Tuning Nanoscale Intrinsic Friction via Quantum Mechanical Descriptors

5th Users' Conference of IT4Innovations

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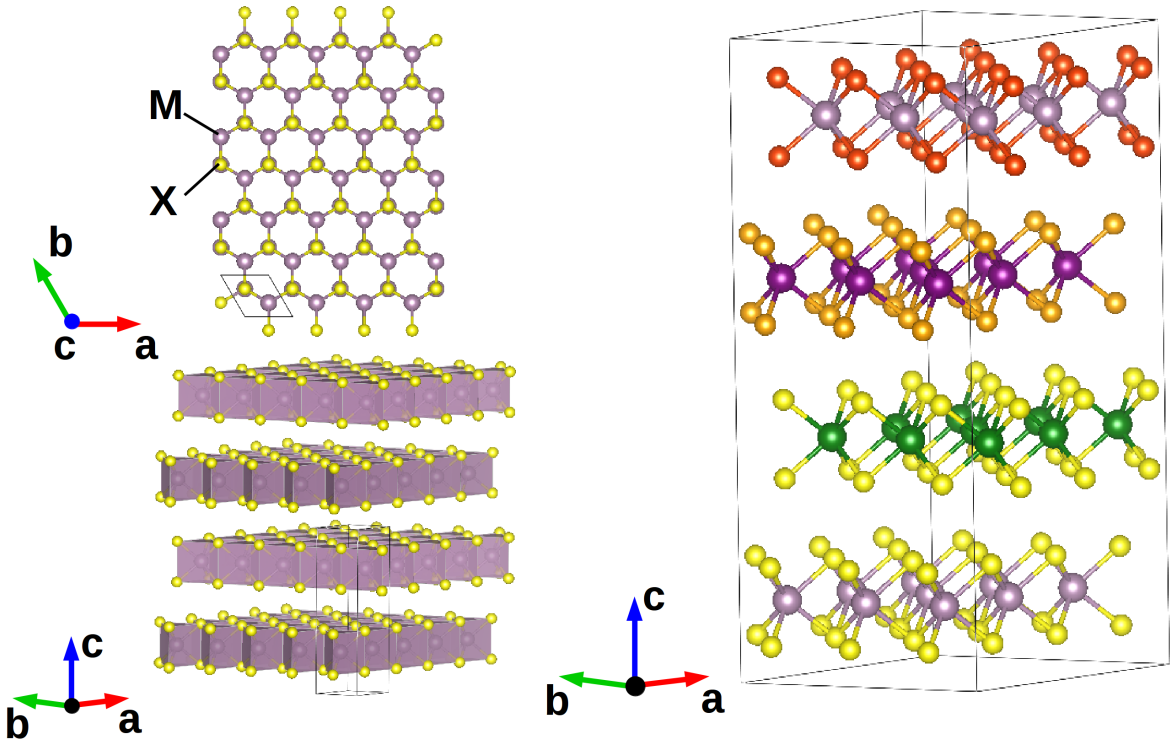
ČESKÉ VYSOKÉ UČENÍ TECHNICKÉ V PRAZE

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)]

Quantum Mechanical Modeling of Intrinsic Friction in Transition Metal Dichalcogenides

IT4Innovation resources

Quantum Mechanical Modeling of Intrinsic Friction in Transition Metal Dichalcogenides

Past projects:

- OPEN-4-20, OPEN-8-2, OPEN-14-9, OPEN-15-48, OPEN-16-13, OPEN-17-16
- $\sim$ 16.5 MCPUh
- Anselm, Salomon, Barbora

Running:

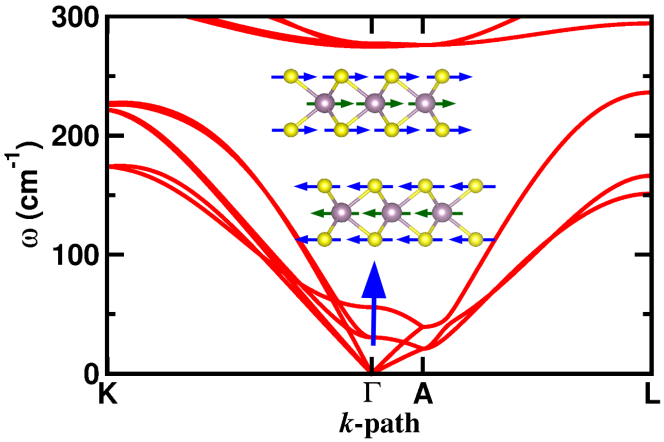
- OPEN-23-37, "harnEss Nanofriction with LIGHT" (ENLIGHT)
- $\sim$ 2.1 MCPUh
- Karolina

