Theoretical spectroscopy of single-layer and few-layers MoS_2

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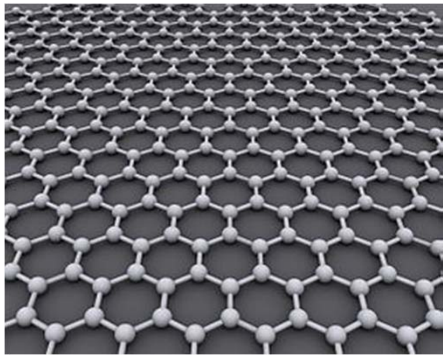
Outline

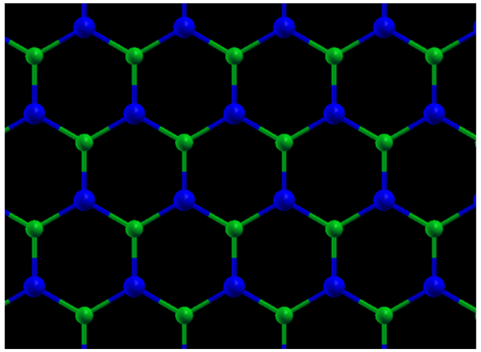
- MoS_2 single-layer electronic structure and excitonic spectra.
- Phonons in MoS_2.
- Raman spectroscopy for determining the number of layers.

MoS_2 single-layer

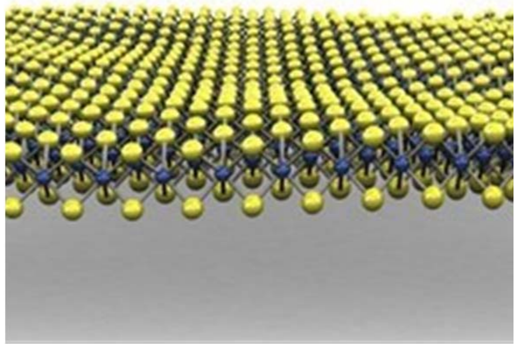
Graphene has focused attention in other 2-dimensional materials



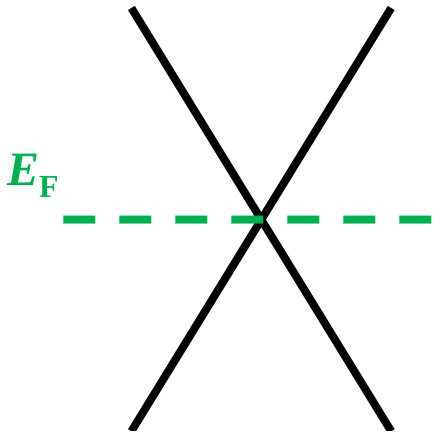
Graphene



Hexagonal boron nitride



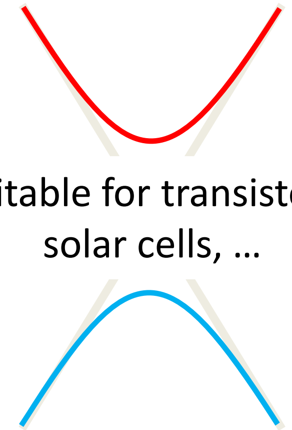
Molybdenum disulfide



No bandgap

“Very” wide band-gap

$\sim$ 6 eV

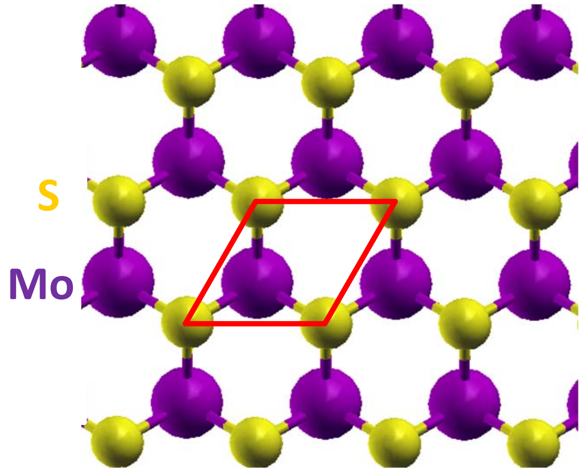


Suitable for transistors, solar cells, …

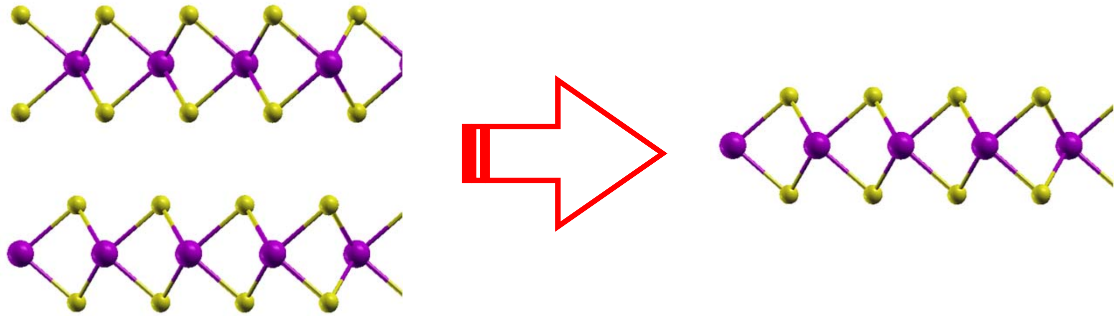
$\sim$ 1.9 eV

MoS_2 single-layer

Hexagonal crystal lattice



Single-layers are obtained from mechanical expholiation from MoS_2 bulk, where layers are attached by van der Walls forces.

