Defects fingerprints in single layer MoS$_2$
by *ab initio*-based STM and AFM simulations

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Acknowledgements

Collaborators:

Dr. Yannick Dappe

Dr. César González

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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

Most common defects:

- PVD: antisites $\rightarrow$ vacS+Mo, vacS2+Mo
- ME, CVD: vacS, vacS2
- But also: vacMo, vacMo+S, ...

Different impact on properties (tuning!) $\rightarrow$ sample characterization

Exploiting atomic defects in molybdenum disulphide monolayers

Jinhua Hong, Zhixin Hu, Matt Probert, Kun Li, Danhui Lv, Xinan Yang, Lin Gu, Nannan Mao, Qingliang Feng, Liming Xie, Jin Zhang, Dianzhong Wu, Zhiyong Zhang, Chuanhong Jin, Wei Ji, Xixiang Zhang, Jun Yuan & Ze Zhang

STEM-ADF image
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)?

<table>
<thead>
<tr>
<th>Clean</th>
<th>V-Mo</th>
<th>V-Mo+S</th>
<th>V-Mo+S2</th>
<th>V-S</th>
<th>V-S+Mo</th>
<th>V-S2</th>
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<tr>
<td>$E_g$(eV)</td>
<td>1.70</td>
<td>0.64</td>
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<td>1.25*</td>
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<td>no gap</td>
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Motivation: selected defects

Are all defects equivalent?

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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)
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

- $H = H_{\text{Tip}} + H_{\text{interaction}} + H_{\text{Sample}}$  \(\xrightarrow{\text{DFT-LDA FIREBALL code}}\)

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

Theoretical STM model

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

\( H = H_{\text{Tip}} + H_{\text{interaction}} + H_{\text{sample}} \)

DFT-LDA FIREBALL code

Au(111) tip


MoS$_2$: 6x4 single layer

- Keldysh-Green’s functions formalism
STM simulations

• **STM images:**

  Determination of atom/defect position $\Rightarrow$ geometric effects should dominate (in principle)
  
  - bright protrusión $\leftrightarrow$ atom closer to tip
  - dark holes $\leftrightarrow$ 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:

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 $\sim$ -2V – 3.4V
STM simulation of pristine MoS$_2$ monolayer

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(WSxM software)

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- 4.0 Å, 4.5 Å, 5.0 Å
- No changes with distance
- Voltage range $\sim$ -2V – 3.4V

$V = -0.1$ (occupied states)

Triangular pattern

DOS

\begin{align*}
\text{energy (eV)} & : -4 & -2 & 0 & 2 & 4 \\
\text{DOS} & : 0 & 1
\end{align*}

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)  
V = +1.9 (empty states)

STM simulated images

- S atoms
- Mo atoms

Geometry effects

DOS compensation

DOS

\[ \text{energy (eV)} \]

-4 -2 0 2 4
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

![STM simulated images](image)

- **Triangular pattern**
  - $V = -0.1$ (occupied states)
  - $V = +1.9$ (empty states)

- **Asymmetric hexagonal pattern**

![DOS chart](image)

- **Geometry effects**
- **DOS compensation**

- Further voltage increase $\rightarrow$ triangular pattern
- Experimental confirmation?
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) $\rightarrow$ three brilliant spots in the neighboring S atoms, not directly over the S
  ($p$-character of the S dangling bond $\rightarrow$ opposite direction to the original bond)

- **Images @ −1.9 V** (filled states) $\rightarrow$ dangling bond effect reduced $\Rightarrow$ 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 $\rightarrow$ lower contribution to current than other S
- Asymmetric position of subs-S $\rightarrow$ sharp peak in DOS of far S neighbor $\rightarrow$ change of contrast
- $V = -1$ V $\rightarrow$ 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

- 2 subs-S no connected to Mo atoms but to S atoms:
  - S-vars atoms in a semioccupied state (sharp peak)
  - bright at low V
  - dark at high V, recovering pristine image

Dependence on applied voltage

V = + 1.9

DOS

V = + 0.5
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

S divacancy – our simulation

DOI: 10.1021/acs.jpcc.6b02073

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:

$V = +1.9$

One or two Mo atoms in an empty S site

("metallic" defects)

Bright protrusión

(regardless of voltaje)
STM simulations: conclusions

- **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
Atomic Force Microscopy simulations

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)**

\[
\Delta f = \frac{f_0}{2\pi kA_0} \int_0^{2\pi} F_{TS} [d + A_0 + A_0 \cos \phi] \cos \phi d\phi
\]

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 $\rightarrow$ force minimum value
  - Type of interaction $\rightarrow$ tip-sample distance at minimum force

- Comparison of force curves $\rightarrow$ discrimination between defects?
AFM simulations of pristine MoS$_2$ monolayer

- 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**

- 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

**Expected nc-AFM images obtained at 3 Å**

- Triangular pattern

**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

- Hexagonal pattern (asymmetric)
AFM simulations of pristine MoS$_2$ monolayer

- **Tip interaction** $\rightarrow$ 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 $\rightarrow$ over a Mo vacancy
- Capture of apex atoms
- Transfer of atoms from sample to tip
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 \rightarrow 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:**

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

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?

<table>
<thead>
<tr>
<th>tipCu</th>
<th>$F_m$(nN)</th>
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<tr>
<td>vacMo</td>
<td>-3.42</td>
<td>1.75</td>
</tr>
<tr>
<td>vacS</td>
<td>-2.07</td>
<td>1.75</td>
</tr>
<tr>
<td>vacS2</td>
<td>-1.85</td>
<td>1.75</td>
</tr>
<tr>
<td>Mo</td>
<td>-0.88</td>
<td>2.50</td>
</tr>
<tr>
<td>vacMo+S</td>
<td>-1.56</td>
<td>2.75</td>
</tr>
<tr>
<td>vacS2+Mo</td>
<td>-1.07</td>
<td>3.00</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>-1.00</td>
<td>3.00</td>
</tr>
<tr>
<td>vacS+Mo</td>
<td>-1.01(-1.51)</td>
<td>3.50(3.75)</td>
</tr>
<tr>
<td>vacS2+Mo2</td>
<td>-0.93(-1.18)</td>
<td>3.75(3.75)</td>
</tr>
<tr>
<td>vacMo+S2</td>
<td>-1.11</td>
<td>4.25</td>
</tr>
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- **@ 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

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<td>1.50</td>
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- **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

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

Cu tip on GB3
Thank you for your attention!