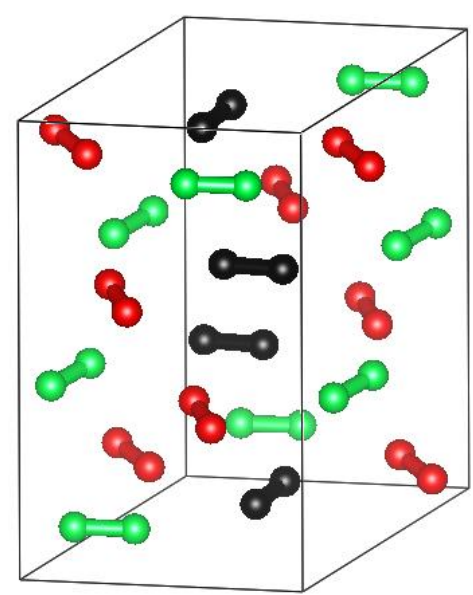


Introduction

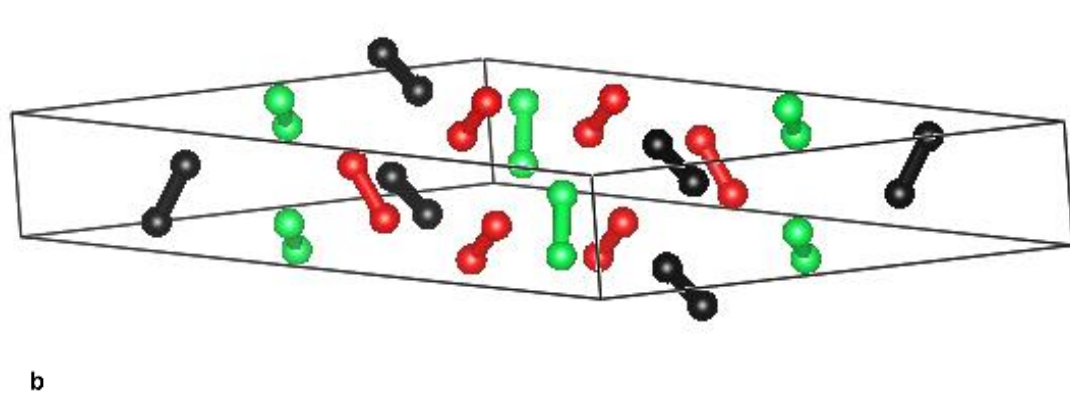
- Under pressures of the megabar regime, a variety of hydrogen solid phases exist [1]
- Phase boundaries have been determined experimentally up to 300 GPa using Infrared and Raman spectroscopies [2]
- Structural information on these phases is however missing due to X-ray diffraction experiments being inconclusive on these systems [3]
- Growing interest of the scientific community for high-pressure solid hydrogen phases because they are potential high-temperature superconductors [1]

For this study:

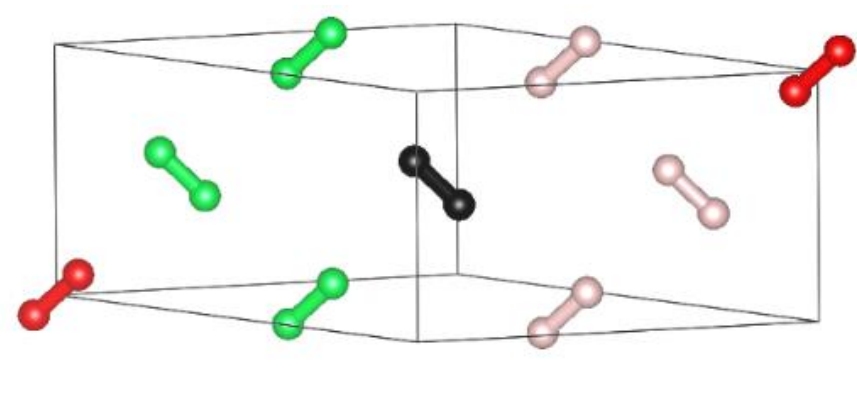
- Use of the *Quantum Espresso* plane waves DFT code
- Use of the *TurboRVB* quantum Monte Carlo code
- Pressure range of interest: 100-350 GPa
- Focus on the II-III phase transition
- Families of methods considered:** Hartree-Fock (HF), Generalized Gradient Approximation (GGA) and hybrid Density Functional Theory (DFT), Random Phase Approximation (RPA), Coupled Cluster (CC), Diffusion Monte Carlo (DMC)
- Four different molecular solid phases of interest:** C2/c-24 (monoclinic), P₂/c-24 (monoclinic), P₆/m-16 (hexagonal), Cmca-12 (orthorhombic)