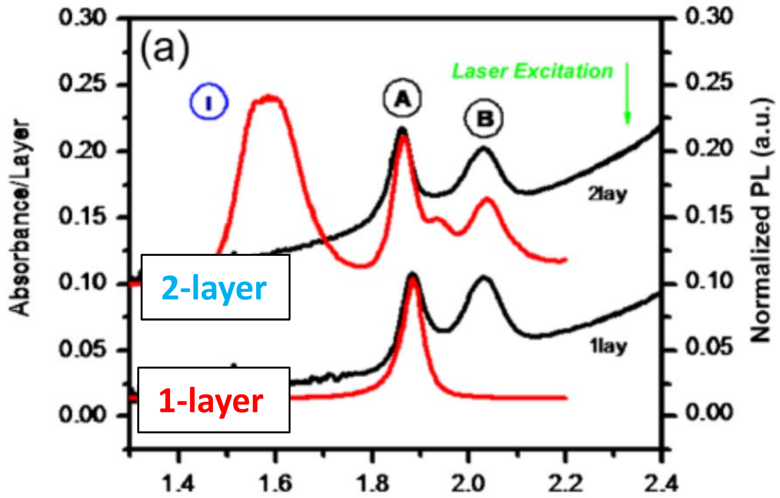


Optical experiments show a transition from indirect bandgap in bulk to a direct bandgap in single-layer.

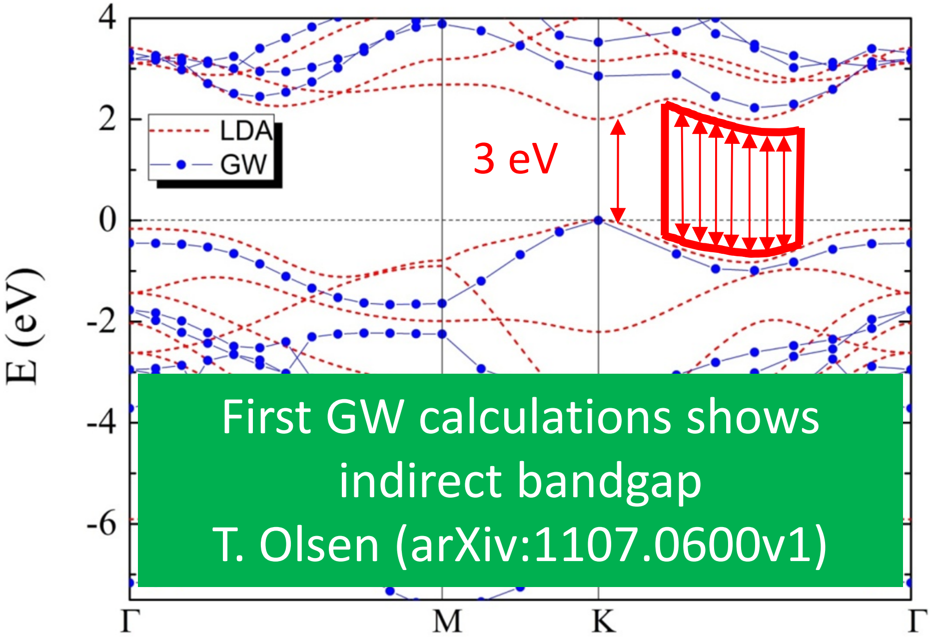
Suitable for transistors and other optoelectronic devices:

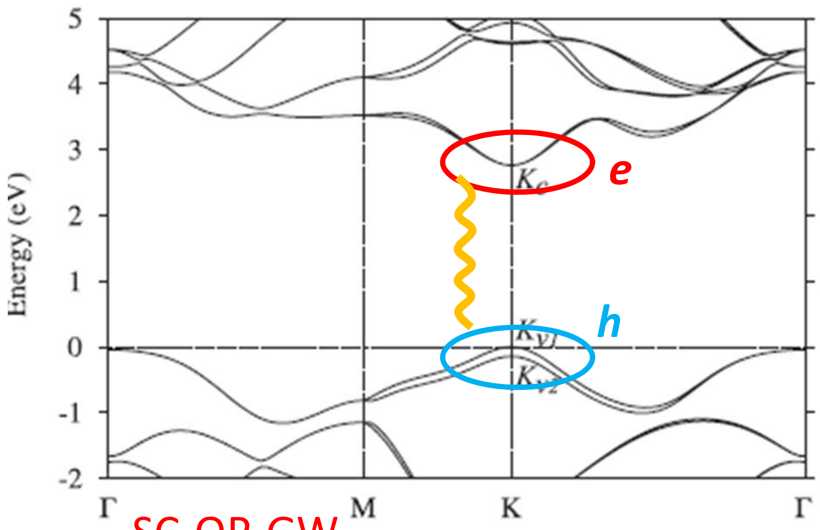
- High mobility (similar to graphene nanoribbons).
- Presumed direct bandgap.
- High quantum efficiency.

