Predicting Crystal Structures by Random Searching

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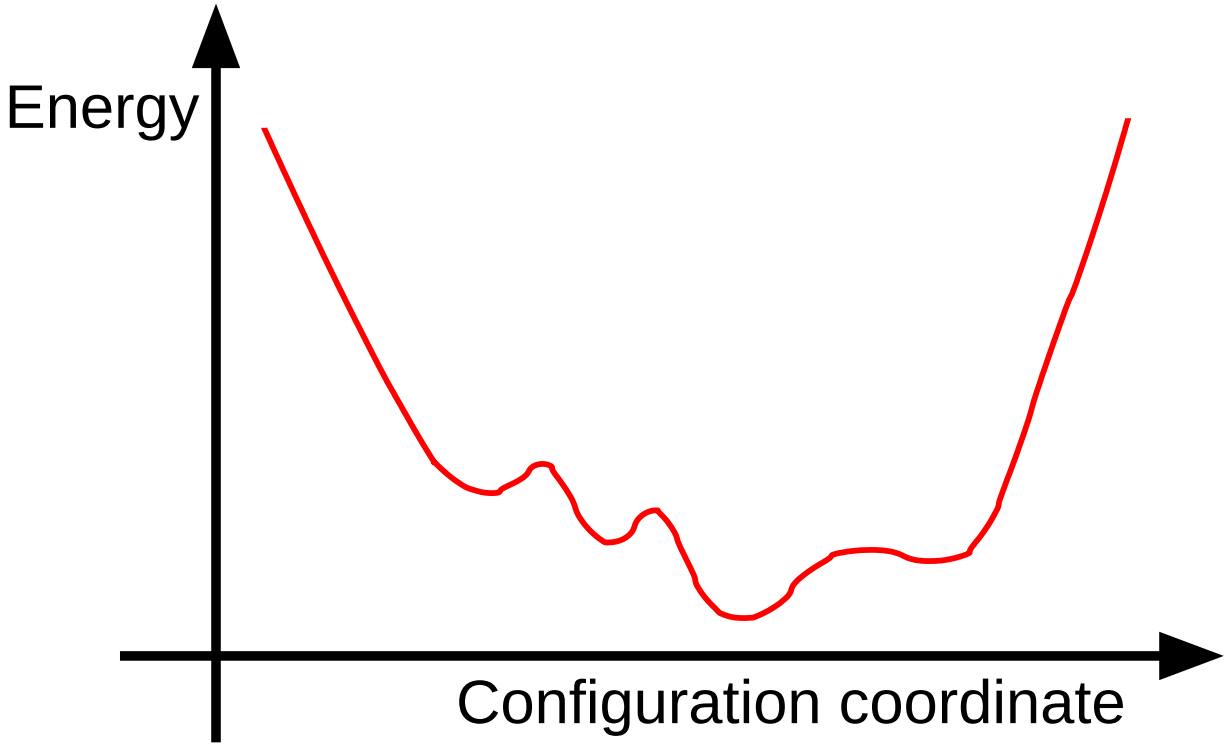
Locating the global minimum of a potential energy surface



"Accurate" methods such as first principles DFT are required

Use CASTEP with ultrasoft pseudopotentials and PBE GGA

Random searching algorithm for crystal structures

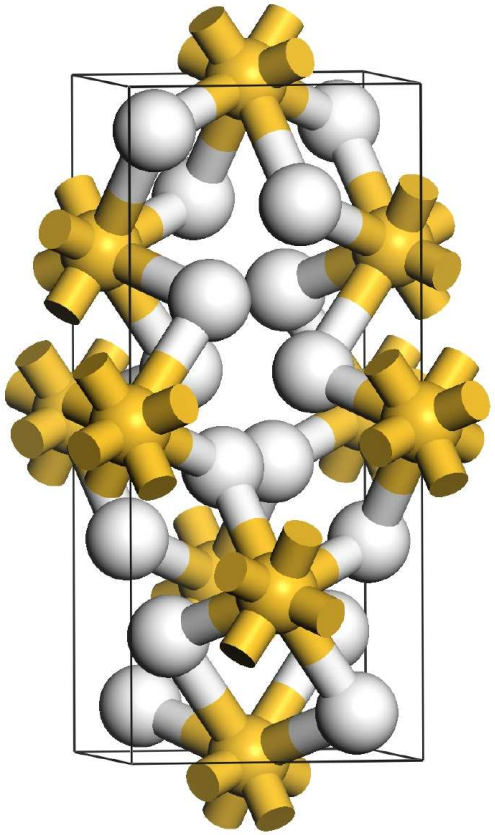
Generate a population of random structures and relax them:

