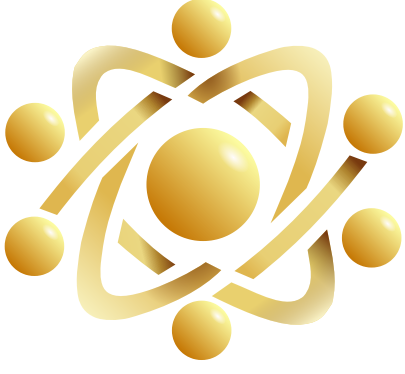
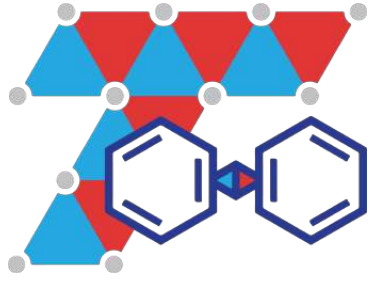
SAPIENZA
UNIVERSITÀ DI ROMA

The key role of quantum electron and ion fluctuations on the hydrogen phase diagram

Lorenzo Monacelli



AB INITIO SIMULATIONS
AND RESEARCH ON
ULTRAFAST MATERIALS



Crafting metallic hydrogen

- Molecular hydrogen dissociates to an atomic phase at high P
- BCS predicts it to be a room-temperature superconductor

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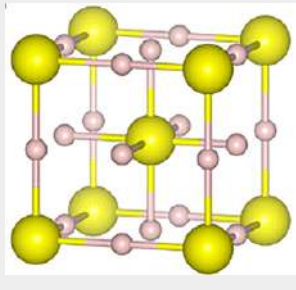
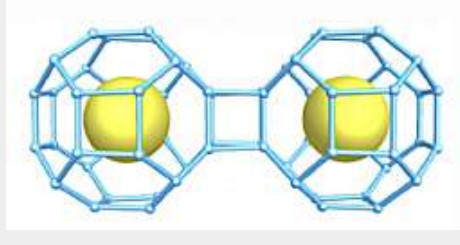
Notable mention:

- H_3S is superconductor at 200 K
- LaH_{10} is superconductor at 250 K

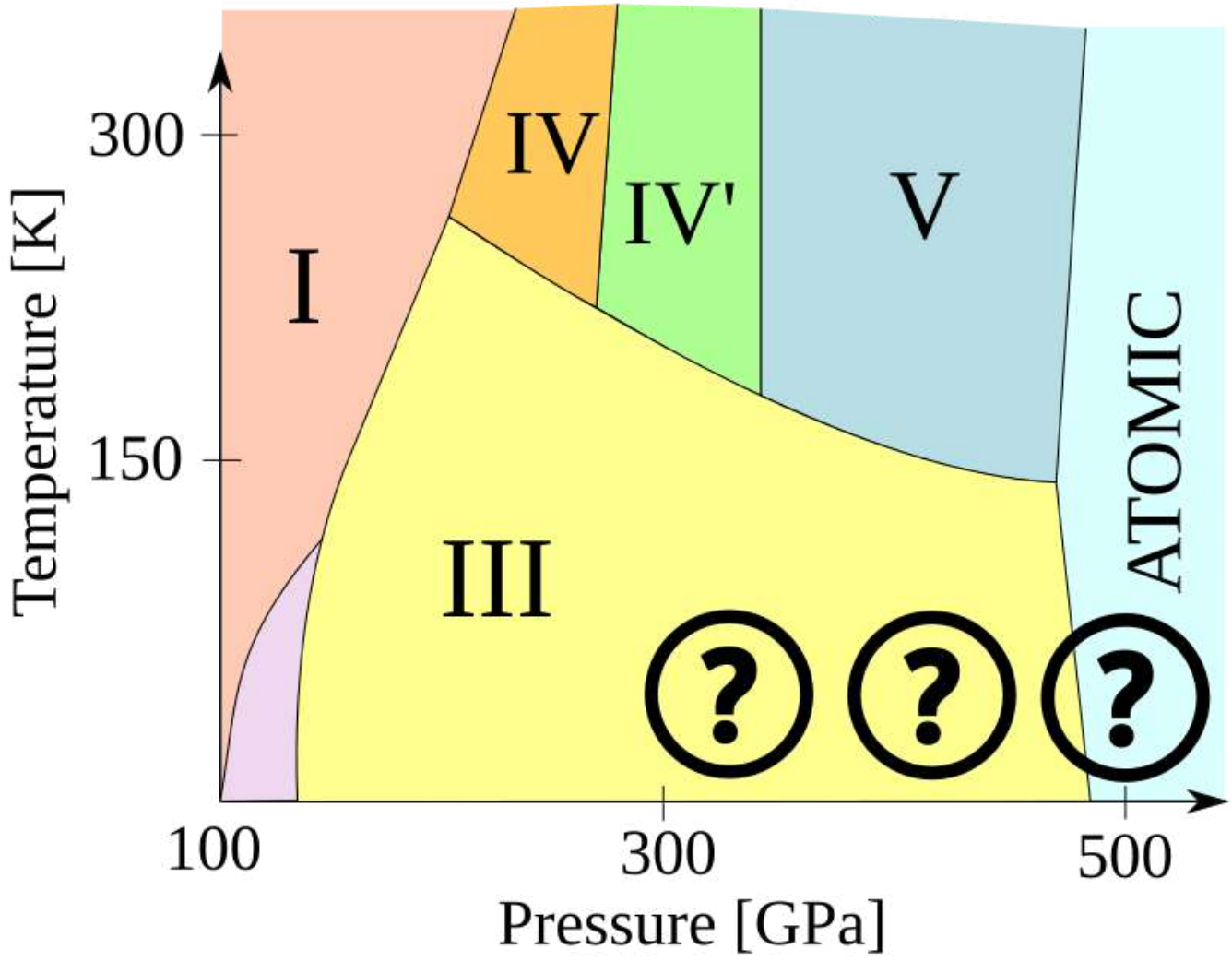


H_3S



LaH_{10}

The phase diagram of hydrogen



Challenges

Experiments

✗ Neutron scattering
✗ X-Ray scattering
✔ Electrical resistivity
✔ Optical spectroscopy
✔ Vibrational spectroscopy