Phys. Rev. Lett. 105 (2010)
Nature nanotech 6 (2010)



MoS_2 single-layer band structure



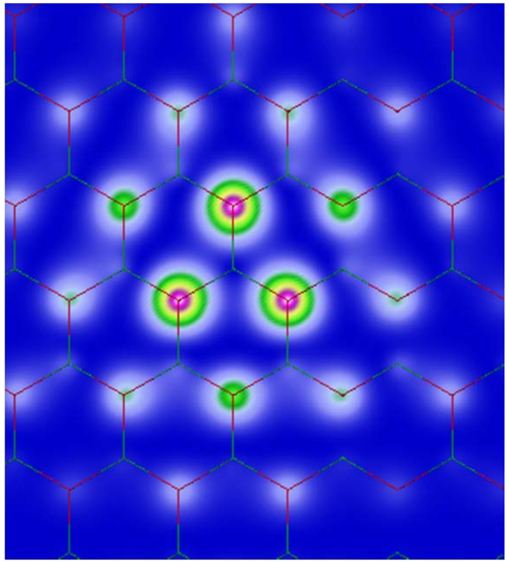


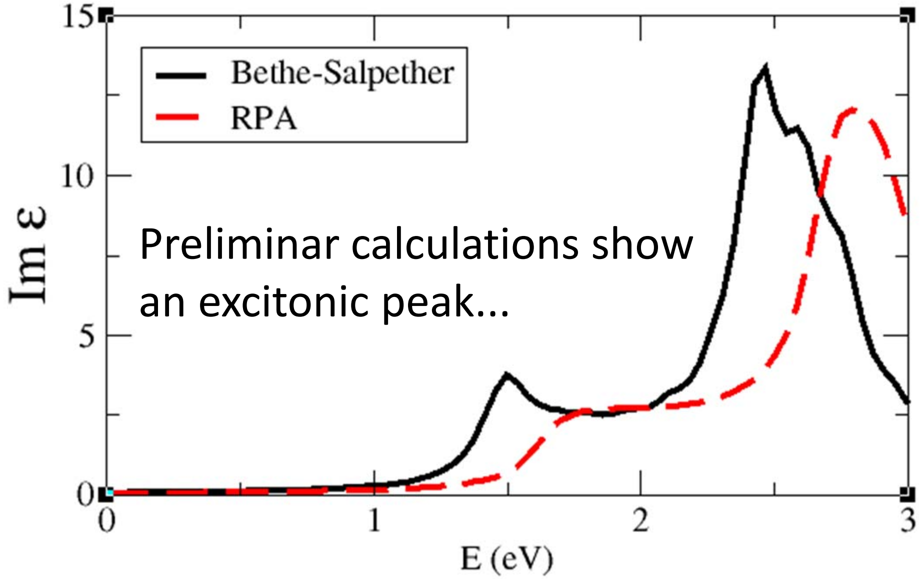
SC-QP-GW
Phys. Rev. B 85, 205302 (2012)

If MoS_2 single-layer has direct or indirect bandgap is not clear:
- The choice of the pseudopotentials.
- The method. LDA, GW, self-consistent GW, etcetera.
- Photoluminescence not always gives the bandgap of the *pure* material.
- Excitonic effects?

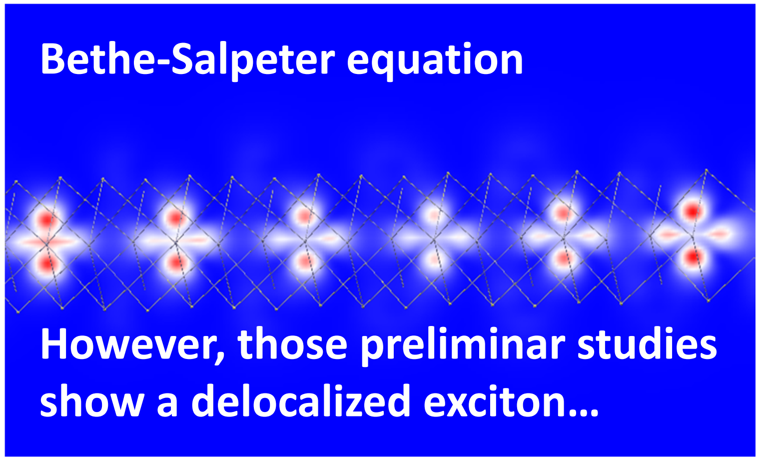
Results in the discussion stage...

MoS_2 single-layer band structure





Do we have a spatially confined exciton as in single-layer BN?



Phonons in MoS_2 single-layer (and bulk)

Phonons and Raman Spectroscopy:

- Determination of the number of layers with atomic resolution.
- Study of the Van der Walls bond.
- Interlayer interaction *versus* dielectric screening.

