Harness Nanoscale Friction in Transition Metal Dichalcogenides

1st Users' Conference

A. Cammarata, P. Nicolini, B. Irving

cammaant@fel.cvut.cz

Czech Technical University in Prague - Advanced Materials Group

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IT4Innovations Centre of Excellence

Ostrava (Czech Republic)
October the 31st – November the 1st 2017

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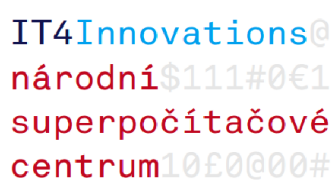


Advanced Materials Group

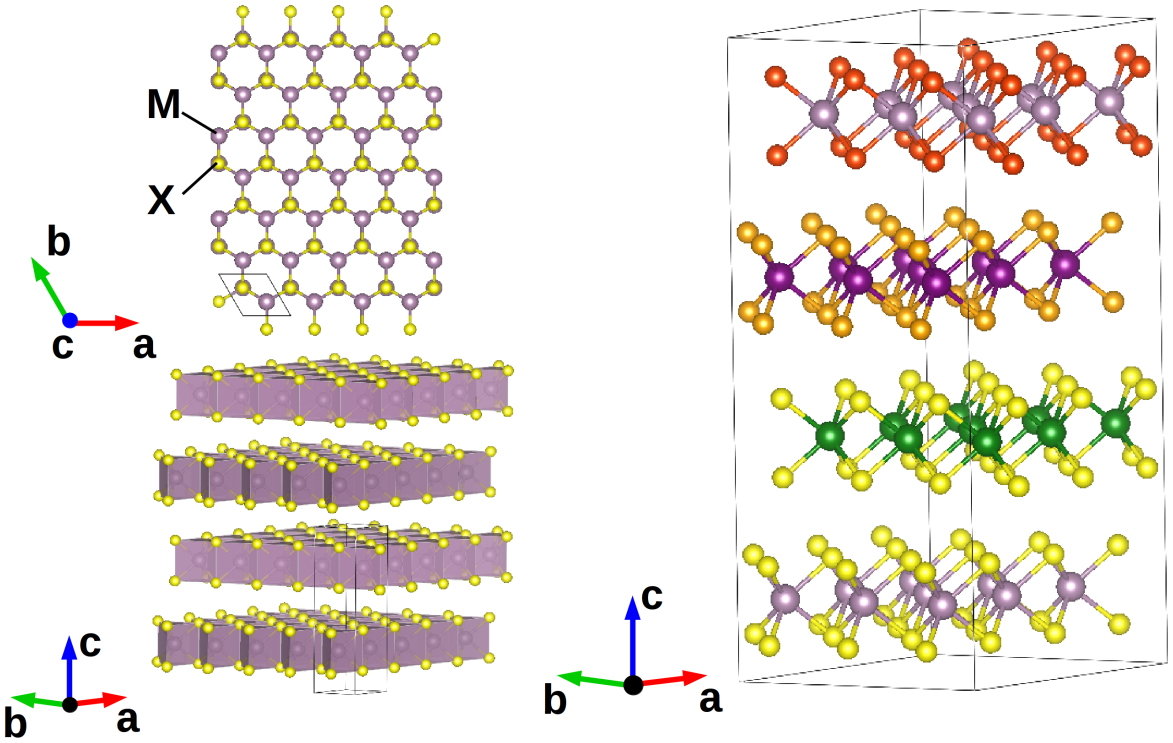
Head: Prof. Tomáš Polcar

Ass't Prof: Antonio Cammarata, Paolo Nicolini

Postdocs: Emilio Frutos, Alberto Fraile, Benjamin Irving, Hakan Yavas, Sener Sen, Kosta Simonović

PhD Students: Martin Daněk, Jamil Missaoui, Florian Belviso

Transition Metal Dichalcogenides



MX_2 Transition Metal Dichalcogenides: flexible chemistry (M = Mo, W, Ti, Zr, V... X = S, Se, Te) ⇒ easy property tuning and wide applicability (lubrication, catalysis, energy storage, electronic devices)

[*Nature Chemistry* **5**, 263 (2013); *Nature* **499**, 419 (2013)]

Transition Metal Dichalcogenides as Dry Lubricants

Dry lubricants: mandatory in extreme conditions like high temperature or under vacuum

- Transition metal dichalcogenides (TMDs)

Experimental discovery of new TMD-based materials with optimal characteristics is challenging and time-consuming, requiring development cycles that include:

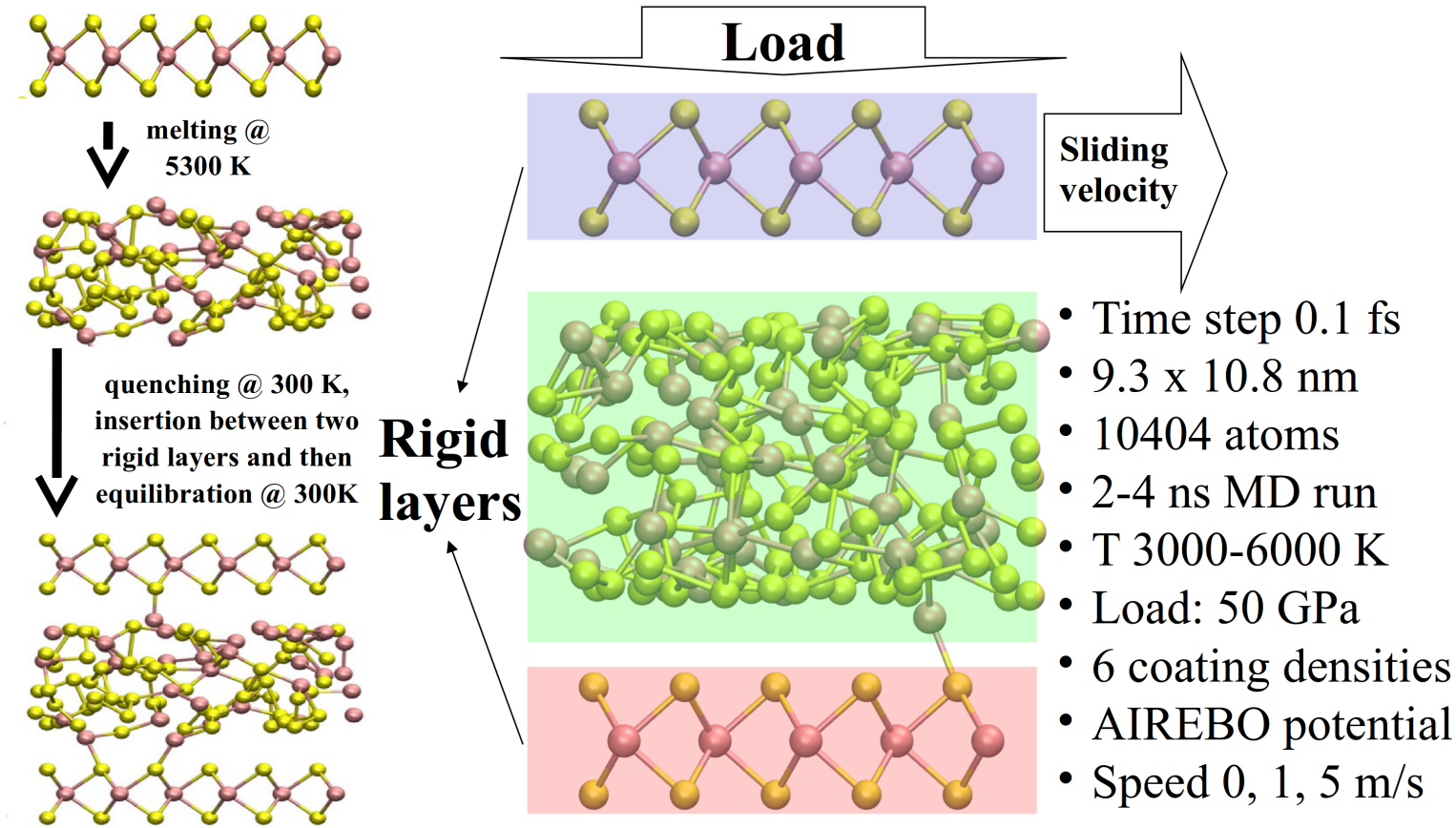
- candidate material identification
- testing
- structural optimization

Computational techniques expedite the process by narrowing the composition-structure phase space for experimental exploration to only the most favorable compounds:
$\Rightarrow$ efficient design of novel TMD materials with improved or new frictional properties

Classical simulations

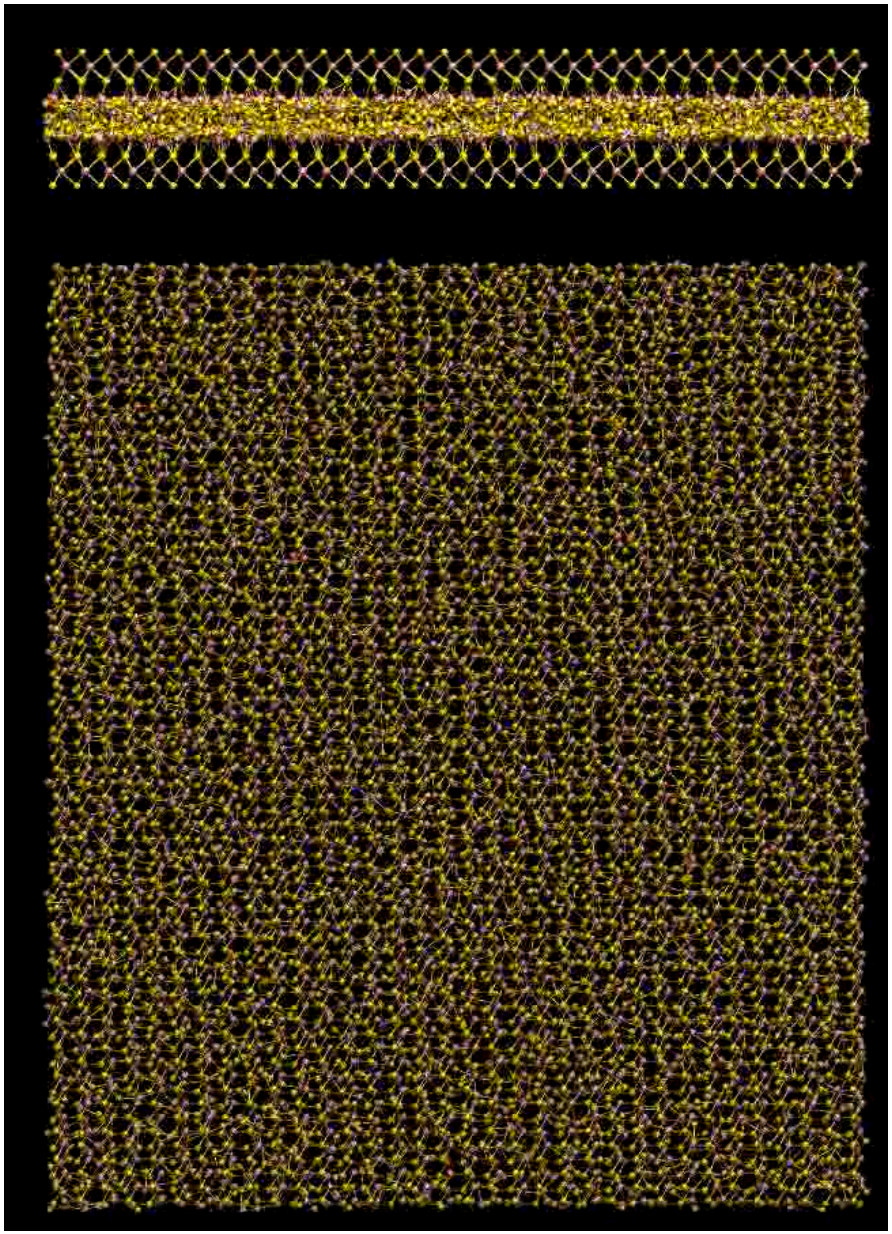
[P. Nicolini, T. Polcar et al. submitted to *Nanoscale*]