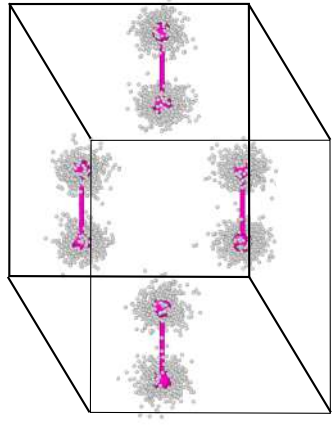
Simulations

- Required accuracy of 1 meV/H
  - ✗ DFT
  - ✔ Diffusion Monte Carlo
- Quantum fluctuations of protons
  - ✗ Classical simulations
  - ✔ Quantum nuclear motion

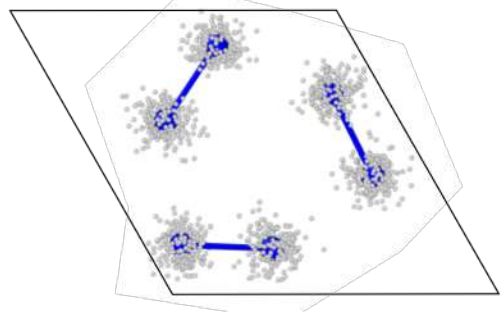
Many possible phases

with strong nuclear quantum fluctuations

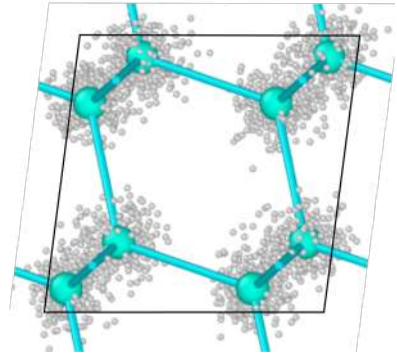
Cmca-4



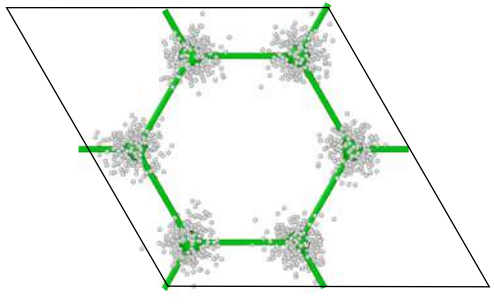
C2/c-24



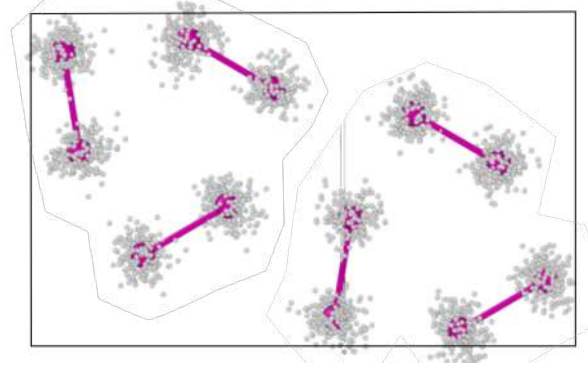
Cs-IV



P62c-24

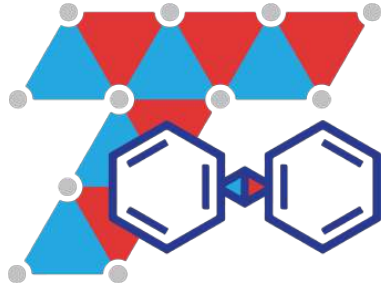


Cmca-12



Theoretical framework

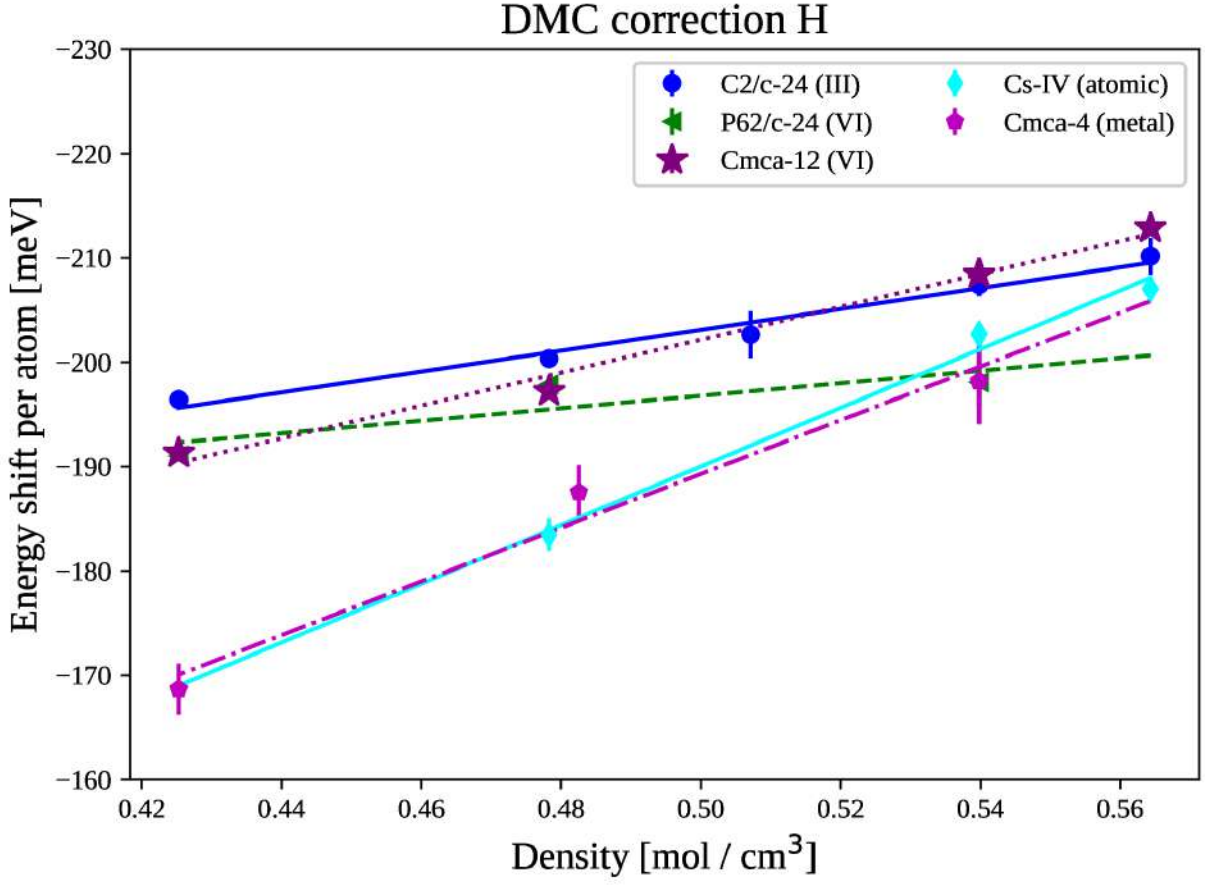
- Simulation of ***electrons*** and ***nuclei*** from first principles
- Adiabatic approximation: ***electrons*** are in their ground state
- The electronic problem is solved using Quantum Monte Carlo as implemented in the TurboRVB code