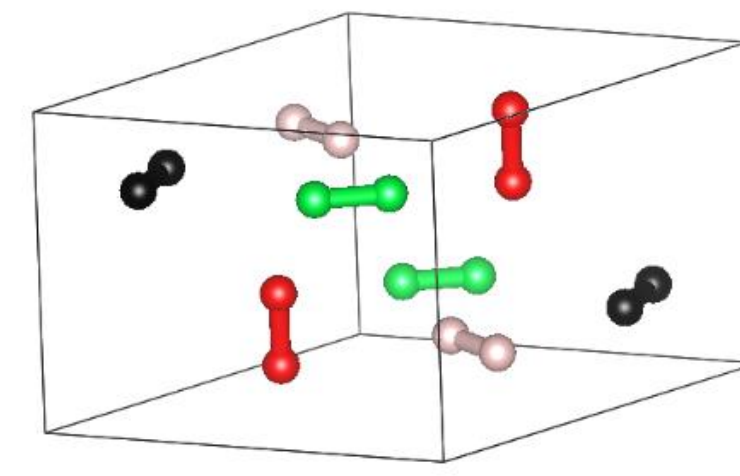
C2/c-24



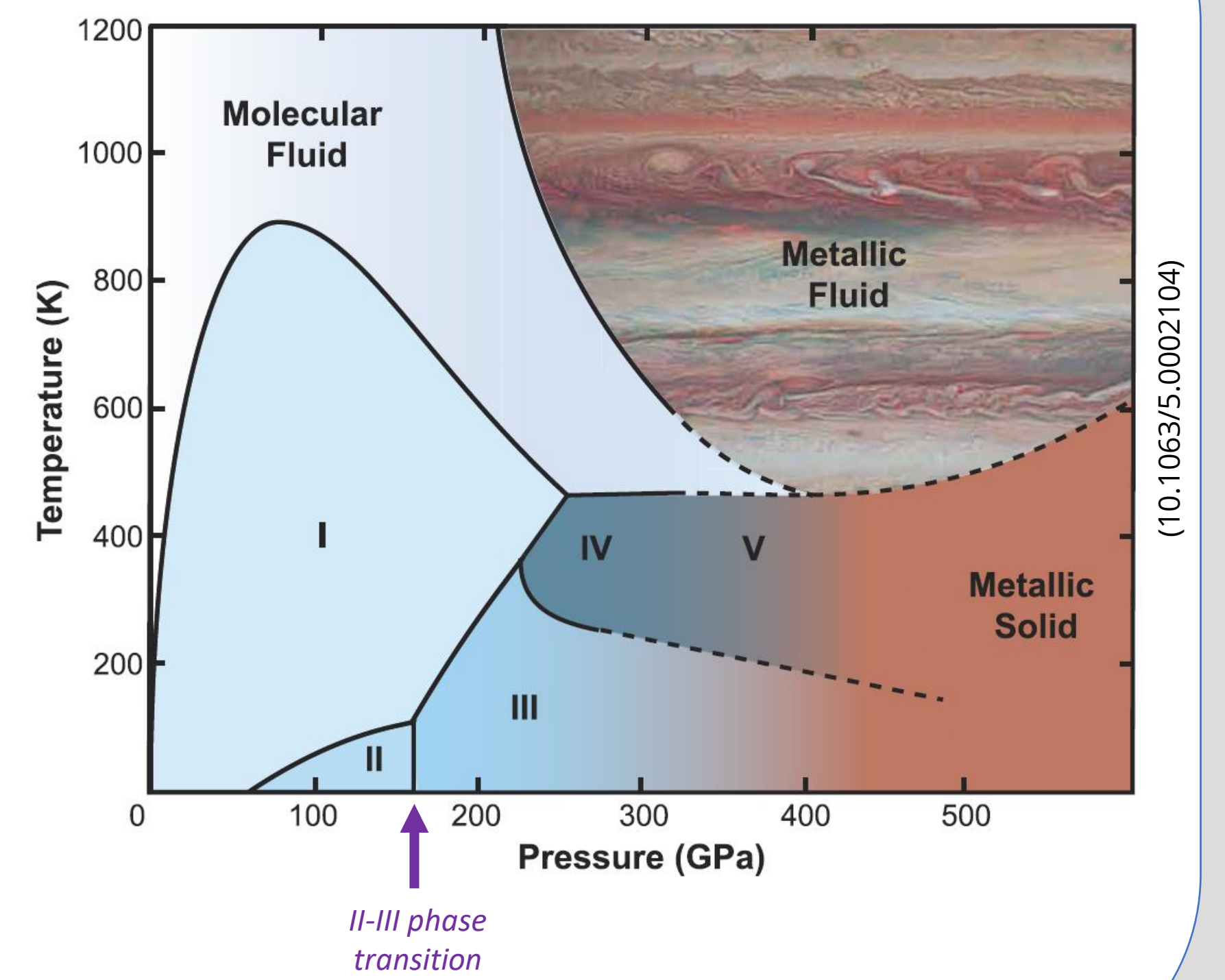
P₂/c-24



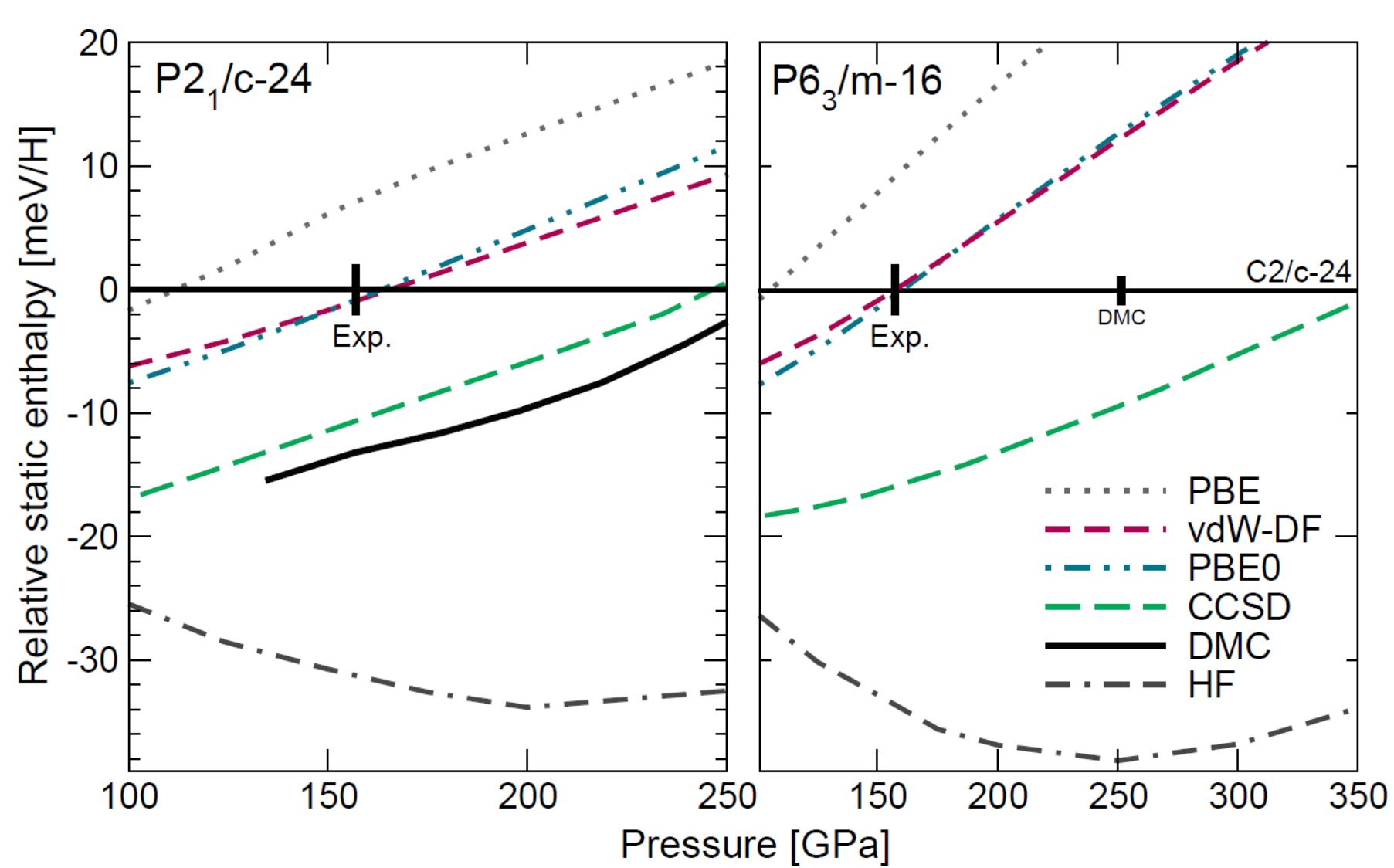
P₆/m-16



Cmca-12



Motivations



- In this work, diverse methods are tested on various high-pressure solid hydrogen phases and compared to CCSD [4] and DMC [5]
- Apparent agreement of vdW-DF and PBE0 with experimental II-III phase transition
- But more advanced CCSD and DMC methods predict the same phase transition to occur at much higher pressures

The large difference between CCSD and DMC correlated methods shows the complexity in determining the numerical phase diagram of hydrogen

RPA and RPAx results

- RPA and RPAx methods are constructed within the DFT framework and rely on the Adiabatic Connection Fluctuation Dissipation Theorem (ACFDT) [6]
- Both methods are based on the exact expression of the correlation energy:

$$E_c = \frac{i}{2} \int_0^1 d\lambda \int \frac{d\omega}{2\pi} \text{Tr} \{ v(\mathbf{r} - \mathbf{r}') [\chi_\lambda(\mathbf{r}, \mathbf{r}', \omega) - \chi_s(\mathbf{r}, \mathbf{r}', \omega)] \}$$

- Like with Time-Dependent DFT, the density response function χ is needed [7]:

$$\chi_\lambda = \chi_s + \chi_s [\lambda v + f_{xc}^\lambda] \chi_\lambda = \chi_s + \chi_s \left[\lambda v + \frac{\partial v_{xc}^\lambda}{\partial n} \right] \chi_\lambda$$