Crystal formation from amorphous phase



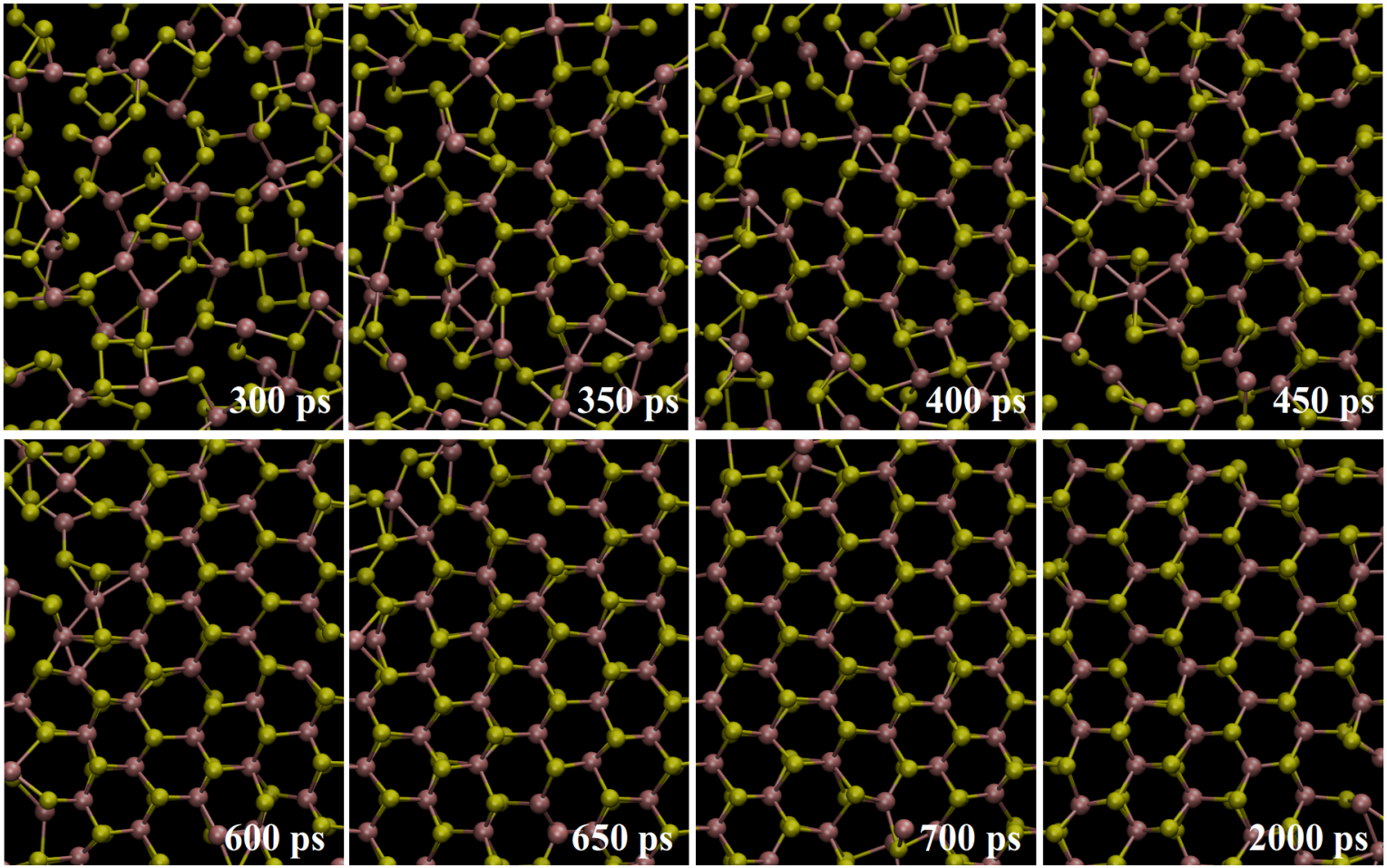
Classical simulations

[P. Nicolini, T. Polcar et al. submitted to *Nanoscale*]



Classical simulations

[P. Nicolini, T. Polcar et al. submitted to *Nanoscale*]



Intrinsic Friction

Friction: **macroscopic** effect of a resultant force that resists sliding or rolling of one object over another

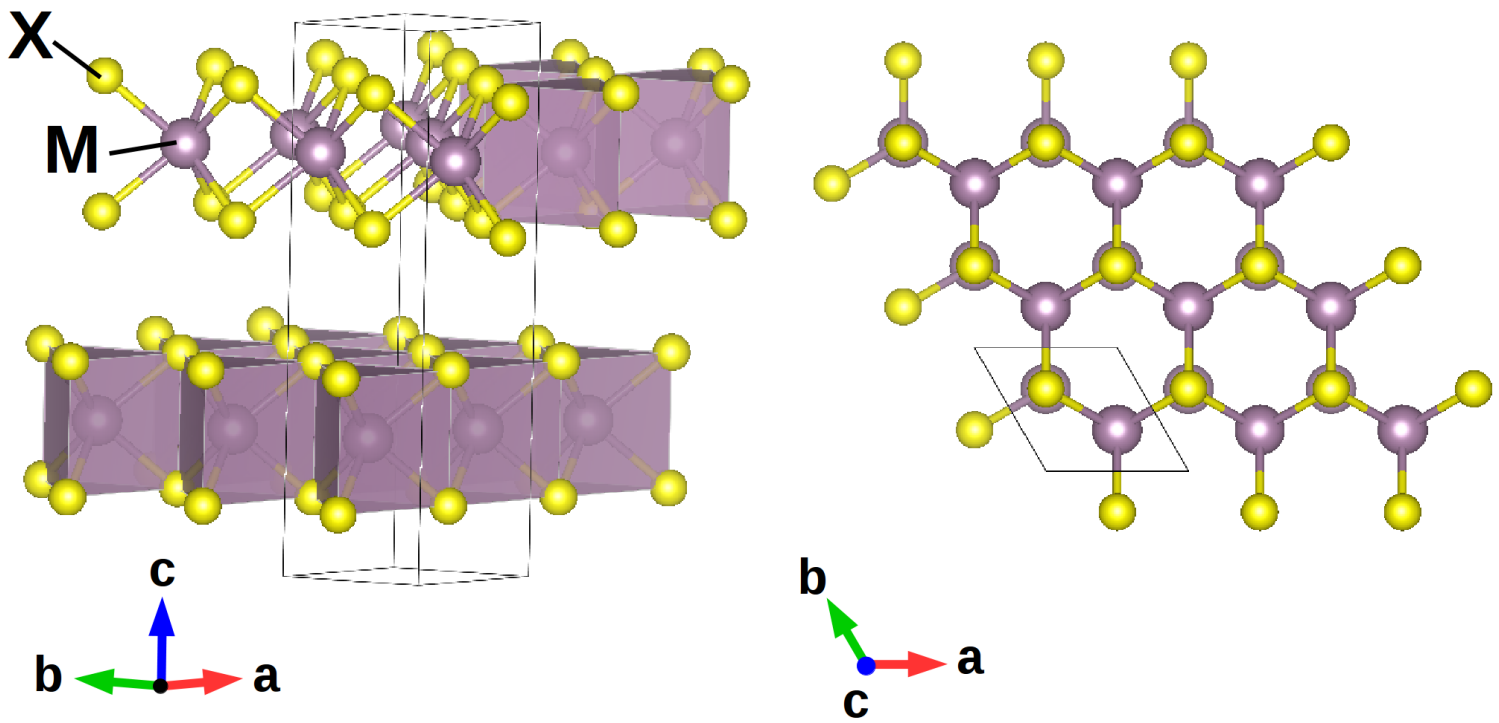
Microscopic Friction: friction generated at the **atomic scale** by the relative motion of few adjacent atom layers in the presence of structural irregularities (dislocations, layer truncations, grain boundary orientation...)

Intrinsic Friction: **microscopic friction** due to only local electronic (atomic type) and structural features (geometry) **without irregularities** $\Rightarrow$ a property *intrinsic* of the system

Quantum Mechanical Modeling of Intrinsic Friction in TMDs

Quantum Mechanical Models of MX_2 TMDs

MX_2 — M = Mo, W; X = S, Se, Te ($P6_3/mmc$)

