

Further random results from random structure searching

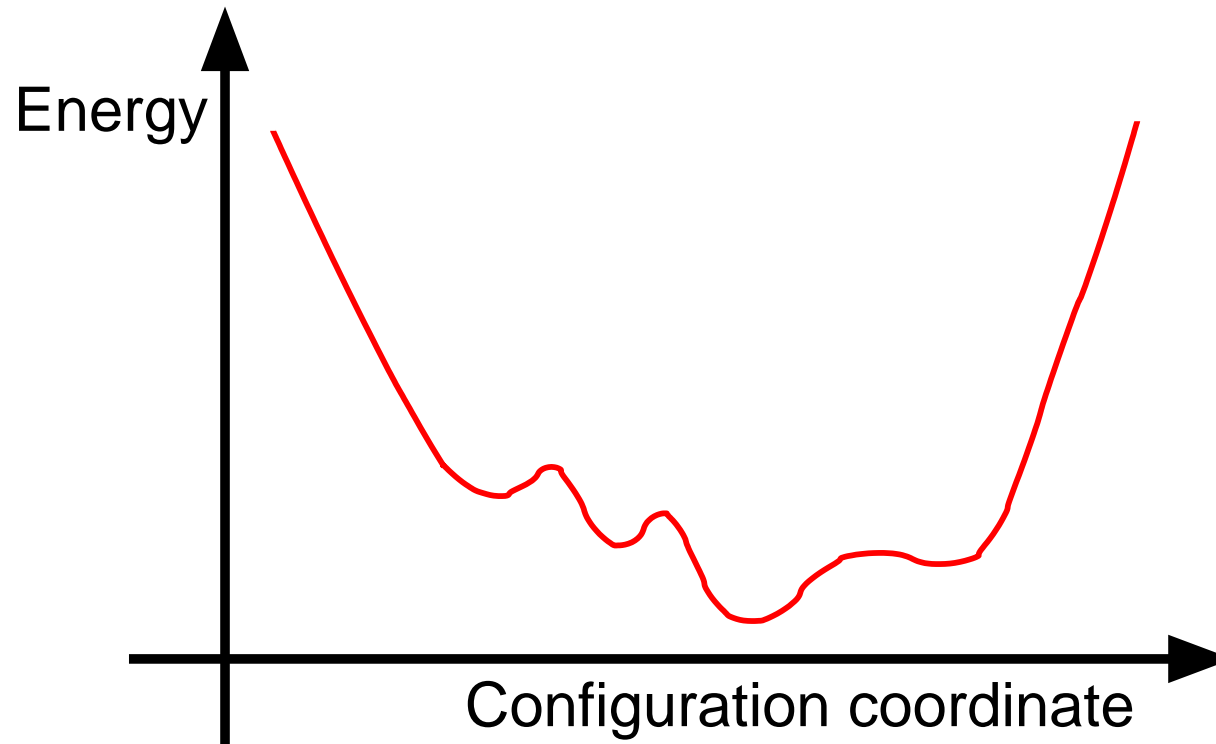
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Locating the global minimum of a potential energy surface



Search method of choice depends on affordable number of energy evaluations
“Accurate” methods such as first principles DFT are required

Random searching algorithm for crystal structures

Generate a population of random structures and relax them:

Choose random unit cell translation vectors

Renormalize the volume to a reasonable range of values

Choose random atomic positions within the cell

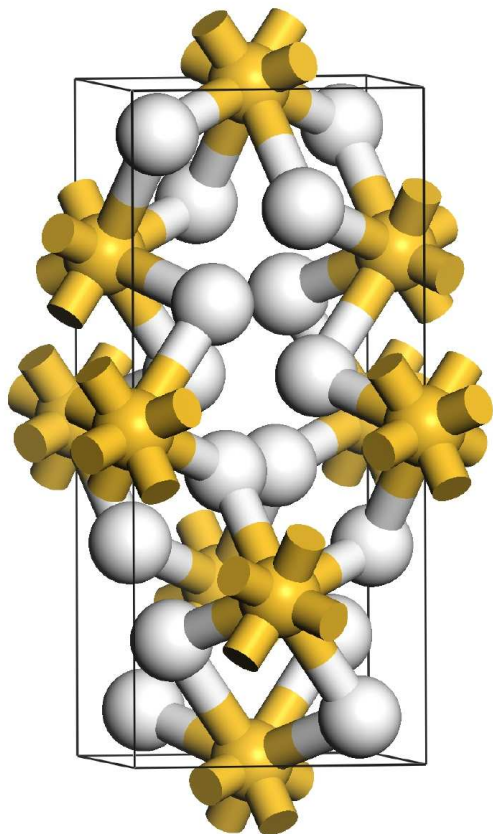
May constrain the initial positions:

Fix the initial positions of some of the atoms (e.g., defect)