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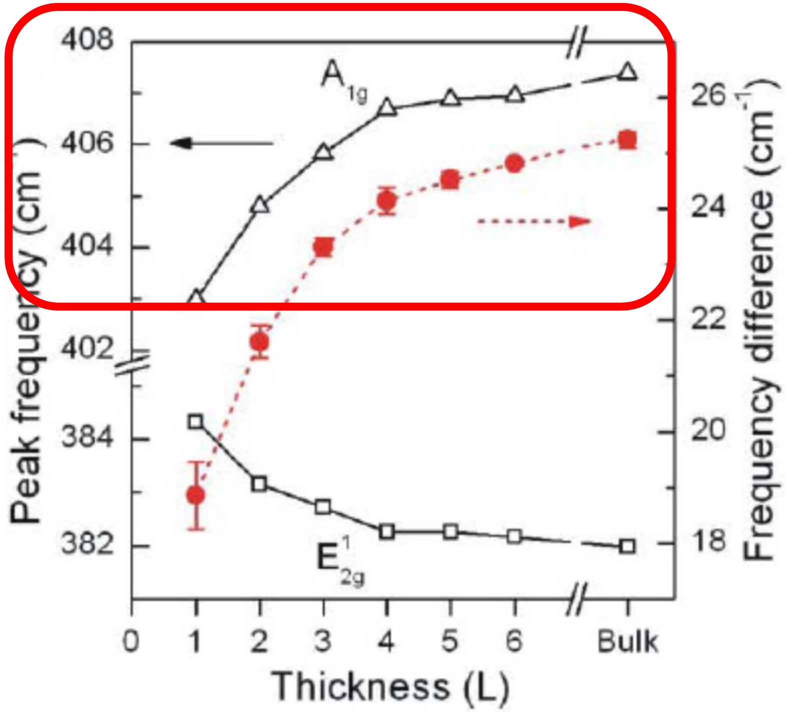
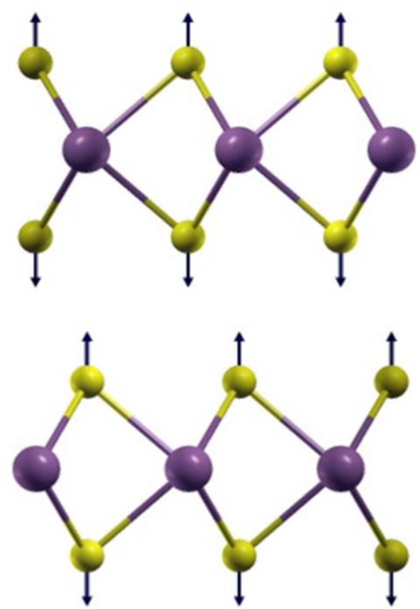


Raman spectra of n-layer MoS_2 samples exhibit:

The frequency of mode A_{1g} increases with the number of layers, presumably by the interlayer interaction.



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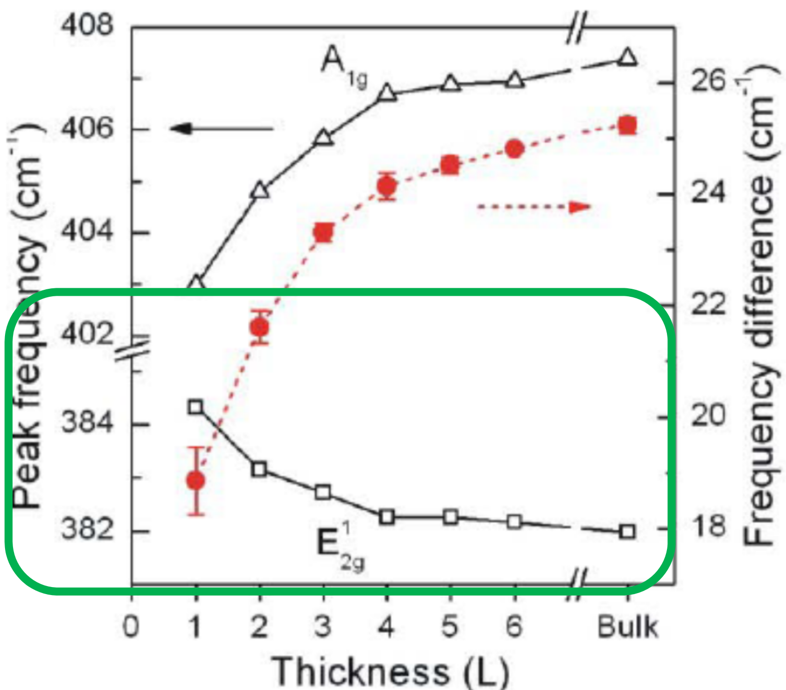
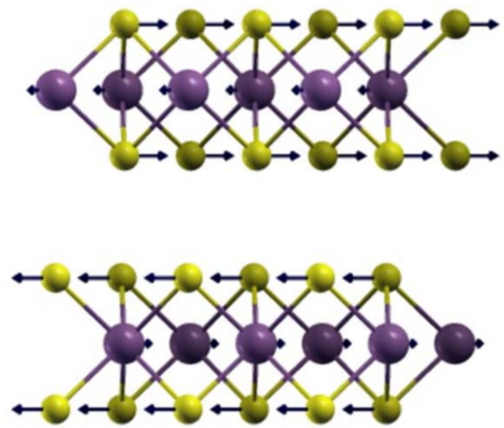