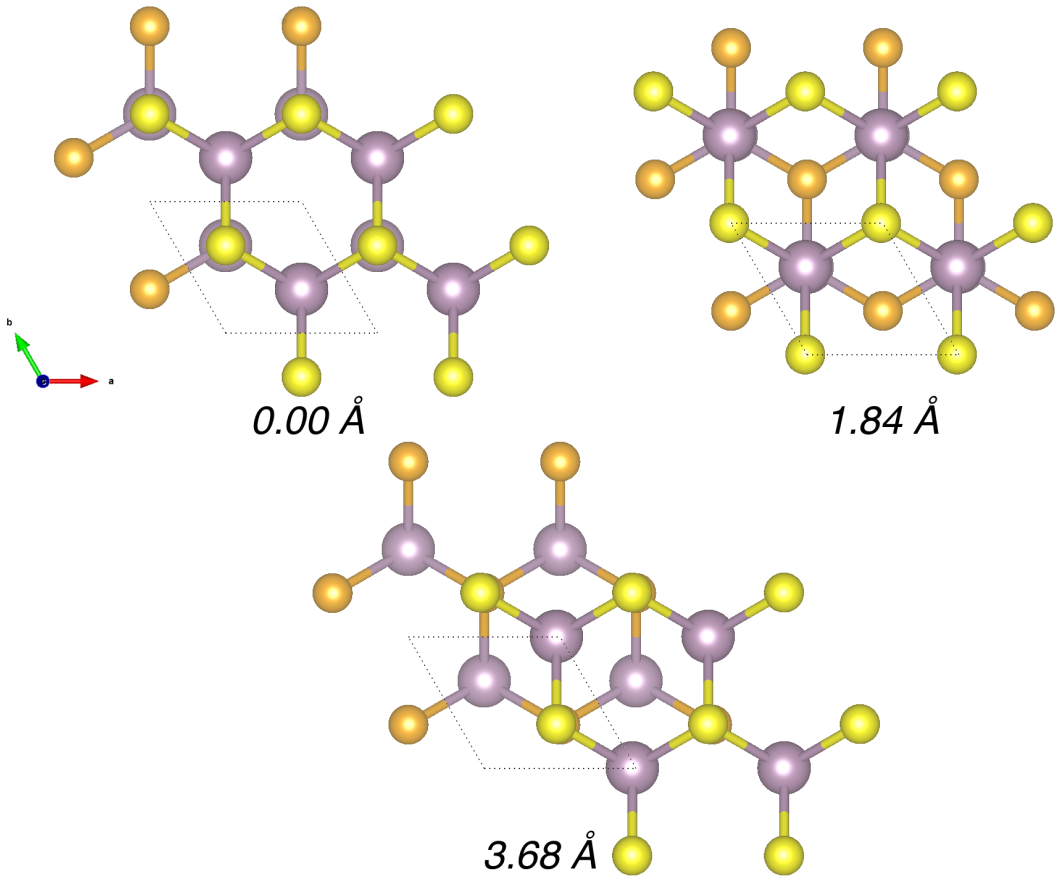


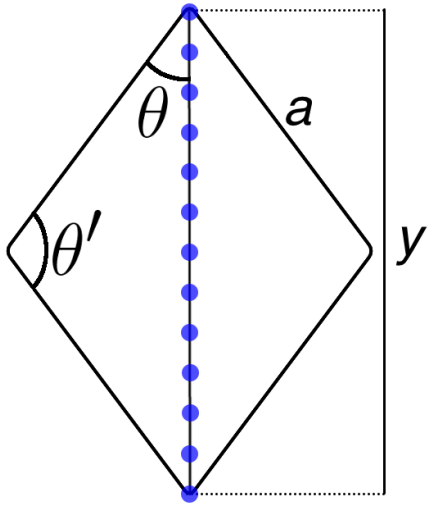
Ab Initio simulations allow to identify and disentangle the electro-structural features that determine the intra- and inter-layer motions affecting the intrinsic friction.

Quantum Mechanical Models of MX_2 TMDs

[B. J. Irving, P. Nicolini, T. Polcar, *Nanoscale 9*, 5597 (2017)]

Most important geometric configurations for MX_2 bilayers:

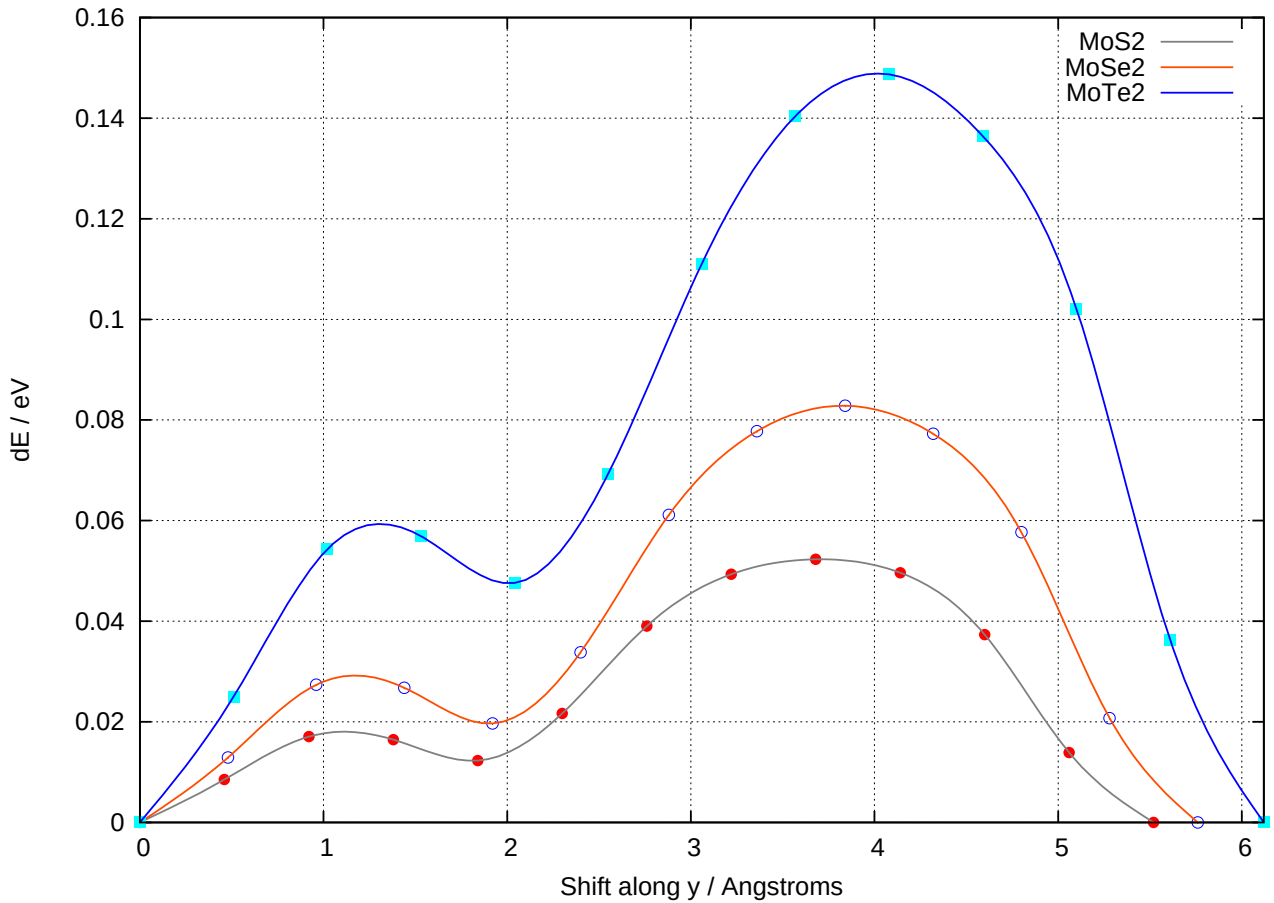




Quantum Mechanical Models of MX_2 TMDs

[B. J. Irving, P. Nicolini, T. Polcar, *Nanoscale 9*, 5597 (2017)]

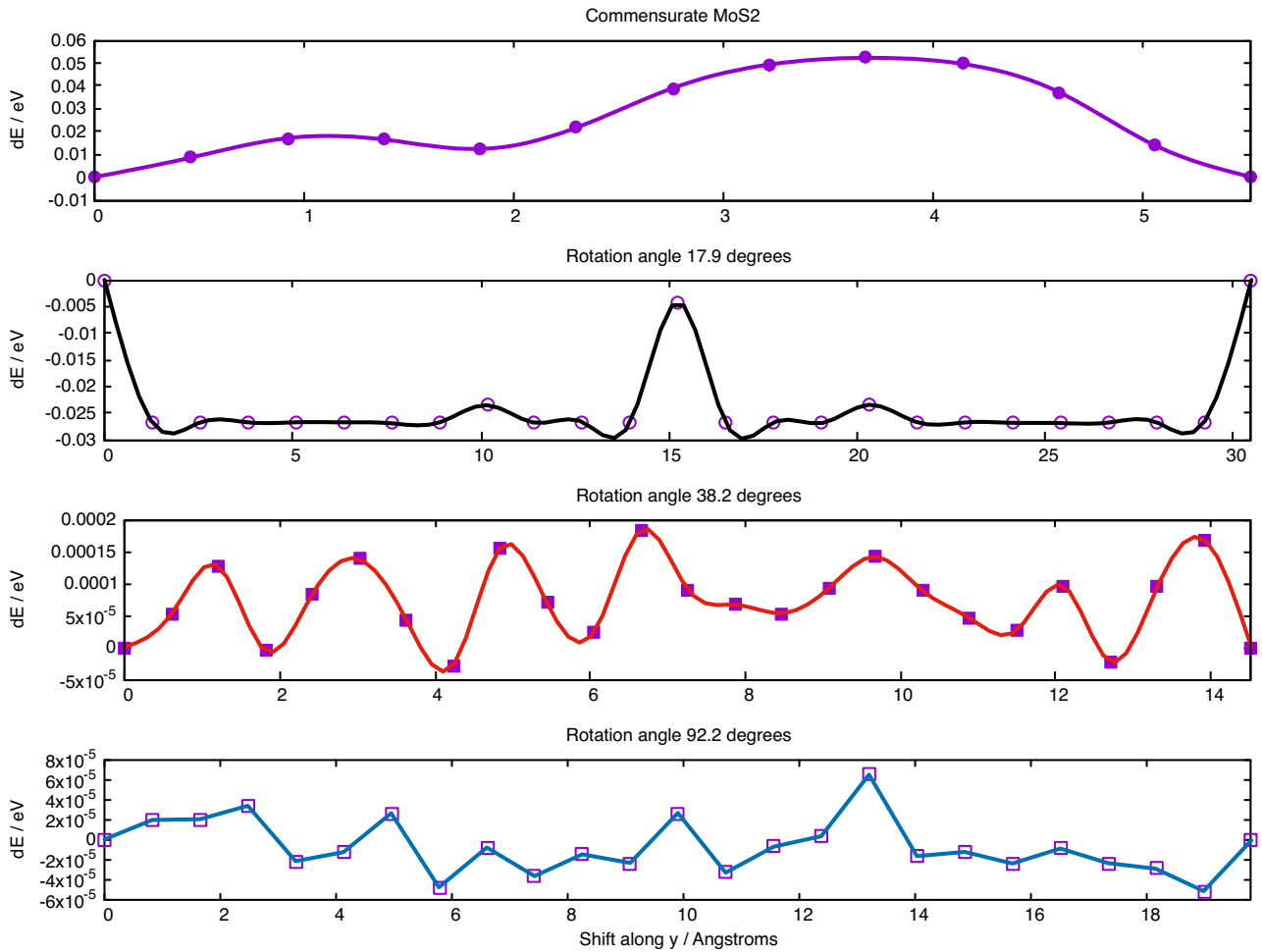
Potential energy profiles for MoX_2 bilayers:



Quantum Mechanical Models of MX_2 TMDs

[B. J. Irving, P. Nicolini, T. Polcar, *Nanoscale 9*, 5597 (2017)]

Incommensuration effects: a greater degree of incommensuration results in a significant easier inter-plane shear



Disentangling Electro-Structural Features

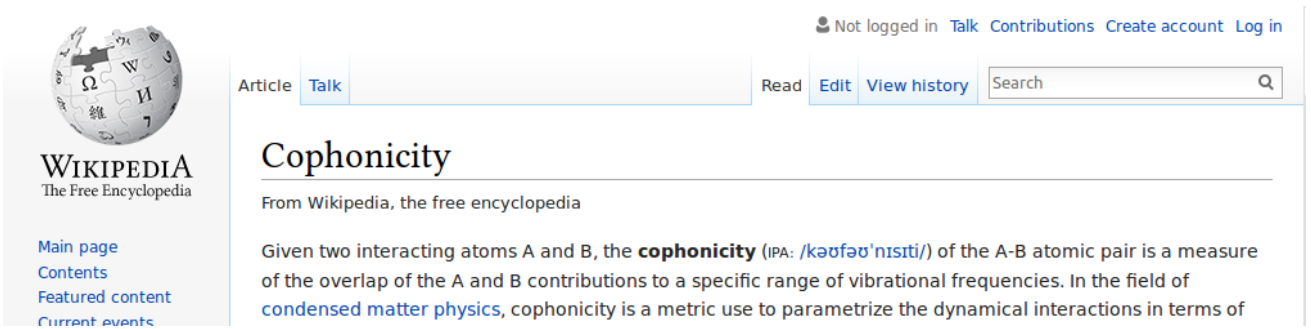
In terms of the classical picture, atoms are called back by a harmonic restoring force with associated frequency $\omega = \sqrt{k_f/\mu}$

lower frequency $\Rightarrow$ sliding promoted

Goal: to improve intrinsic friction, that is, to lower the sliding-related frequencies