- Energies are evaluated with a Δ sampling with DFT-BLYP

Theoretical framework

We evaluate energies DFT-BLYP and correct them based on the density and phase with DMC energies



L Monacelli *et al.*, *Nature Physics*, 19, 845 (2023)

Theoretical framework

- Nuclear wave-function is solved with a Variational Monte Carlo
- The nuclear trial density matrix $\hat{\rho}$ is a Gaussian

$$\langle R|\hat{\rho}|R\rangle \propto \exp\left[-\frac{1}{2}\sum_{ab}(R_a - \mathcal{R}_a)\Phi_{ab}(R_b - \mathcal{R}_b)\right]$$

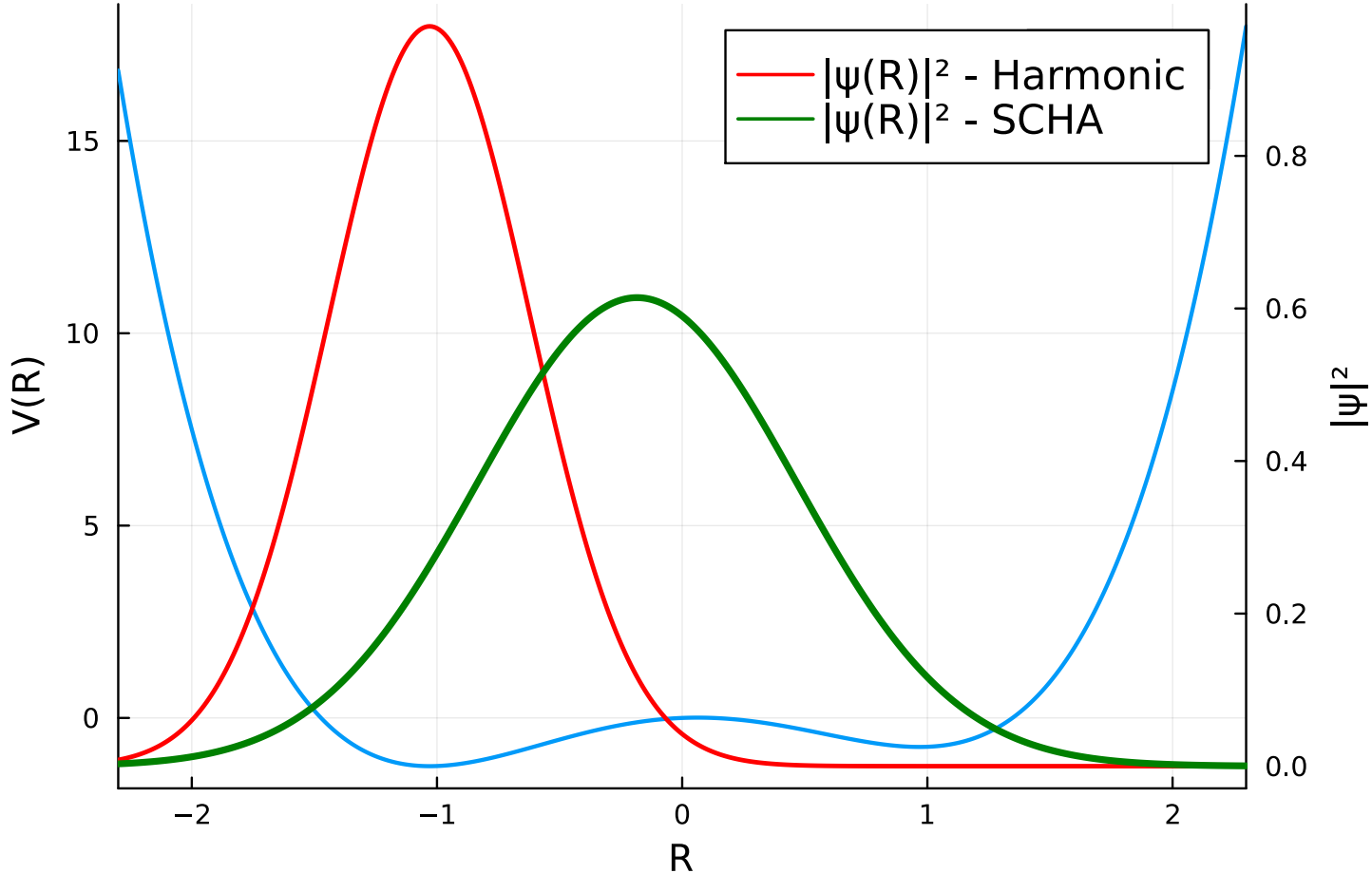
- We optimize the centroids $\mathcal{R}$ and fluctuations Φ
- Minimization of the free energy with a trial nuclear density matrix $\hat{\rho}$

$$\min_{\hat{\rho}} F[\hat{\rho}] = \underbrace{\left\langle \hat{H} \right\rangle}_{U} + \underbrace{k_b T \left\langle \ln \hat{\rho} \right\rangle}_{-TS}$$

- Given F we can simulate the thermodynamics of the system.
- Implemented in the SSCHA code (www.sscha.eu)

L. Monacelli *et al.*, *Physical Review B*, 98, 024106 (2018)
L. Monacelli *et al.*, *Journal of Physics: Condensed Matter*, 33, 363001 (2021)

