SAND2022-2866C

Interactions of environmental species with pristine and defective MoS_2

N. Scott Bobbitt and Michael Chandross

Sandia National Laboratories, Albuquerque NM

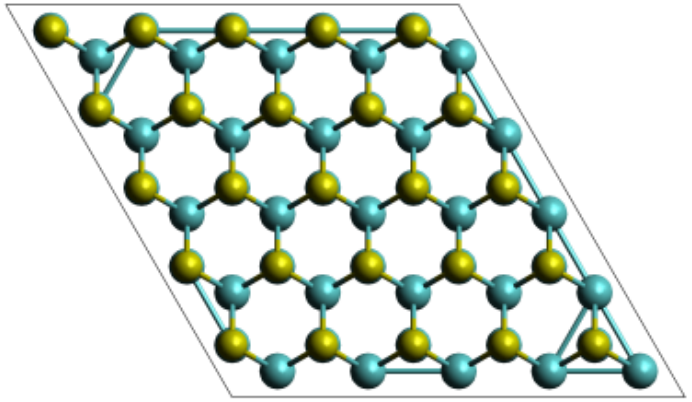
Tribology Letters, **69**, 96, (2021)
Bobbitt, Chandross, *in prep*

Sandia National Laboratories

LDRD Laboratory Directed Research and Development

ASC

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

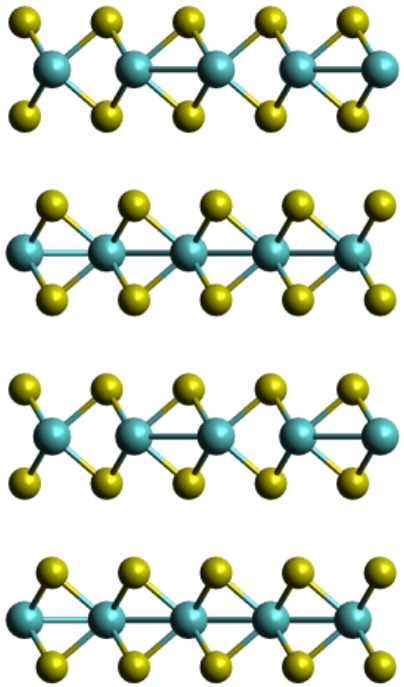


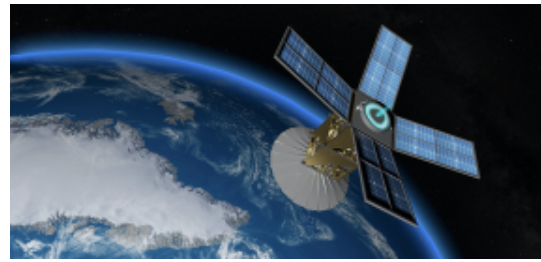
MoS_2 (molybdenum disulfide) is a metal dichalcogenide that forms hexagonal 2D layered sheets similar to graphene.

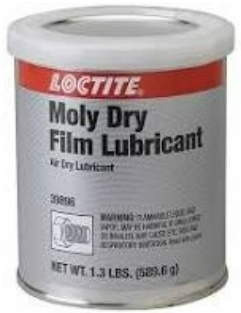
MoS_2 is a semiconductor used in microelectronics and also a catalyst used in hydrodesulfurization and hydrogenation reactions.

Also widely used as a dry lubricant, often for aerospace applications.

Extremely low coefficient of friction.







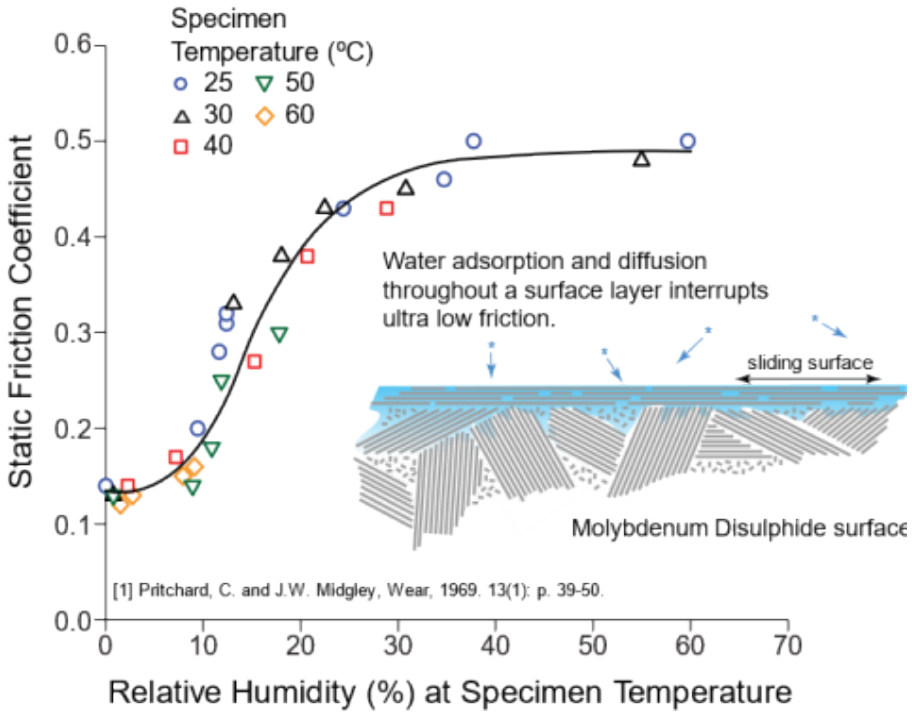
A 2017 ARPA-E commissioned study estimated up to 22.8 Quads (25% of total consumption) can be saved in the US alone by deployment of friction & wear reducing technologies[1]

An annual savings potential of ~ 1.0 – 1.5% GDP ($250 billion / year in 2020) by reducing wear and friction[2-4]

References:
1. ARPA-E report, “Tribology Opportunities for Enhancing America’s Energy Efficiency,” (2016) contract no. DE-AR00282
2. Jost, H. Peter. “*Lubrication: Tribology; Education and Research; Report on the Present Position and Industry's Needs*” (submitted to the Department of Education and Science by the Lubrication Engineering and Research) Working Group. HM Stationery Office, 1966.
3. Jost, H. Peter. "*Tribology—origin and future*." Wear 136.1 (1990): 1-17.
4. Jost, H. Peter. "*Tribology micro & macro economics: A road to economic savings*." Tribology & Lubrication Technology 61.10 (2005): 18

Lubrication can save a lot of money and energy!

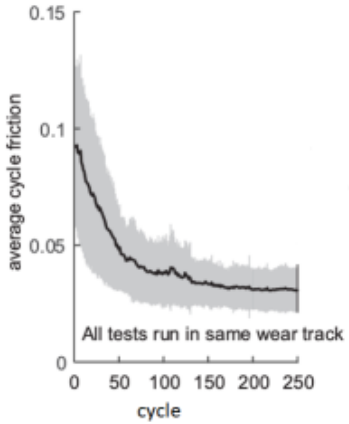
Humidity increases the friction coefficient.



Water reduces effectiveness of MoS_2 lubricants.

For some applications, devices must sit idle for years and be able to work on first try.

Limits utility for many applications, requires larger margins in engineering.



Mechanism of water/aging effect is poorly understood.

Hypotheses:

- water induces hydrogen bonds between lamella
- water prevents flakes forming into large sheets
- oxygen from atmosphere oxidizes MoS_2 into MoO_3
- water from bulk diffuses up to surface (re-run-in)

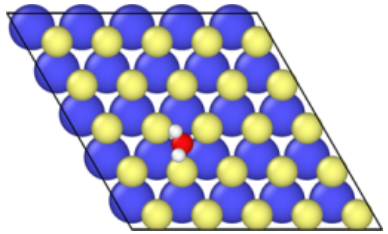
GOAL: To understand water adsorption on MoS_2 in realistic conditions and how that affects friction.

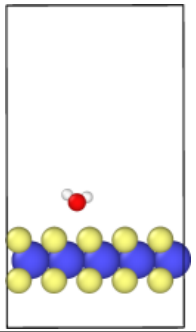
First we compute water binding energy on monolayer of MoS_2 using DFT

MoS_2 generally thought to be slightly hydrophobic (contact angle ≥ 70°). How does water interact with defects?

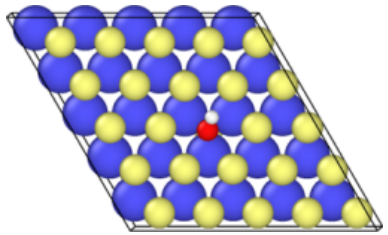
DFT calculations
VASP, PBE functional with D3 dispersion

No defect

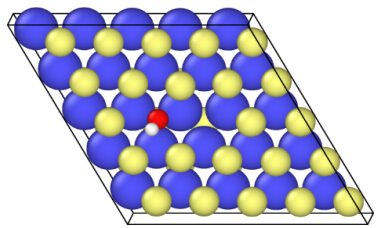




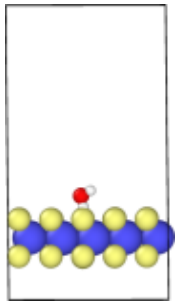
-12 kJ/mol



1 S vacancy

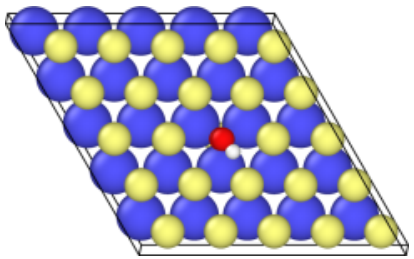


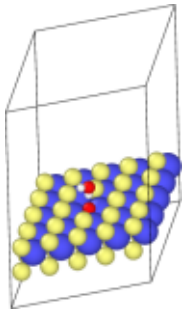
2 S vacancy, adj



-22 to -23 kJ/mol

O sub





-31 kJ/mol

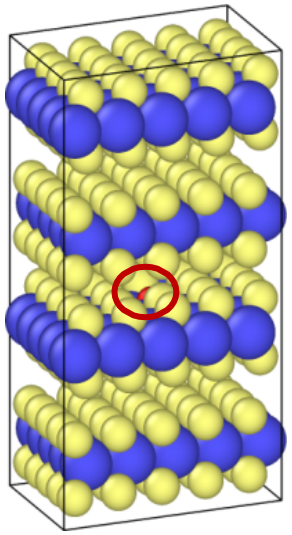
Defects bind water stronger than pristine MoS_2

Water Adsorption in Bulk MoS_2

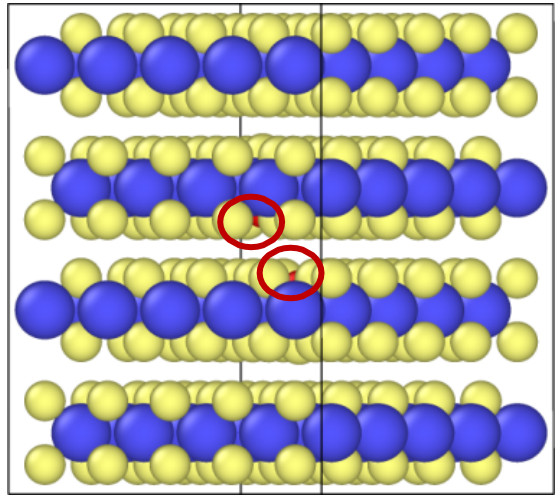
Adsorption on monolayer is informative but we also care about water in bulk MoS_2.

Consider 4 different structures with different arrangements of defects.

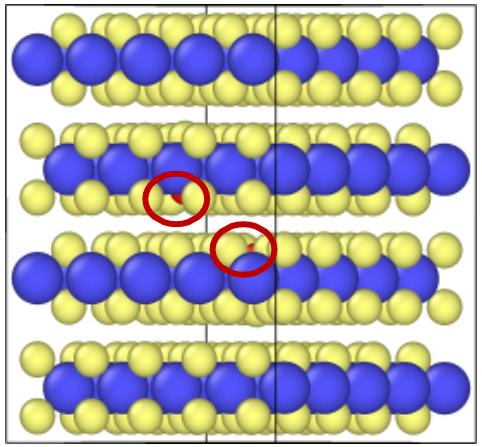
Structure I: 1 defect (S vacancy or O substitution)
Structure II: 2 defects on opposing sheets
Structure III: 2 defects on opposing sheets, farther away
Structure IV: 2 adjacent defects on same sheet



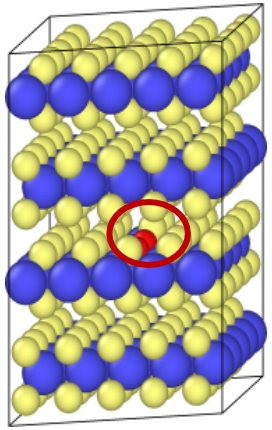
Structure I



Structure II



Structure III



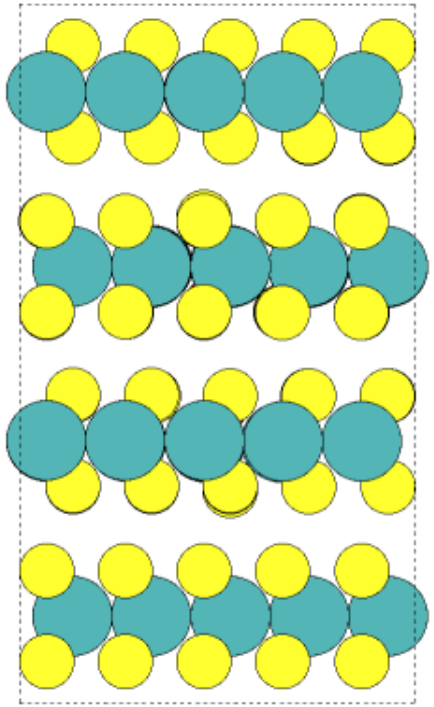
Structure IV

kJ/mol	Total Energy
	Change
No Defect	221.5
S-I	-0.5
S-II	-1.9
S-III	2.0
S-IV	-18.3
O-I	134.1
O-II	44.3
O-III	134.3
O-IV	69.3

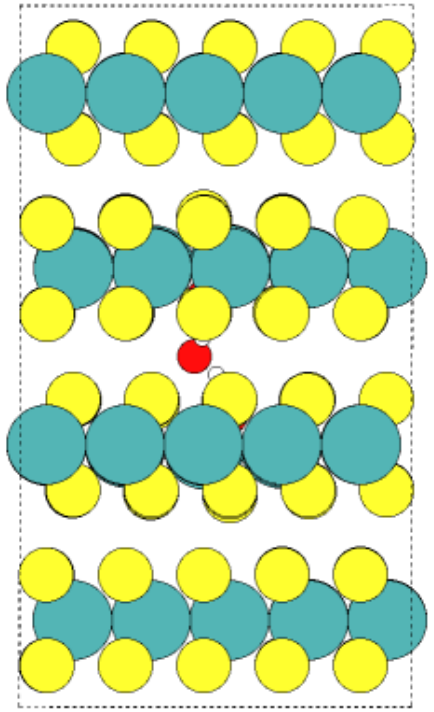
Water adsorption on S vacancies neutral or slightly favorable.