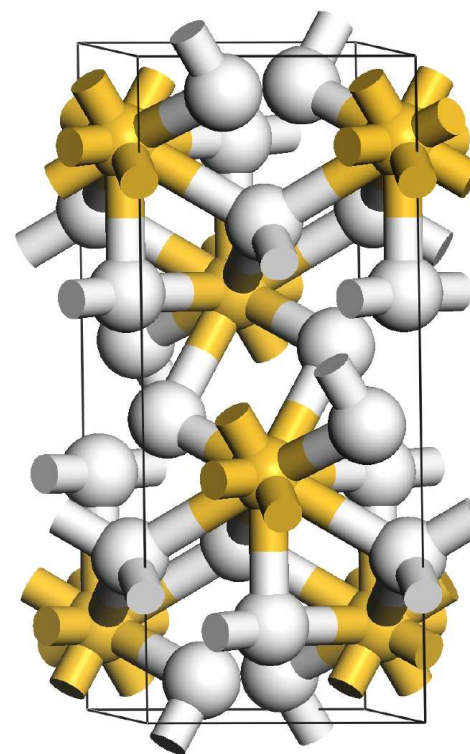
Insert molecules randomly (rather than atoms)

Choose a particular space group

The $I4_1/a$ and $C2/c$ structures of silane



$I4_1/a$



$C2/c$

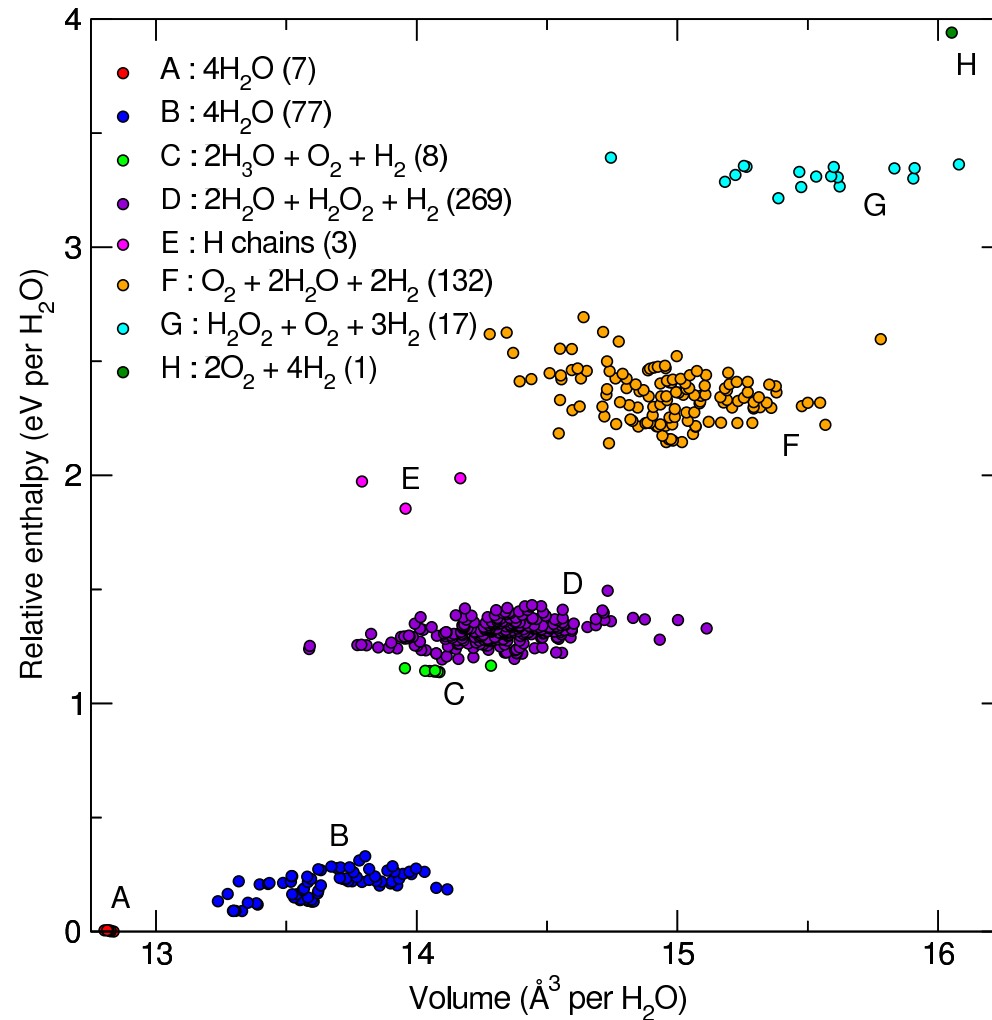
Golden spheres: silicon atoms; white spheres hydrogen atoms

Pickard and Needs, Phys Rev Lett 97, 045504 (2006)