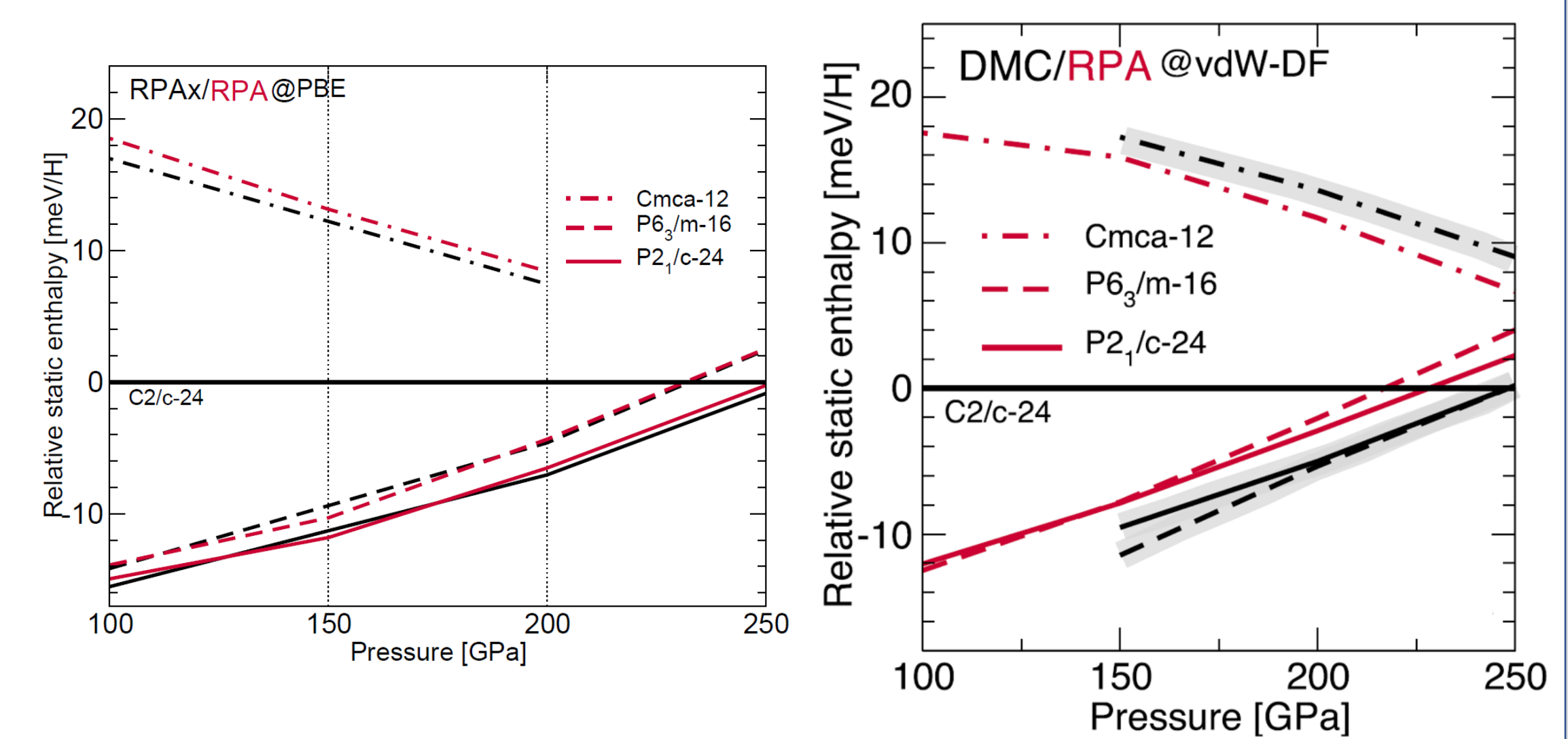
- For RPA: $f_{xc}^\lambda = 0$
- For RPAx: $f_{xc}^\lambda = f_x^\lambda$

- The total RPA energy is notably composed of the RPA correlation energy and the exchange energy, determined using the EXact Exchange method (EXX):

$$E_{tot}^{RPA} = T_s + V_{ext} + E_H + E_x^{EXX} + E_c^{RPA}$$

- On diverse systems, RPA and RPAx methods have shown a high level of accuracy for moderate computational costs [7,8]

- Not possible to relax structures using RPA or RPAx in *Quantum Espresso* yet: RPA and RPAx calculations done on PBE and vdW-DF geometries instead



- RPA@PBE and RPAx@PBE provide similar results on all phases of interest
- RPA@vdW-DF is in very good agreement with the DMC results we obtained using the *TurboRVB* code on the same set of vdW-DF geometries