Adsorption on pristine or O dopants highly unfavorable due to structure changes.

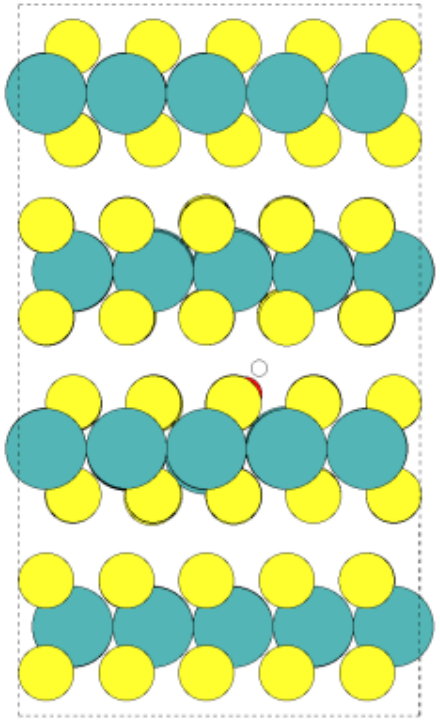
Interlayer space too tight for water molecule, but S vacancy permits adsorption.



Dry



Water on O sub

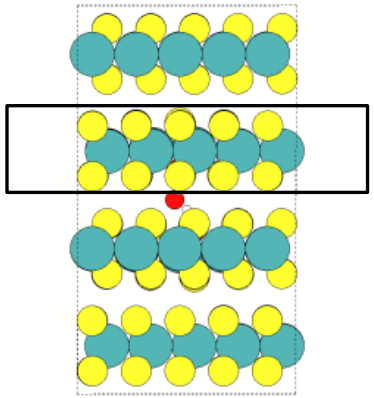


Water on S vacancy

3D periodic boundaries

Chance in vertical (Z) position of Mo layer above the water.

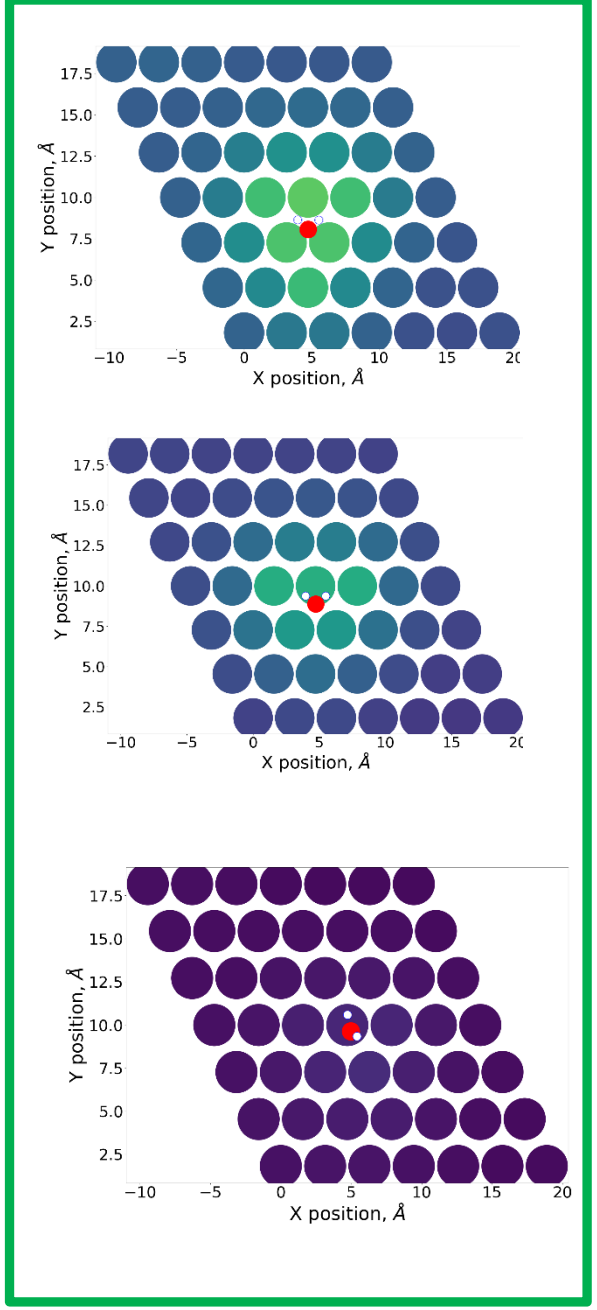
Bulk

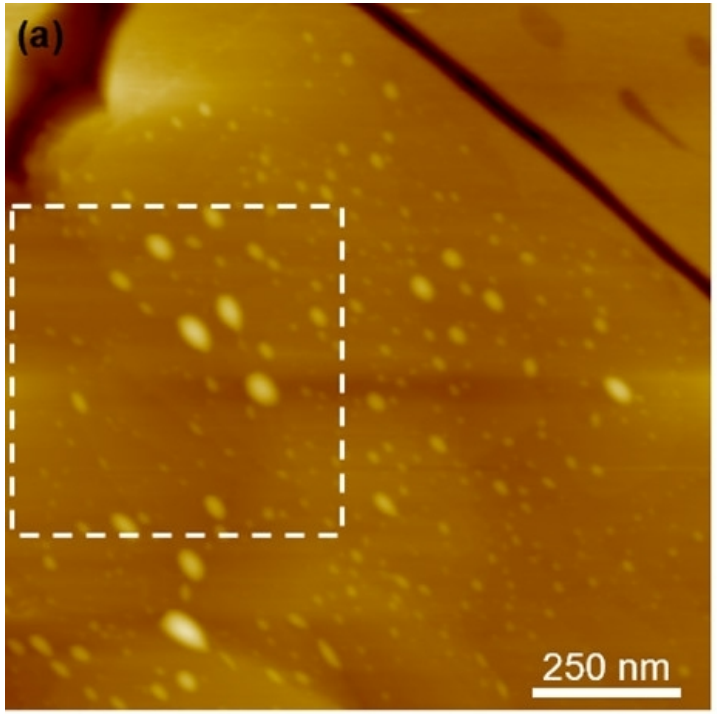


No defect

Oxygen sub

S vacancy



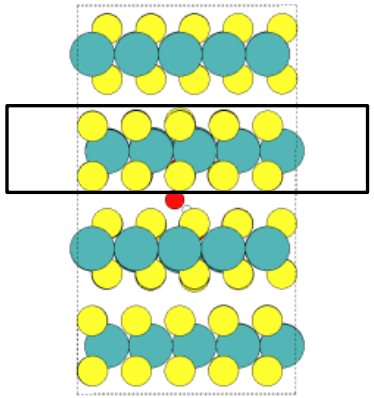


AFM image of water bubbles in MoS_2 on Au111

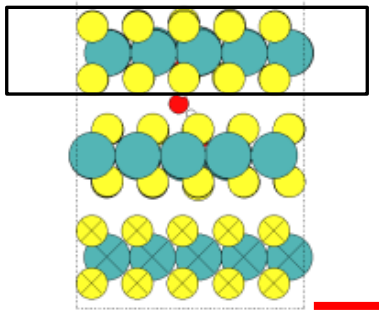
Batteas et al., ACS Nano 2020, 14, 12, 16939-16950

Chance in vertical (Z) position of Mo layer above the water.