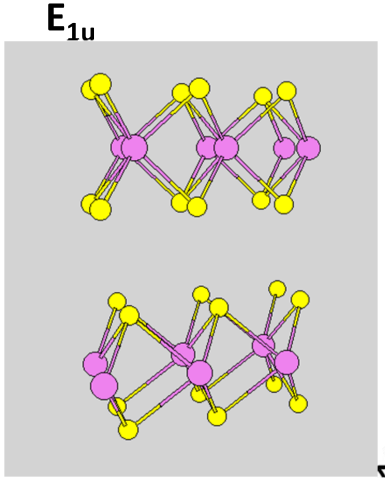
Raman spectra of n-layer MoS_2 samples exhibit:

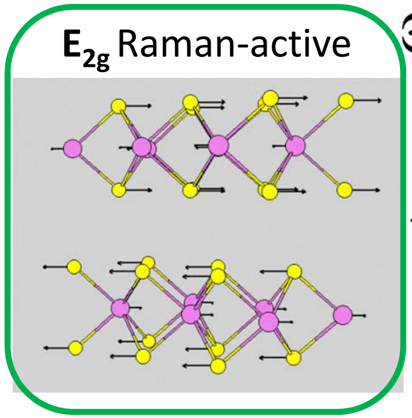
For this phonon mode, the frequency decreases.
Intuition says that interlayer interaction tends to increase the frequency.