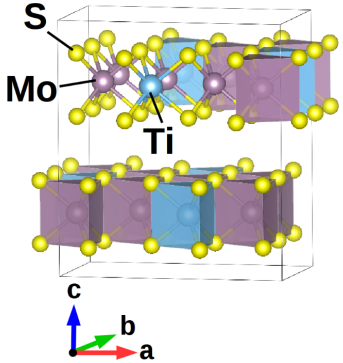
A big thank you to the IT4I support for the prompt resolution of technical issues and requests

Material Design

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

Phonon eigendisplacements are a complete basis for the geometric description of layer sliding



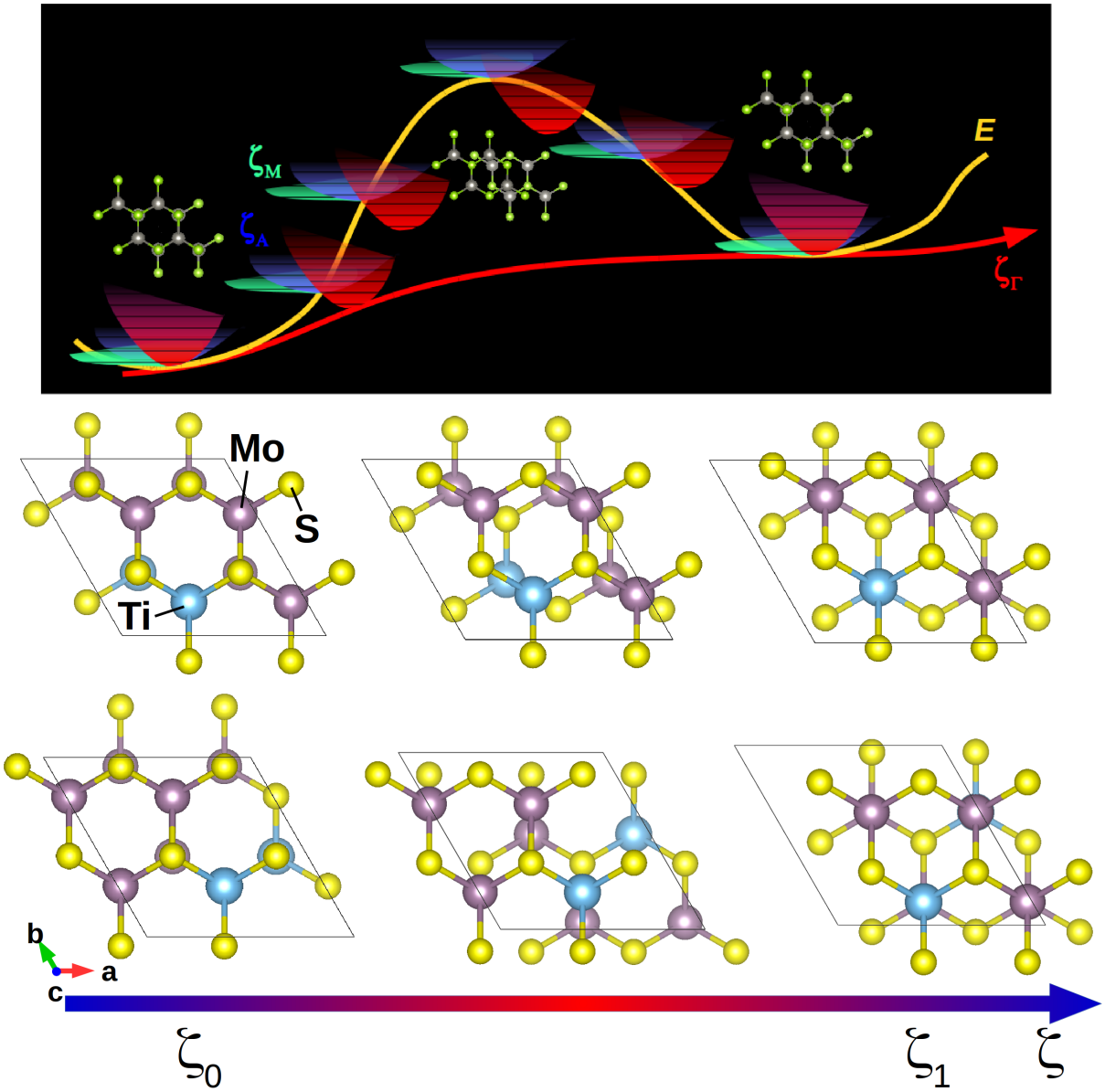


- Identification of the vibrational modes related to layer sliding (**sliding modes**)
- Relations among mode frequencies, covalency, orbital polarization, distortions, cophonicity...
- Selection of proper geometry and chemistry