Bulk



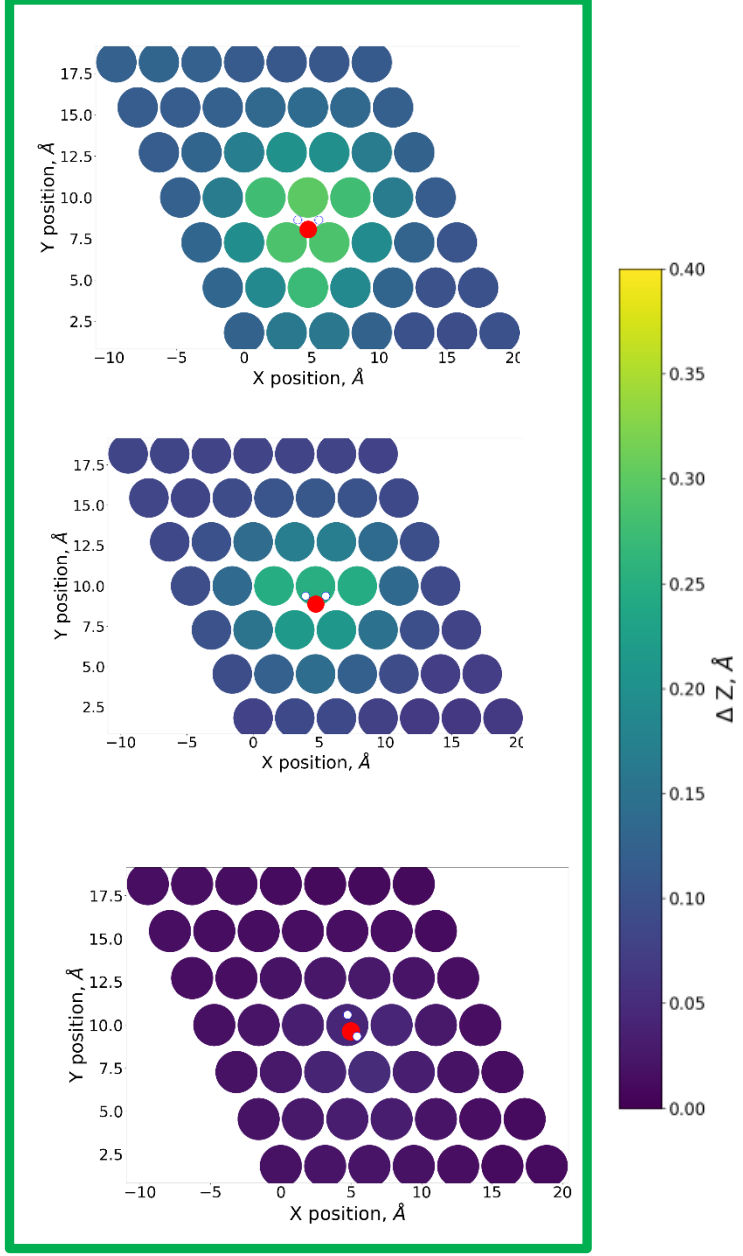
Surface

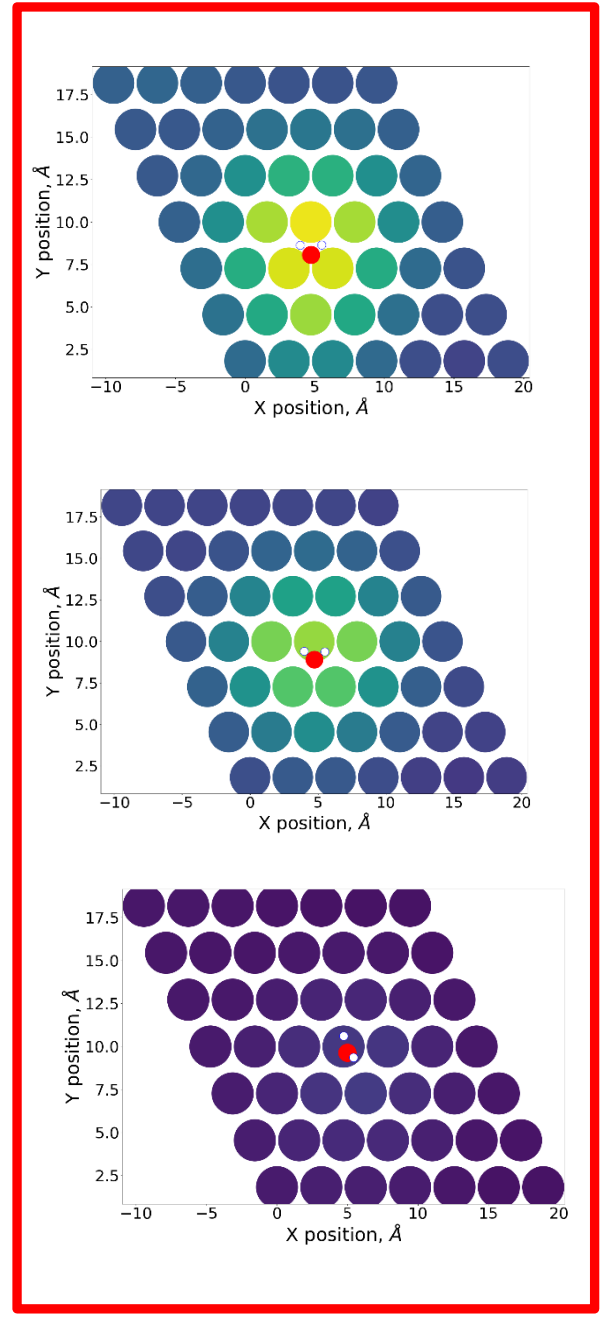


No defect

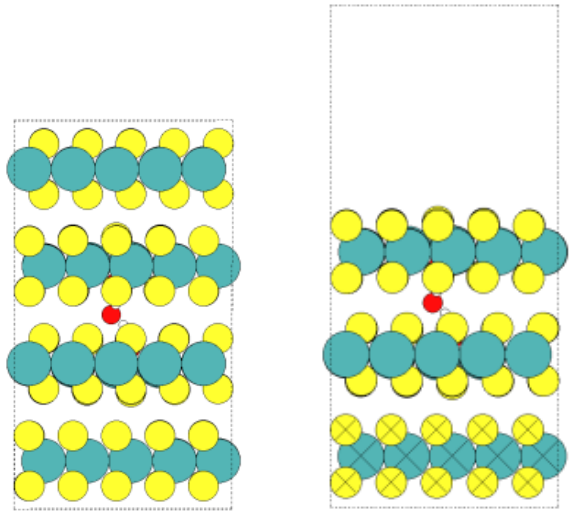
Oxygen sub

S vacancy





kJ/mol	Bulk	Surface	Diff
No Defect	221.5	214.7	-6.8
S vac I	-0.5	-1.3	-0.8
S vac II	-1.9	-5.1	-3.1
S vac III	2.0	-1.8	-3.9
S vac IV	-18.3	-21.5	-3.1
O sub I	134.1	128.1	-6.0
O sub II	44.3	39.0	-5.3
O sub III	134.3	127.7	-6.6
O sub IV	69.3	65.1	-4.2



Bulk

Surface

Water is adsorbed to bulk MoS_2 during synthesis and is very difficult/impossible to remove.

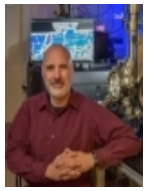
Water adsorption under surface layer consistently more favorable than in bulk MoS_2.

This implies water will migrate from bulk to the surface layers, impacting the tribology.

Defect density: 1 (or 2) vacancies per 200 S atoms

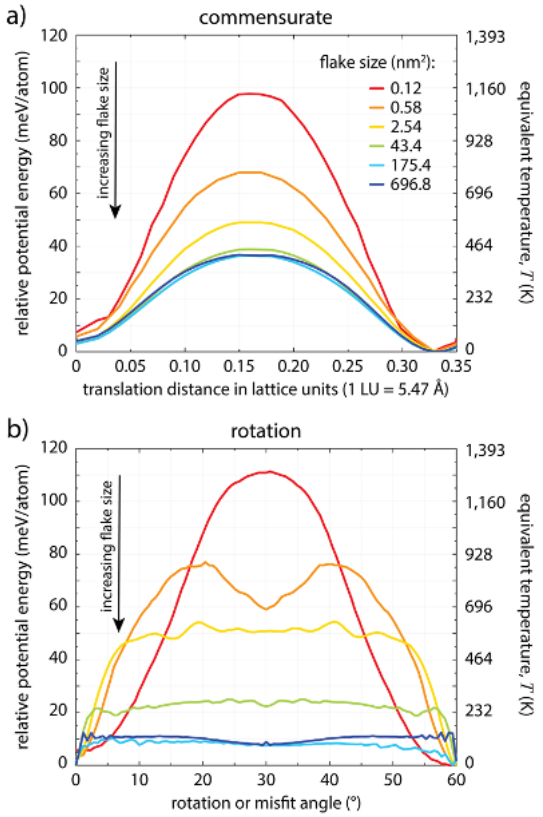
Naturally occurring MoS_2: ~1% vacancies

Water's effects on friction



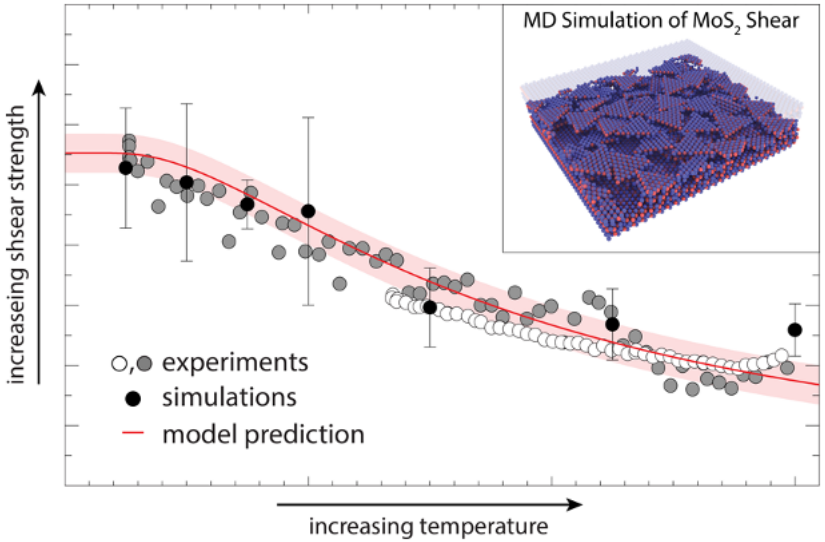
Mike Chandross

Prior work at SNL developed a model for predicting friction in MoS_2 based on energy barriers from NEB (nudged elastic bands) calculations.



Computed energy barriers

$$\tau(T) = \tau_0 f_{slide}$$
$$= \tau_0\left[1 - \exp\left(-\frac{T_i + T_\tau}{T}\right) - \exp\left(-\frac{T_c}{T}\right) + \exp\left(-\frac{T_\tau + T_c}{T}\right)\right]$$



Predictions of shear strength

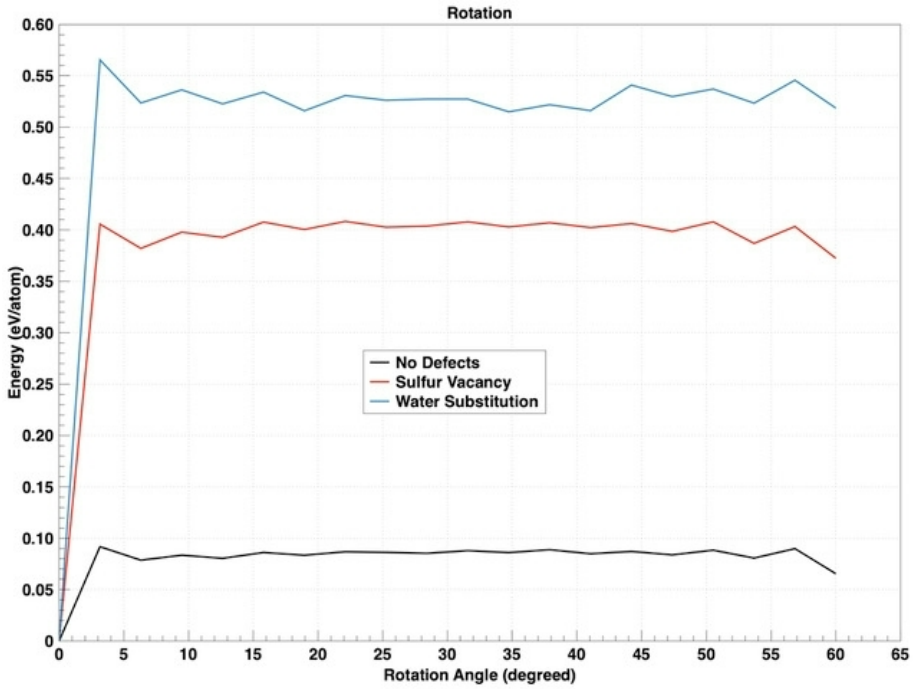
Good agreement with experiments

Curry, J.F., Hinkle, A.R., Babuska, T.F., Wilson, M.A., Dugger, M.T., Krick, B.A., Argibay, N. and Chandross, M., 2018. *ACS Applied Nano Materials, 1*, pp.5401-5407.

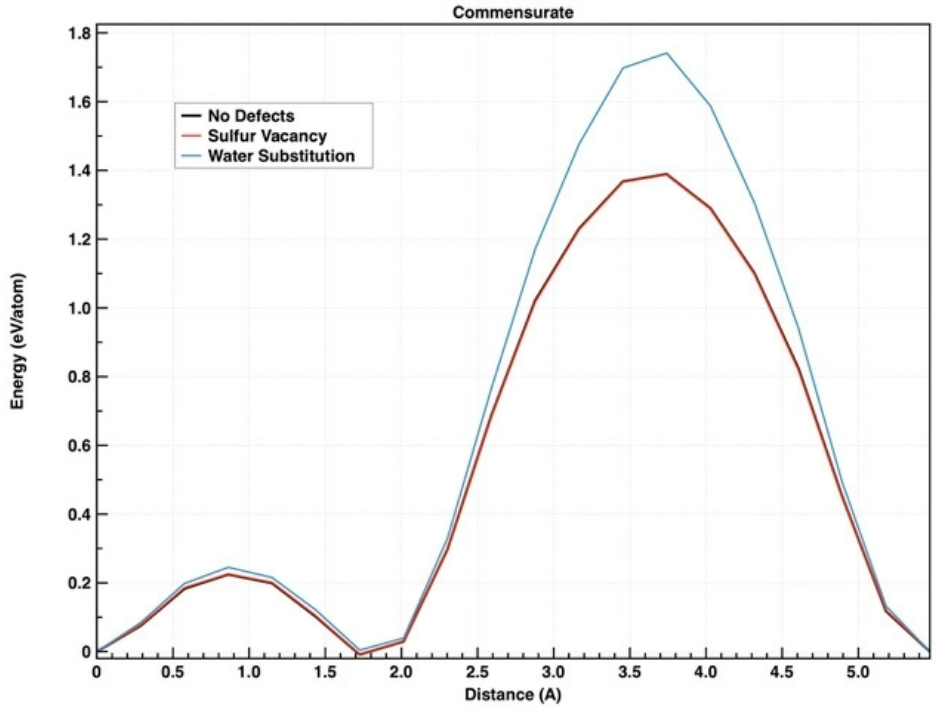
Water's effects on friction

Rotation and sliding (commensurate) barriers are higher with water molecule present.

Previous modeling work indicates the rotational barrier is the most important.



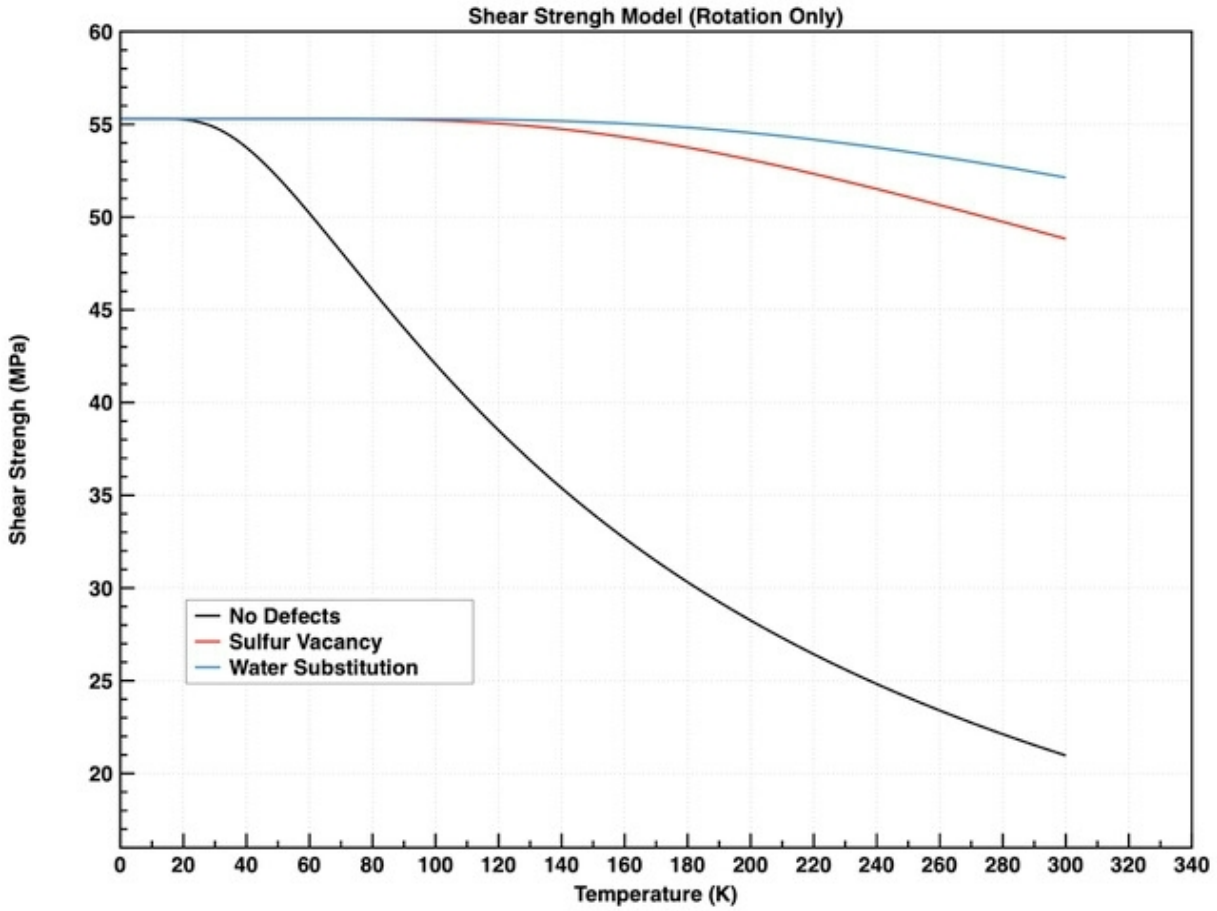
Rotation Barrier



Sliding Barrier

Energy barriers computed in LAMMPS with a flake sliding across a layer containing 1 defect.