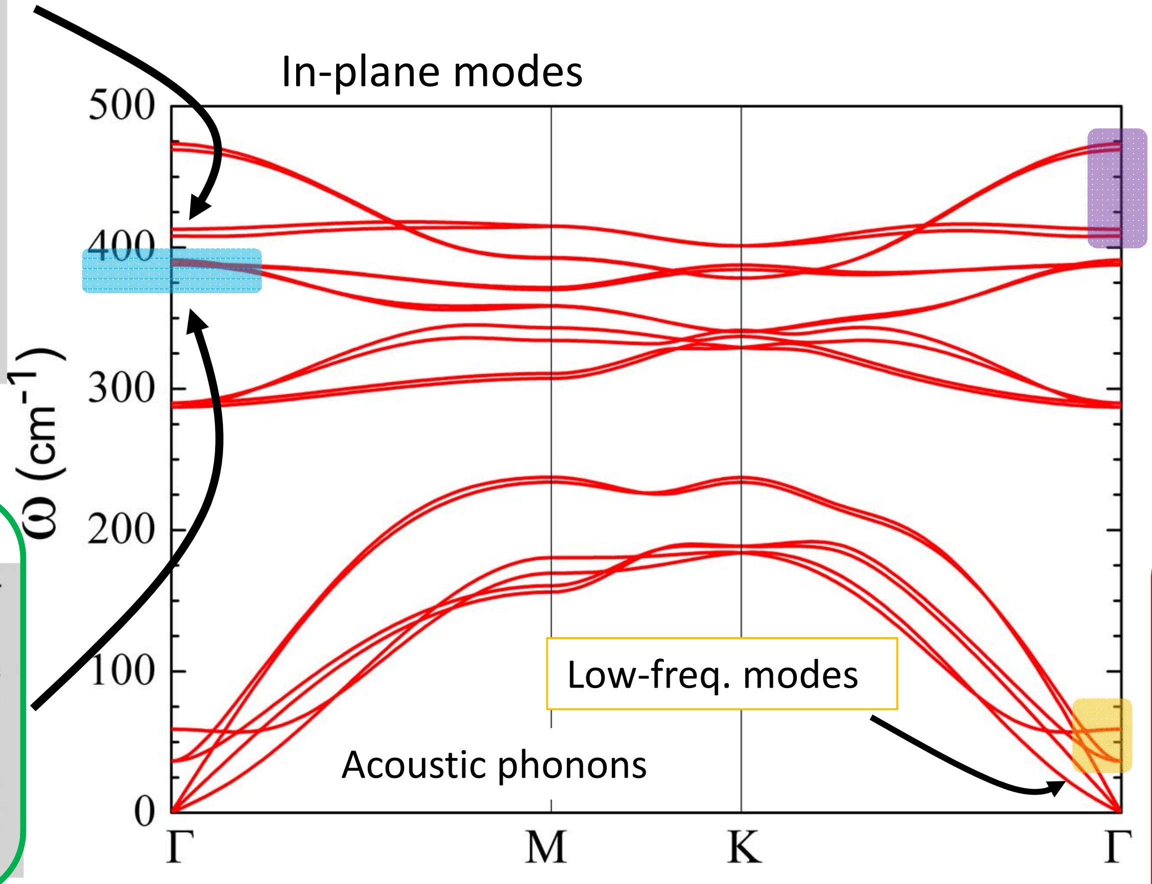


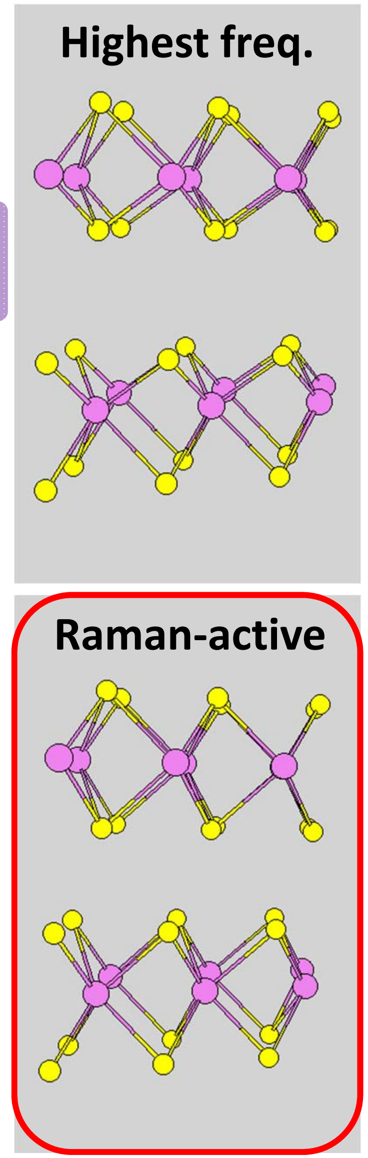
Theoretical modelling of phonons of MoS_2 n-layer systems for a better understanding

Phonons in MoS_2 (bulk)



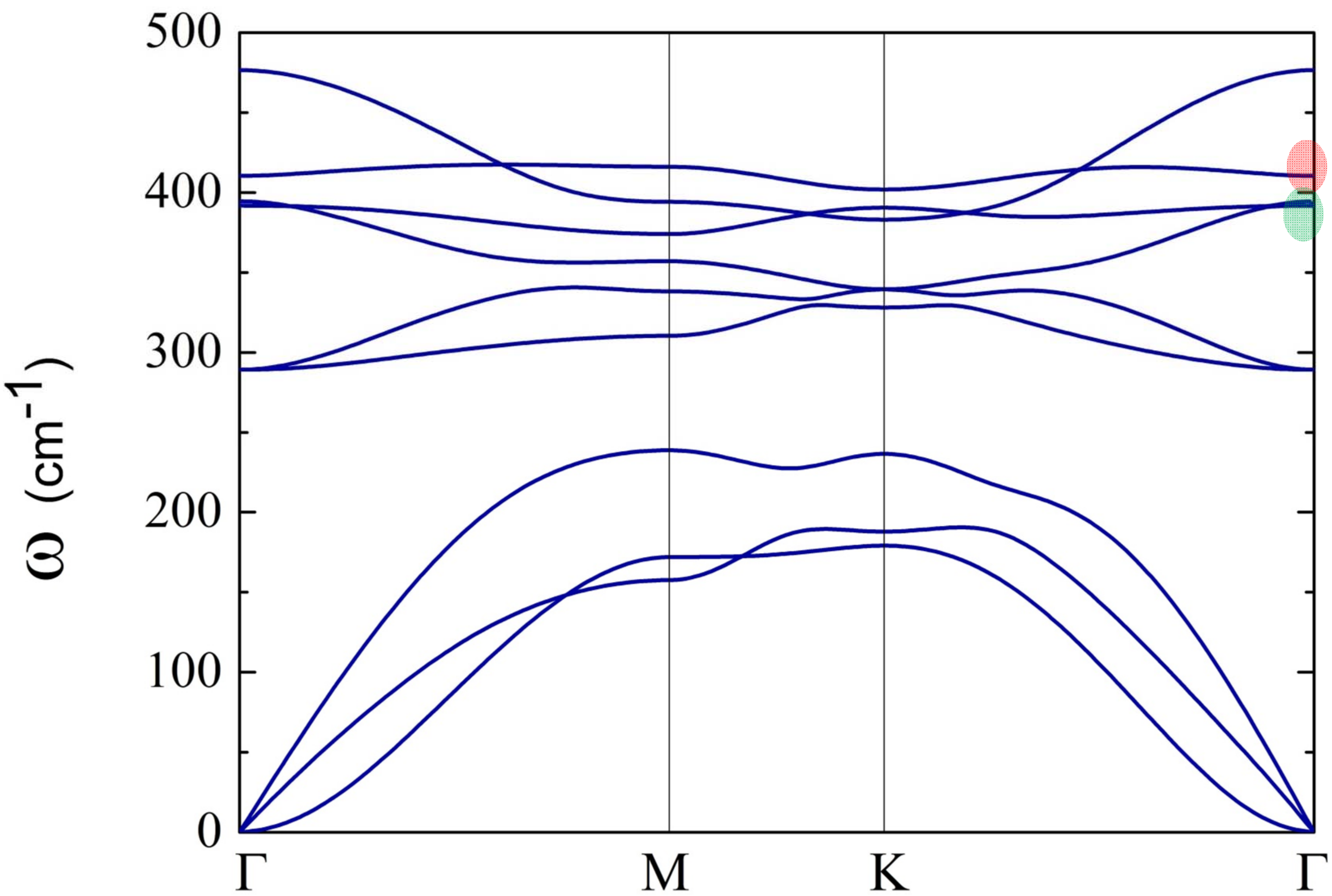






Low-freq. modes: Useful for detecting the number of layers.