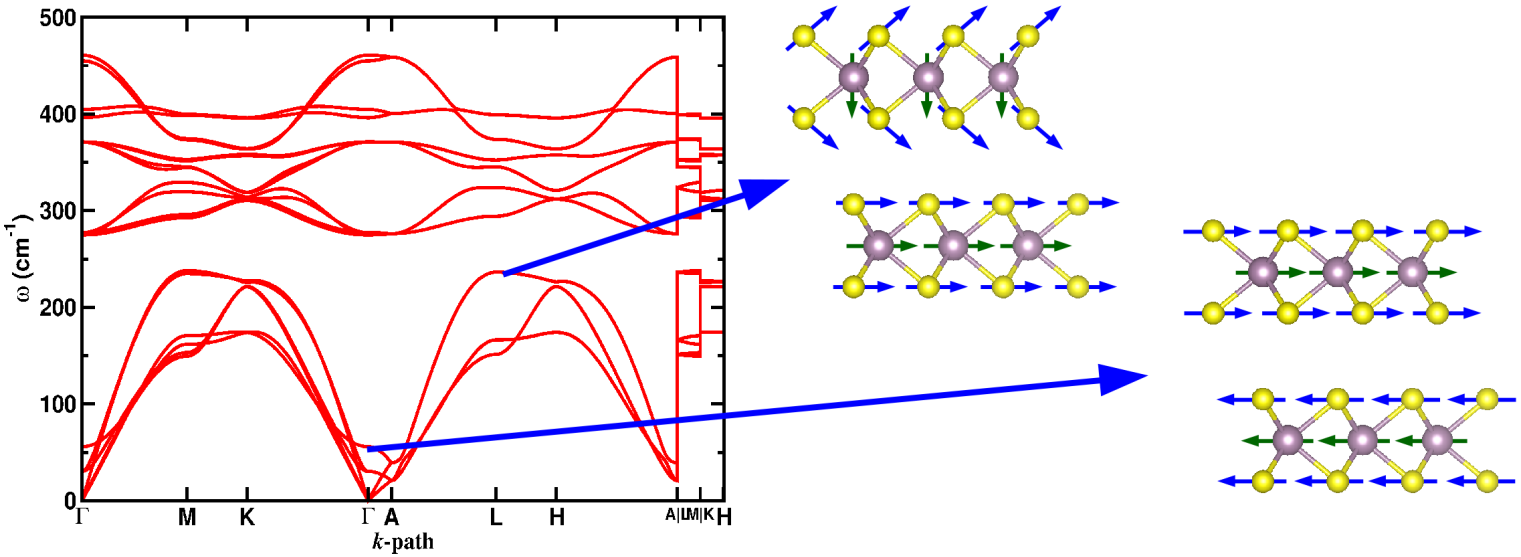
We parameterize the electronic and structural features by means of simple descriptors:

- Dynamic features: Cophonicity
- Electronic density: Covalency, Orbital Polarization
- Structural Distortions: Group Theory



Dynamic Analysis

Phonon Band Structure



- Identification of the vibrational modes related to layer sliding
- Each mode corresponds to a harmonic restoring force with force constant k_f: $\omega = \sqrt{k_f/\mu}$
- The lower the frequency, the weaker the restoring force, the higher the atomic displacement amplitude

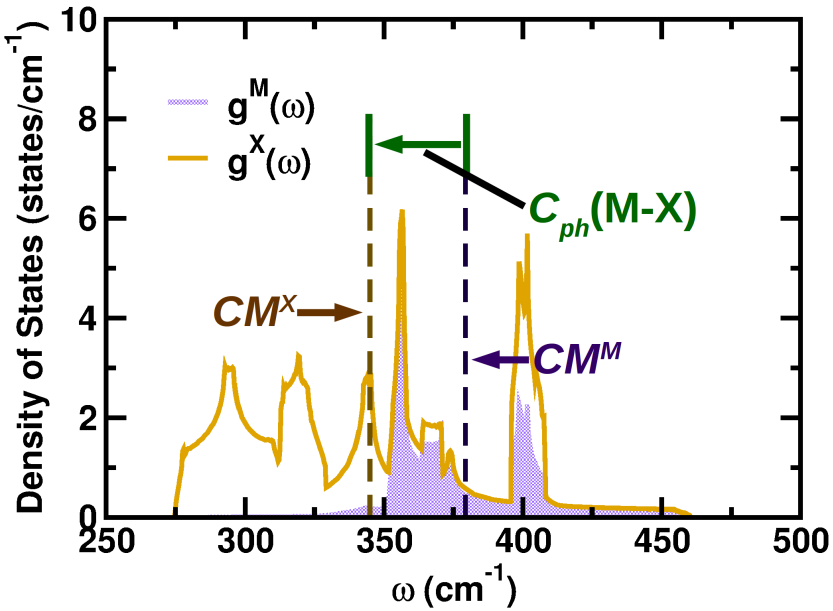
Optimal $\omega \Rightarrow$ optimal layer sliding

We need a descriptor (metric) to quantify how changing the atomic type affects specific phonon frequencies

The *Cophonicity* Metric

[A. Cammarata, T. Polcar, *Inorg. Chem.* **54**, 5739 (2015)]

The phonon density of states can be decomposed into atomic contributions of the M-X atomic pair, which is the smallest unit that generates the dynamical interactions



The relative position C_{ph}(M-X) of CM^M with respect to CM^X is $C_{ph}(\text{M-X}) = CM^M - CM^X$

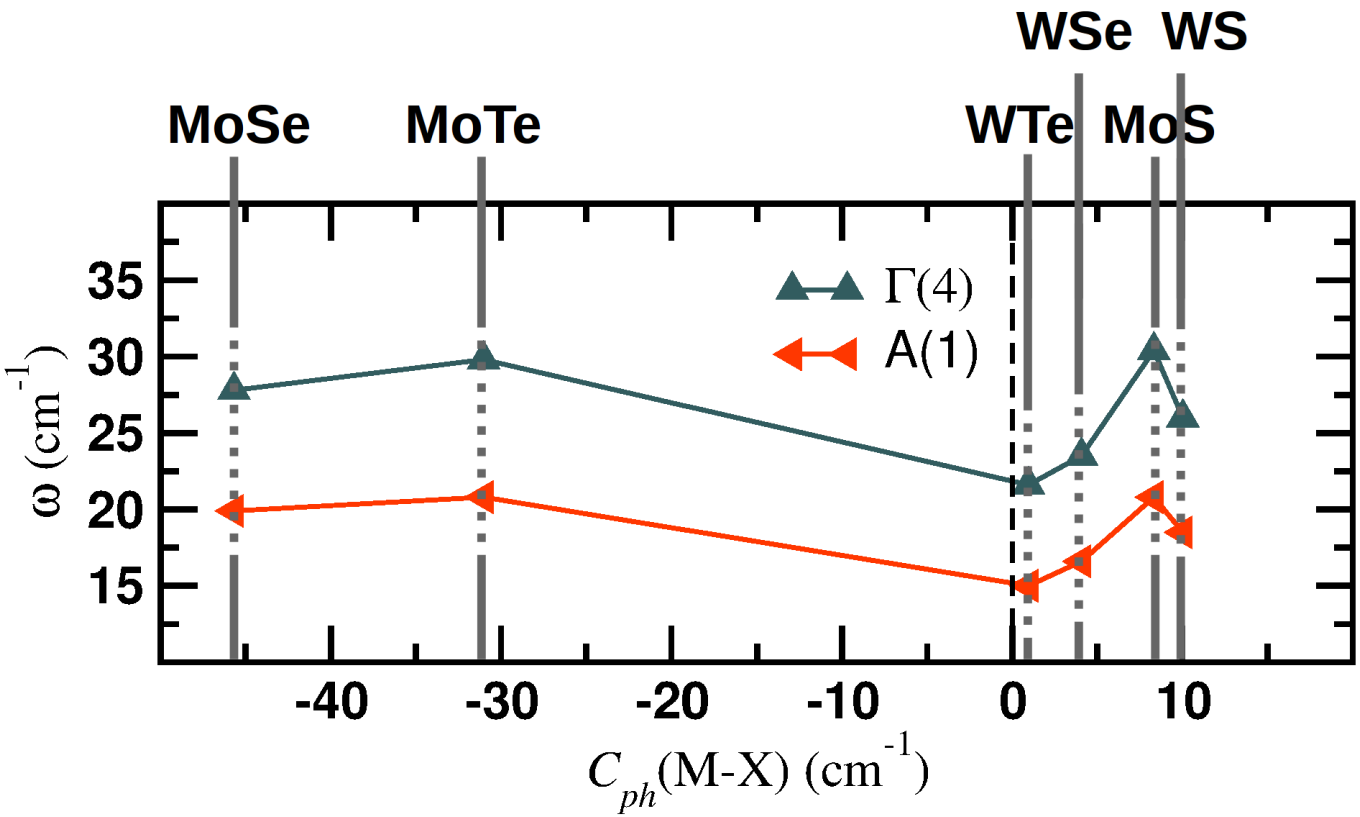
We call C_{ph}(M-X) the **cophonicity** of the M-X atomic pair

Cophonicity is a measure of the overlap of the single atomic contributions to a specific frequency range.

Results

Tuning Frequency with Cophonicity

Mode frequency is minimum when $C_{ph} \simeq 0$ cm^{-1}



How can we control M-X pair cophonicity?