Design of new TMD: Ti:MoS_2

Normal-Modes Transition Approximation

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



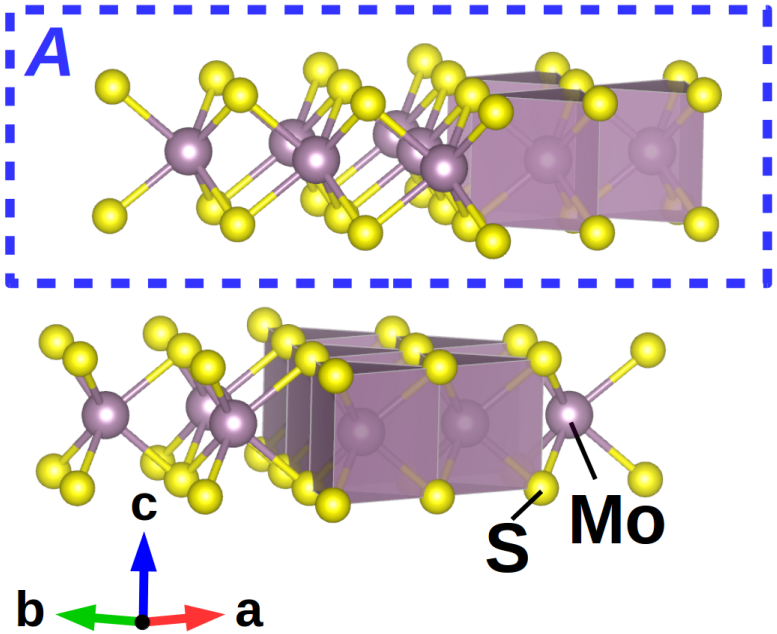
Design of Friction and Energy Dissipation

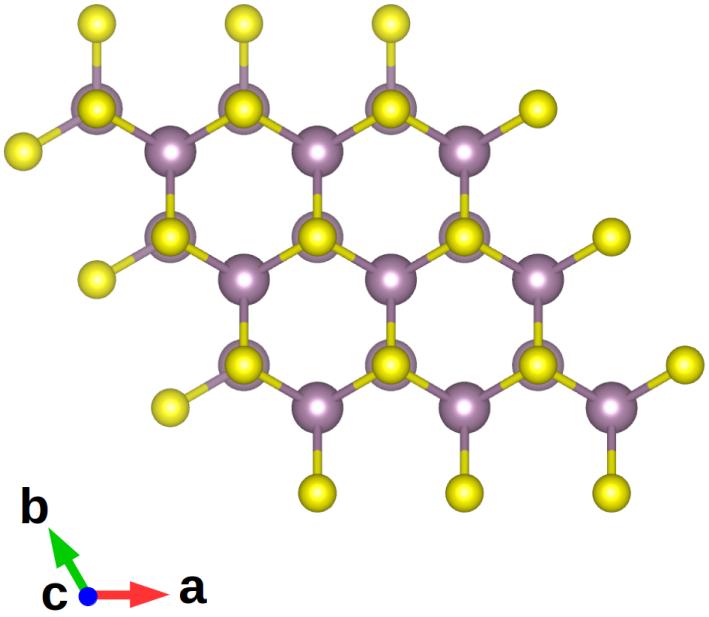
[A. Cammarata, P. Nicolini et al. *Phys. Rev. B* **99**, 094309 (2019)]

Chemistry and geometry of the stable structure determine energy dissipation, thus frictional properties, via phonon-phonon scattering processes:

$$\mathcal{P}_{jj'}^{j''} \propto nn'(n''+1)|\Phi_{jj'j''}|^2. \quad (1)$$

Identification of such dissipation channels ($\Phi_{jj'j''}$) allows to control frictional properties in non-equilibrium conditions.