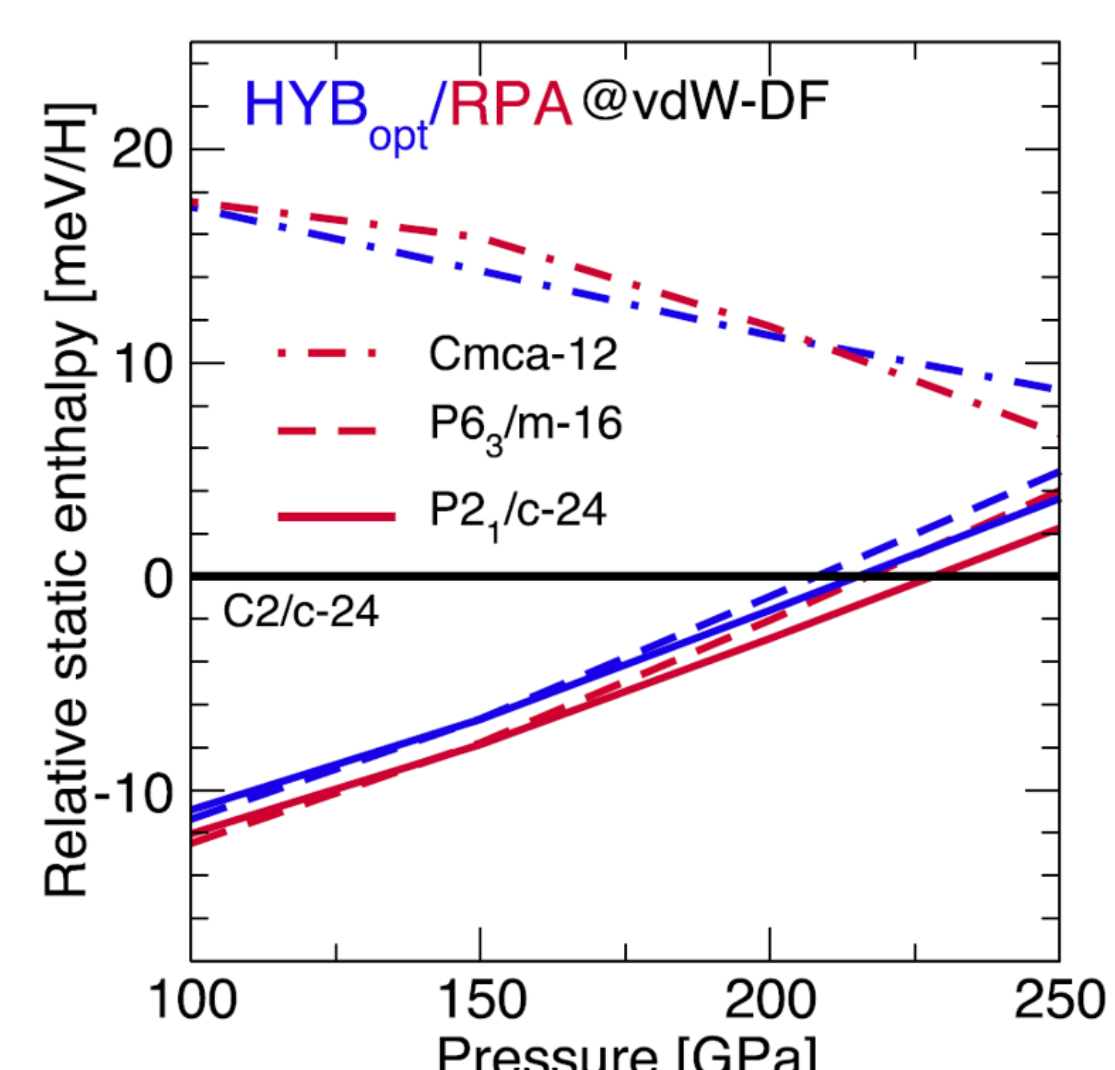
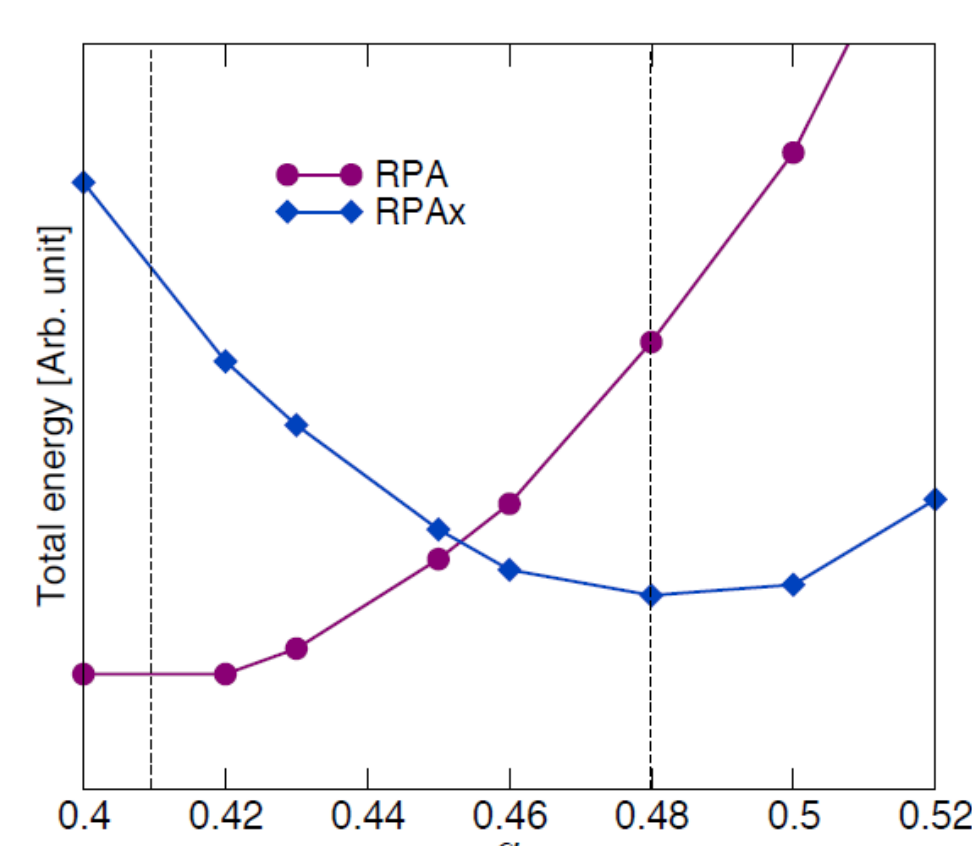
The RPA method presents an excellent accuracy-cost ratio on high-pressure solid hydrogen phases

Hybrid PBE0 results

- Standard PBE0 hybrid functional admits $\alpha=25\%$ of exact exchange
- Difference in results between PBE025 and HF confirms the importance of optimizing the fraction of exact exchange for PBE0 on these systems: done by calculating the RPA and RPAx energy on top of the equilibrium geometry and orbitals predicted by PBE0 α on a single H₂ molecule