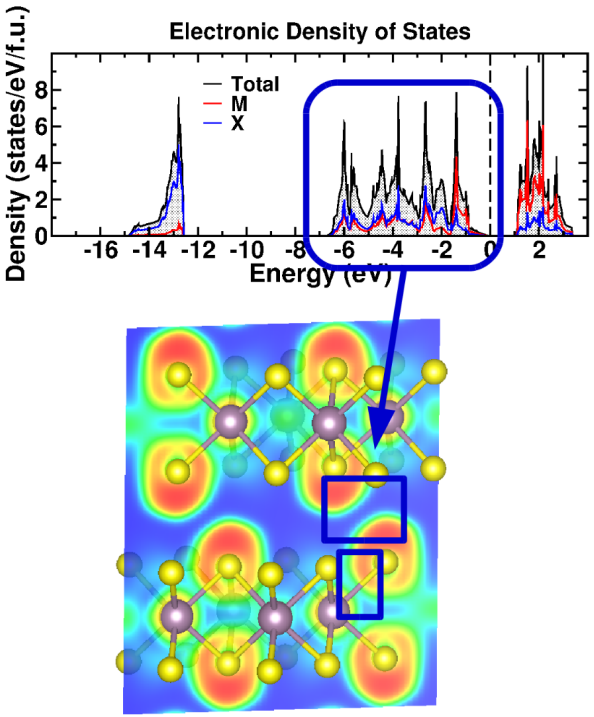
Results

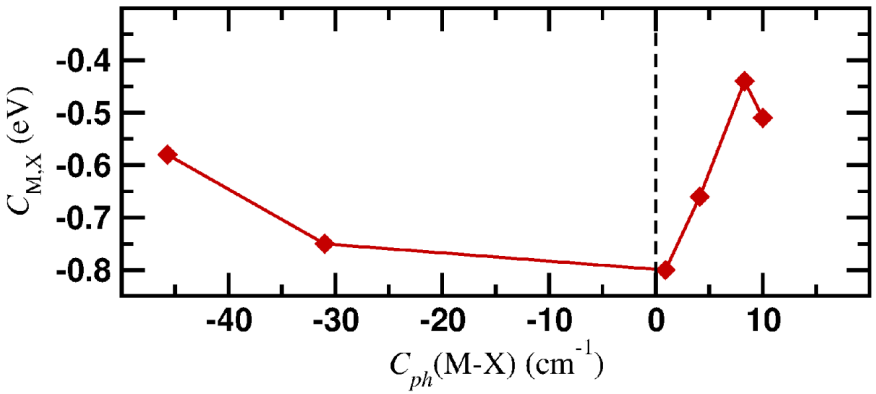
Tuning Cophonicity with Covalency and Structural Distortions

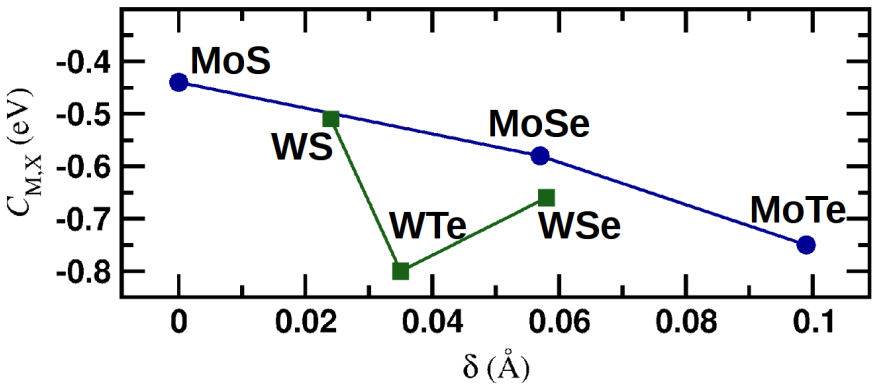
Cophonicity is related to M–X bond covalency and the structural distortions

M-X bond covalency $C_{M,X}$

A. Cammarata et al.
J. Chem. Phys. **141**, 114704 (2014)
Chem. Mater. **26**, 5773 (2014)



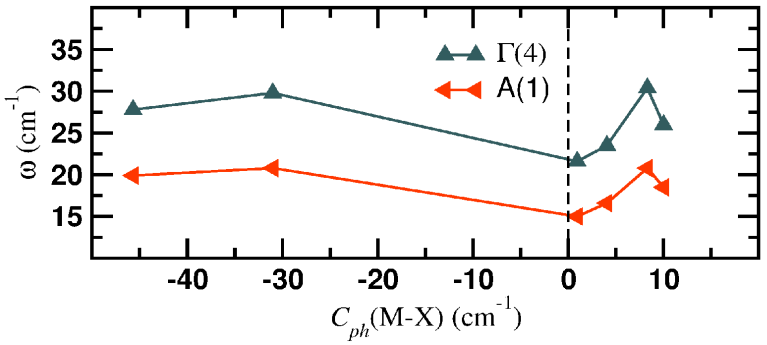


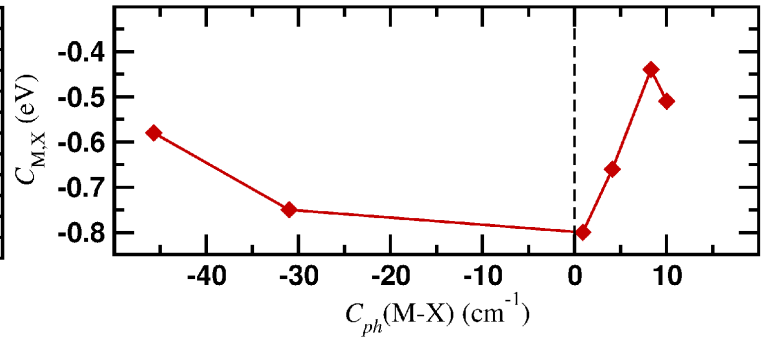


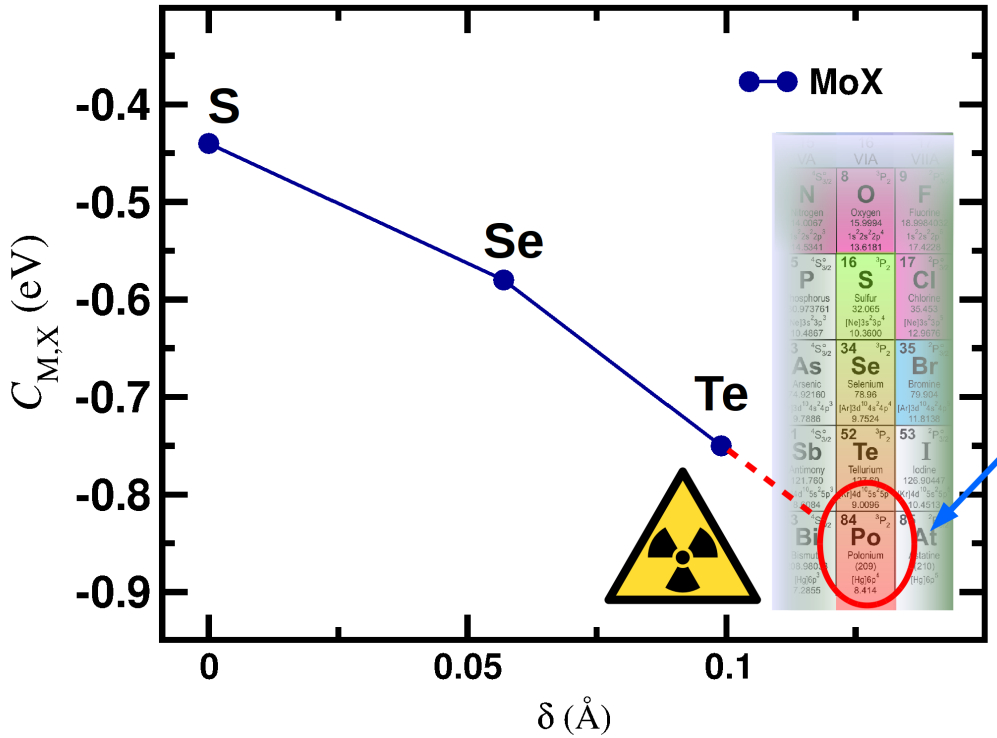
Let's now design a new TMD!

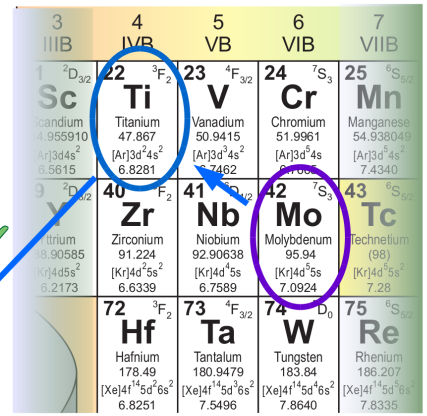
Designing a new TMD

[A. Cammarata, T. Polcar, *Inorg. Chem.* **54**, 5739 (2015)]



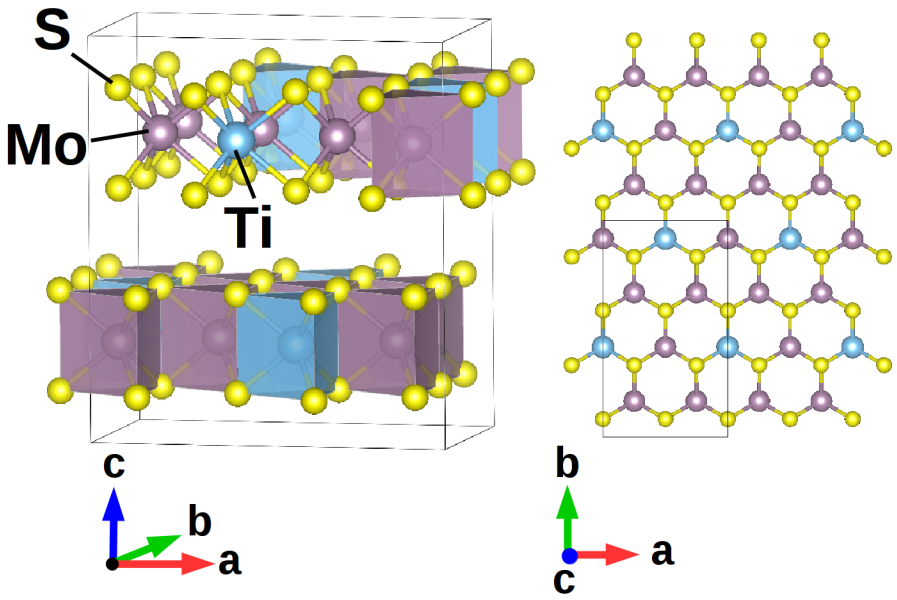






The Ti:MoS_2 System

[A. Cammarata, T. Polcar, *Inorg. Chem.* **54**, 5739 (2015)]