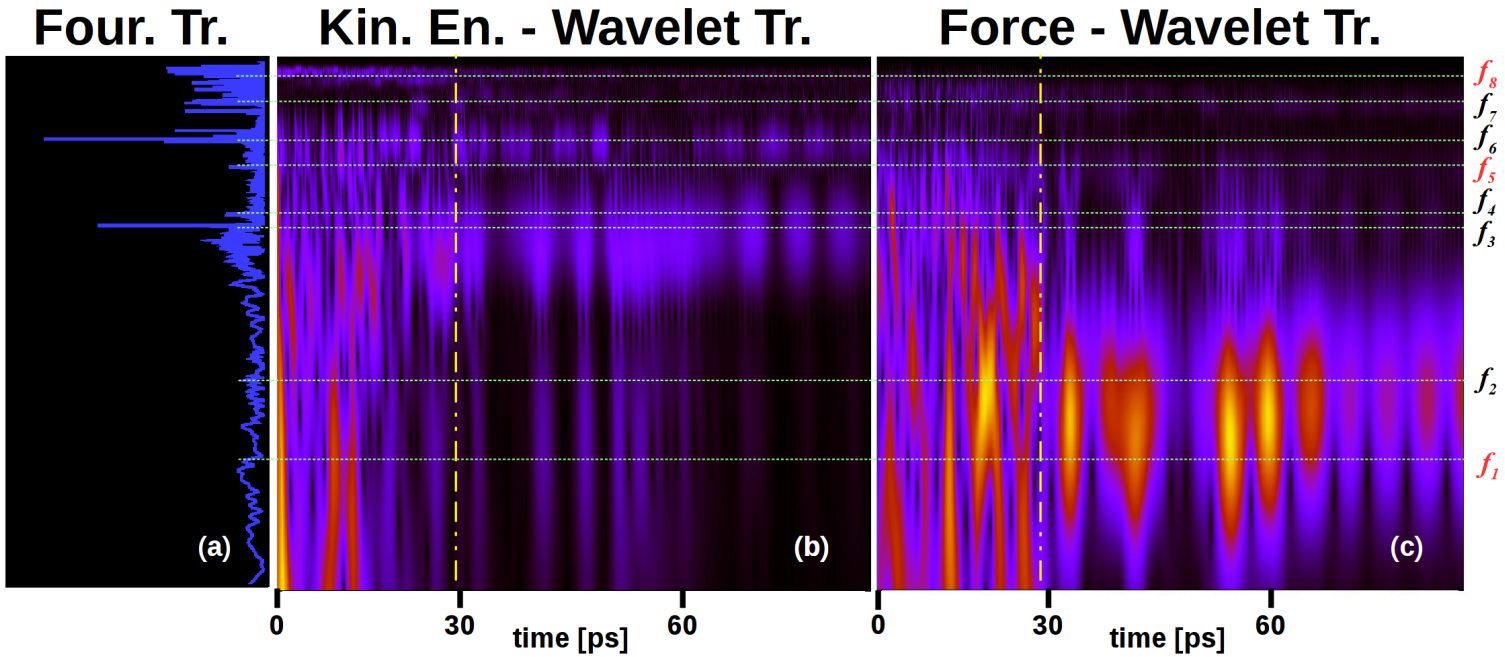




Design of Friction and Energy Dissipation

[A. Cammarata, P. Nicolini et al. *Phys. Rev. B* **99**, 094309 (2019)]

Layer sliding occurs until sliding modes own enough energy



Anharmonic third-order effects can be evaluated by using second-order force constants only:

$$V = \frac{1}{2}\sum_j \omega_j^2 |Q_j|^2 + \frac{1}{6}\sum_{j,j',j''} \Phi_{jj'j''} |Q_j||Q_{j'}||Q_{j''}| \approx$$

$$\approx \frac{1}{3}\sum_j \omega_j^2 |Q_j|^2 + \frac{1}{3}\sum_j \frac{1}{\omega_j^2} \left|\ddot{Q}_j\right|^2$$

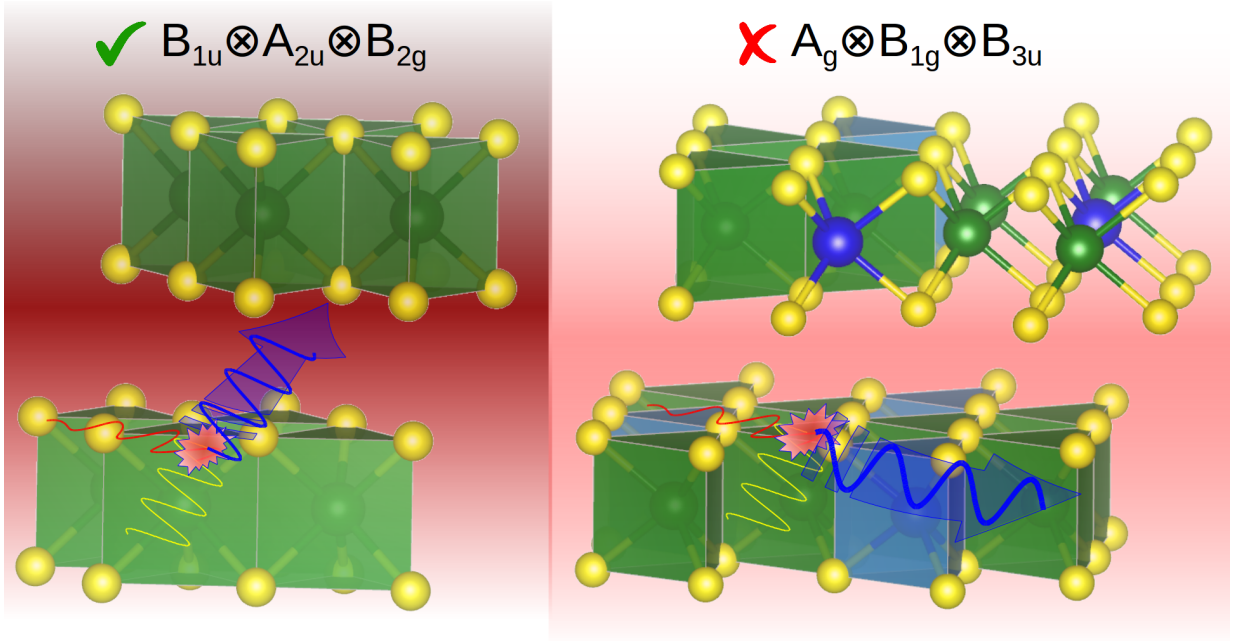
Phonon-Phonon Scattering Selection Rules