Phonons in MoS_2 (single-layer)



A_{1g} phonon mode at lower frequency

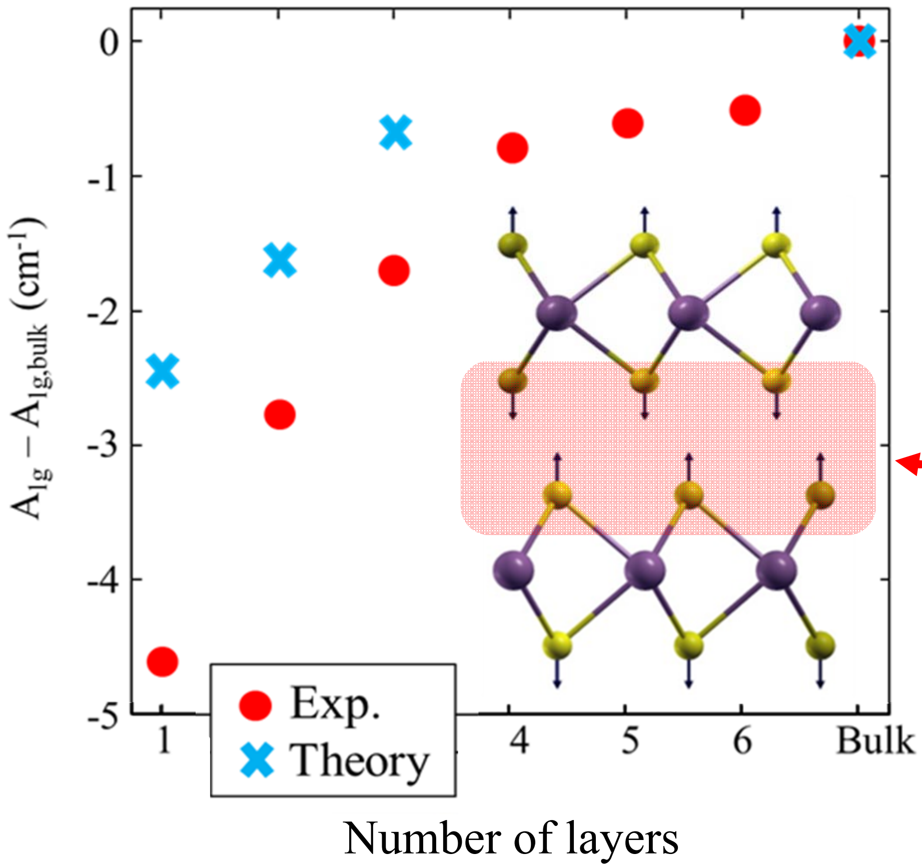
E_{2g} phonon mode at higher frequency

E_{1g} = E_{2u} are now a degenerate mode

Extinction of low-frequency modes

Raman spectroscopy

A_{1g} mode



- Upshift of the frequency with the number of layers.
- Important interaction between sulfur atoms of neighboring layers (equivalent to add an "string" between layers).
- Atomic force constant:

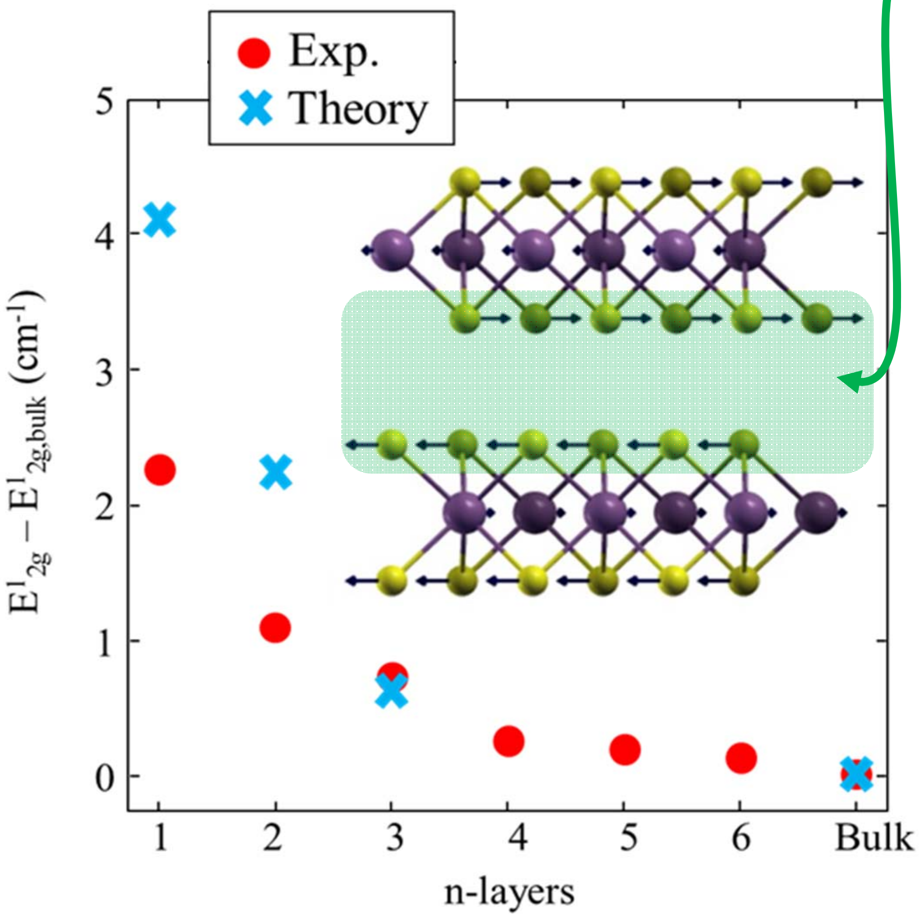
$$C_{I\alpha,J\beta}(\boldsymbol{q}) = -\frac{dF(I,\alpha)}{du(J,\beta)}$$

- In this case is negative and tends to increase the frequency.