$I4_1/a$ has been found in experiments by Eremets *et al.*

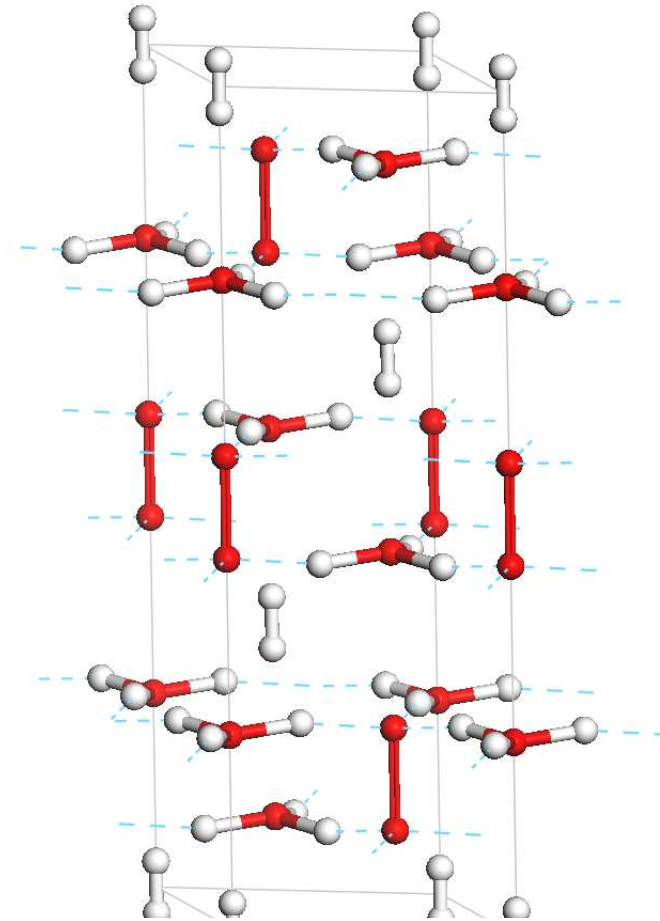
When is H₂O not water?

“X-ray-induced dissociation of H₂O and formation of an O₂-H₂ alloy at high pressure”, Mao *et al.*, *Science* 314, 636 (2006)