Choose random unit cell translation vectors
Renormalize the volume to a reasonable range of values
Choose random atomic positions within the cell

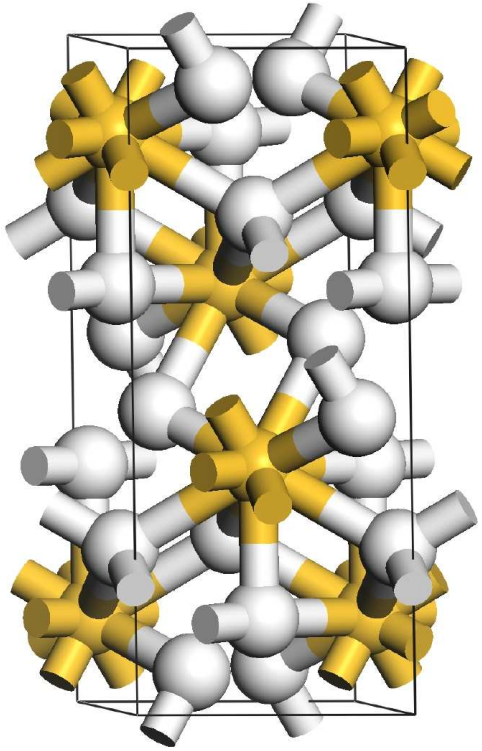
May impose constraints:

Fix the initial positions of some of the atoms (e.g., defect)
Choose initial positions from local minimum + shake
Insert molecules randomly (rather than atoms)
Choose to search within structures with a particular space group