Self-Consistent Harmonic Approximation



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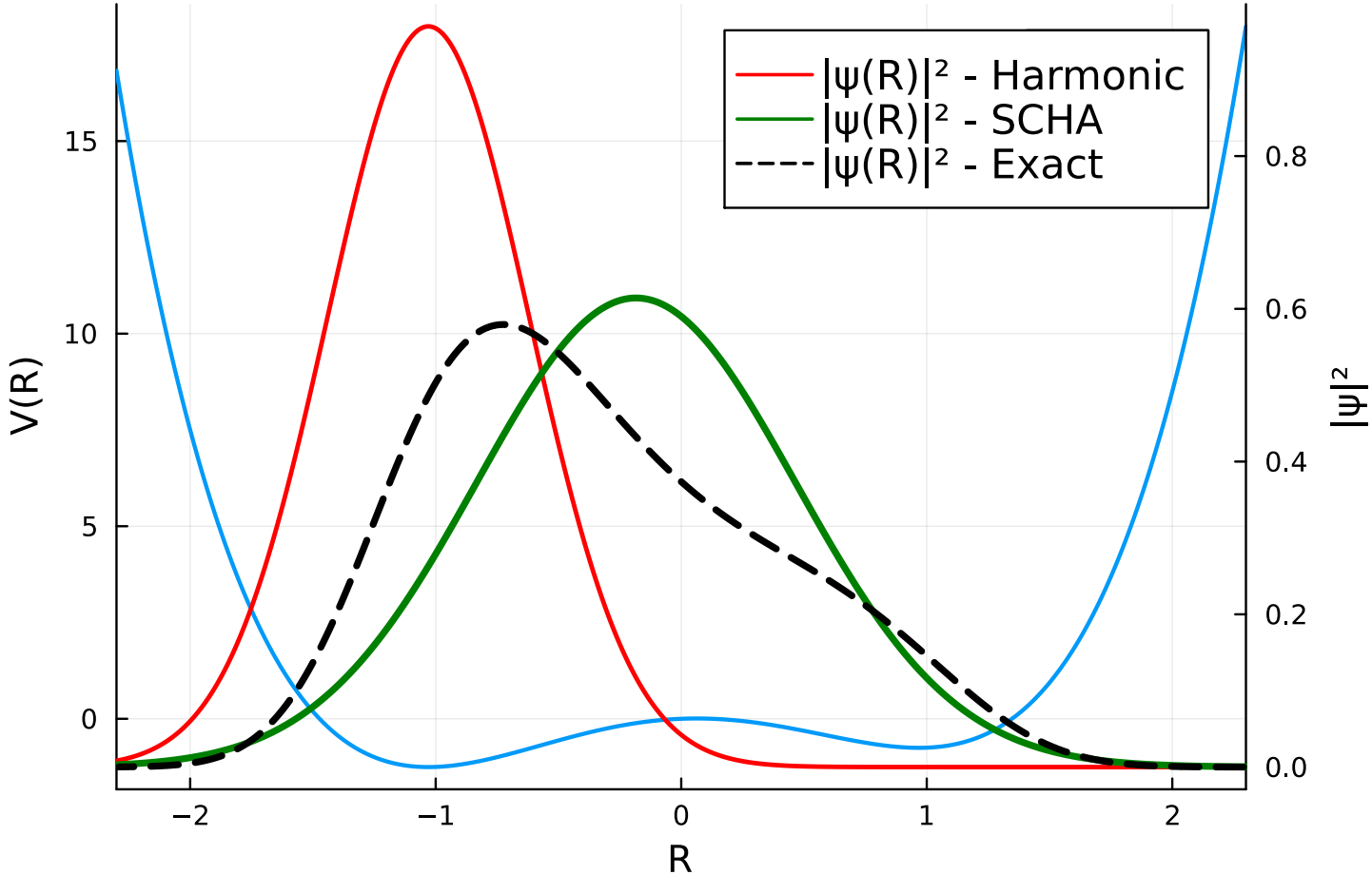
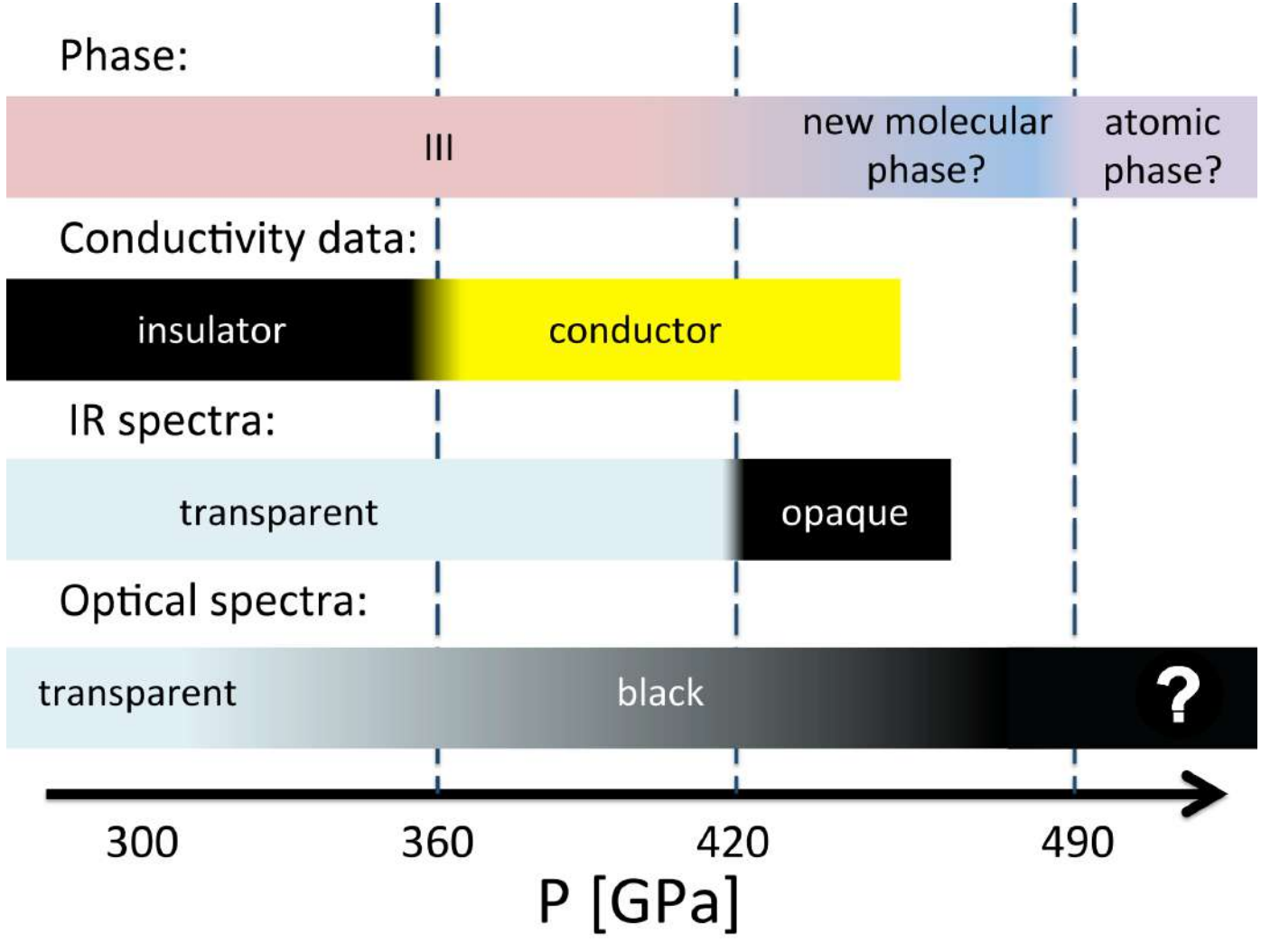


