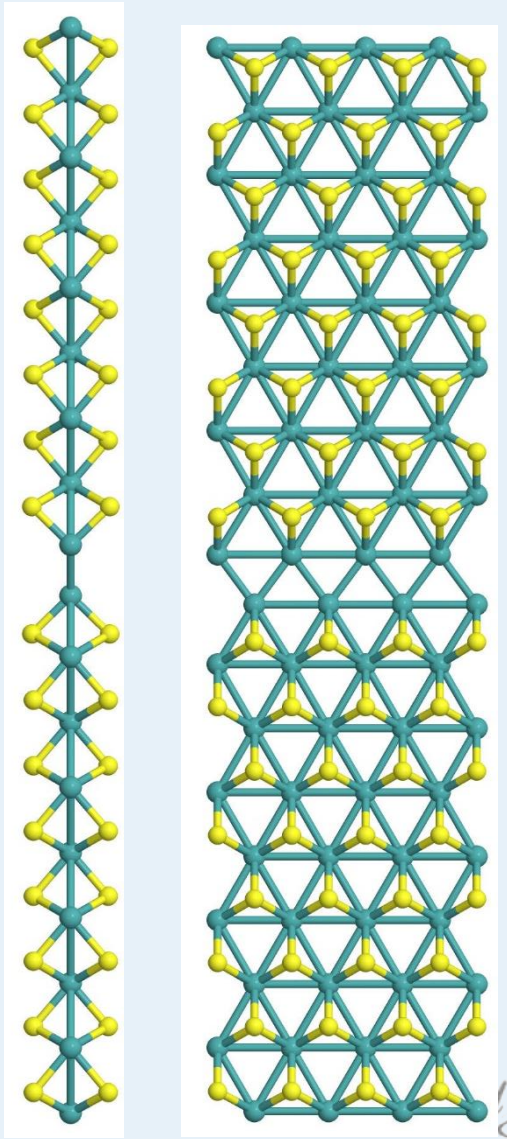


Universidad de Granada

Work in progress: extended defects (grain boundaries -GBs)

Cu tip on GB3





Thank you for your attention!