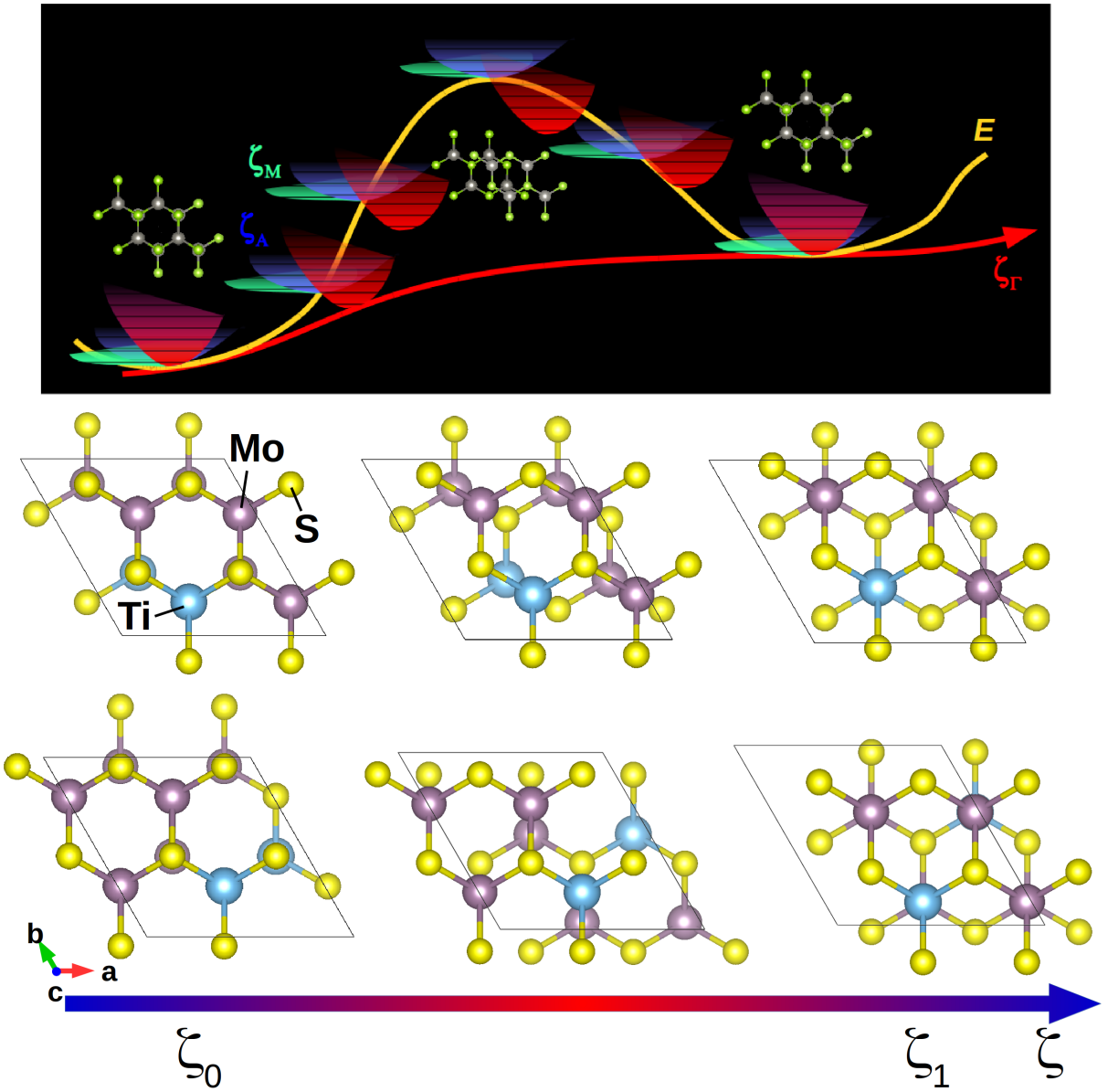


- The **most stable** among the explored MX_2, comparable to MoS_2
- **Lowest sliding frequencies** expected, comparable to WSe_2 and WTe_2

System	ΔH_f (eV/f.u.)	δ (Å)	$C_{M,X}$ (eV)	C_{ph}(M-X) (cm^{-1})	$\omega(\Gamma)_{4-5}$ (cm^{-1})	$\omega(A)_{1-4}$ (cm^{-1})
MoS	0.00	0.00	-0.44	8.3	30	21
MoSe	2.79	0.06	-0.58	-45.7	28	20
MoTe	5.94	0.10	-0.75	-31.0	30	21
WS	1.23	0.02	-0.51	10.0	26	18
WSe	4.27	0.06	-0.66	4.1	24	17
WTe	7.63	0.03	-0.80	0.9	22	15
Ti:MoS	0.04	0.17	-0.76	4.6	$\omega(\Gamma)_4$ 22 $\omega(\Gamma)_5$ 23	$\omega(A)_{1-2}$ 15 $\omega(A)_{3-4}$ 16

Normal-Modes Transition Approximation

[A. Cammarata, T. Polcar, *Phys. Rev. B* **96**, 085406 (2017)]

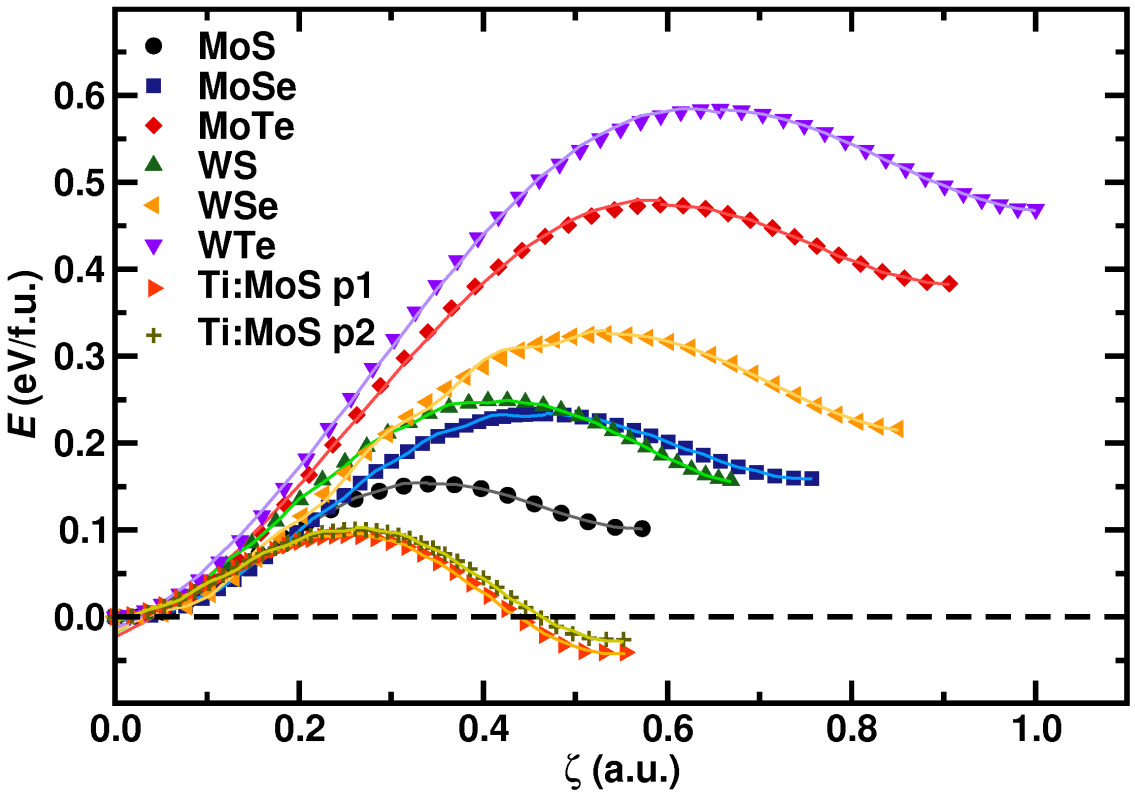


Normal-Modes Transition Approximation

[A. Cammarata, T. Polcar, *Phys. Rev. B* **96**, 085406 (2017)]

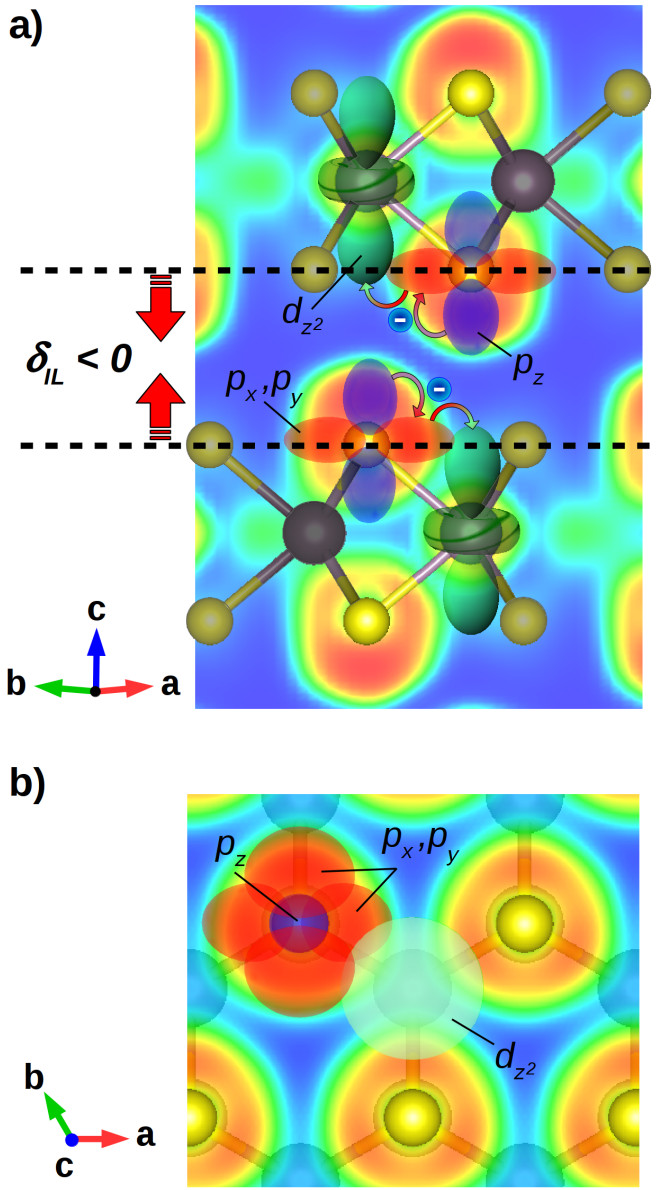
Along a general configurational coordinate ζ, the total potential energy E can be approximated as a sum of contributions from all the K normal modes:

$$E(\zeta) = \sum_{k=1}^{K} \frac{1}{4}\omega_k^2 C_k^2 \left[1 - \cos\left(\frac{\pi}{C_k}\zeta - \theta_k\right)\right] \quad (1)$$



MX_2 Under Load

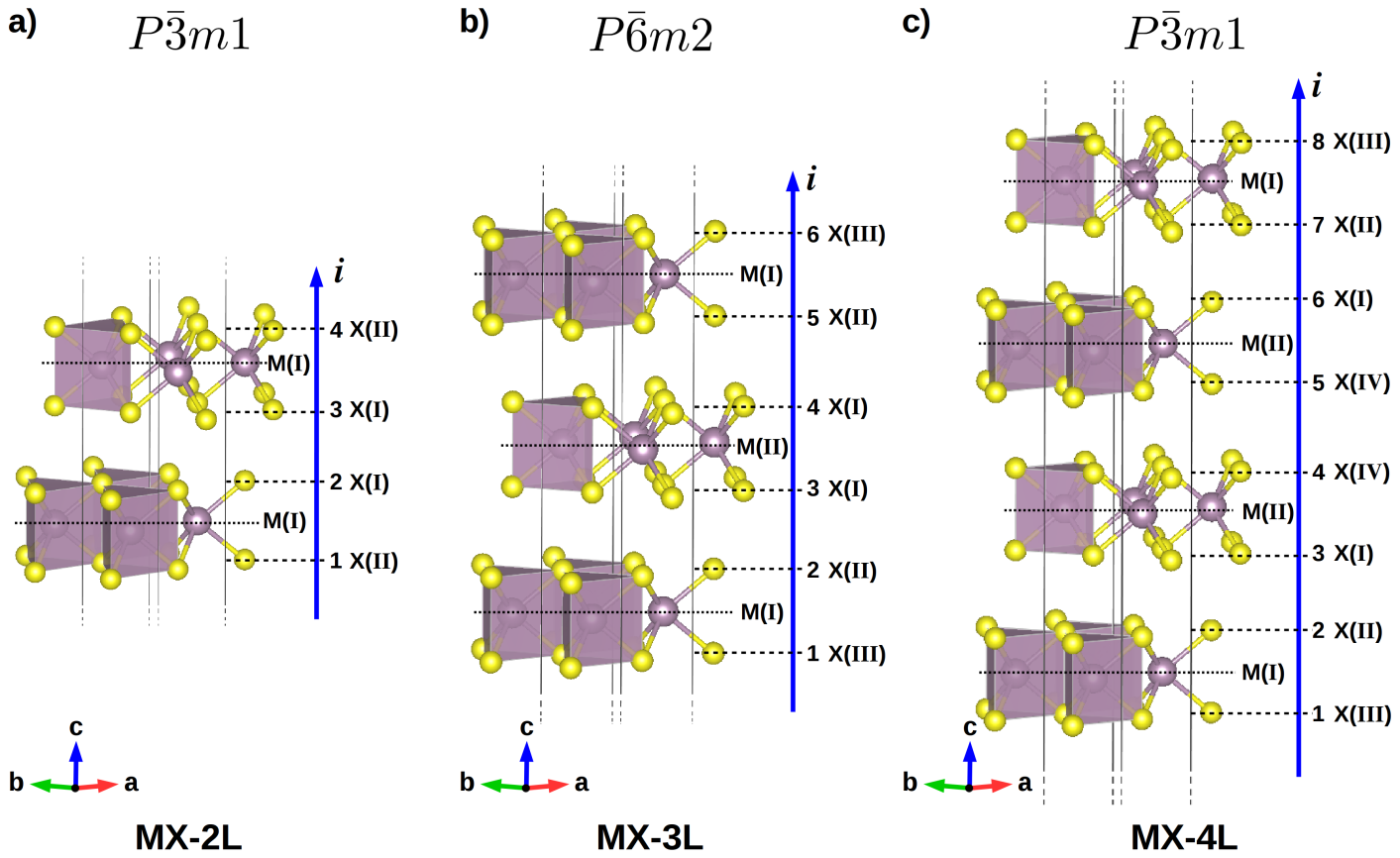
[A. Cammarata, T. Polcar, *RSC Adv.* **5**, 106809 (2015)]