Experimental hydrogen phase diagram

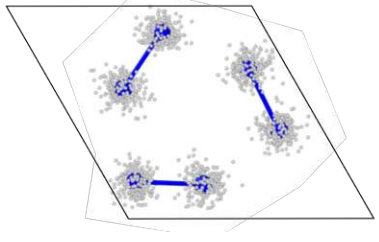


M. I. Eremets *et al.*, *Nature Physics*, 15, 1246 (2019)
P. Loubeyre *et al.*, *Nature*, 577, 631 (2020)

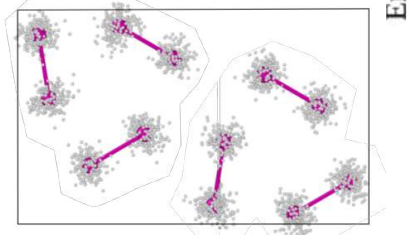
Discovery of phase VI

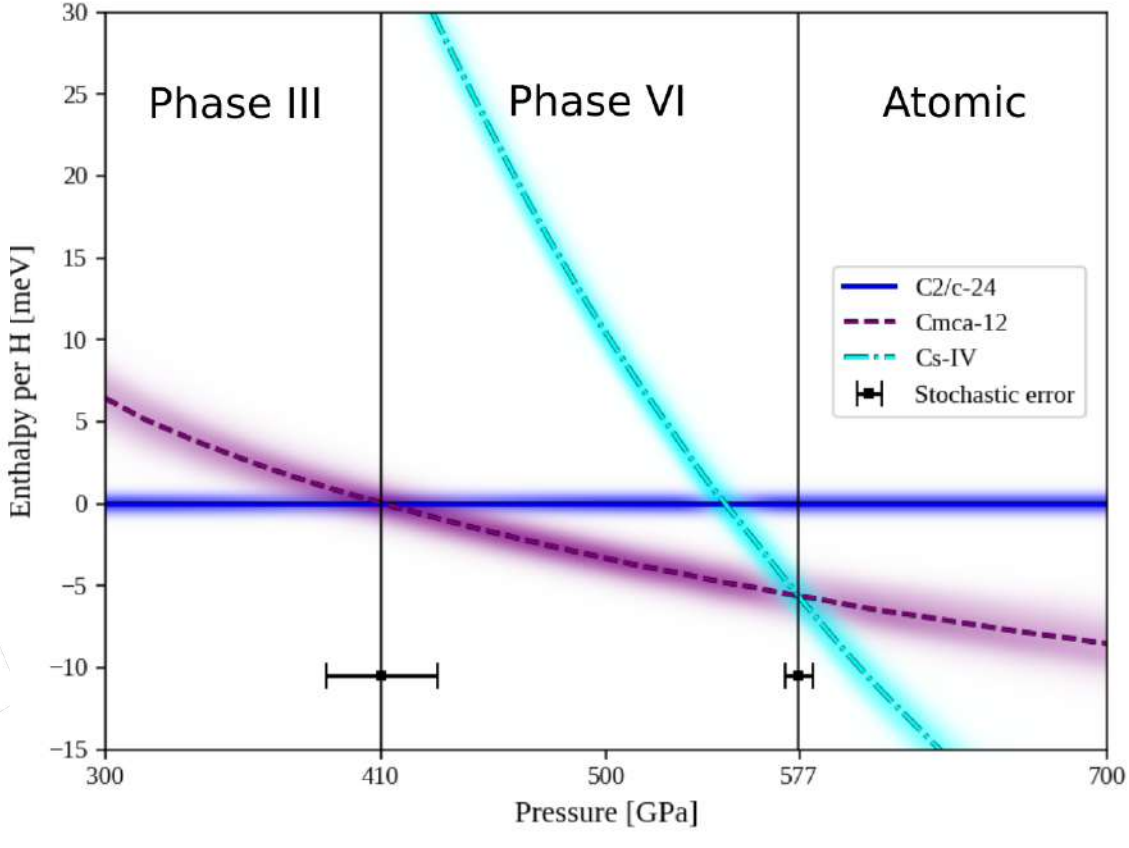
enthalpy with quantum fluctuations

Phase III
(C2/c-24)

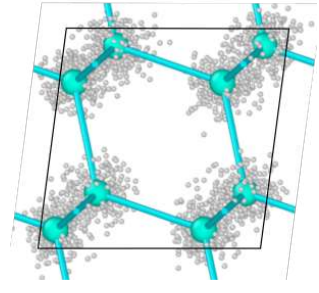


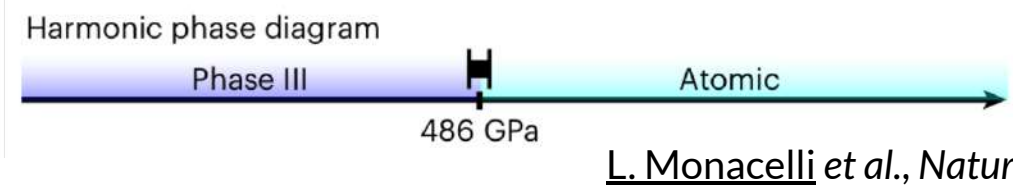
Phase VI
(Cmca-12)





Atomic
(Cs-IV)