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



$I4_1/a$



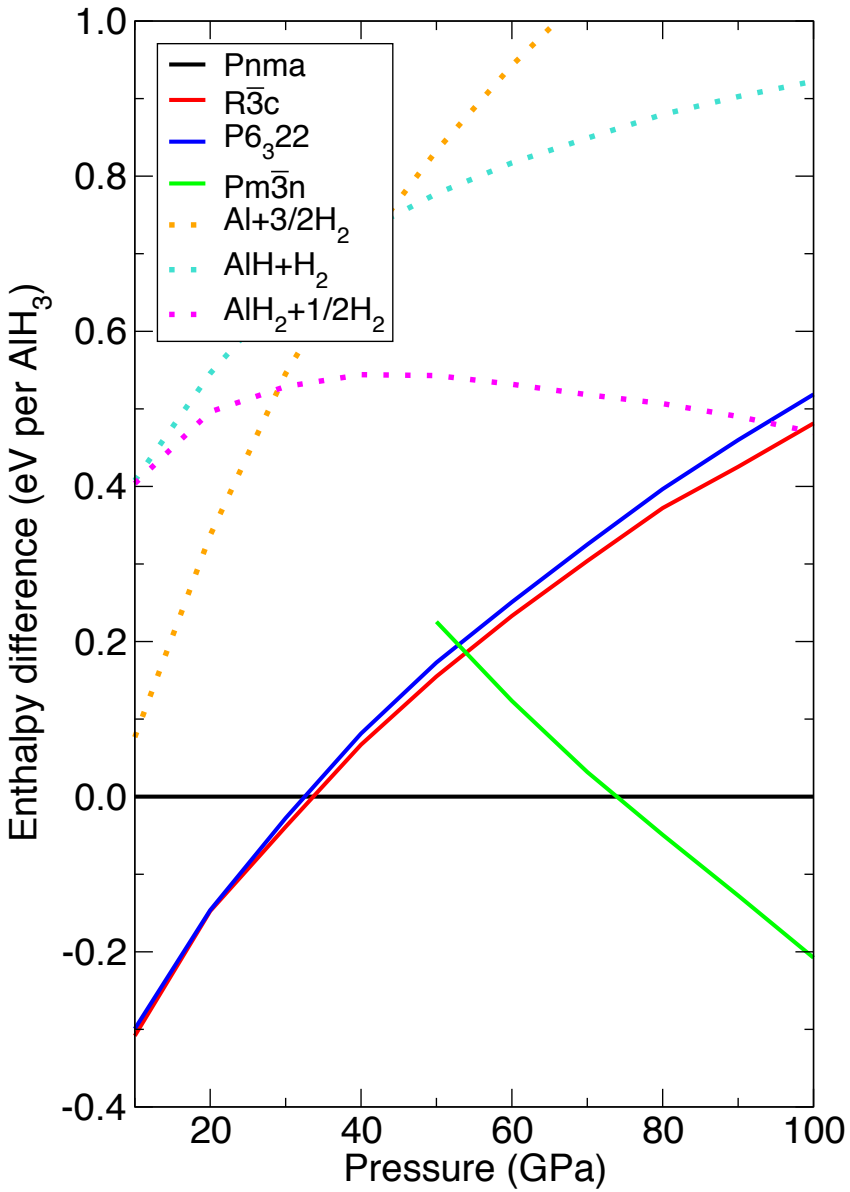
$C2/c$

Golden spheres: silicon atoms; white spheres hydrogen atoms

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

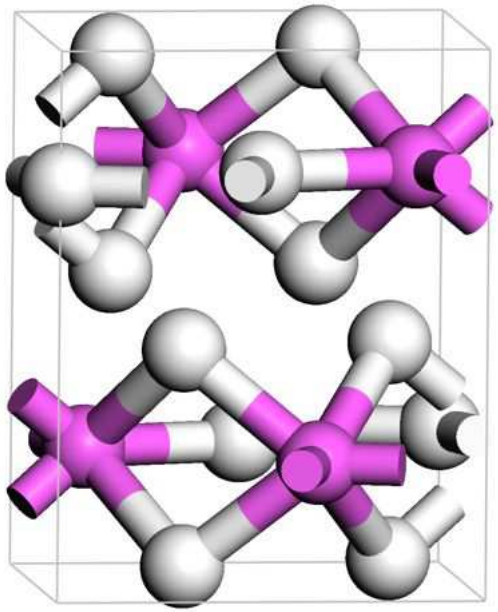
$I4_1/a$ found in experiment! Eremets *et al.*, *Science* 319, 1506 (2008)

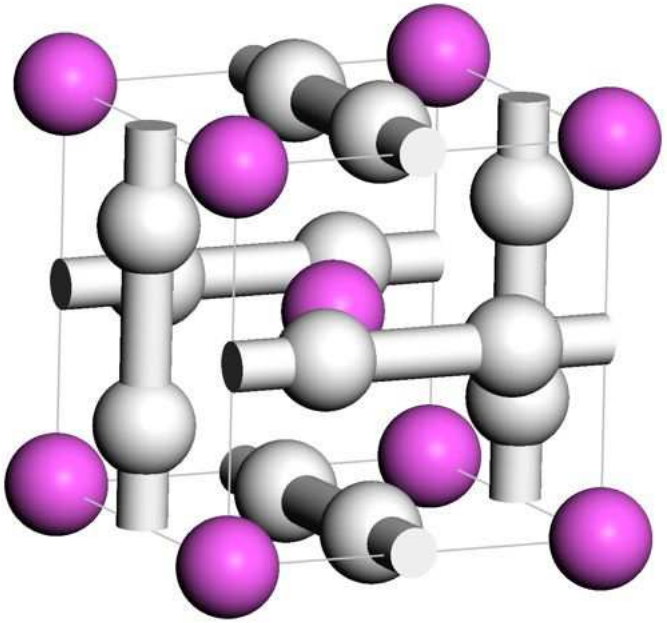
Aluminum Hydride AlH_3 - Enthalpy versus Pressure



Pickard and Needs, *Phys Rev B* 76, 144114 (2007)