The weak interlayer interaction implies the up-shift of the phonon frequency

Raman spectroscopy

E^1_{2g} mode



- Interlayer interaction is weaker.
- Self-interaction term:

$$C_{I\alpha,J\beta}\,(\mathbf{0}) = \sum \frac{dF(I,\alpha)}{du(J,\beta)}$$

- This term has a long-range contribution (it depends on the dielectric tensor) and a short range contribution.
- Short-range cont. is mostly the same for single-layer and bulk.
- The dielectric tensor is much higher in bulk and makes the interaction weaker.

The decrease of frequency is related with a stronger dielectric screening of the longrange Coulomb interaction

Conclusions

- Combination of Raman and phonon calculations gives an accurate counting of layers and a detailed investigation of interlayer interaction.

Incoming work

- GW + BSE results of MoS_2.
- Van der Walls interaction.
- Raman spectroscopy at high pressures.

Acknowledgments

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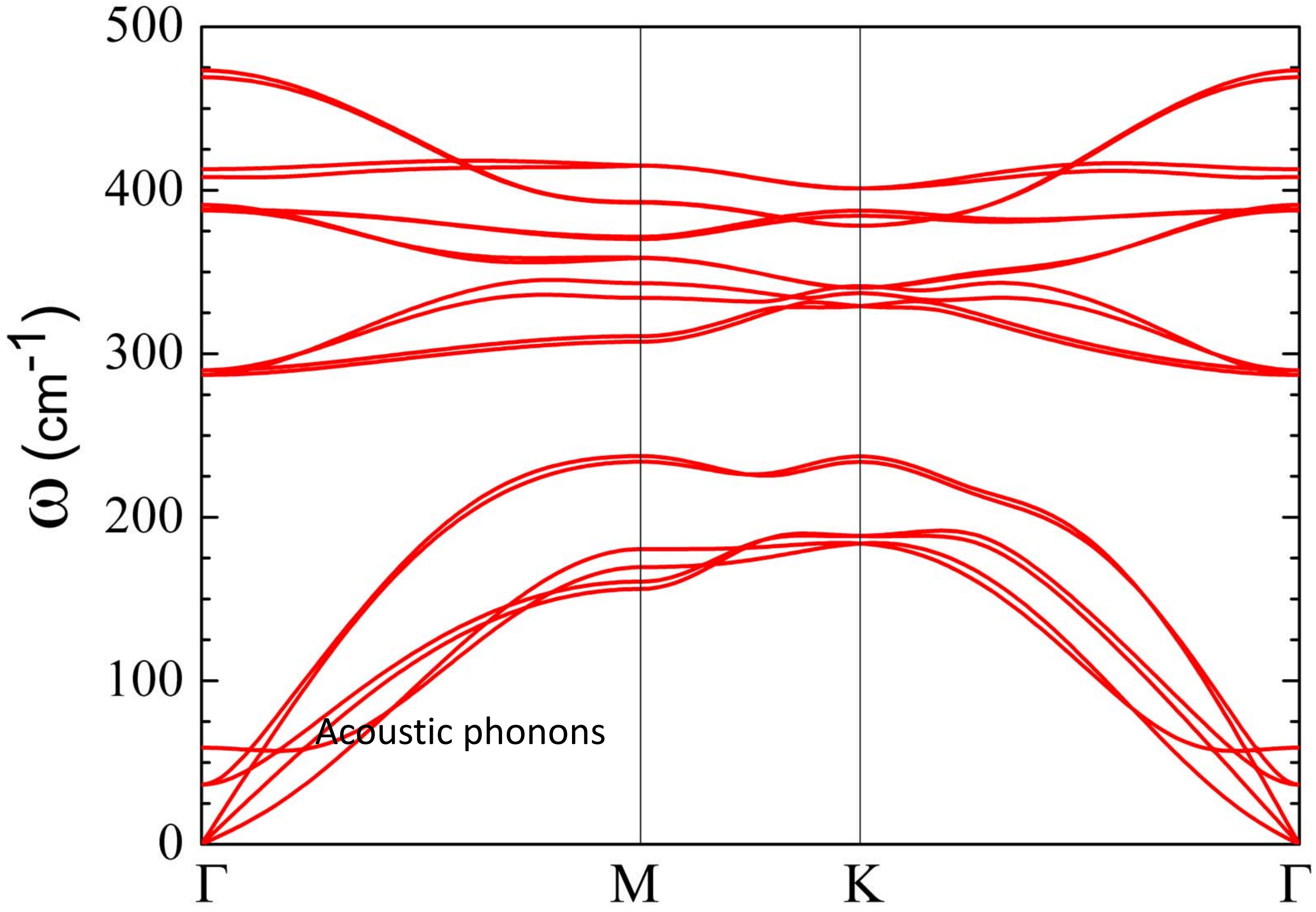
Thanks for your attention

Phonons in MoS_2 (bulk)



Low-frequency phonons