[A. Cammarata *RSC Adv.* **9**, 37491 (2019)]

Anharmonic scattering among p phonons is allowed if the direct product among the phonon representations contains the totally symmetric representation:

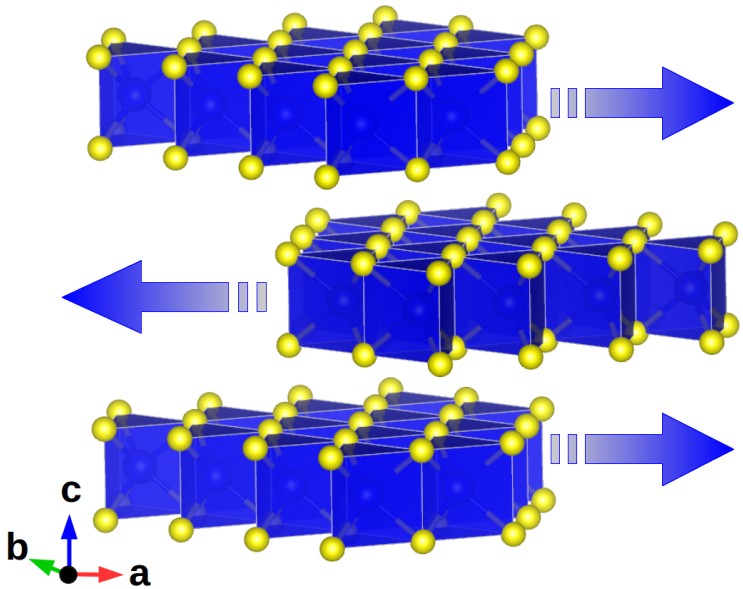
$$\Phi_{\lambda^1\lambda^2\ldots\lambda^p} \neq 0 \Rightarrow \Gamma^{e_\lambda} \otimes \cdots \otimes \Gamma^{e_{\lambda^p}} \subseteq A \tag{2}$$

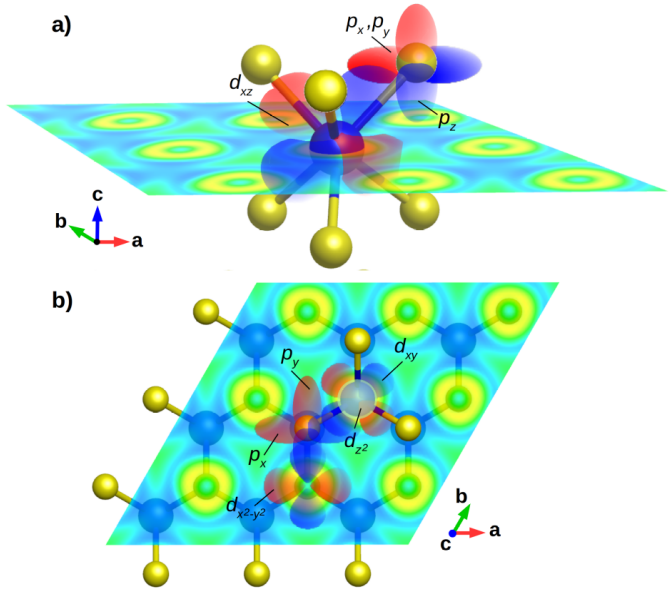
- no need to compute Φ to check if scattering is allowed
- control of symmetries $\Rightarrow$ control of anharmonic processes (friction, energy transfer/dissipation...)