Aluminum Hydride AlH_3 - Structures





$Pnma$

Insulating

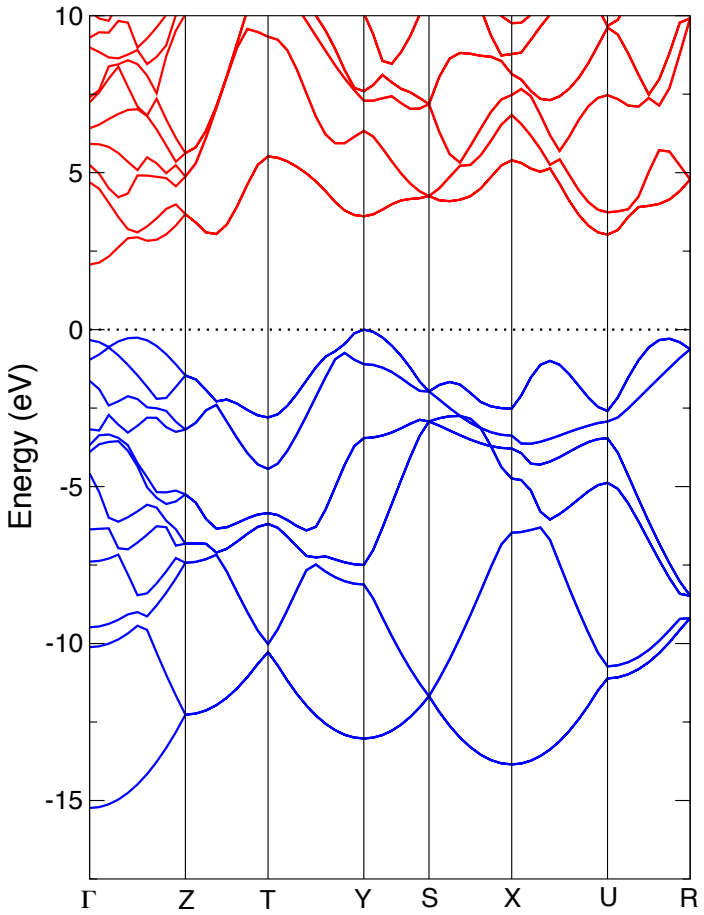
$Pm\bar{3}n$

Metallic

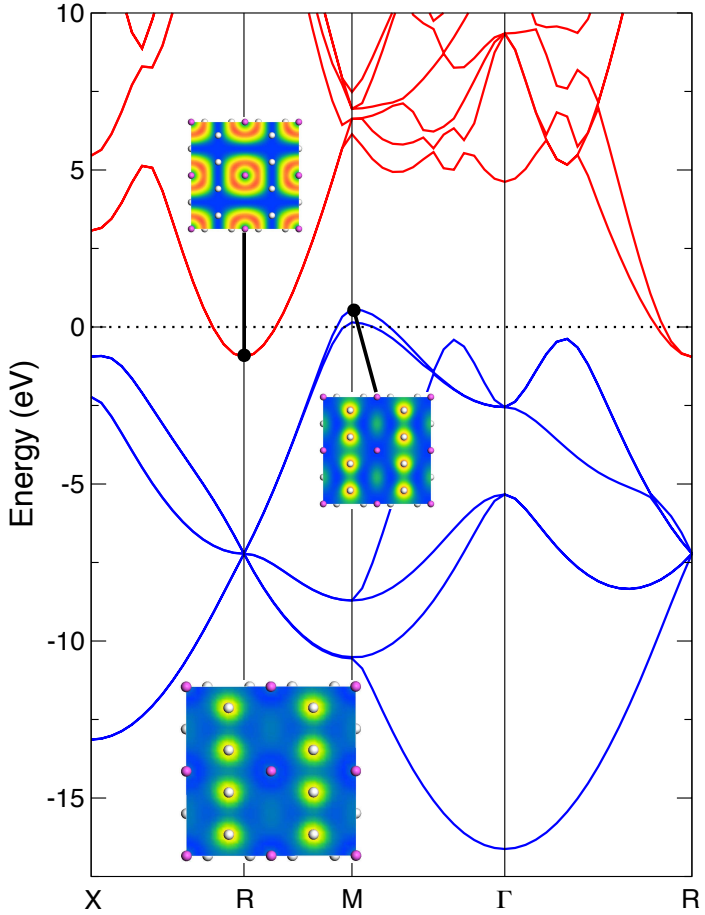
Pickard and Needs, *Phys Rev B* 76, 144114 (2007)

$Pm\bar{3}n$ found in experiment!
Goncharenko *et al.*, *Phys Rev Lett* 100, 045504 (2008)