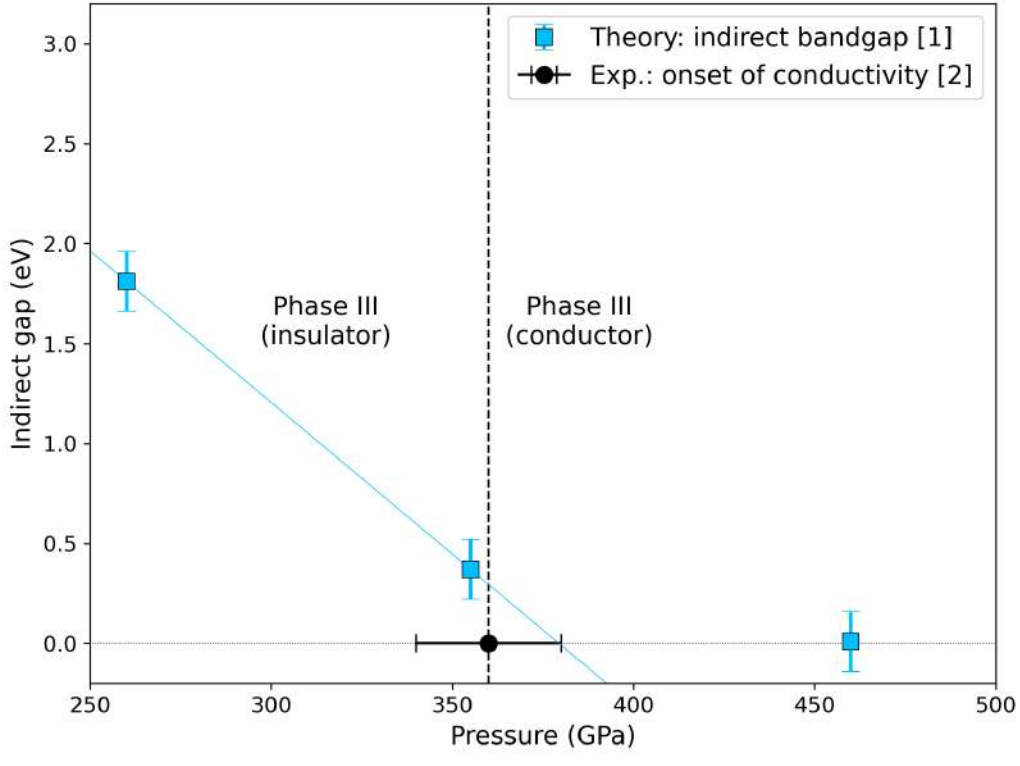




L. Monacelli *et al.*, *Nature Physics*, 19, 845 (2023)

Metallization: theory vs. experiments

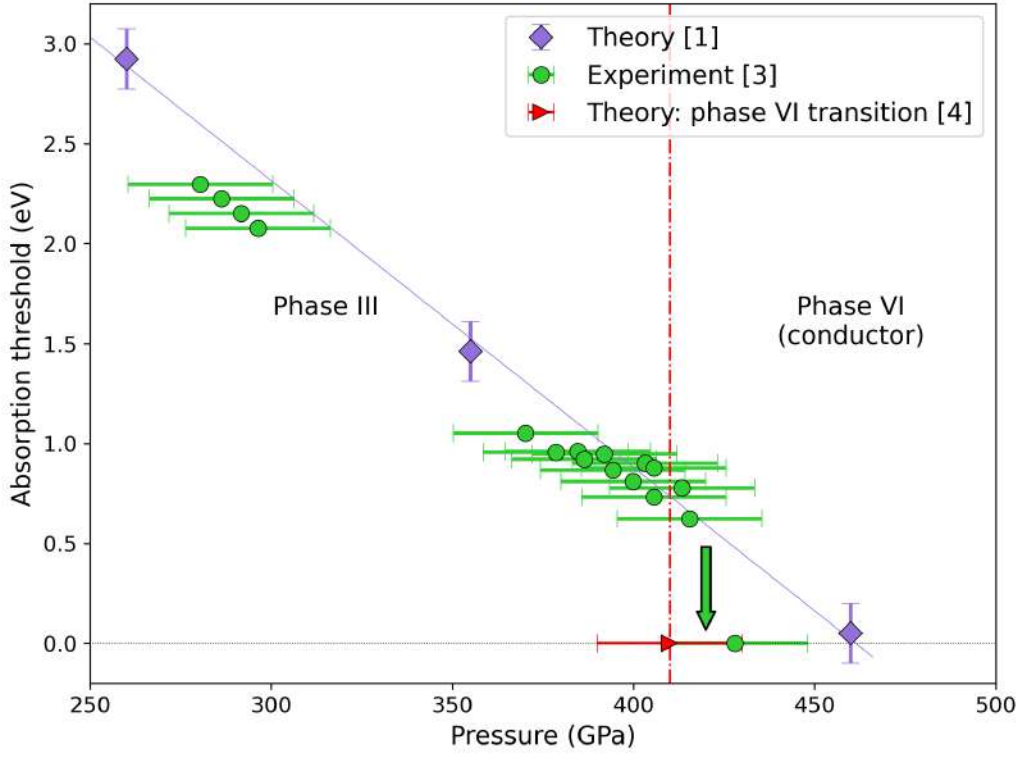
- Simulation of phase III bandgap
- Account for
  - Discontinuity in the XC functional
  - Electron-phonon interaction
- Conductivity onset is due to the closure of the bandgap



[1] L. Monacelli *et al.*, *Nature Physics*, 16, 73 (2021)
[2] M. I. Eremets *et al.*, *Nature Physics*, 15, 1246 (2019)

Metallization: theory vs. experiments

- Simulation of phase III absoprtion
- Account for
  - Discontinuity in the XC functional
  - Electron-phonon interaction
- Good agreement below 410 GPa
- Between 360 GPa and 410 GPa phase III is a **transparent metal**
  - Like ITO employed in LED displays
  - Due to the small plasma frequency



[1] L. Monacelli *et al.*, *Nature Physics*, 16, 73 (2021)
[3] P. Loybeyre *et al.*, *Nature*, 577, 631 (2020)
[4] L. Monacelli *et al.*, *Nature Physics*, 19, 845 (2023)