- Interlayer charge distribution is determined by the p_z orbital of the X atoms
- Under load, electronic charge flows from inter- to intralayer region via p_x and p_y orbitals of X atom:
  X $p_z \rightarrow$ X $p_x, p_y \rightarrow$ M e_g
- Cophonicity is independent of the load and restricts the frequency variation against the applied load

MX_2 *n*-layer systems

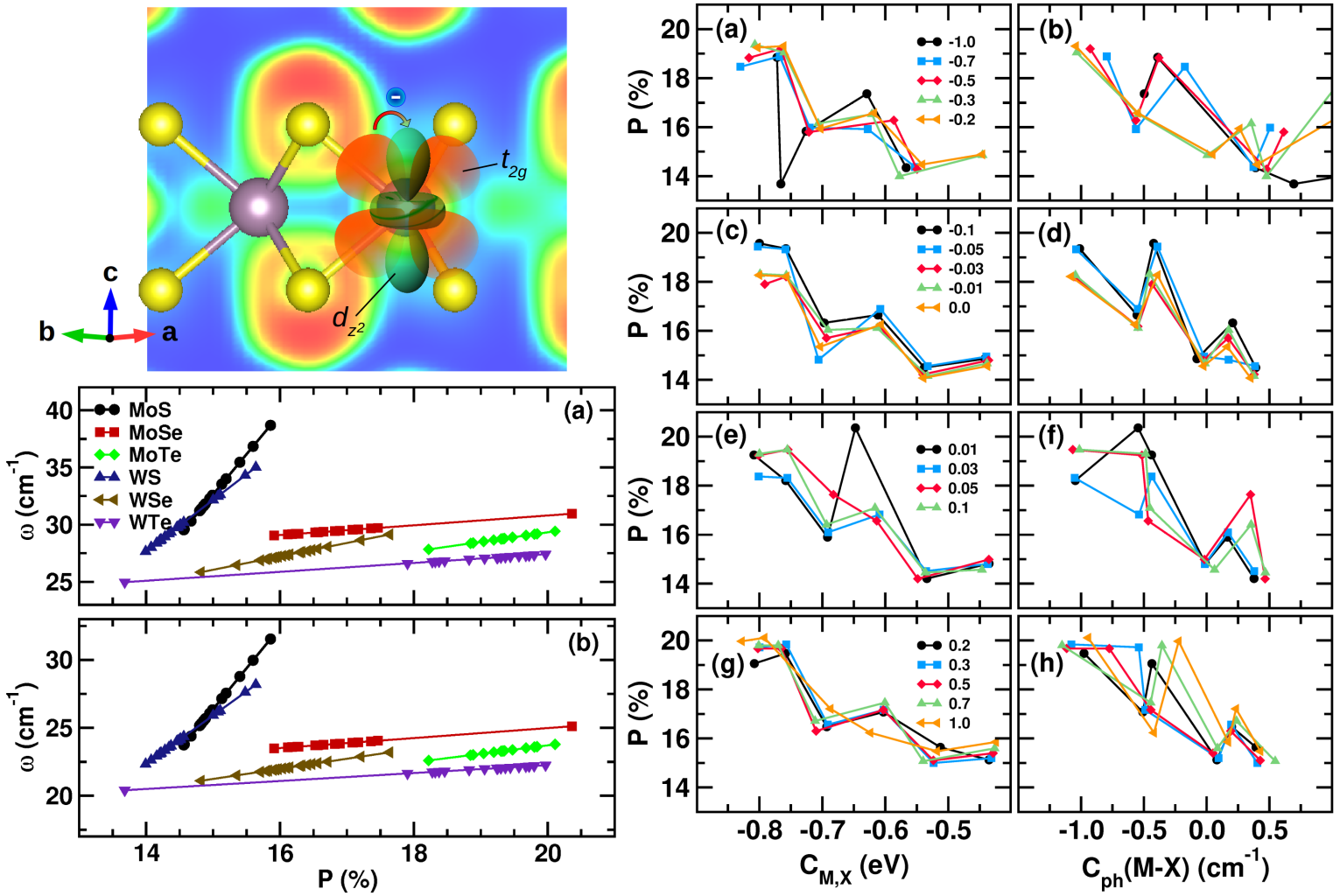
[A. Cammarata, T. Polcar, *Phys. Chem. Chem. Phys.* **18**, 4807 (2016)]



Cophonicity $\Rightarrow$ Inter-layer orb. pol. $\Rightarrow$ Electro-vibrational coupling

Charged MX_2 Systems

[A. Cammarata, T. Polcar, *Nanoscale* **9**, 11488 (2017)]



Cophonicity and covalency as a knob to control electron-phonon coupling

Conclusions and Future Directions

Results:

- Crystal MoS_2 formation from amorphous phase by temperature quenching
- The greater the incommensuration, the easier the inter-plane shear
- New lattice dynamic metric proposed: *cophonicity*
- New promising tribological material proposed: Ti:MoS_2
- NMTA method decomposes MEPs into phonon contributions
- External Load and perturbation of charge neutrality affect sliding-related vibrational modes
- Cophonicity and covalency are a knob to control the electron-phonon coupling

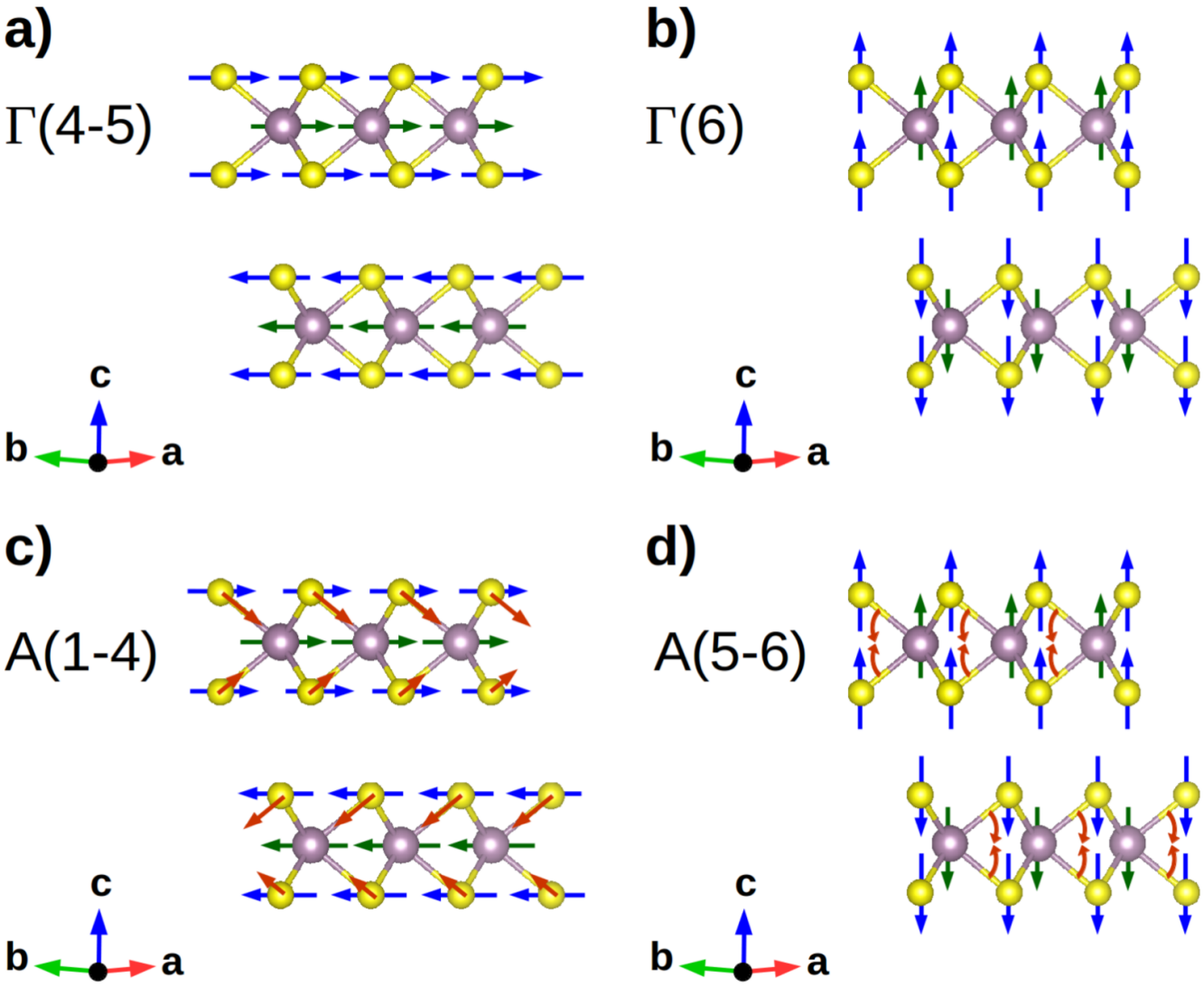
Future Directions:

- Activation/deactivation of selected modes to favor/disfavor layer sliding, exfoliation, internal heat dissipation...
- Applications beyond tribology: Metal-Insulator transitions, linear dielectric response, nonlinear Second Harmonic Generation, phase matchability, ionic conduction...