- Minimal energy obtained with 41% of exact exchange for RPA, 48% for RPAx

RPAx being a more accurate method than RPA, calculations will be performed with the PBE048 (=HYB_{opt}) functional instead of PBE041



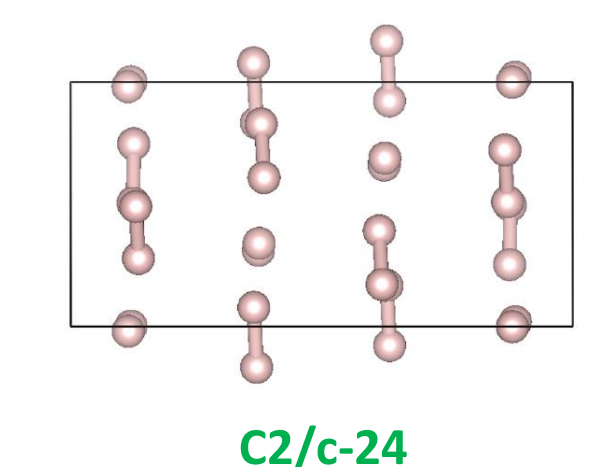
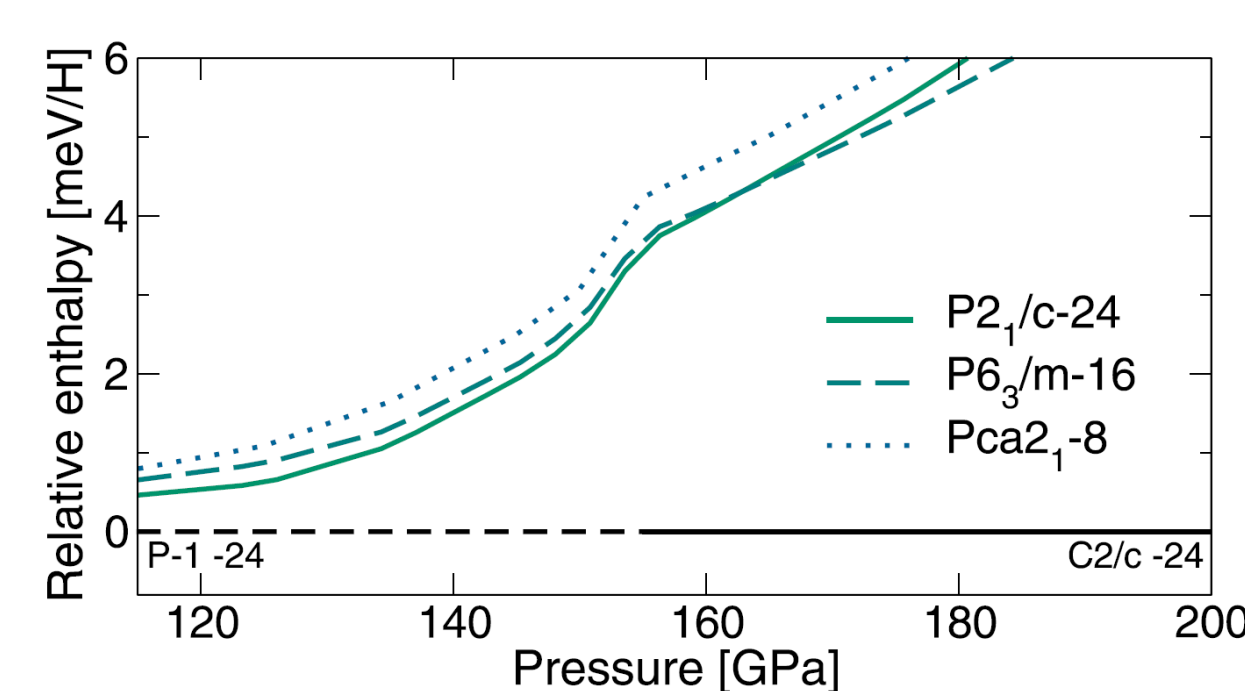
- Contrary to the PBE025 method, PBE048 hybrid calculations performed on vdW-DF geometries deliver improved results, in satisfying agreement with RPA
- The good agreement between RPA and HYB_{opt} confirms that the exact exchange proportion to use for PBE0 should be much larger than 25%
- The 48% value found on a single H₂ molecule also appears to be the suited proportion to study pure extended hydrogen systems

Interesting performance of HYB_{opt}, given its accuracy and it being much more affordable than RPA, RPAx and DMC in terms of computation costs