Water's effects on friction



Energy barriers are higher when water is present, results in higher friction.

Water causes higher friction but not a large effect.

What happens to MoS_2 in real atmosphere?

How much water is really adsorbed in MoS_2 exposed to air?

How much do defects matter?

MoS_2 is often used in space, but satellites are manufactured on Earth

The atmosphere contains humidity.

Realistic temperatures:		Atmosphere composition:
278 K	(41 F)	78 % nitrogen
298 K	(77 F)	21 % oxygen
313 K	(104 F)	1 % Ar
		0-95% RH (0-7% H_2O)

Grand canonical Monte Carlo simulations using Lennard-Jones potentials

TraPPE for O_2 and N_2
TIP3P for water
Mo and S taken from Gu et al, *Physical Chemistry Chemical Physics* **2017**, *19*, 3039-3045.

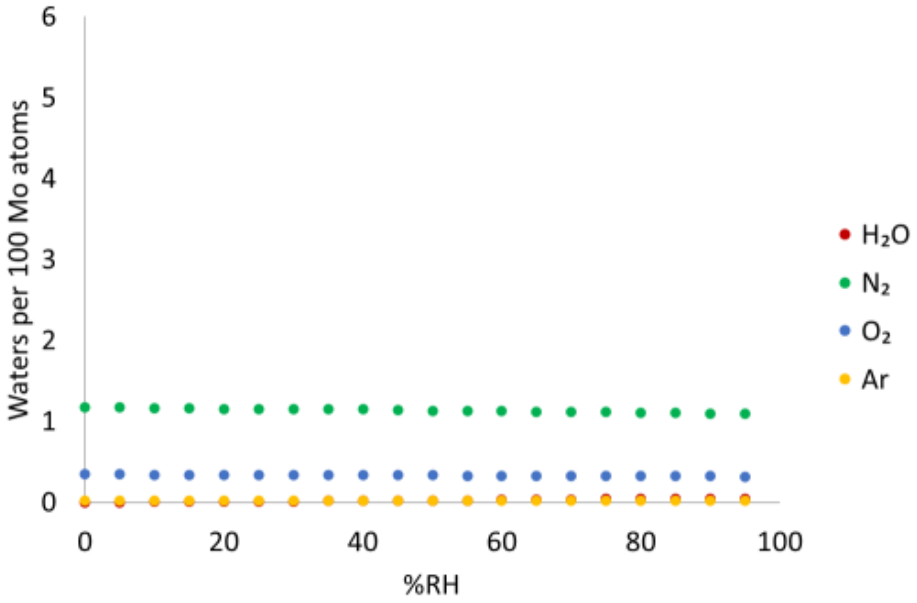
GCMC simulations done in RASPA

Multipurpose simulation code developed by Randy Snurr and David Dubbeldam.

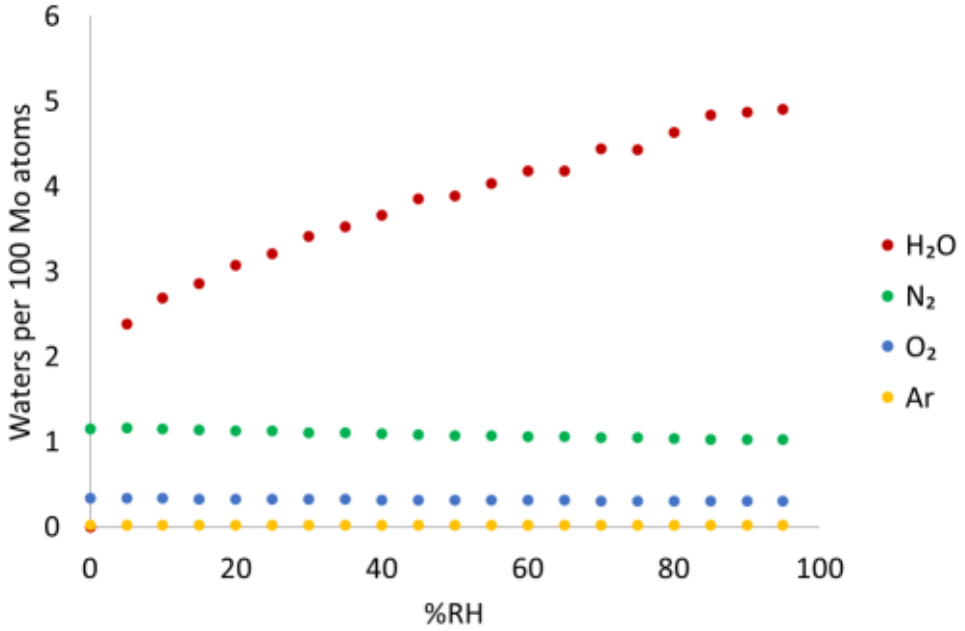
https://github.com/iRASPA/RASPA2

Pristine MoS_2 is hydrophobic.

About 1% S vacancies, adsorbed phase is 60-80% water.



Defect free MoS_2, 313 K

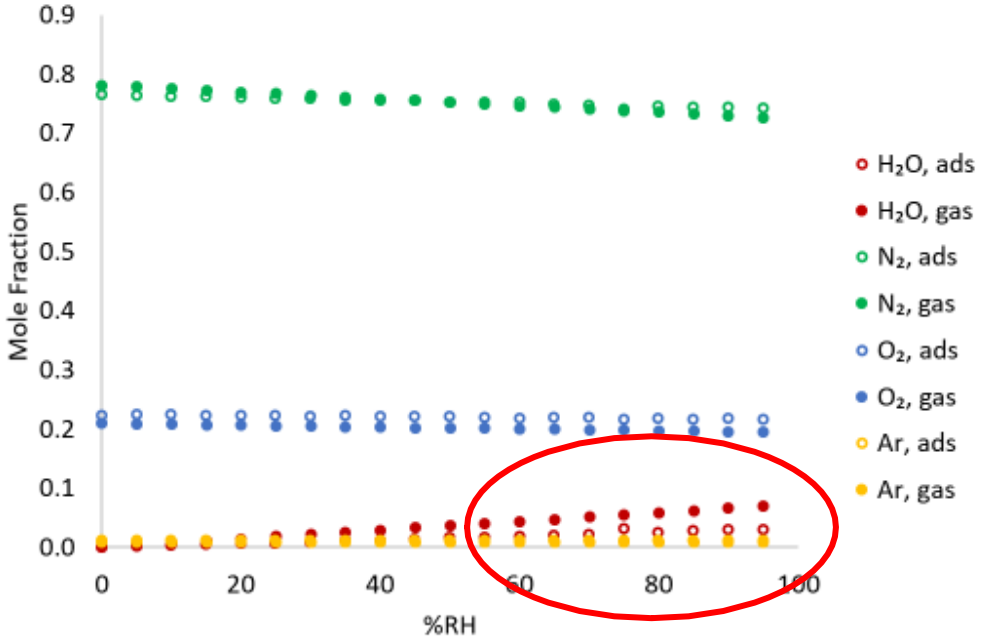


2.3 x 10^{13}/cm^2 defects, 313 K

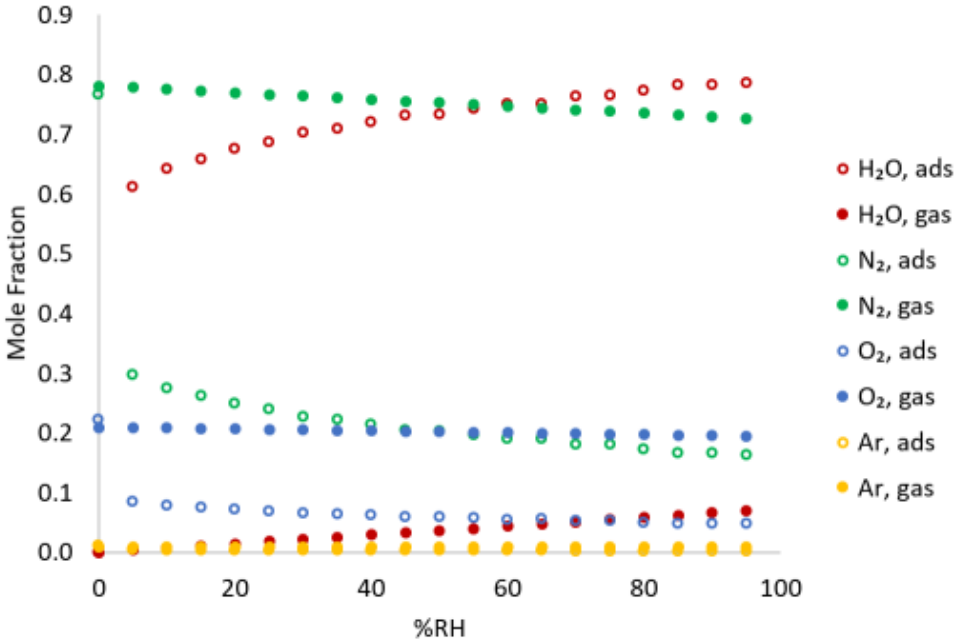
Adding a moderate density of defects greatly increases water uptake.

Adsorbed phase contains less water than gas phase.

This indicates pristine MoS_2 is hydrophobic. Adding defects makes it hydrophobic.

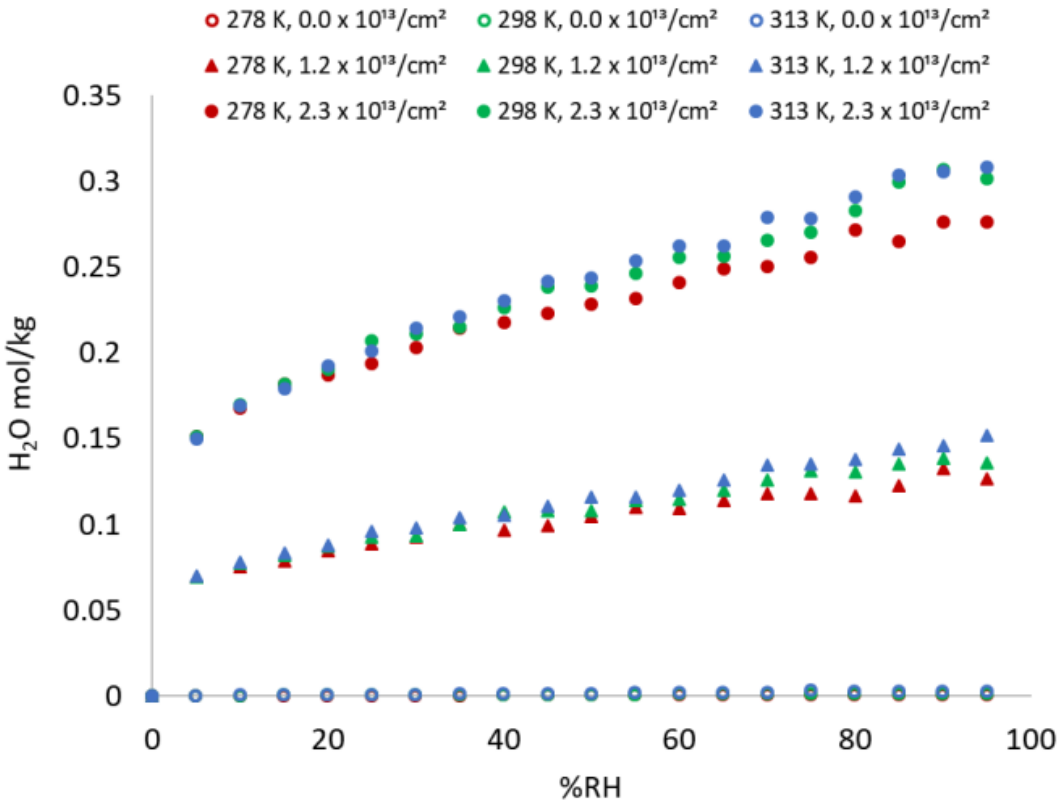


Defect free MoS_2, 313 K



2.3 x 10^{13}/cm^2 defects, 313 K

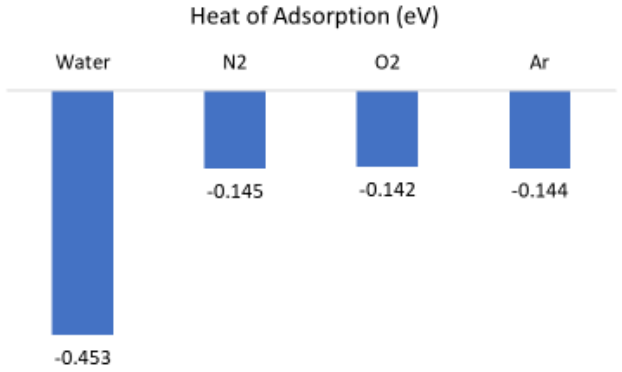
Adding a moderate density of defects greatly increases water uptake.