Thank you very much for your kind attention

Dynamic Analysis

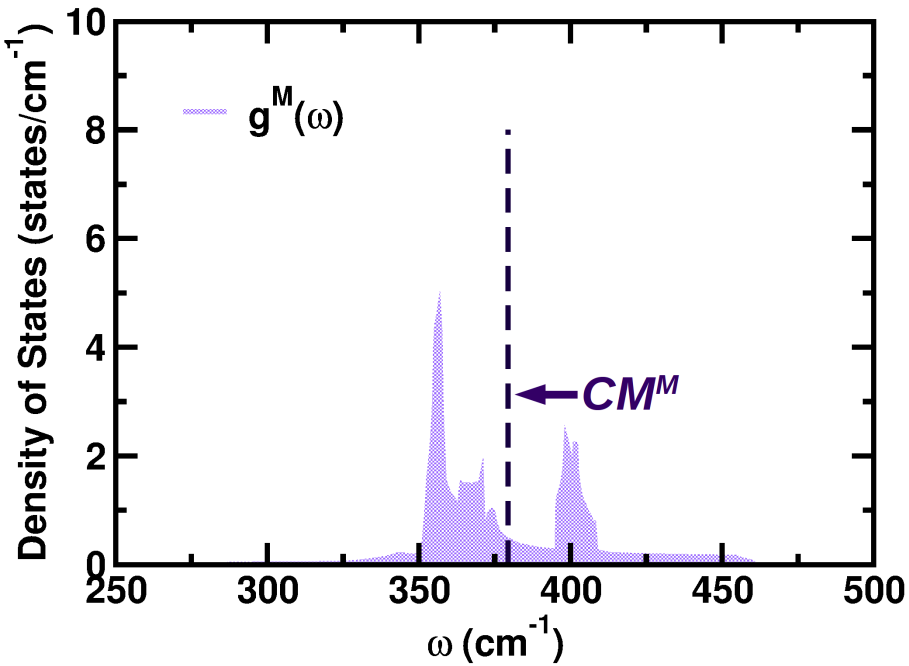
Example of sliding-related modes



The *Cophonicity* Metric

[A. Cammarata, T. Polcar, *Inorg. Chem.* **54**, 5739 (2015)]

In a specific range $[\omega_0, \omega_1]$, the center mass CM^M of $g^M(\omega)$ is defined as $CM^M = \frac{\int_{\omega_0}^{\omega_1} \omega g^M(\omega) d\omega}{\int_{\omega_0}^{\omega_1} g^M(\omega) d\omega}$

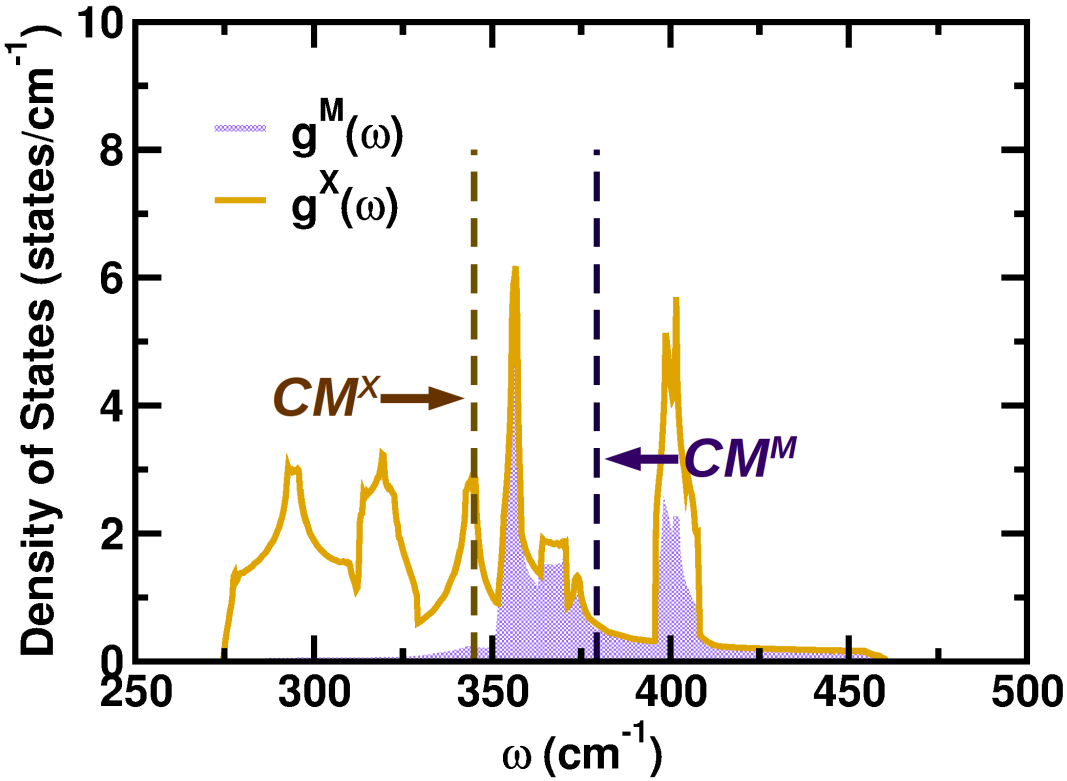


We call $\int_{\omega_0}^{\omega_1} g^M(\omega) d\omega$ the **phonicity** of the M atom

The *Cophonicity* Metric

[A. Cammarata, T. Polcar, *Inorg. Chem.* **54**, 5739 (2015)]

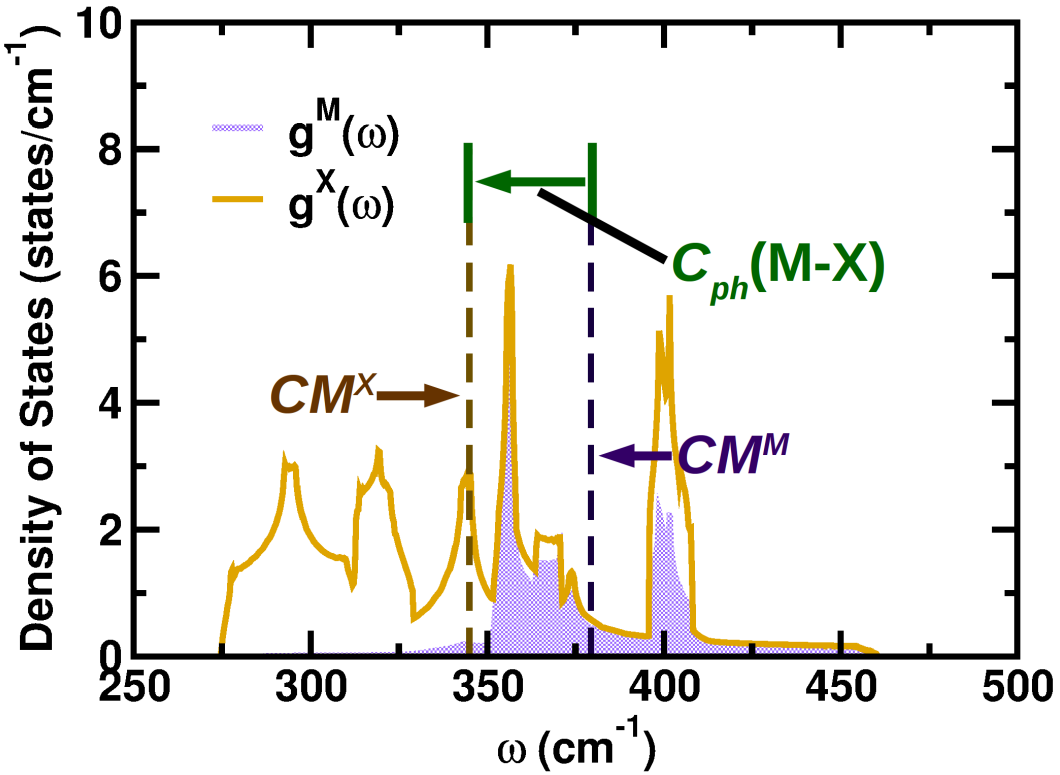
In general, M and X atomic contributions are centered around distinct phonon frequencies



The *Cophonicity* Metric

[A. Cammarata, T. Polcar, *Inorg. Chem.* **54**, 5739 (2015)]

The relative position C_{ph}(M-X) of CM^M with respect to CM^X is $C_{ph}(\text{M-X}) = CM^M - CM^X$



We call C_{ph}(M-X) the **cophonicity** of the M-X atomic pair

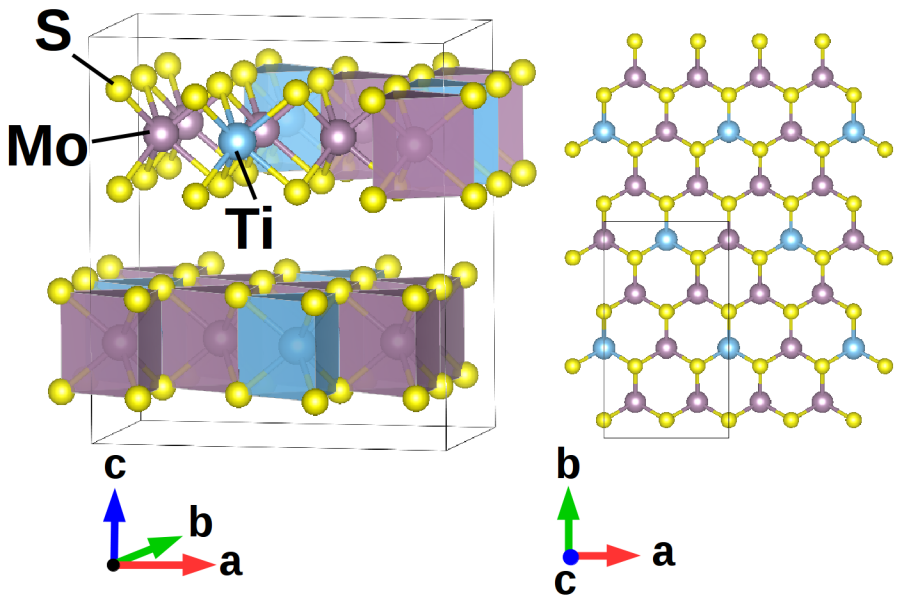
Computational Details

- Geometries: Hexagonal $P6_3/mmc$ (SG# 194)
- closed shell configuration
- Density Functional Theory, General Gradient Approximation (DFT-GGA): Perdew-Burke-Ernzerhof (PBE) (Phys. Rev. Lett. **77**, 3865 (1996))
- DFT-D2 Grimme correction (J. Comp. Chem. **27**, 1787 (2006))
- Vienna Ab-initio Simulation Package (VASP)
- Plane-wave cut-off: 700 eV
- PHONOPY package
- Monkhorst-Pack mesh: $7 \times 7 \times 5$ for VASP, $41 \times 41 \times 41$ for PHONOPY

The Ti:MoS_2 System

Cmcm (SG 63), relaxed structure

[A. Cammarata, T. Polcar, *Inorg. Chem.* **54**, 5739 (2015).]



Lattice parameters: $a = 6.46321$, $b = 11.19461$, $c = 12.56747$				
Mo	4c	0	0.16767	1/4
Ti	4c	0	0.41744	1/4
Mo	8g	1/4	0.16767	1/4
S	8f	0	0.58487	0.12745
S	8f	0	0.08424	0.12685
S	16h	0.74866	0.33385	0.12831