Metallization: theory vs. experiments

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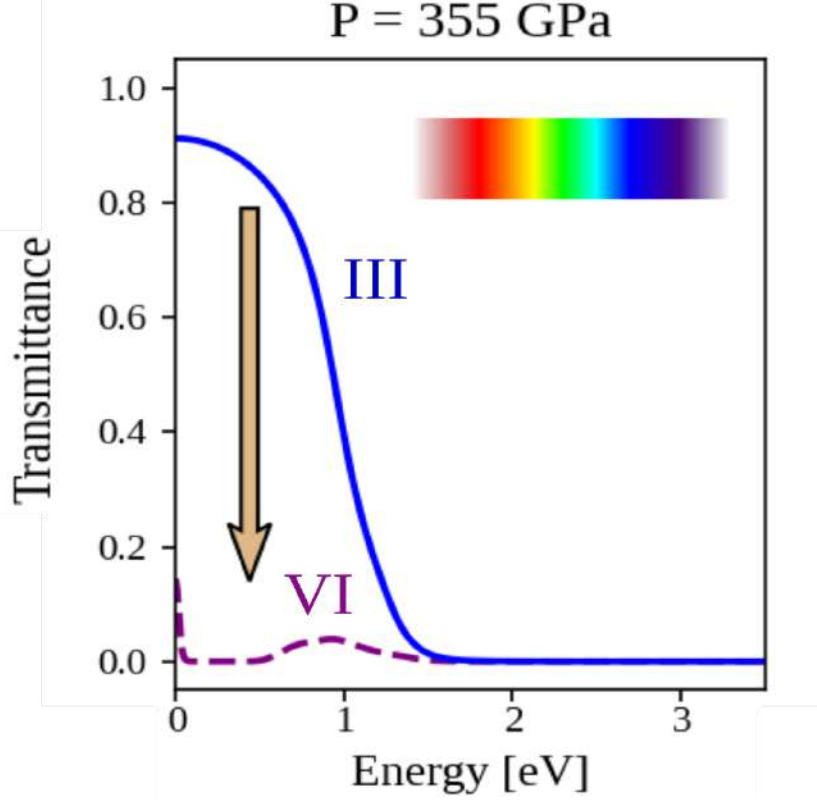
  - Electron-phonon interaction
- Good agreement below 410 GPa
- Between 360 GPa and 410 GPa phase III is a **transparent metal**
- Phase VI is opaque above 355 GPa



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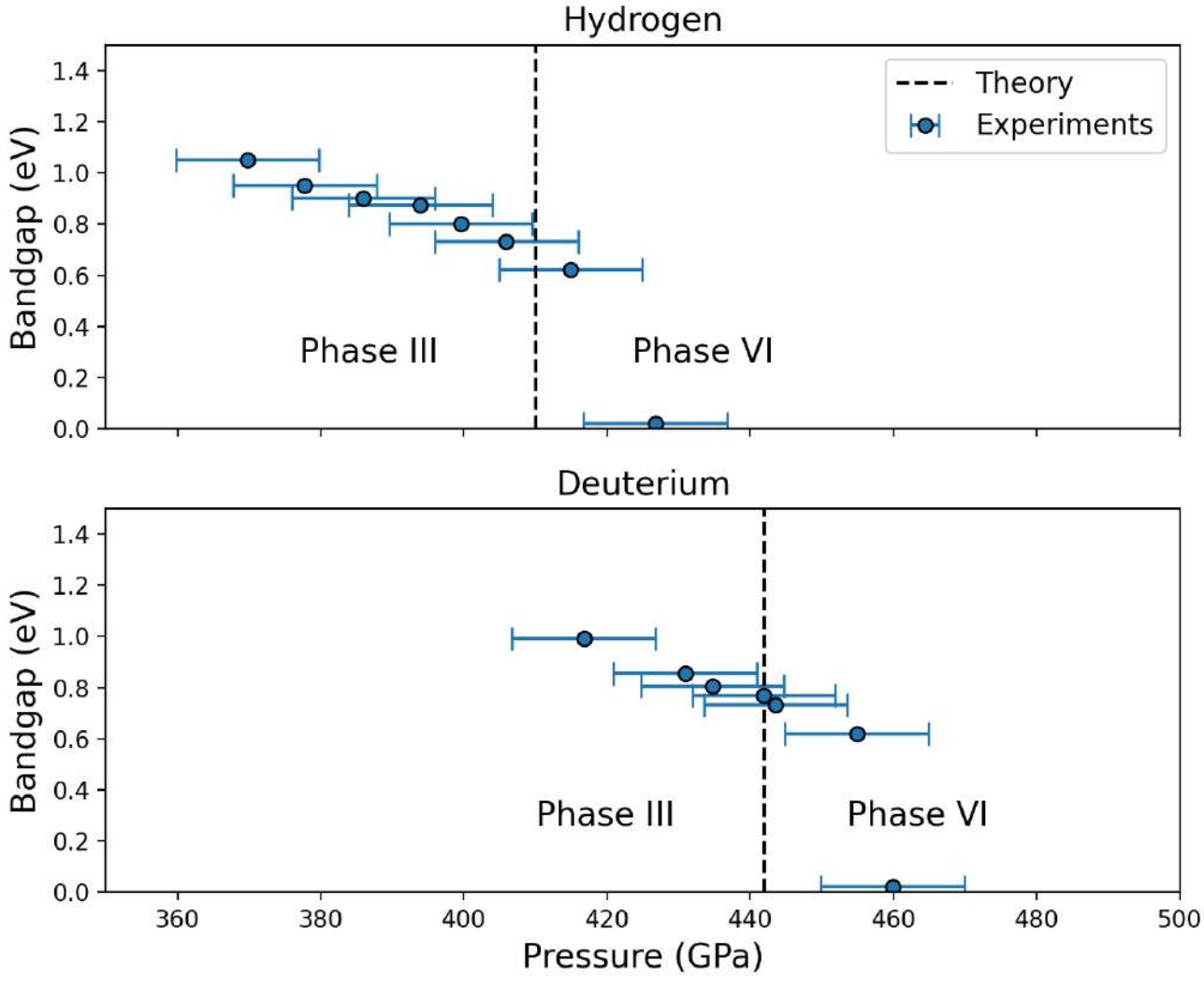
[4] L. Monacelli *et al.*, *Nature Physics*, 19, 845 (2023)