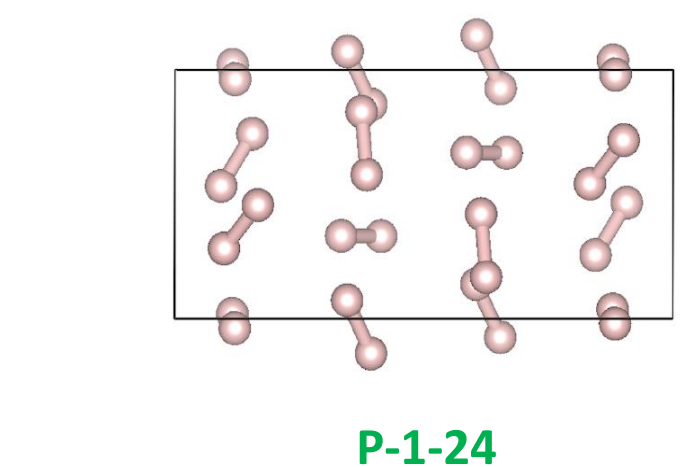
Role of the starting geometry

- Despite the significant lack of accuracy, vdW-DF returns better enthalpy curves than PBE: vdW-DF geometries should be closer to the true geometries than PBE geometries do
- Performing hybrid DFT or RPA/RPAx calculations on a different set of geometries will yield different enthalpy curves
- The change of PBE geometries to vdW-DF geometries leads to a shift in pressures of about 20 GPa: impact rather small, the geometry is not the main source of error in the calculation of enthalpy curves

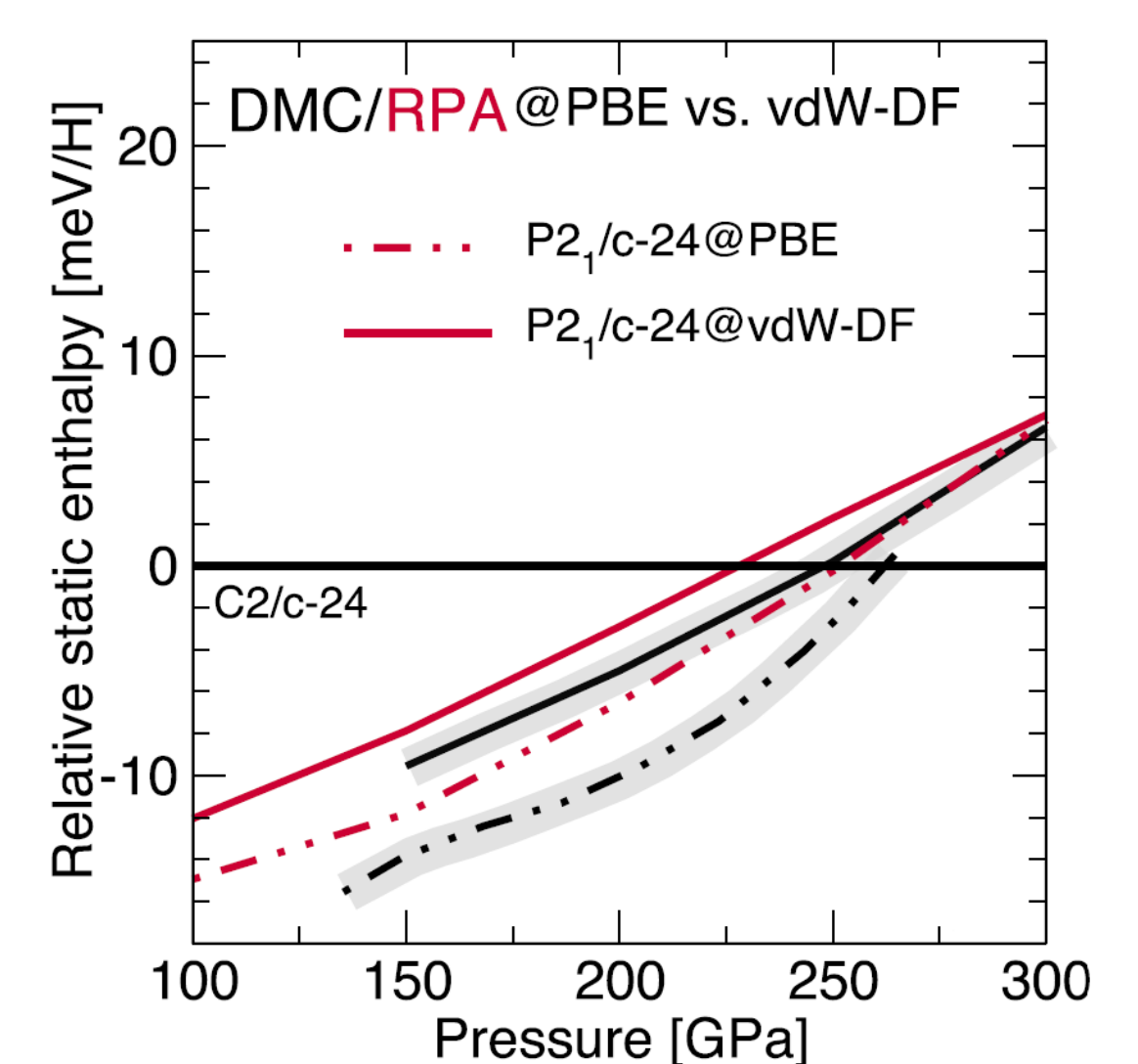
But the geometry still has a major impact: the use of better HYB_{opt} geometries leads HYB_{opt} RPA and DMC to predict a phase never considered before, P-1-24, to be a promising candidate for the phase II structure [9]



C2/c-24
Monoclinic phase where H₂ molecules are all arranged within the (a,c)-plane