Control of energy dissipation in sliding low-dimensional materials

[A. Cammarata, T. Polcar *Phys. Rev. B* **102**, 085409 (2020)]





- The atomic orbital population and the atomic contribution to sliding phonon modes determine the nanofrictional response
- Reduced amount of energy dissipation is found when the bond character is more ionic and the layer sliding is realized by a faster motion of the chalcogen atoms

Conclusions and Future Directions

Results:

- New lattice dynamic metric proposed: *cophonicity*
- New tribological material proposed: Ti:MoS_2
- Cophonicity, covalency and orbital populations are a knob to control the electron-phonon coupling and tune the friction-related vibrational modes
- Phonon-based description of friction and energy dissipation
- Control of friction and energy dissipation via fine tuning of phonon modes and anharmonic interactions

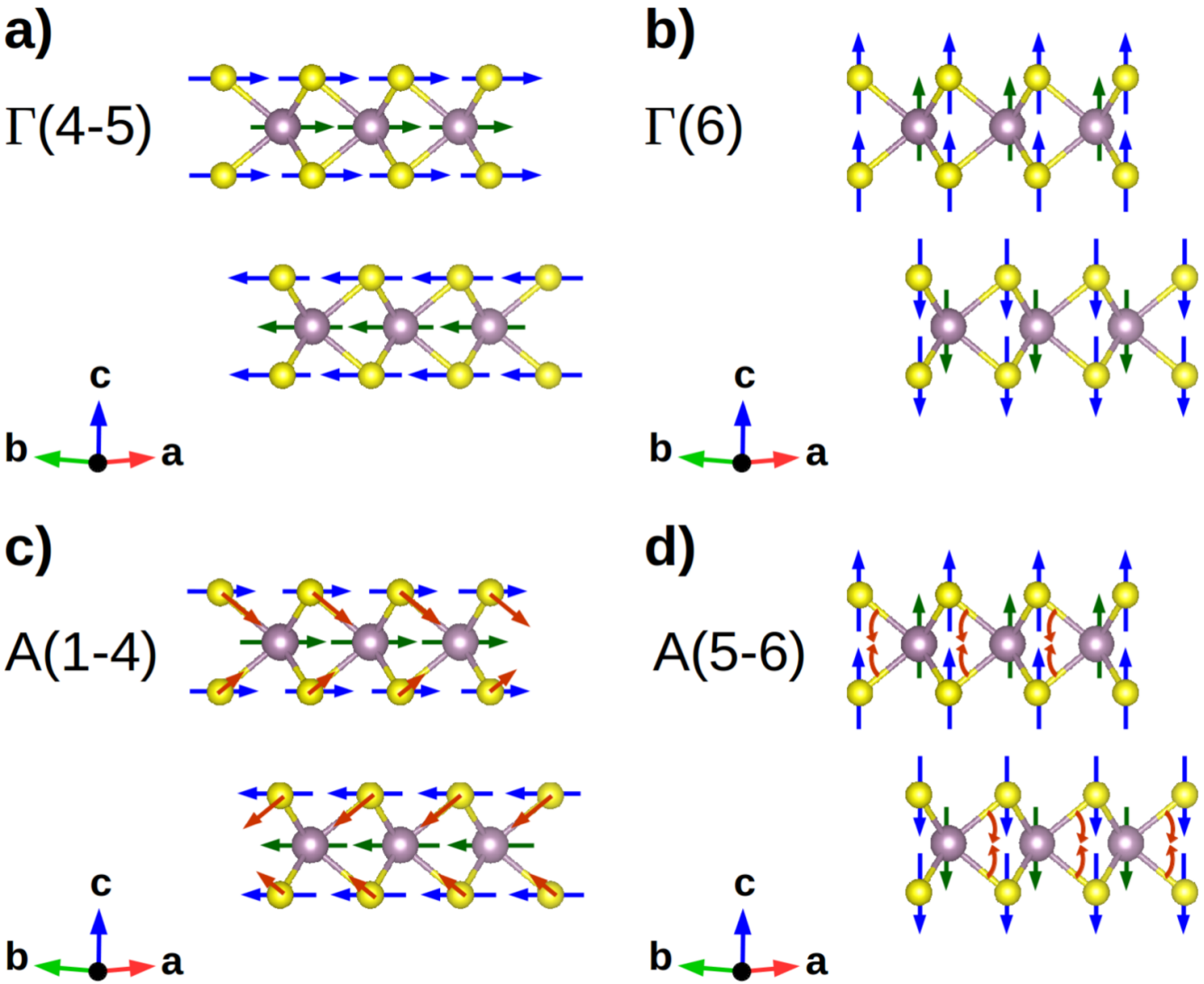
Future Directions:

- Activation/deactivation of selected processes to favor/disfavor layer sliding, exfoliation, directional heat transfer...
- 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