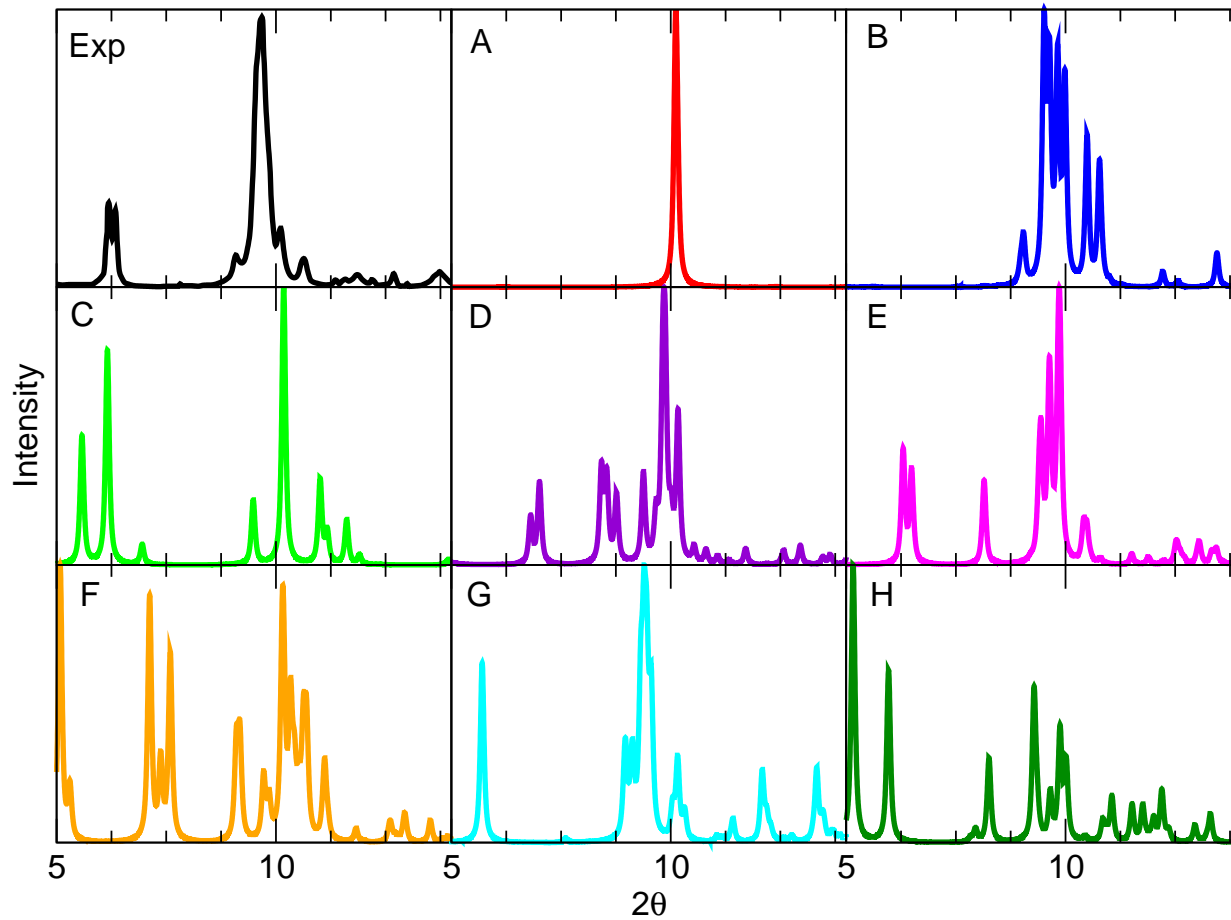
Pickard and Needs, unpublished

The $R\bar{3}m$ structure



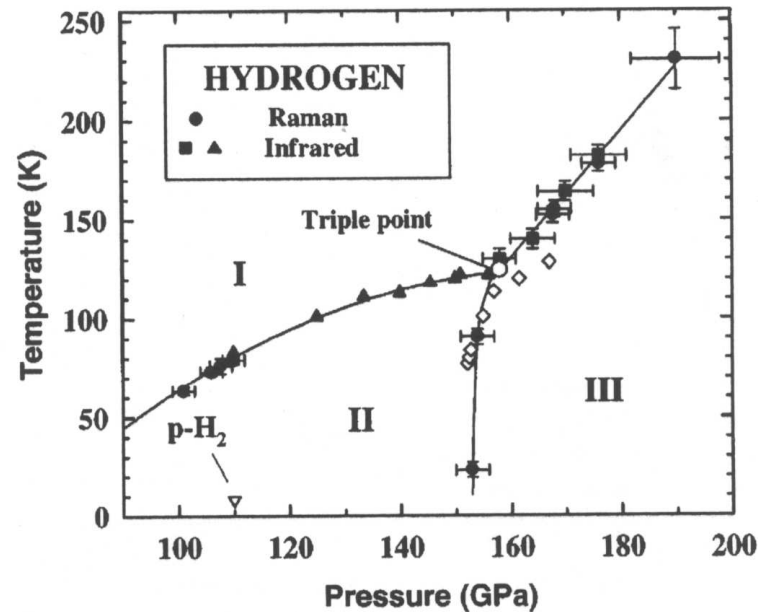
Oxygen atoms in red and hydrogen atoms in white

When is H₂O not water?