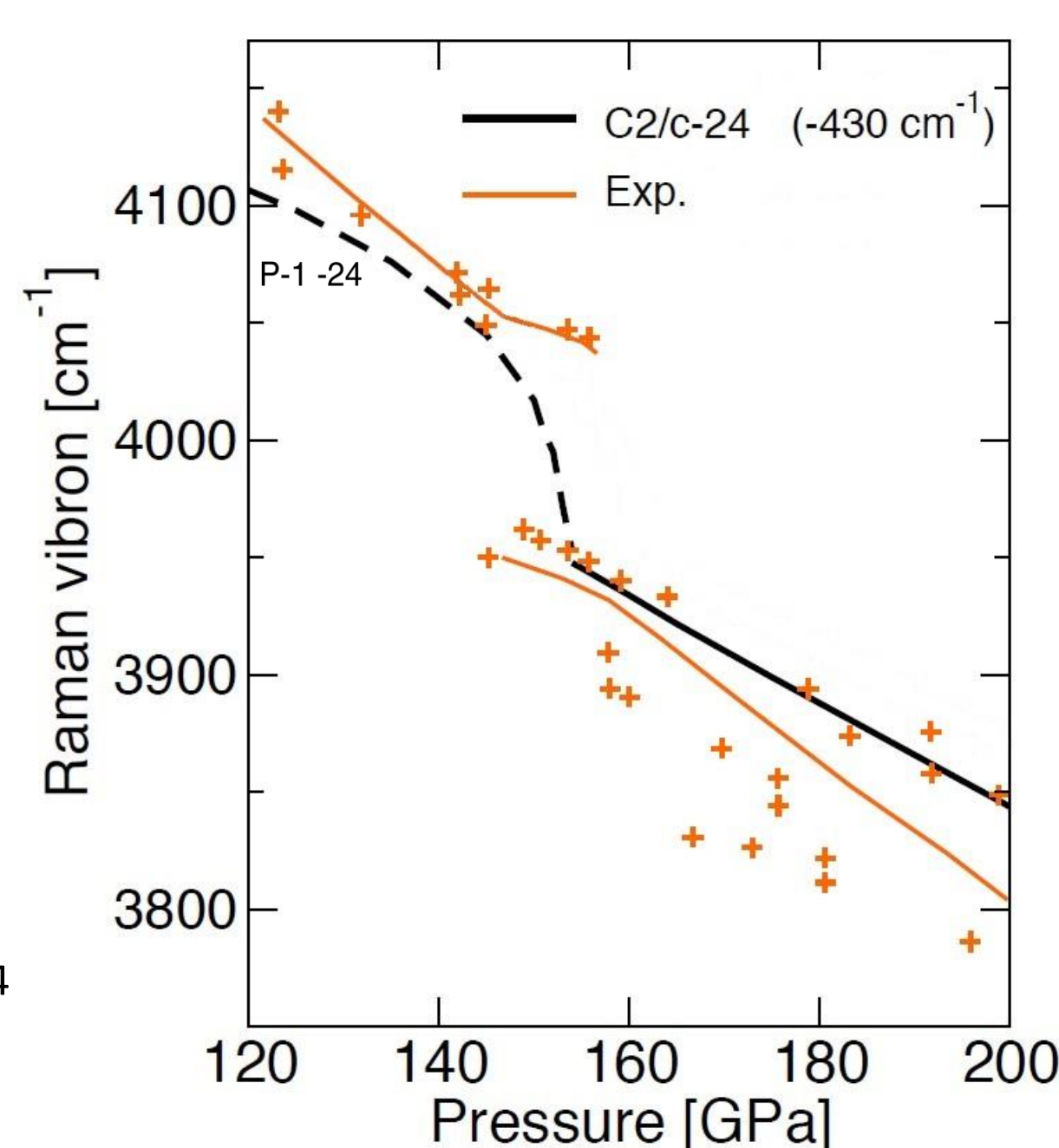


P-1-24
Triclinic phase close to C2/c-24 except that part of the H₂ molecules are rotated out of the (a,c)-plane



The II-III phase transition

- Without the consideration of vibrations in the calculations, HYB_{opt} RPA and DMC find that phase III corresponds to C2/c-24 while phase II corresponds to P₂/c-24 [9]
- When vibrations are considered, with the improved HYB_{opt} geometries, the phase P-1-24 is predicted to become more stable than any of the other structures suggested [9]
- The calculated Raman spectrum shows that the evolution of the frequency of the vibron agrees with experiments [10]. This is true only when moving from C2/c-24 to P-1-24. The shift is much larger when transitioning from C2/c-24 to P₂/c-24 [9]
- The decrease in the frequency of the vibron when transitioning from C2/c-24 to P-1-24 can be explained by the strengthening of the intramolecular bond of the H₂ molecules that are rotated out-of-plane, since they lose their in-plane stability, leading to a shortening of their H-H bond distance [11]



Summary

- PBE048, RPA and RPAx methods offer satisfying accuracy-cost ratios on high-pressure solid hydrogen phases [9]
- All three methods predict phase III to consist of the C2c-24 phase, while the prediction for phase II varies from P₂/c-24 and P-1-24, depending on the additional effects being considered during the calculations
- Along with DMC, they predict the II-III phase transition to occur close to 250 GPa, almost 100 GPa higher than experimental results [1]
- The large discrepancy noted with experiments is likely due to numerous factors: incorrect geometries, non-consideration of vibrations and quantum nuclear effects in the calculations,... [9,12]
- Future works should focus on evaluating the impact of each factor on the numerical results obtained so far

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