Aluminum Hydride AlH_3 - Bandstructures

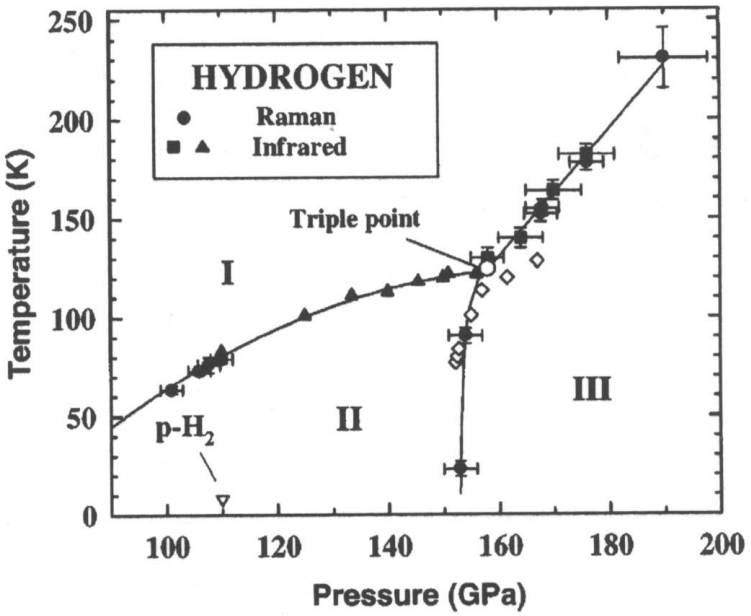


$Pnma$



$Pm\bar{3}n$

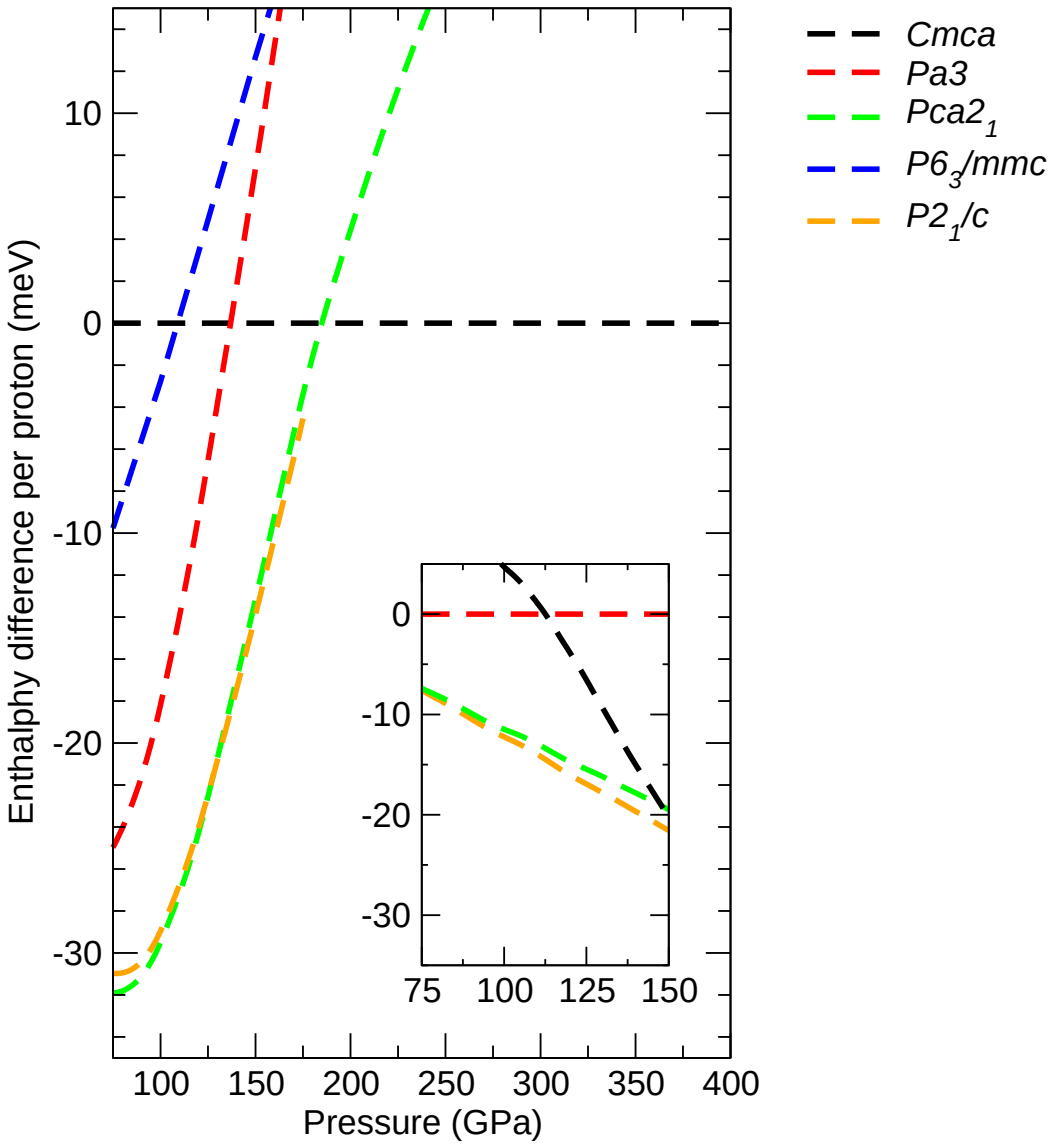
Phase diagram of solid hydrogen



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

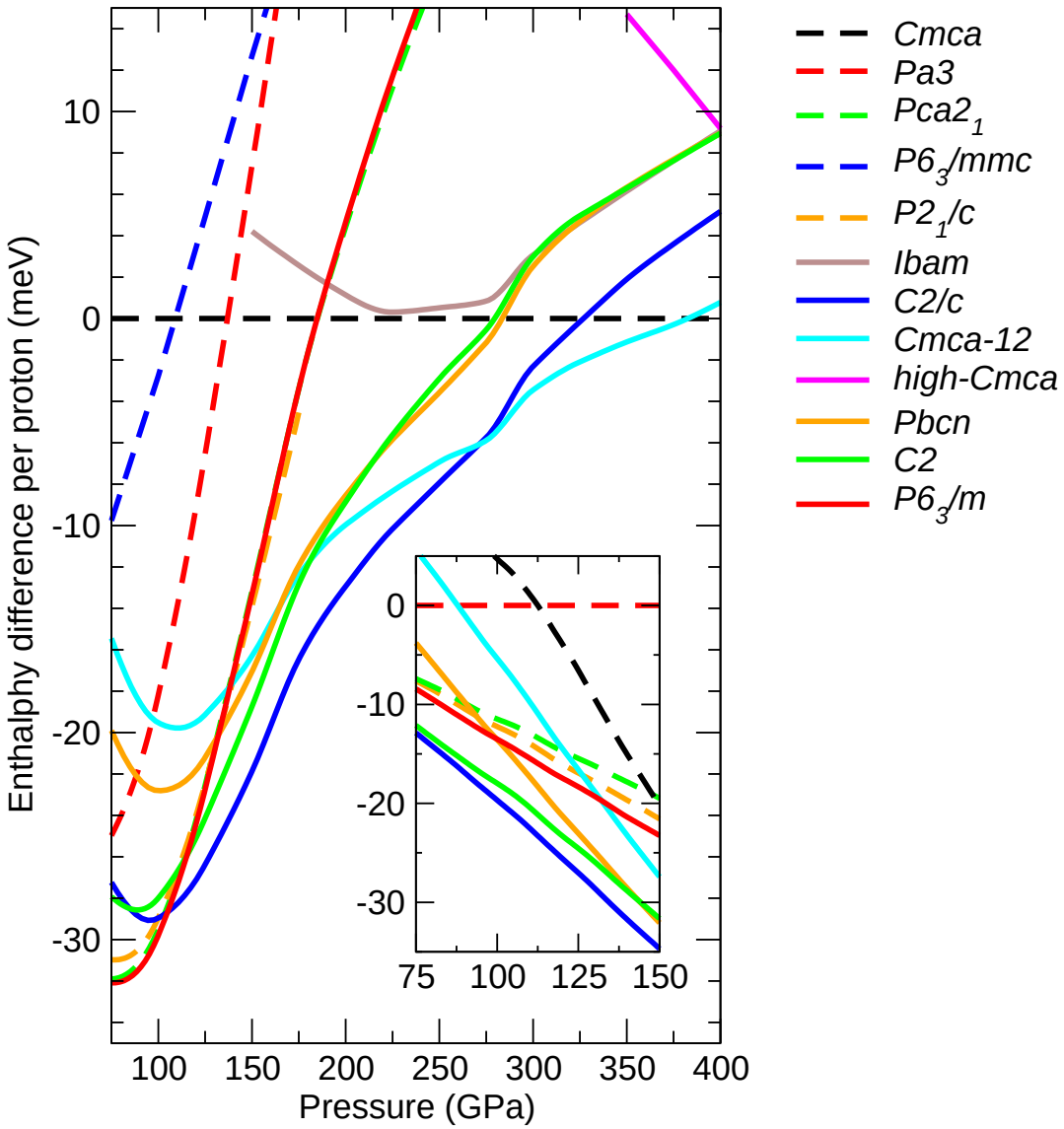
- Hydrogen atoms scatter X-rays weakly ⇒ Difficult for experiments
- Large zero point motion and small energy differences ⇒ Difficult for theory
- Perform structural search on static structures and add harmonic zero point energy (biased against atomic structures which should be stable at very high pressures)