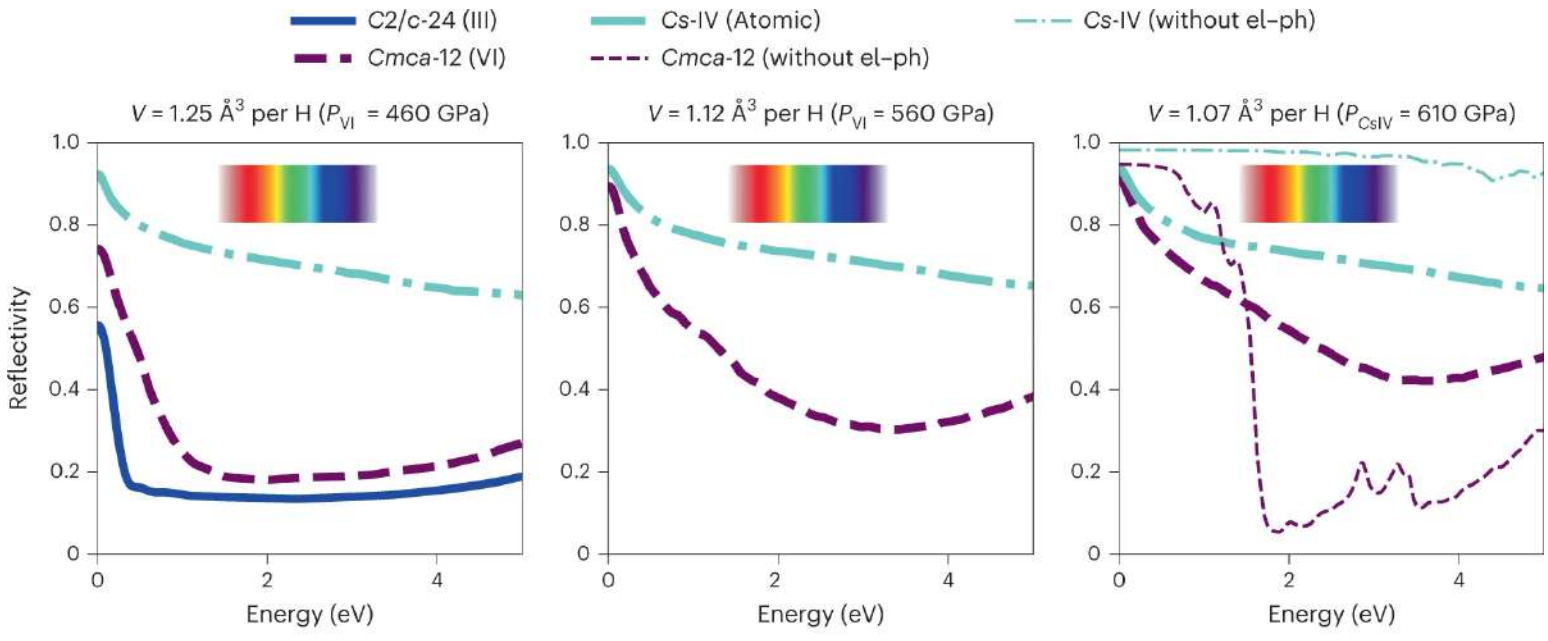
Experiments confirm our predictions

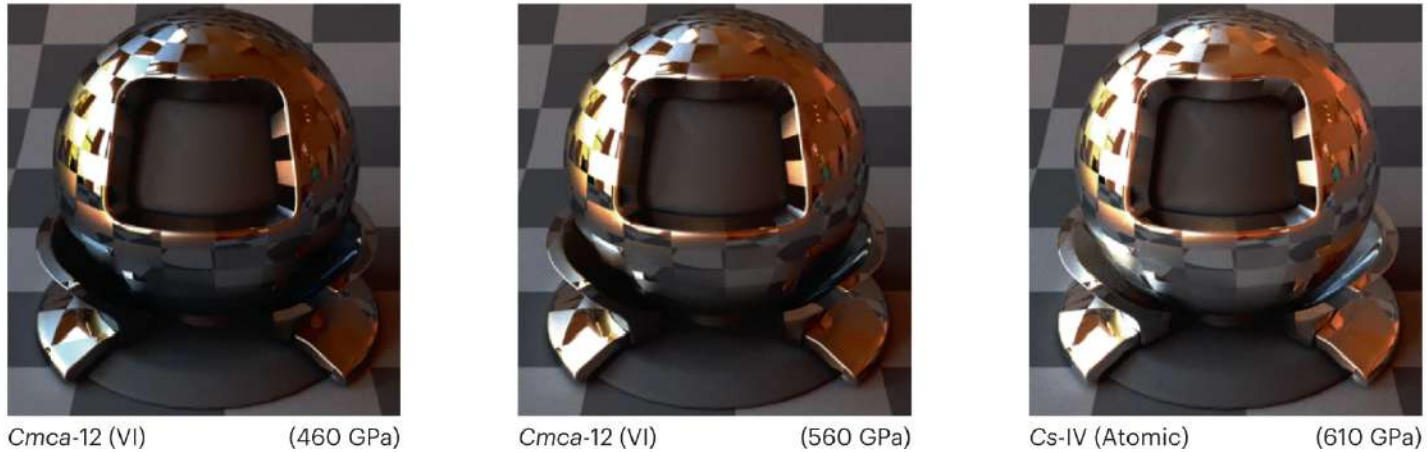


P. Loubeyre *et al.*, *Physical Review Letters*, 129, 035501 (2022) - presented for the first time in May 2022.

L. Monacelli *et al.*, *Nature Physics*, 19, 845 (2023) - preprint in January 2022.

How does it look under visible light?





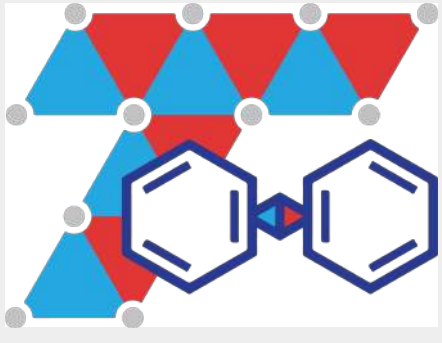
Cmca-12 (VI) (460 GPa) Cmca-12 (VI) (560 GPa) Cs-IV (Atomic) (610 GPa)

Conclusions

State-of-the-art theoretical simulations are predictive

Diffusion Monte Carlo

Focus on the electronic structure.



sissaschool.github.io/turborvb_website/

Stochastic Self-Consistent Harmonic Approximation

For nuclear quantum and anharmonic effects on nuclear motion

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