3 different defect densities (S vacancies)

2.3 x 10^{13} defects/cm^2 corresponds to 1% S vacancies which is close to naturally occurring MoS_2

Bobbitt, Chandross, *in prep*

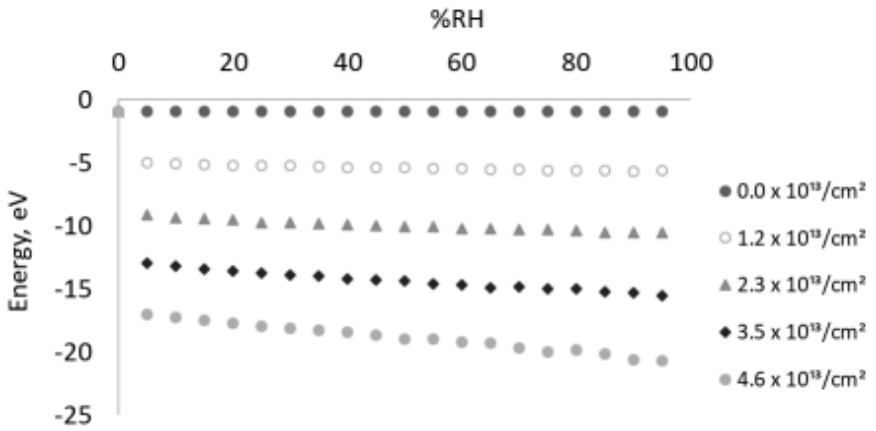


Water heat of adsorption ~3 times higher than other gases.

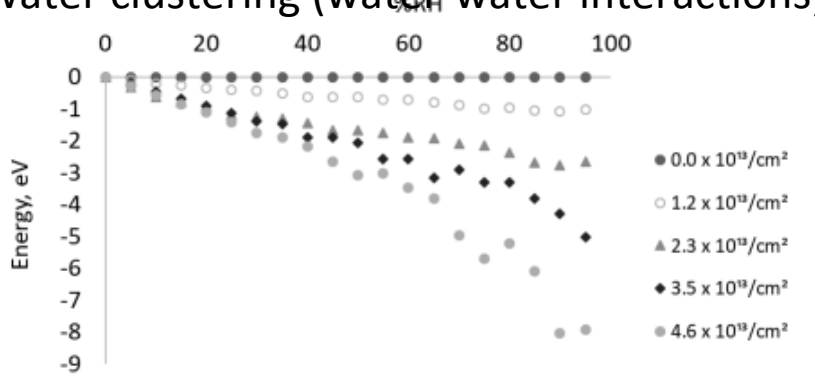
Water will dominate most favorable sites (defects)

Adsorbate-adsorbate increases exponentially at high humidity.

Indicates water clustering (water-water interactions).

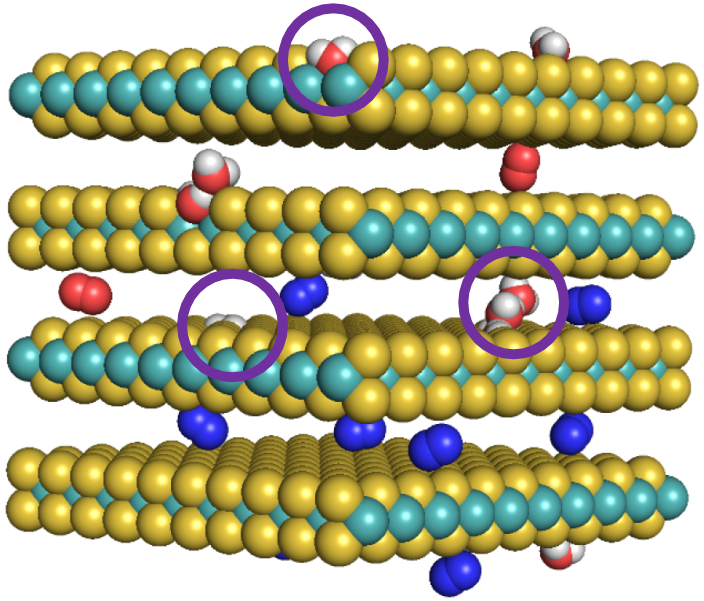


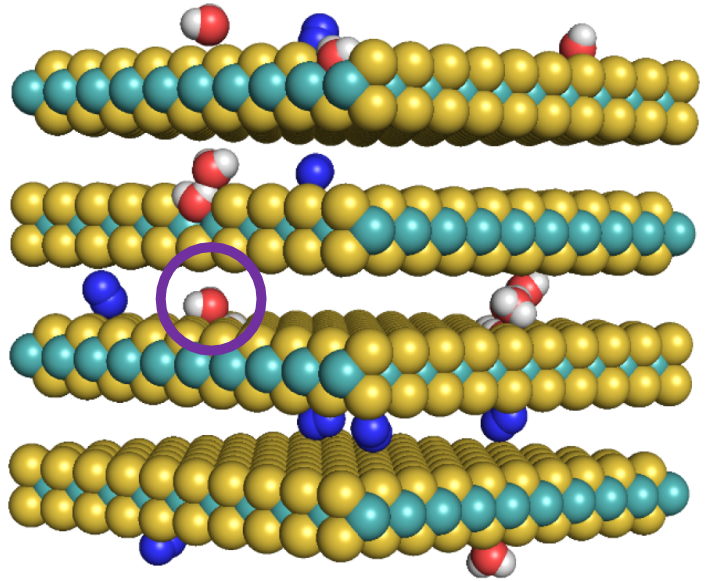
Adsorbate-MoS_2 energy



Adsorbate-adsorbate energy

Two random snapshots
2.3 x 10^{13}/cm^2 defects
298 K, 50% RH

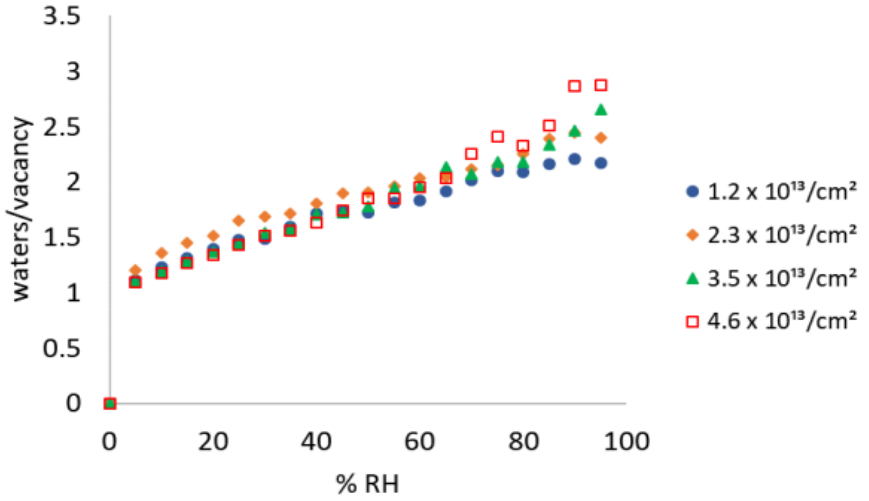




Water molecules are clustered around S vacancy sites.

At lowest humidity, average 1 water molecule per defect

High humidity has 2-3 waters per defect.



Connecting Water to Friction

1. Friction measurements indicate **HIGHER** friction in humid environment.
2. MD simulations indicate **LOWER** friction for **LARGER** flake sizes.
3. DFT simulations indicate **HIGHER** work function with **LARGER** flake sizes.

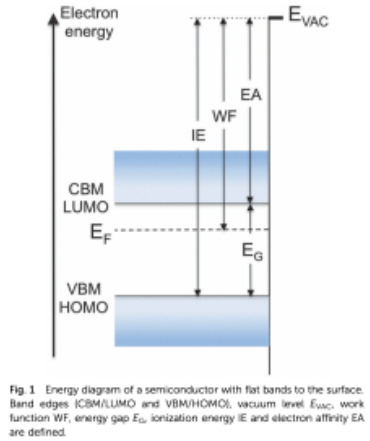
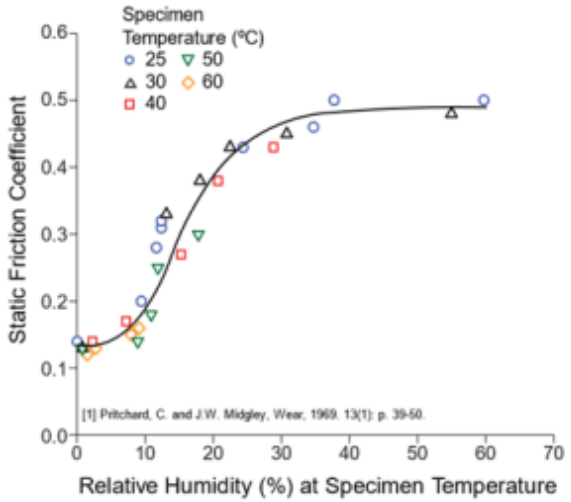
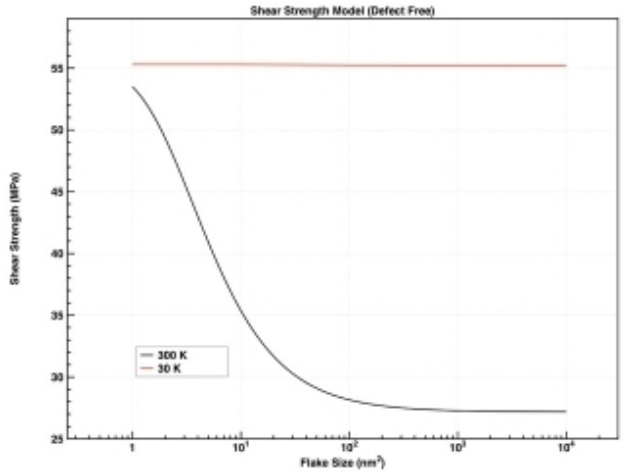


Fig. 1 Energy diagram of a semiconductor with flat bands to the surface. Band edges (CBM/LUMO and VBM/HOMO), vacuum level E_{VAC}, work function WF, energy gap E_G, ionization energy IE and electron affinity EA are defined.

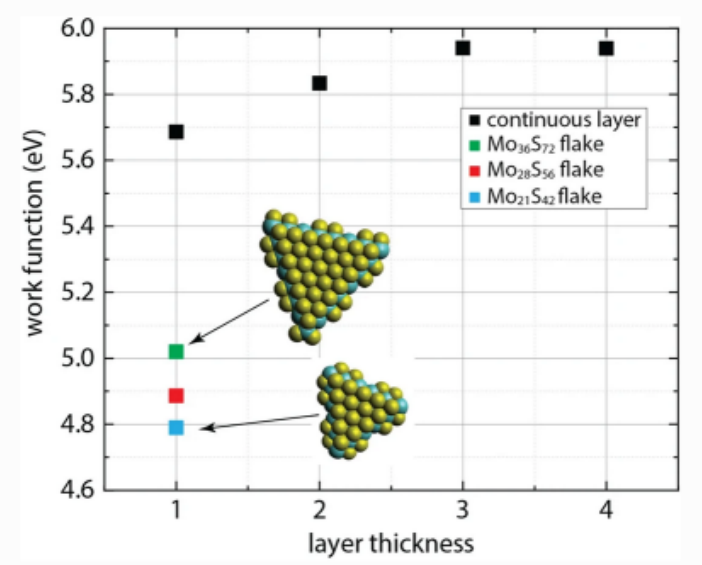
1.



2.

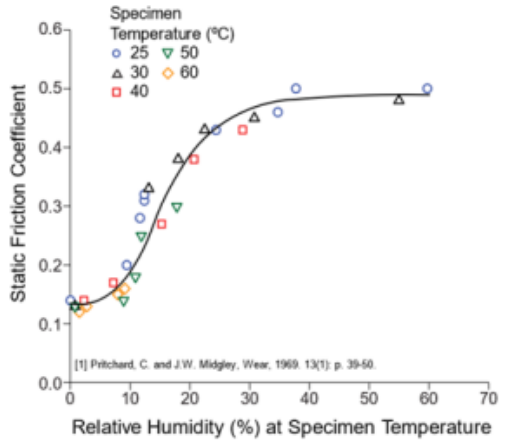


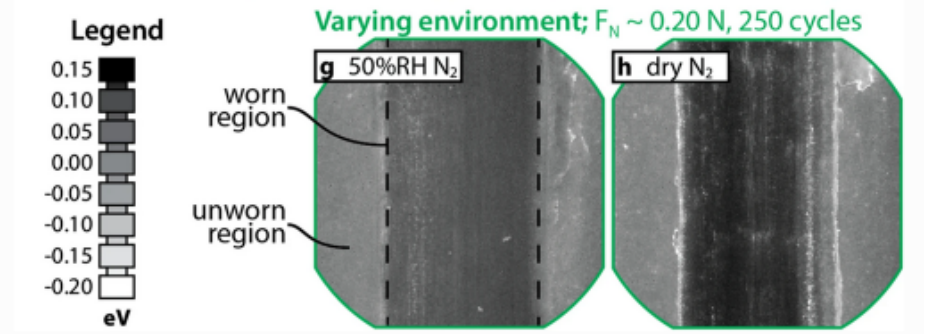
3.