X-ray diffraction patterns from experiment of Mao *et al.* and groups A-H

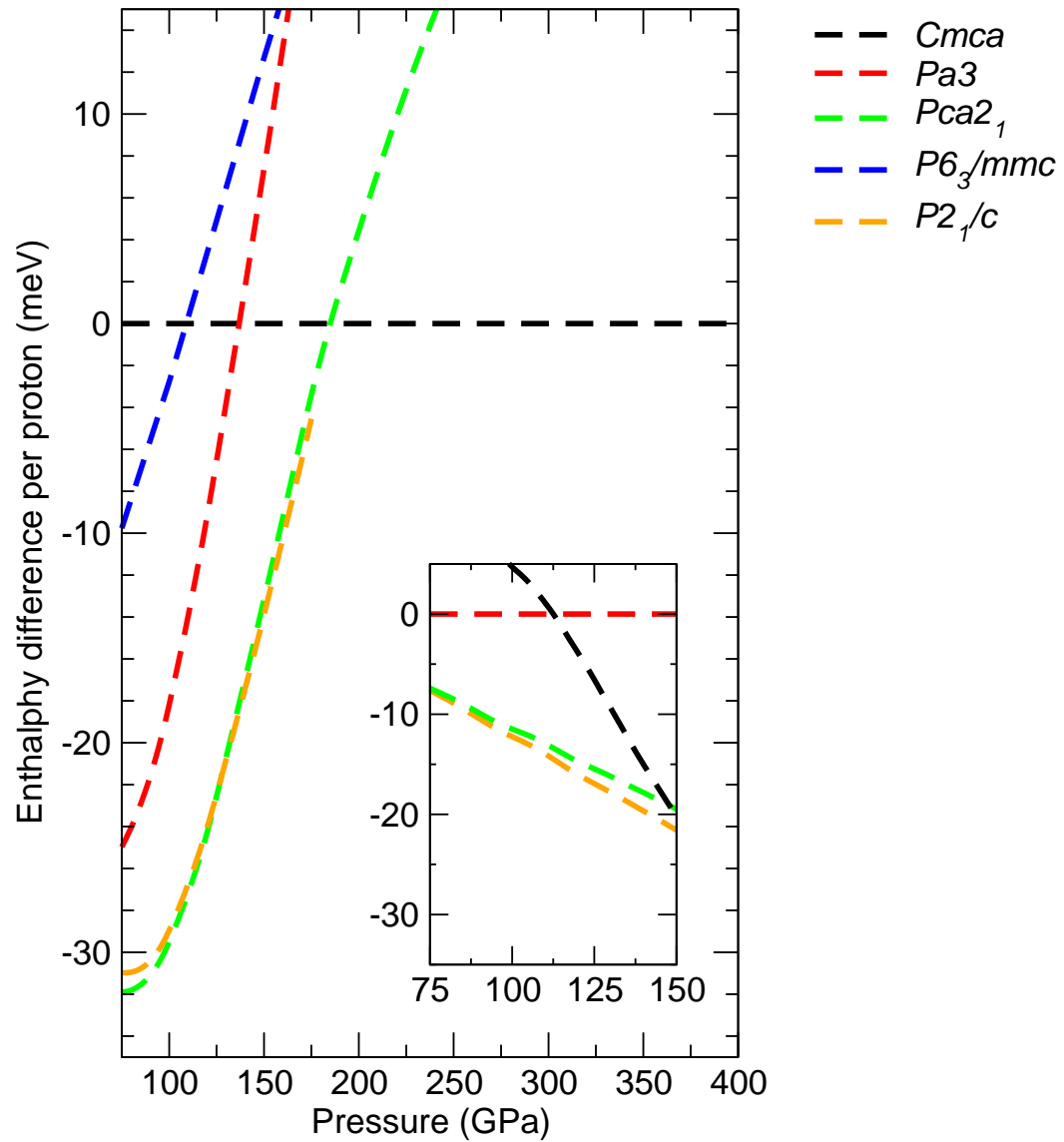
Phase diagram of solid hydrogen



Mazin *et al.*, *Phys Rev Lett* 78, 1066 (1997)

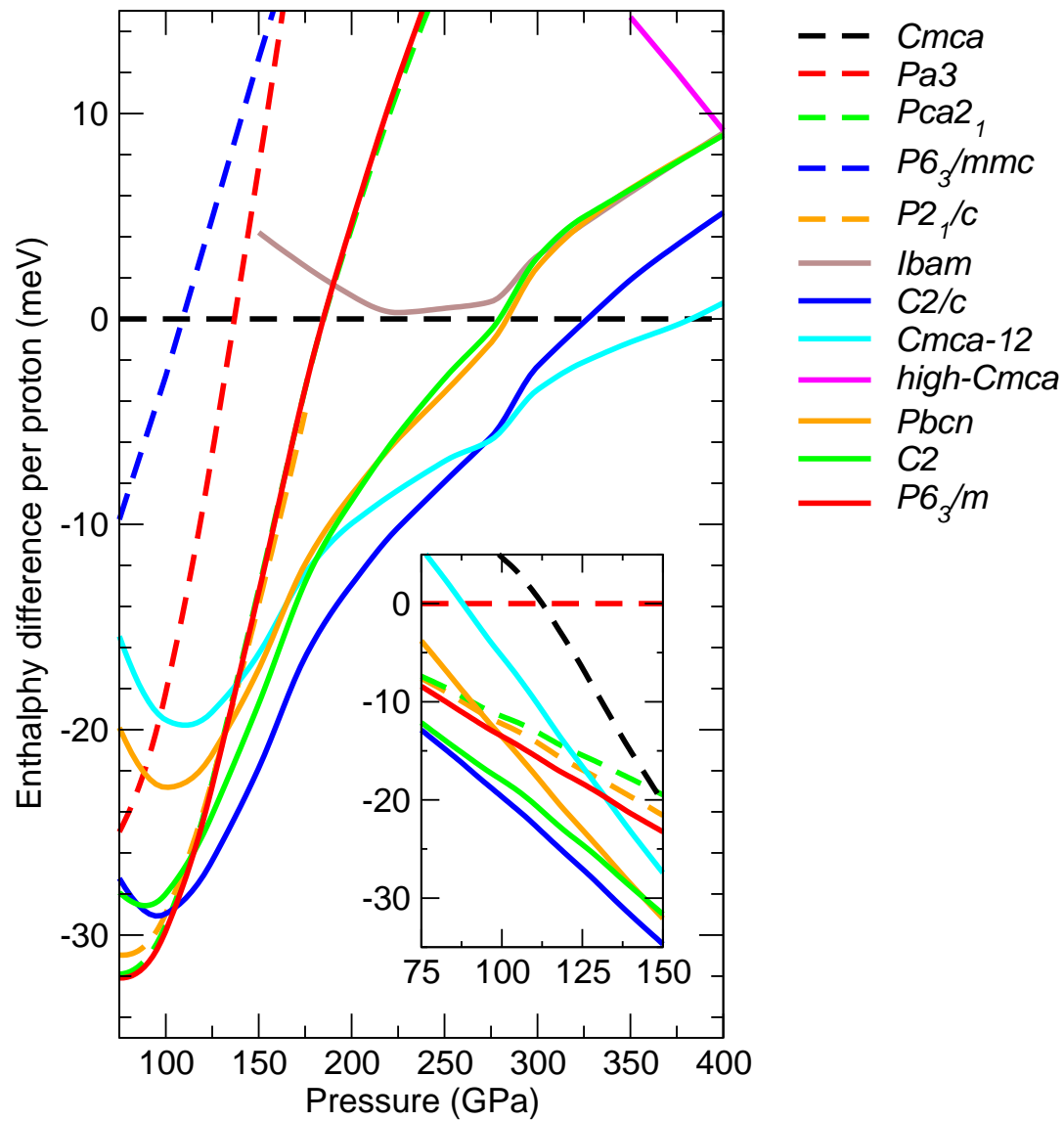
- Hydrogen atoms scatter X-rays weakly \Rightarrow Difficult for experiments
- Large zero point motion and small energy differences \Rightarrow Difficult for theory
- Perform structural search on static structures and add harmonic zero point energy (very poor approximation at very high pressures)