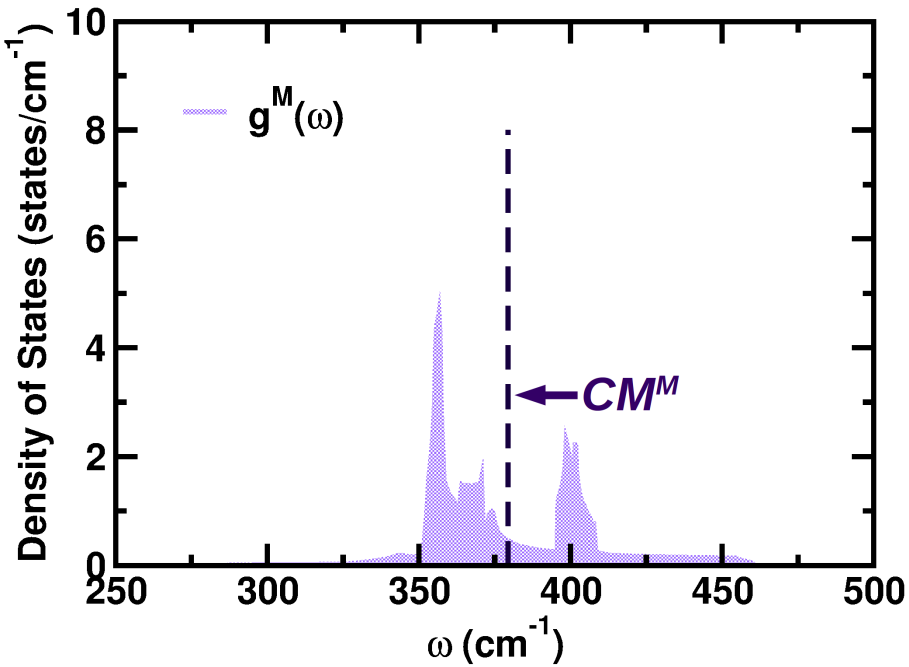
Example of sliding-related modes



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 $CM^M = \frac{\int_{\omega_0}^{\omega_1} \omega g^M(\omega) d\omega}{\int_{\omega_0}^{\omega_1} g^M(\omega) d\omega}$

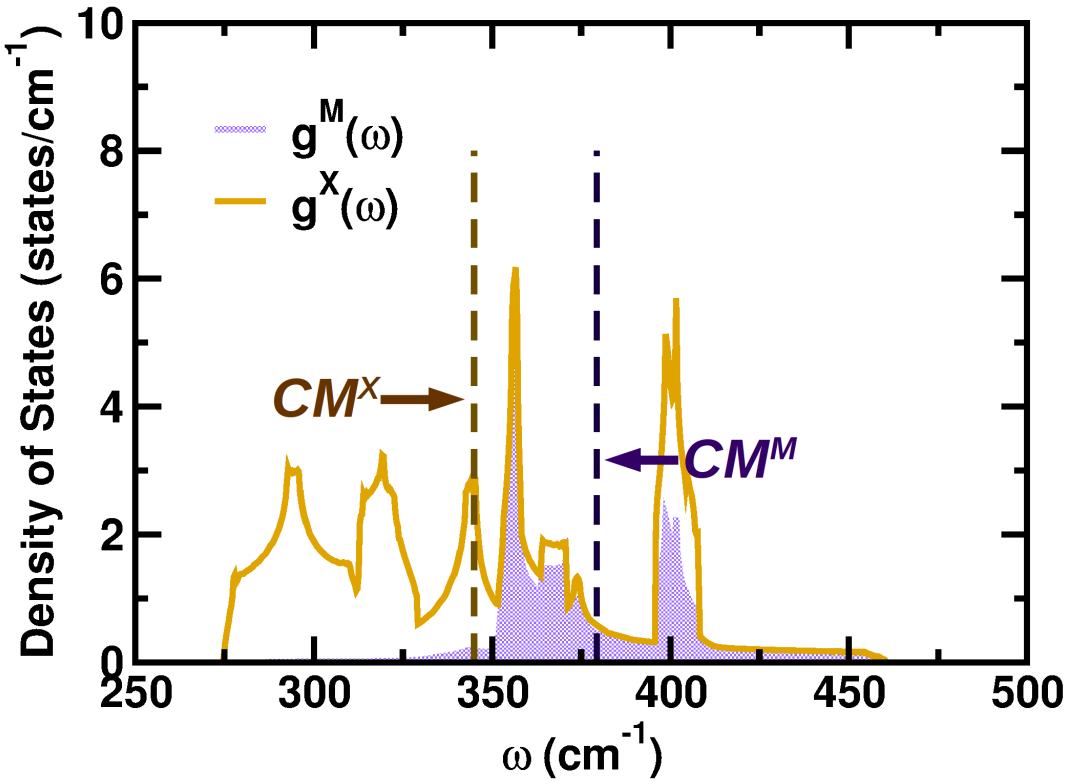


We call $\int_{\omega_0}^{\omega_1} g^M(\omega) d\omega$ the **phonicity** of the M atom