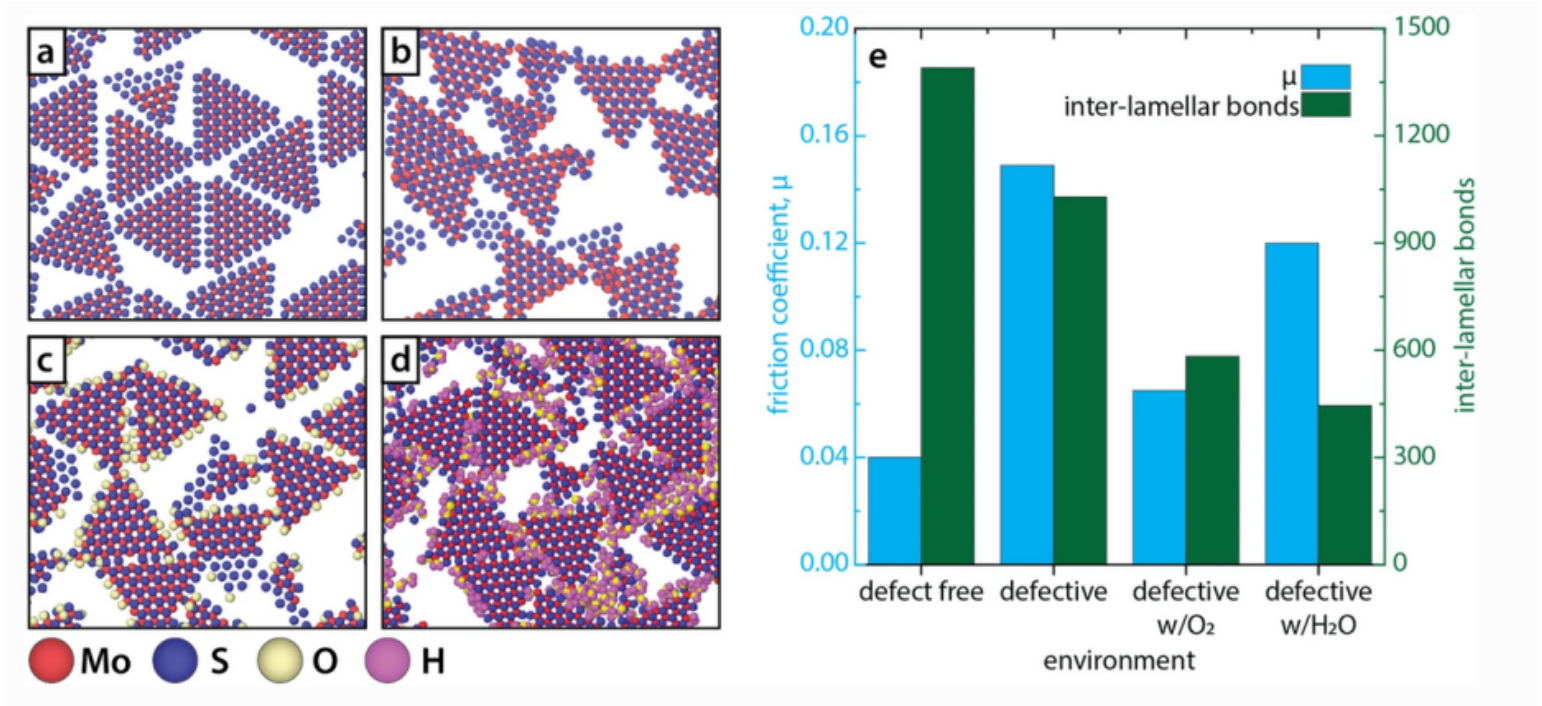


Connecting Water to Friction

1. Friction measurements indicate **HIGHER** friction in humid environment.
2. MD simulations indicate **LOWER** friction for **LARGER** flake sizes.
3. DFT simulations indicate **HIGHER** work function with **LARGER** flake sizes.
4. Work function (measured by PEEM) **LOWER** in humid environments.
   a. *This process is reversible which implies physisorption not oxidation*.







In dry conditions, MoS_2 flakes self-order into large lamellae: good for low friction.

Water disrupts formation of larger flakes, results in higher friction coefficient.

This is indicated by lower number of inter -lamellar bonds.

This work first to provide a cohesive explanation of how water increases friction in MoS_2 using both experiments and simulation.

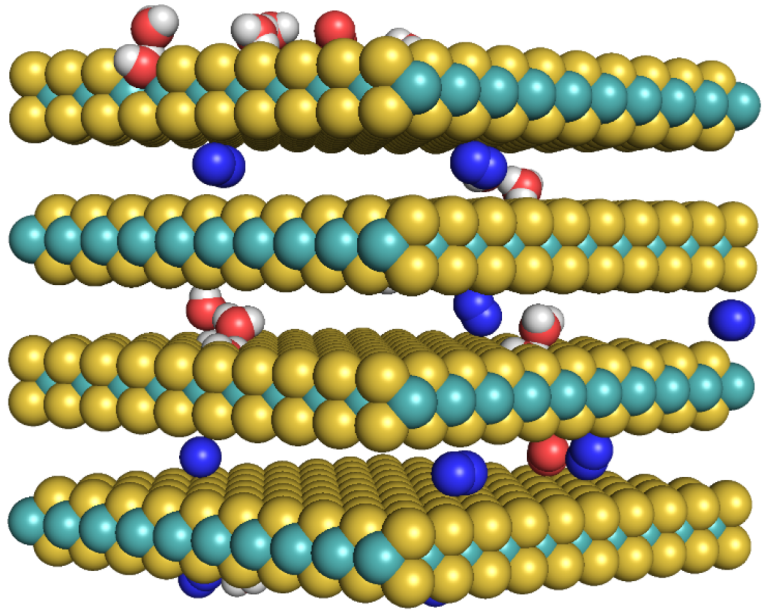
Conclusions:
Adsorption of environmental species on MoS_2

1. Pristine MoS_2 generally hydrophobic but defects greatly increase affinity for water.

2. All defect sites adsorb water at low (5%) relative humidity.

3. Adsorbed water on defect sites increases barrier to sliding and therefore friction coefficient.

4. Water interrupts formation of large flakes which results in higher friction coefficient.



313 K, 80% RH

Mike Chandross

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND XXXXXXX

Thanks for listening!

Questions?

We are hiring postdocs!
Come work in beautiful New Mexico!

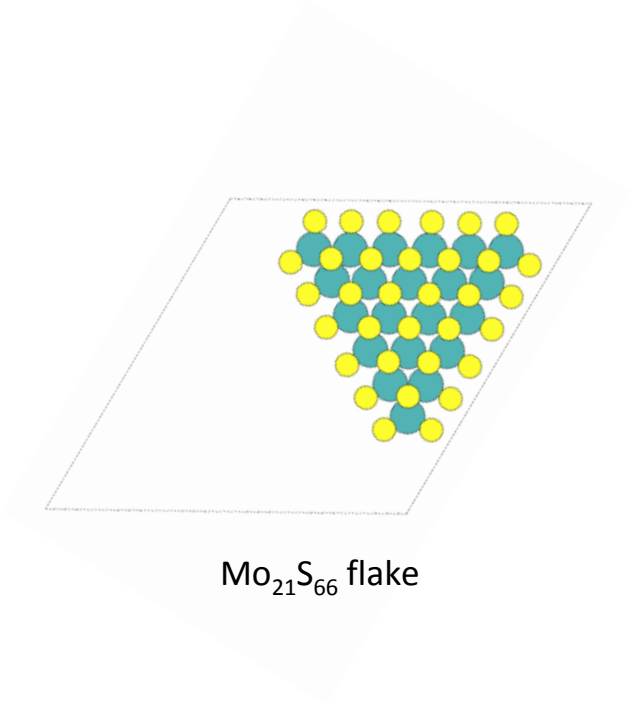
For info: sbobbit@sandia.gov

THE SECRET ARCHIVES

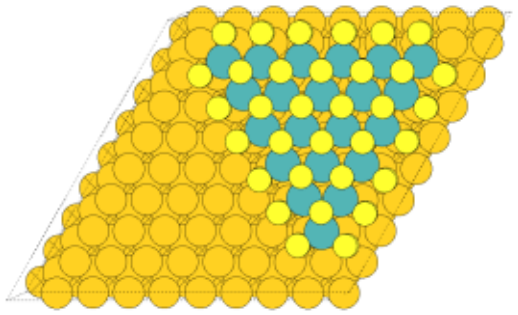
Future work: MoS_2/Au composites

Goal is to improve MoS_2 resistance to humidity by compositing with other materials, e.g. Au

MoS_2/Au composites are known to work but unclear why.



$Mo_{21}S_{66}$ flake



$Mo_{21}S_{66}$ flake on Au111

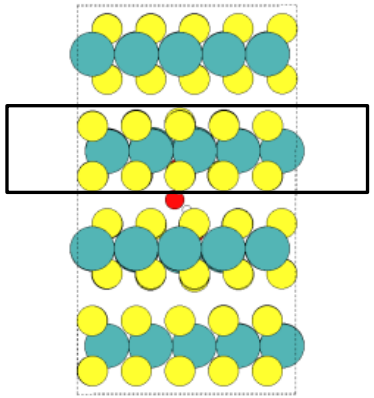
Structure	Avg Diff BE (kJ/mol) [3 sites]
No Defects	+4.8
S vacancy	+2.8
O substitution	+1.3

Early DFT calculations suggest water affinity is **weaker** when flake is on Au substrate.

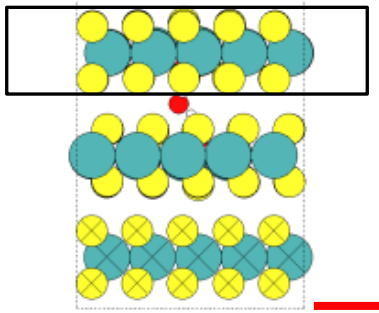
MoS_2/Au composite might be more resistant to humidity.

Chance in vertical (Z) position of Mo layer above the water.

Bulk

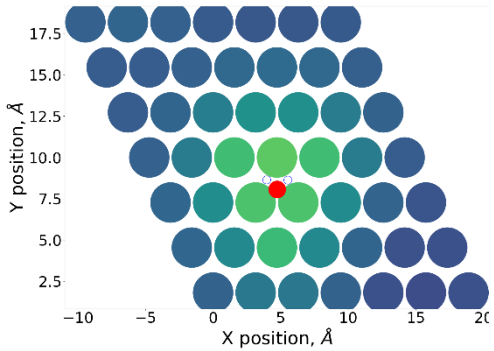


Surface

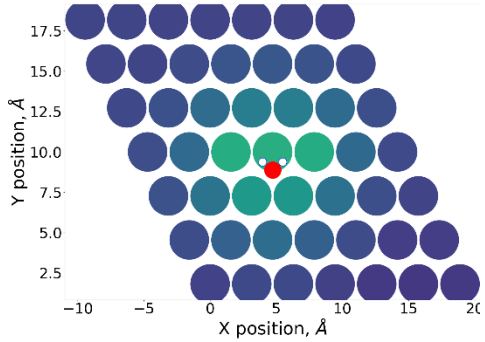


What happens at surface, where shearing occurs?