Phase diagram of solid hydrogen



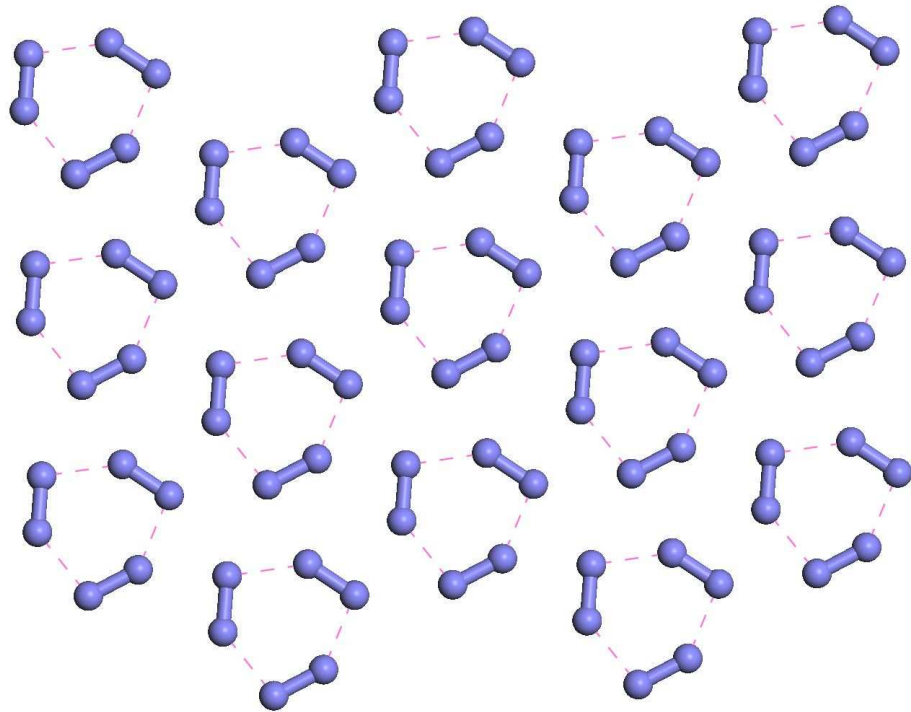
Pickard and Needs, *Nature Physics* 3, 473 (2007)

Phase diagram of solid hydrogen

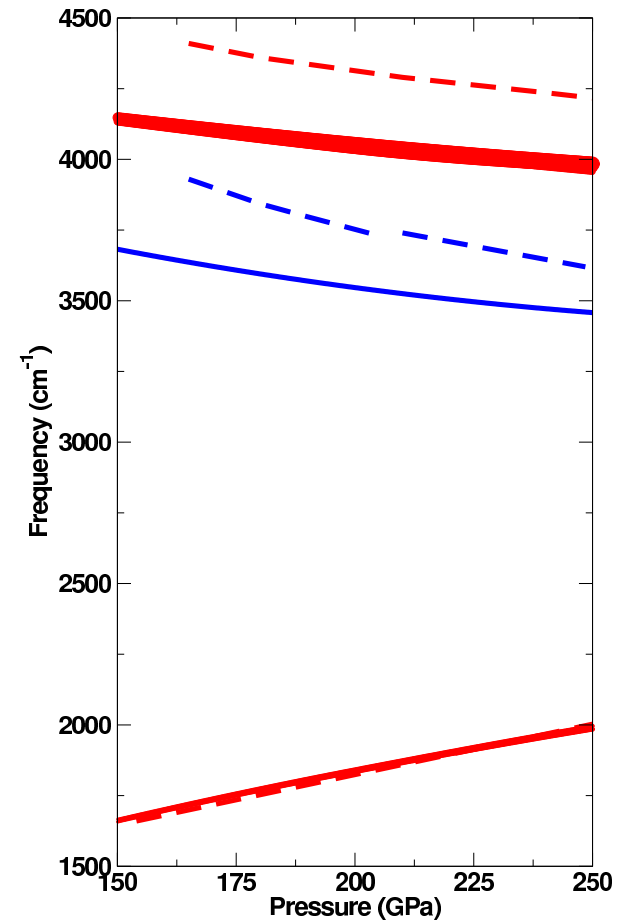


Pickard and Needs, *Nature Physics* 3, (2007)

The $C2/c$ layered structure - Phase III?