The *Cophonicity* Metric

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

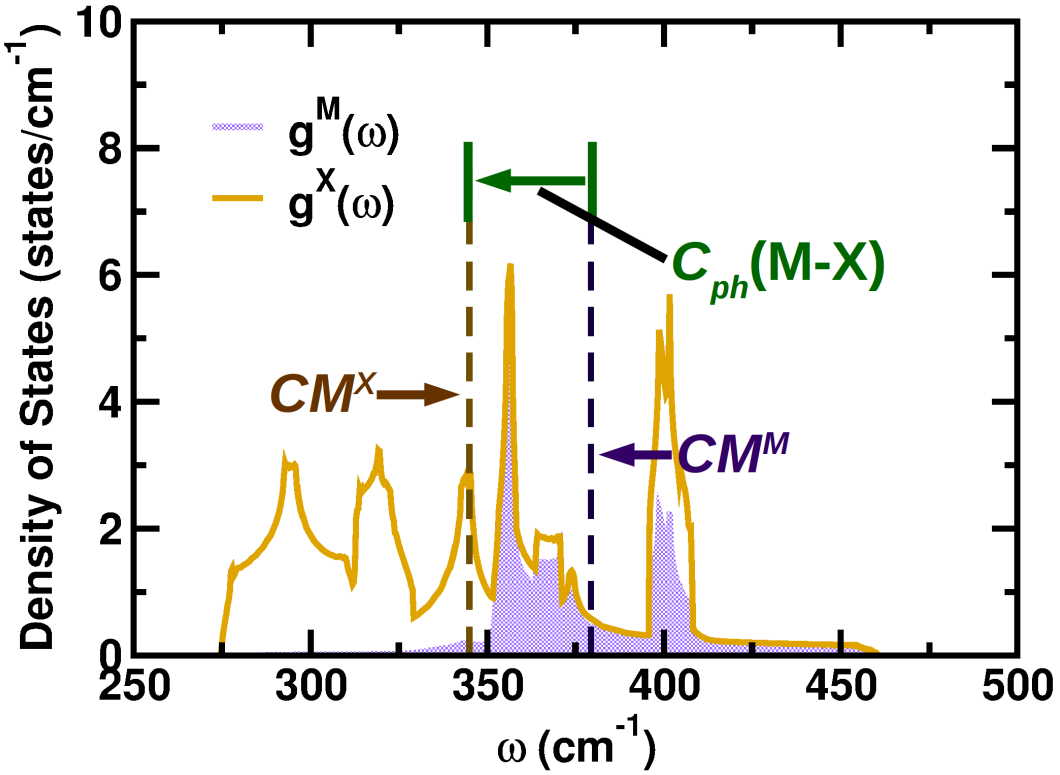
In general, M and X atomic contributions are centered around distinct phonon frequencies



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

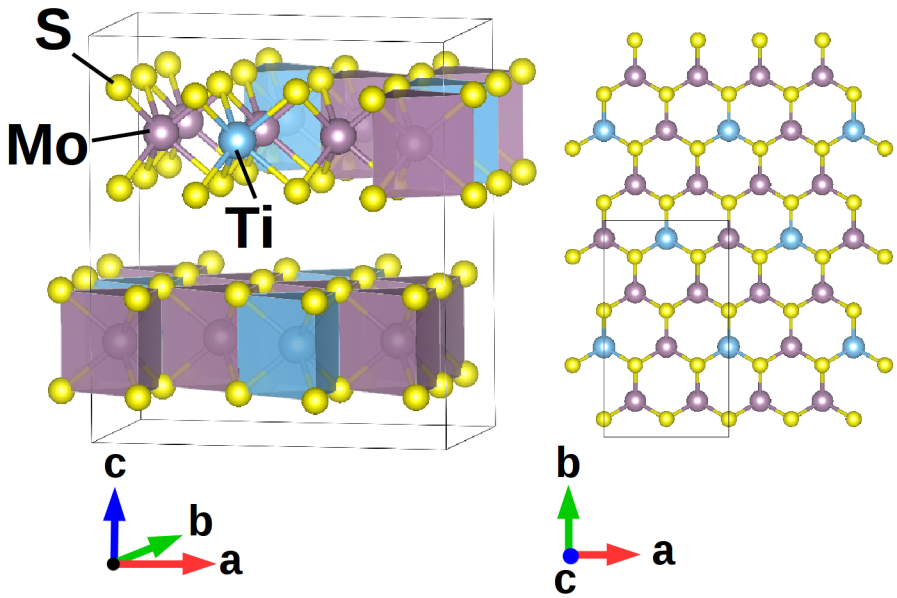
Computational Details

- 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