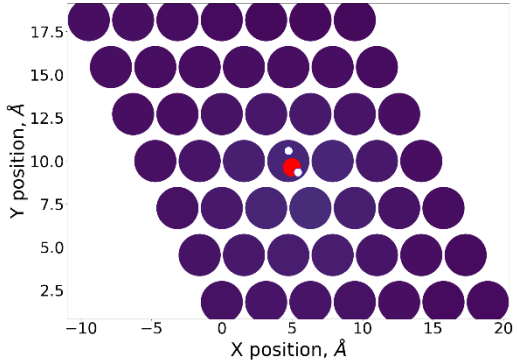
No defect

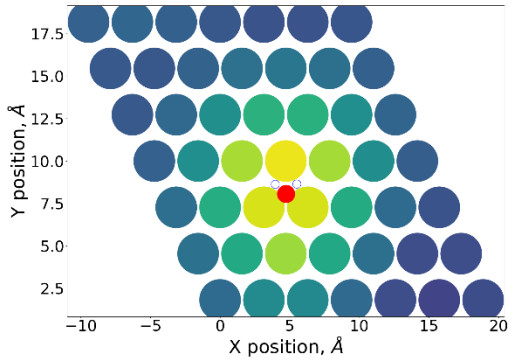


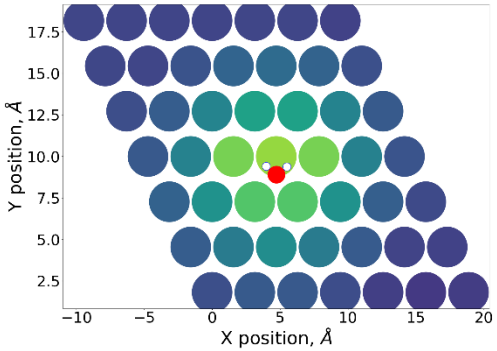
Oxygen sub

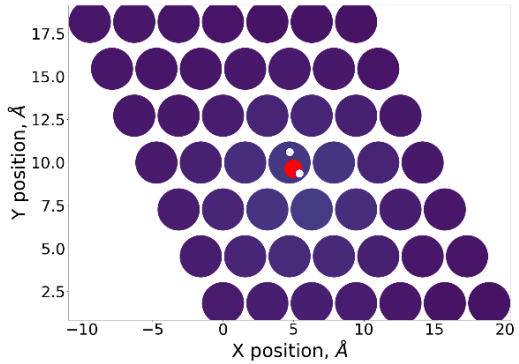


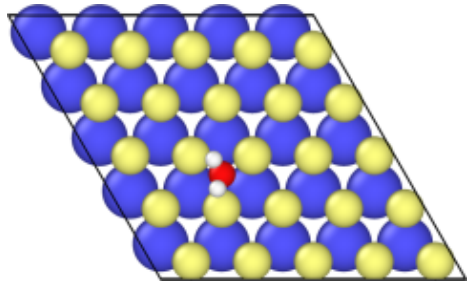
S vacancy



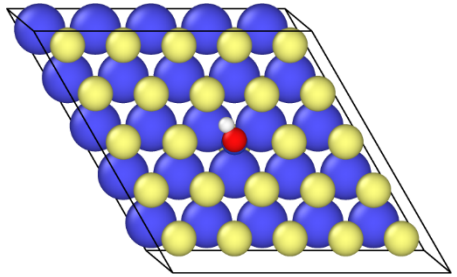




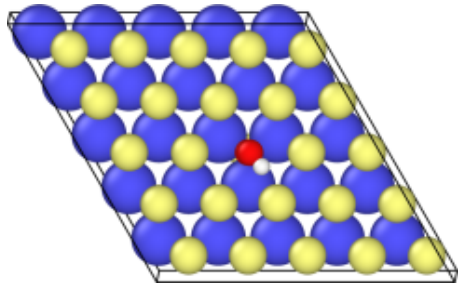




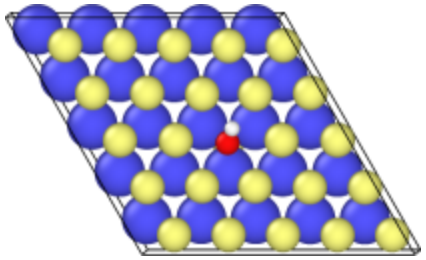
No defect



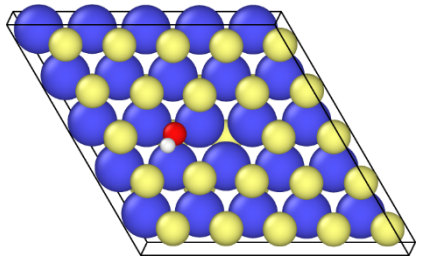
N sub



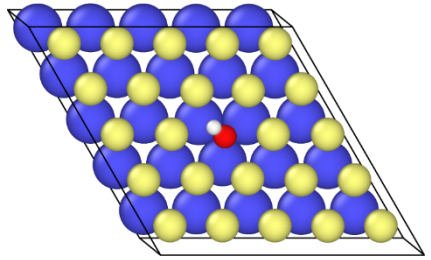
O sub



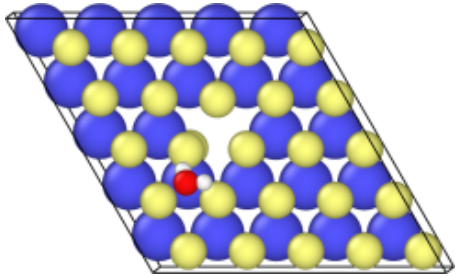
1 S vacancy



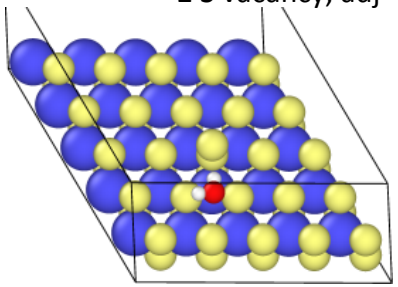
2 S vacancy, adj



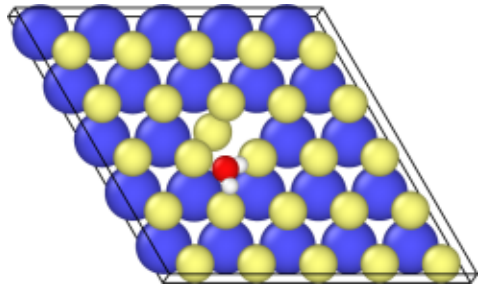
2 S vacancy, stack



Mo vacancy



S adatom

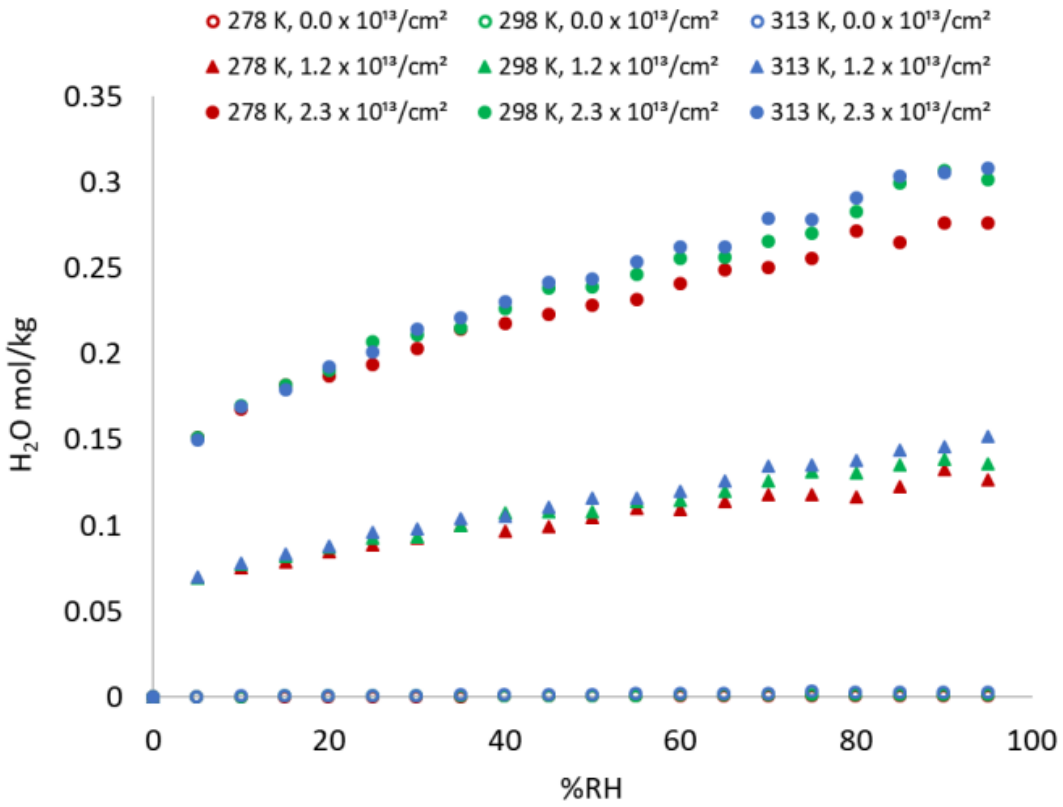


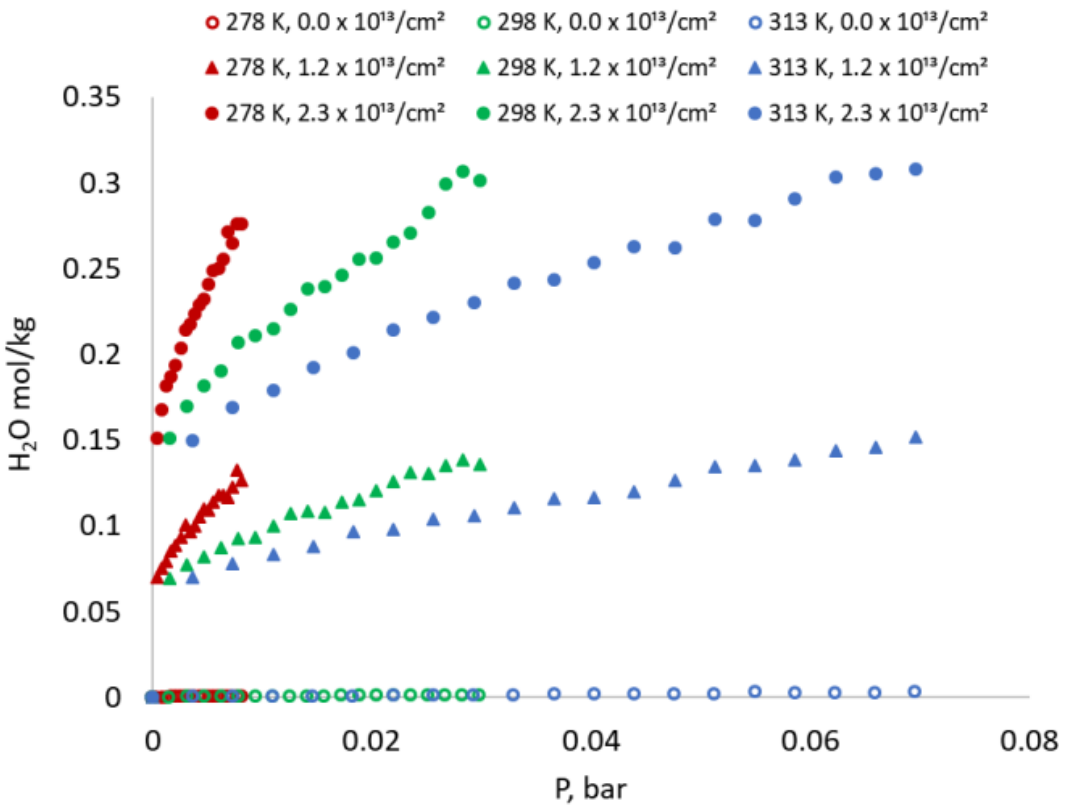
S sub Mo

In pristine MoS_2, water sits in hollow between Mo atoms

Forms H-bond with N and O dopants

Water sits on site of S vacancy



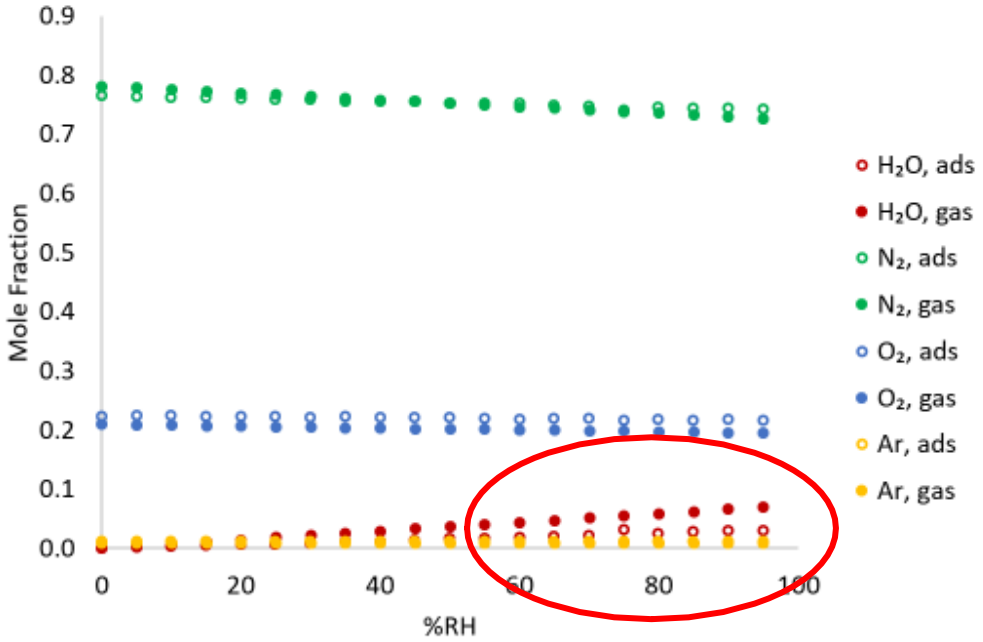


At a given partial pressure of water, uptake decreases with increasing temperature.

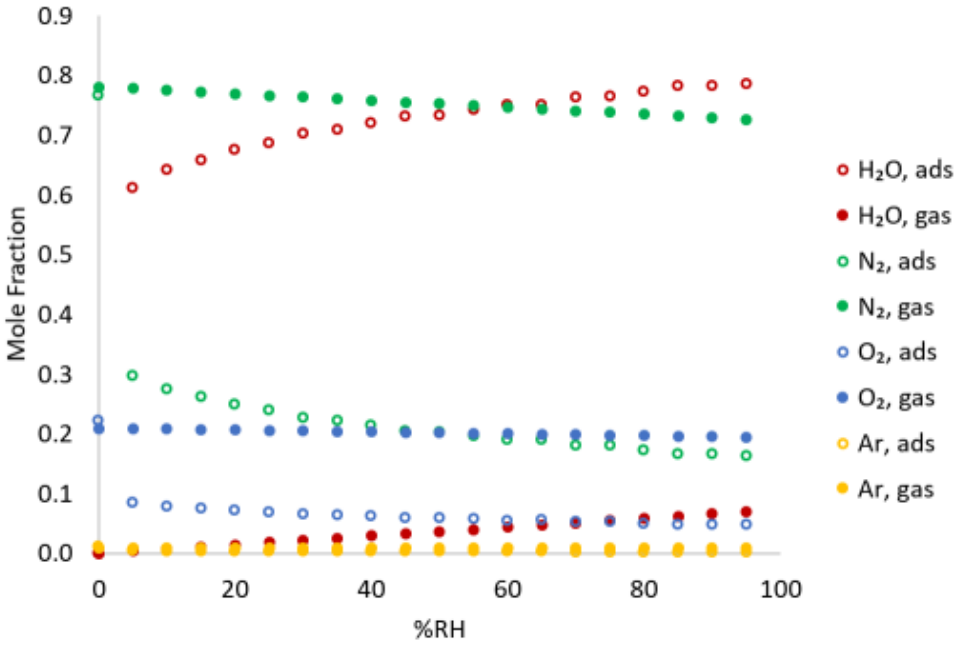
At given %RH, uptake decreases with temperature due to increased vapor pressure.