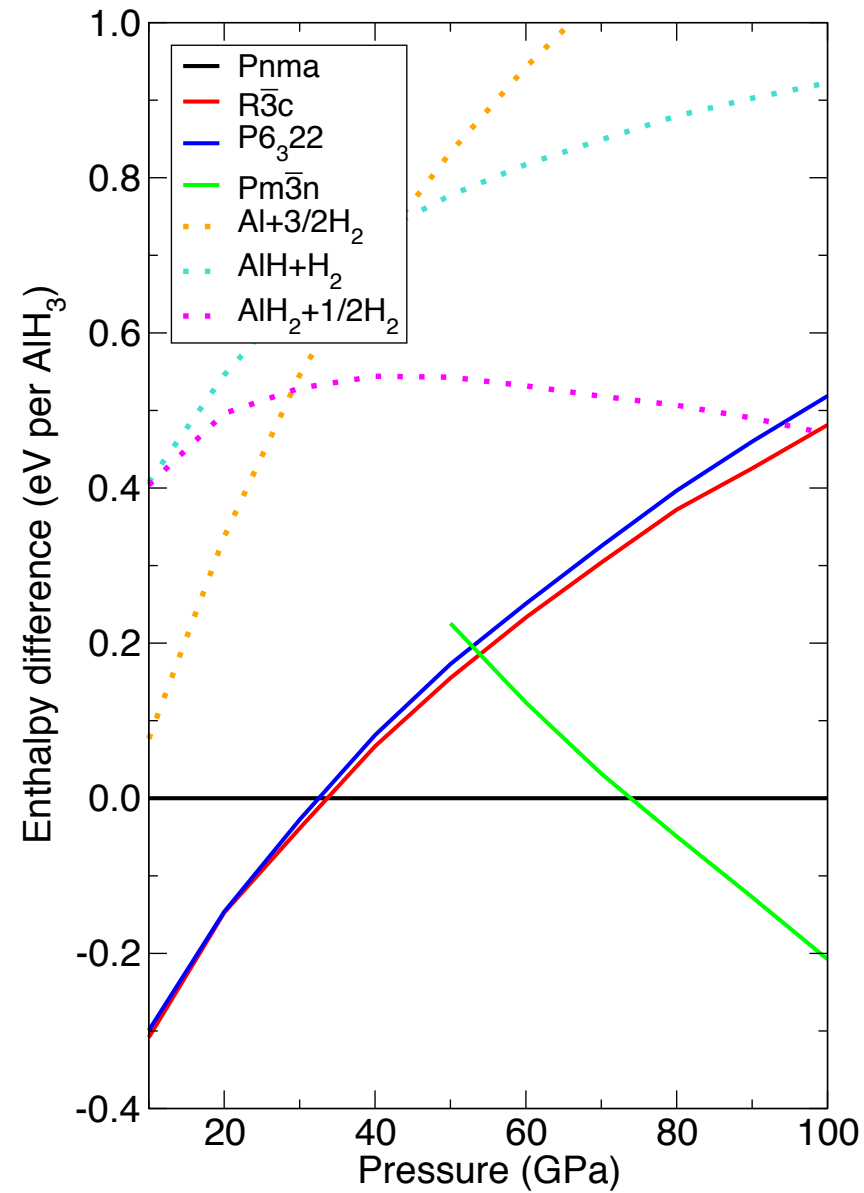


$C2/c$



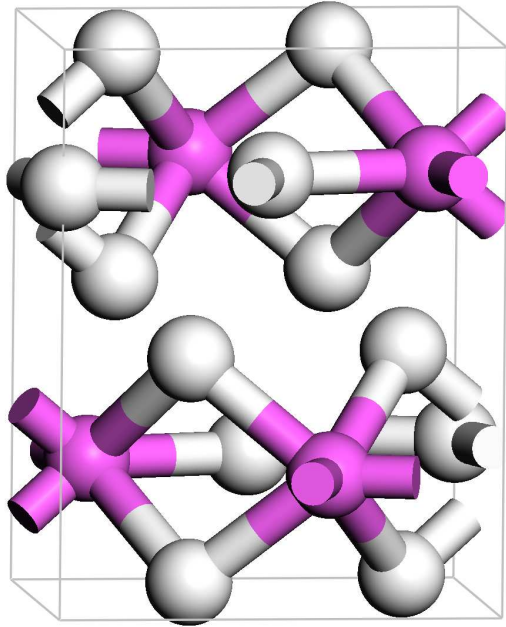
IR and Raman frequencies

Aluminum Hydride AlH_3 - Enthalpy



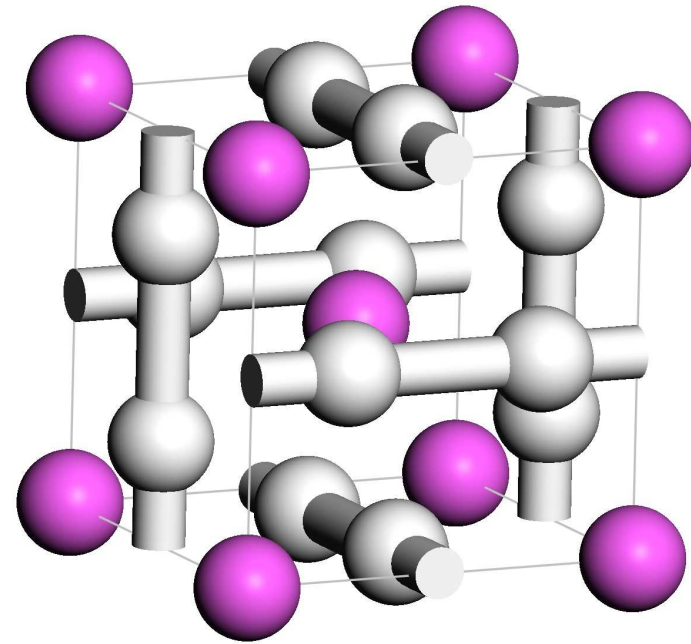
Pickard and Needs, unpublished

Aluminum Hydride AlH_3 - Structures



Pnma

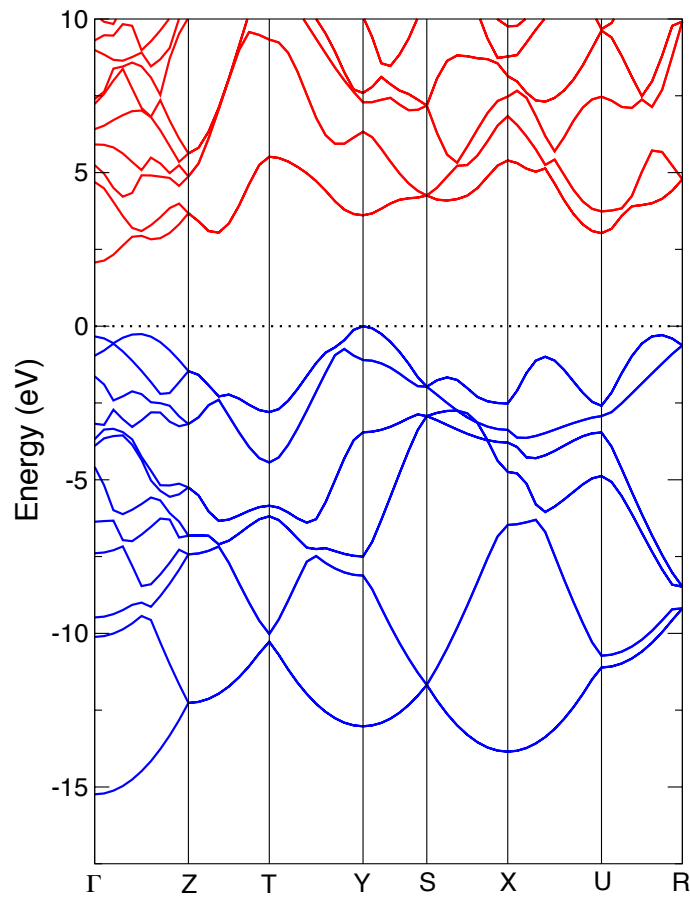
Insulating