Phase diagram of solid hydrogen



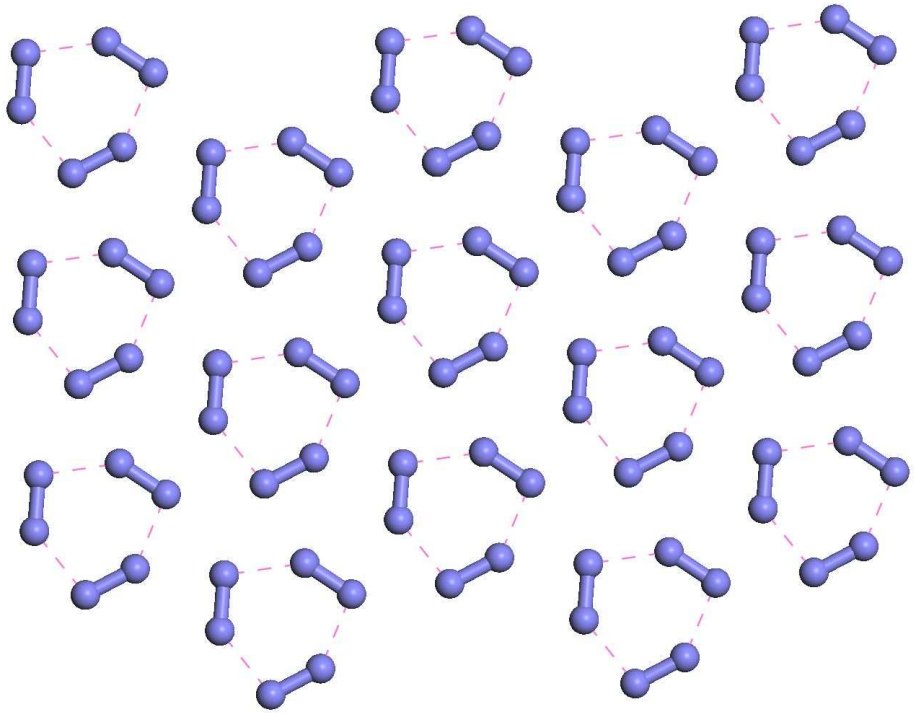
Pickard and Needs, *Nature Physics* 3, 473 (2007)

Phase diagram of solid hydrogen

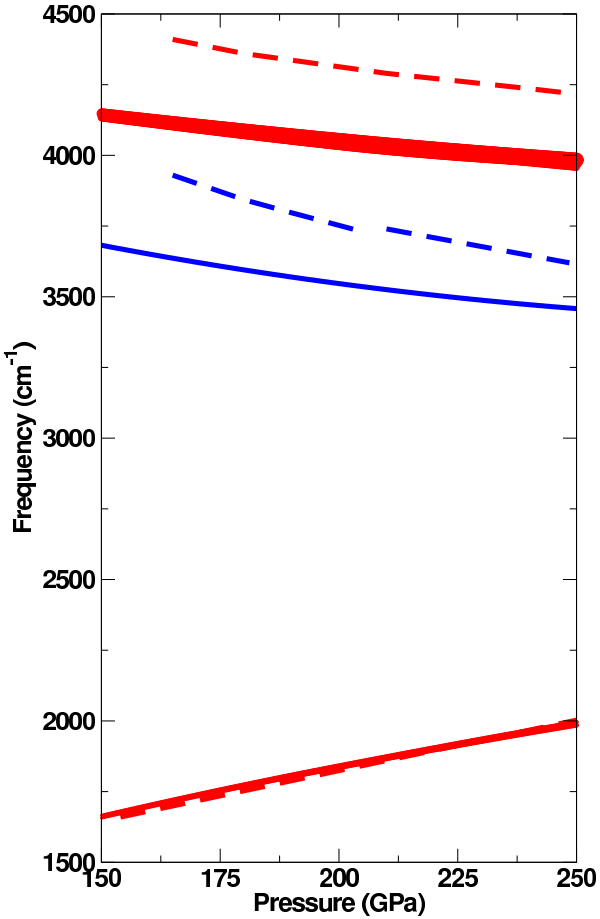


Pickard and Needs, *Nature Physics* 3, 473 (2007)