Adsorbed phase contains less water than gas phase.

This indicates pristine MoS_2 is hydrophobic. Adding defects makes it hydrophobic.



Defect free MoS_2, 313 K

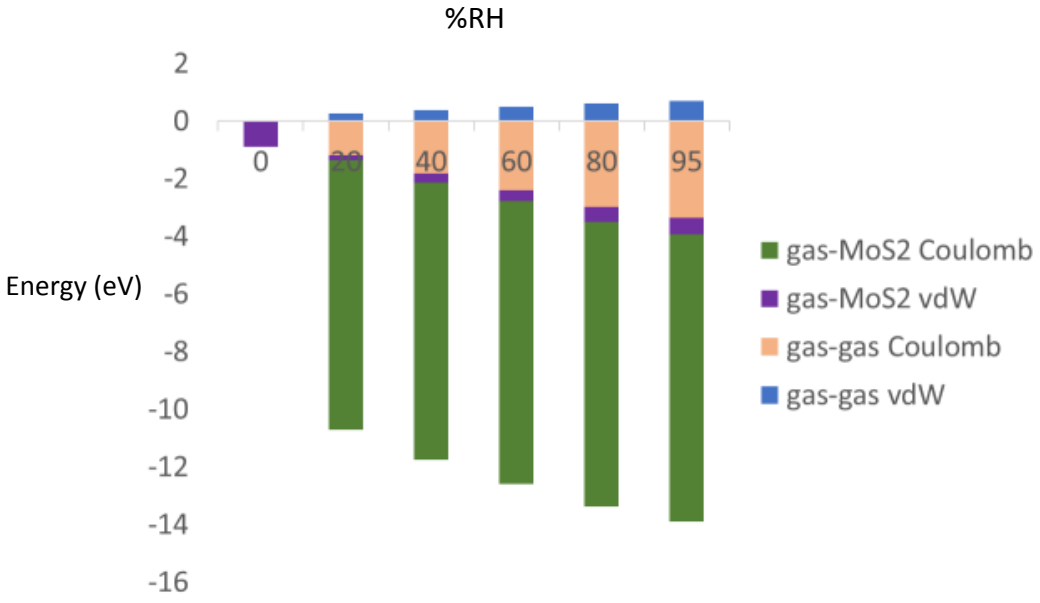


2.3 x 10^{13}/cm^2 defects, 313 K

Adding a moderate density of defects greatly increases water uptake.

Total gas-gas (guest-guest) and gas-MoS_2 (guest-host) energy (all components)

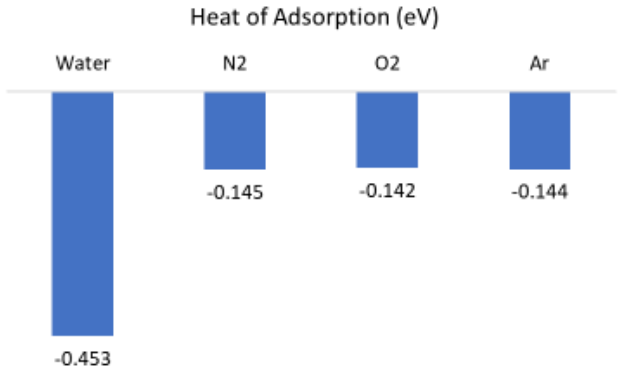
298 K
2.3 x 10^{13} cm^{-2} defects



0% RH contains no water. No O_2-N_2,O_2-O_2, N_2-N_2 interactions.

Water adsorption largely driven by Coulomb interactions.

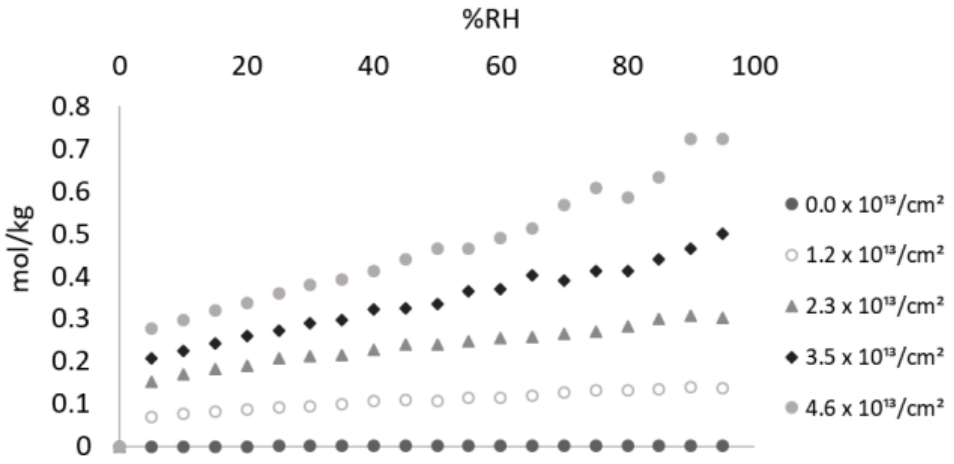
Significant water-water and water-MoS_2 interactions.



Water heat of adsorption ~3 times higher than other gases.

Water will dominate most favorable sites (defects)

Adsorption isotherms, 298 K

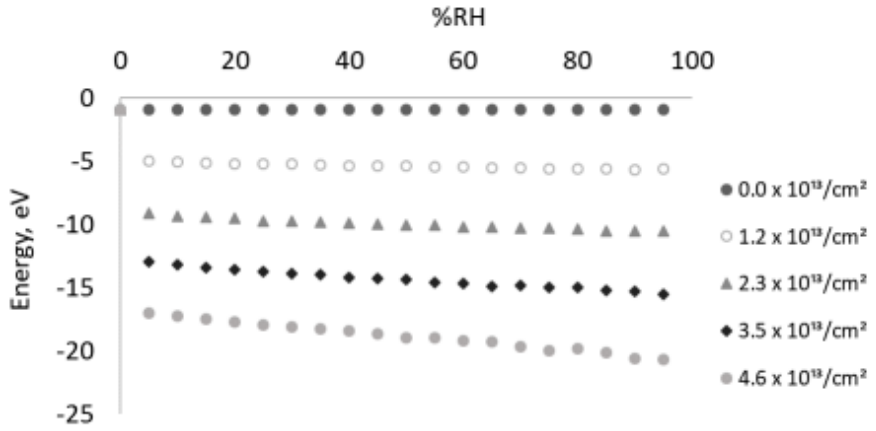


Water uptake increases with defect density.

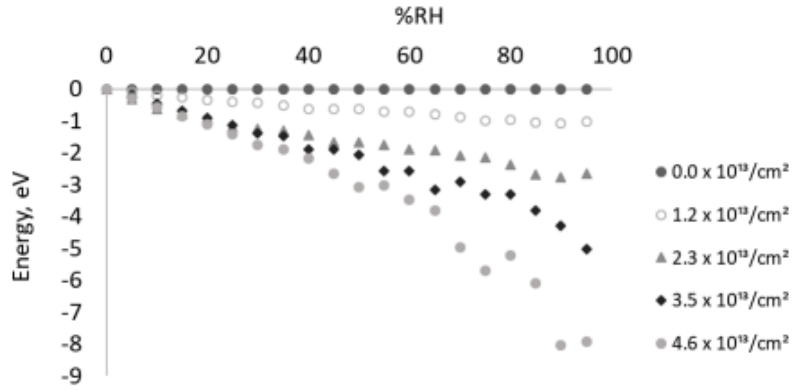
Adsorbate-MoS_2 energy remains fairly linear while adsorbate-adsorbate increases exponentially.

Indicates water clustering (water-water interactions).

Adsorbate-MoS_2 energy



Adsorbate-adsorbate energy



Total gas-gas (guest-guest) and gas-MoS_2 (guest-host) energy (all components)

eV	guest-guest			guest-host		
%RH	Total	vdW	Coulomb	Total	vdW	Coulomb
0	0.00	0.00	0.00	-0.91	-0.90	0.00
20	-0.92	0.25	-1.17	-9.55	-0.18	-9.36
40	-1.44	0.38	-1.82	-9.91	-0.31	-9.61
60	-1.89	0.50	-2.39	-10.19	-0.40	-9.79
80	-2.37	0.62	-2.99	-10.39	-0.51	-9.87
95	-2.66	0.69	-3.35	-10.54	-0.59	-9.95

0% RH contains no water. No O_2-N_2 O_2-O_2, N_2-N_2 interactions.

Water adsorption largely driven by Coulomb interactions.

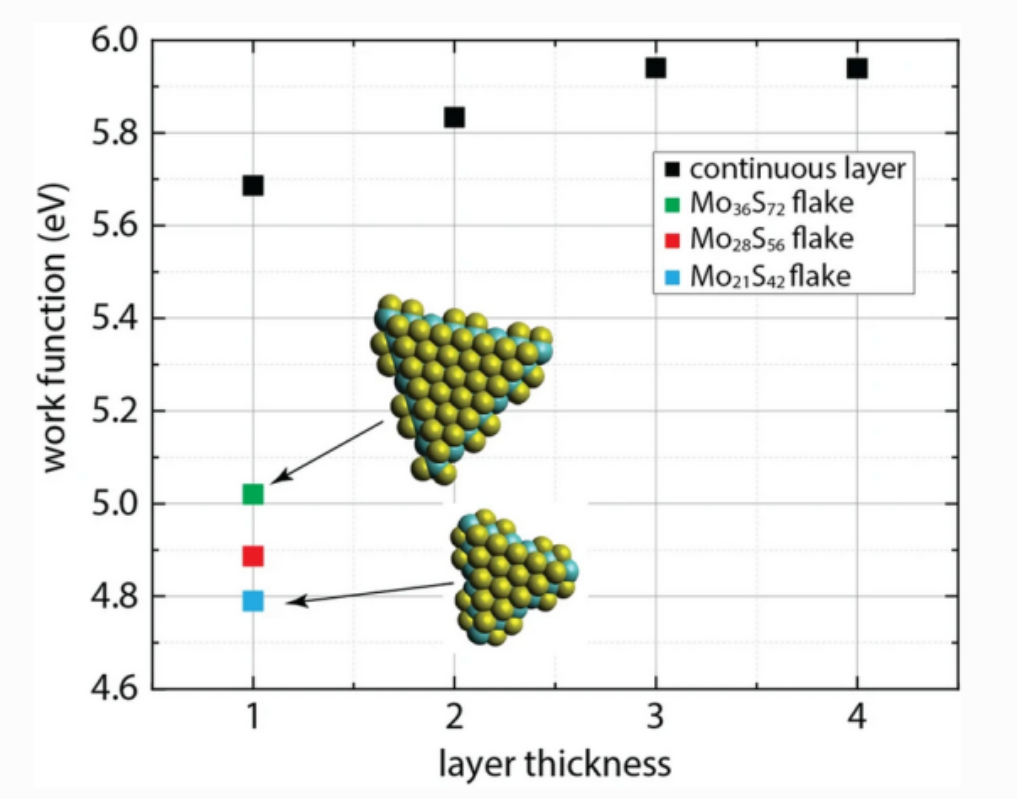
Significant water-water and water-MoS2 interactions.

Avg heat of adsorption

%RH	Water	N_2	O_2	Ar
5	-0.453	-0.145	-0.142	-0.144
20	-0.438	-0.145	-0.142	-0.144
40	-0.420	-0.144	-0.142	-0.143
60	-0.407	-0.145	-0.143	-0.144
80	-0.404	-0.145	-0.143	-0.145
95	-0.401	-0.146	-0.143	-0.149

Water heat of adsorption ~3 times higher than other gases.

Water will dominate most favorable sites (defects)



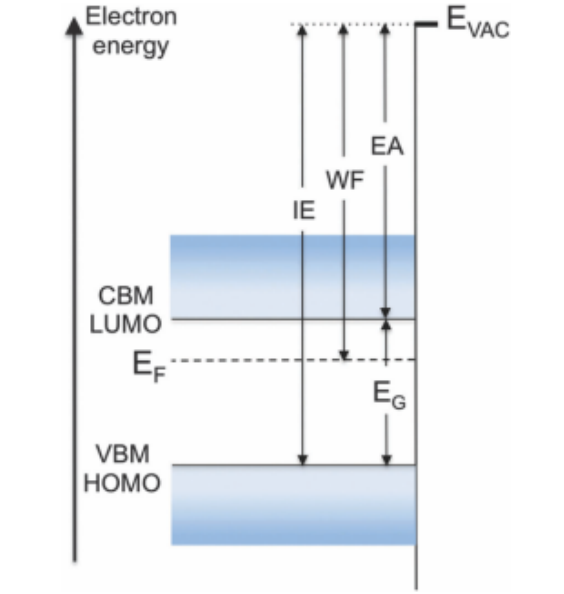


Fig. 1 Energy diagram of a semiconductor with flat bands to the surface. Band edges (CBM/LUMO and VBM/HOMO), vacuum level E_{VAC}, work function WF, energy gap E_G, ionization energy IE and electron affinity EA are defined.

DFT calculations indicate work function of flakes increases with size.