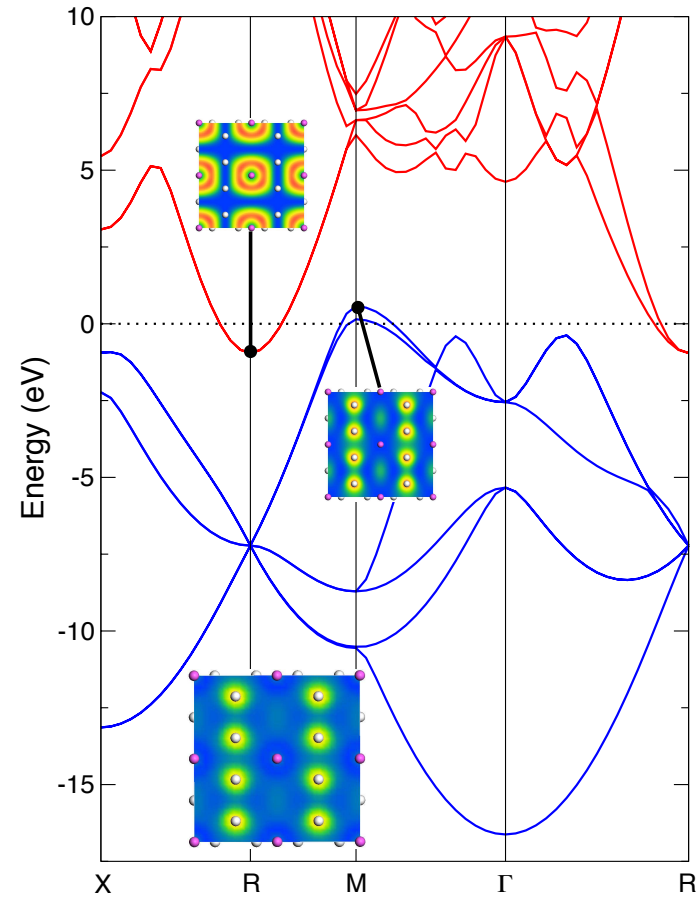
Pm\bar{3}n

Metallic

Aluminum Hydride AlH_3 - Bandstructures



$Pnma$



$Pm\bar{3}n$

Pickard and Needs, unpublished

Perspective

- The “simplest possible” random searching algorithm is useful for finding crystal structures
- Finding crystal structures may be simpler than we thought?