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

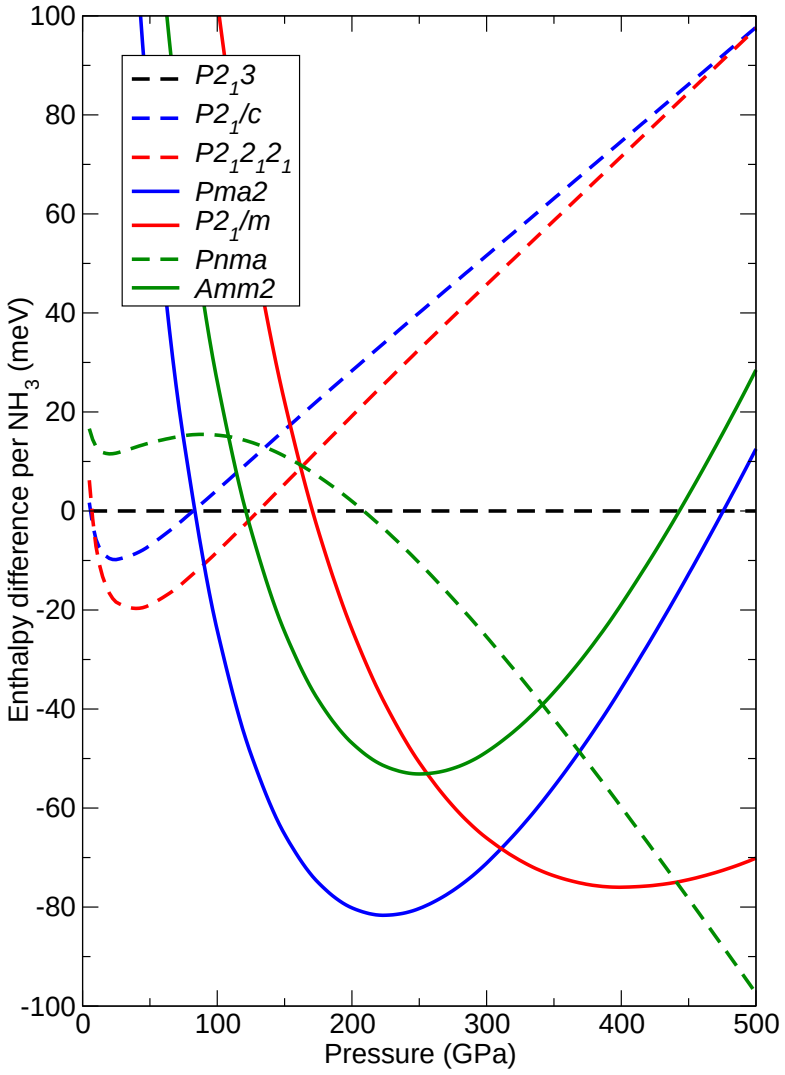


$C2/c$



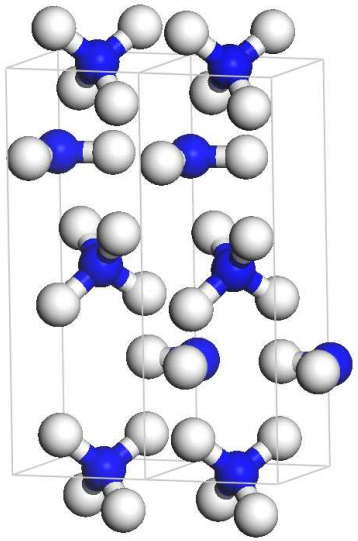
IR and Raman frequencies

Ammonia NH_3 - Enthalpy versus Pressure



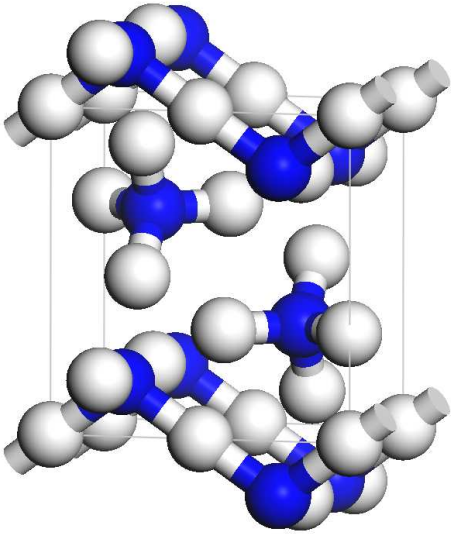
Pickard and Needs, unpublished

Ammonia NH_3 - Structures



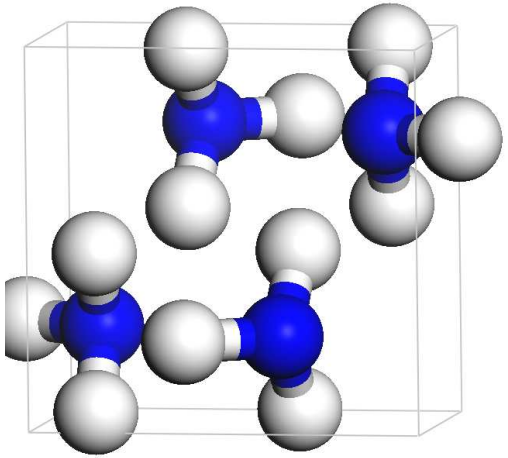
$Pma2$

Ionic



$P2_1/m$

Ionic



$Pnma$

Molecular

Pickard and Needs, unpublished

Perspective

- The "simplest possible" random searching algorithm is useful for finding crystal structures

- Use of constraints can improve performance

- Finding crystal structures with a few atoms per cell may be simpler than we thought

Post doc position available:
http://www.tcm.phy.cam.ac.uk/vacancies.html