Decomposition and Terapascal Phases of Water Ice

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Density functionals for water at TPa pressures

- Van der Waals interactions are known to be important in ice structures at low pressures

- Can include van der Waals interactions using empirical (Tkatchenko and others) or parameter free density functional methods (Langreth and others)

- Including van der Waals interactions tends to contract structures

- The uniform limit becomes relevant at very high densities

- Empirical methods generally do not obey the uniform limit and (probably) do not give an accurate description of the linear response to an applied potential

- We don't really know what to do, so we use the PBE-GGA density functional, which satisfies the uniform limit and gives a good account of linear response

- All energy scales tend to increase as the density increases

Terapascal pressures

1 GPa $\simeq 10^4$ atmospheres

Pressure at the centre of the Earth $\simeq$ 350 GPa $=$ 0.35 TPa

Pressure at the centre of Jupiter $\simeq$ 8 TPa

Pressures at the centres of large exoplanets up to 100 TPa

Maximum pressure in diamond anvil cell $\simeq$ 0.4 TPa (0.64 TPa now!)

Can achieve multi-TPa pressures in shock wave experiments

Ramped compression achieves multi-TPa pressures at lower temperatures

Aluminium subjected to 400 TPa in an underground nuclear explosion

Development of apparatus for multi-TPa experiments, laser driven shock waves, precompression, National Ignition Facility (NIF) etc.

Relevance of water at terapascal pressures

- It has been speculated that water ice is present in the core of Jupiter at pressures as high as 6.4 TPa, also in Saturn at 1 TPa

- Icy planetary cores could be strongly eroded by contact with a hydrogen-rich mantle

- Pressure at which water ice metallizes?

- Does water ice decompose at high pressures?

- To investigate these issues we need to know what the most stable structures look like at TPa pressures

The stability of structures

H_2O is a stable stoichiometry of the binary H:O system.

At low pressures and temperatures, the reaction

$$H_2O \rightarrow H_yO_z + H_{2-y}O_{1-z}$$

is endothermic for all y and z, $0 < y < 2, 0 < z < 1$

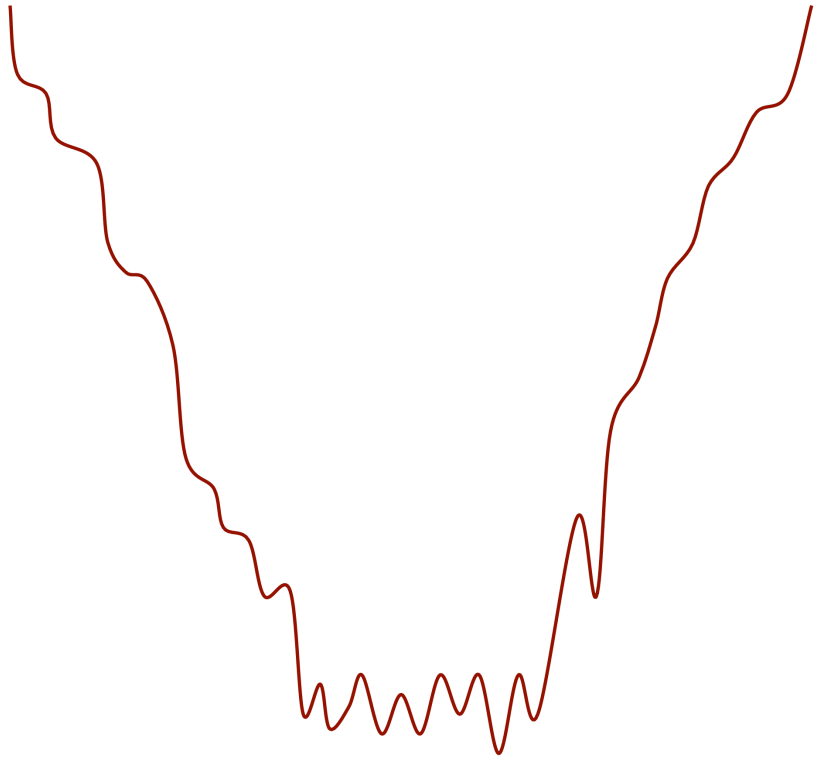
(1) Local or mechanical stability: harmonic phonons have real frequencies (also stable against elastic distortions)

(1a) Local or mechanical stability: structure sits in a potential well, but some phonons are unstable

(2) Stability against decomposition into two other compounds

Structure searching can typically find types (1) and (2), but not (1a)

Energy landscape



Minima at low energies, could have multiple funnels

Ab Initio Random Structure Searching

Use Density Functional Theory methods as the type of bonding may be uncertain

- Make a random unit cell
- Throw the required numbers of each atom type into the cell at random
- Relax under the quantum mechanical forces and stresses
- Repeat until happy or computing credits run out
- Look at lowest-energy or other interesting structures

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

Pickard and Needs, *J Phys: Condensed Matter* 23, 053201 (2011)

Ab Initio Random Structure Searching

- Easy to understand
- Easy to do
- Biased towards getting the right answer
- Teaches you chemistry
- Loves modern computers

Philosophy and extensions

- When you don't know anything, select initial structures from a uniform random distribution

- When you know something for sure impose it directly, when you think something is likely to be true, bias the search towards it

- Can constrain search to exclude very-low-symmetry structures

- Impose chemical ideas through a careful choice of the initial structures - chemical units, distances between atoms, coordination number

- Can use experimental data as constraints

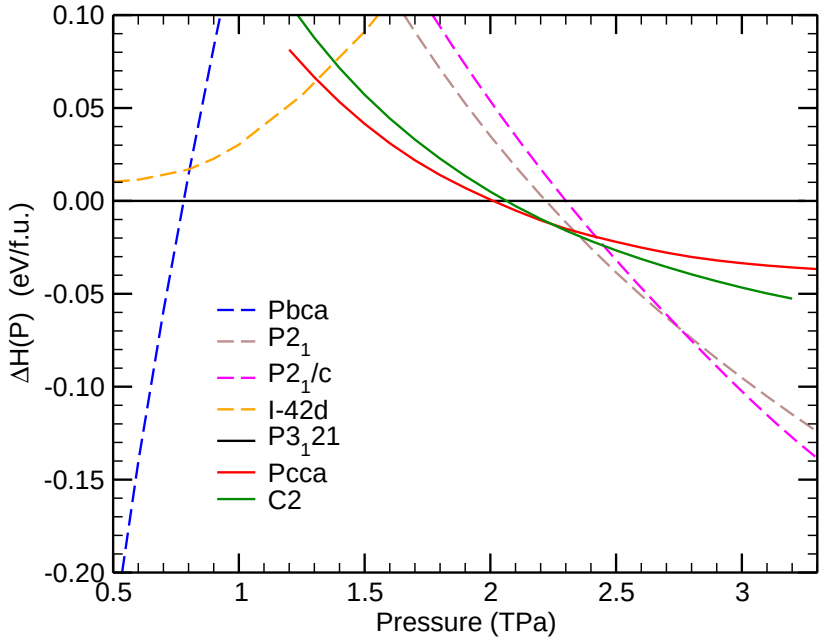
- "Shake" structures

Results from structure searching

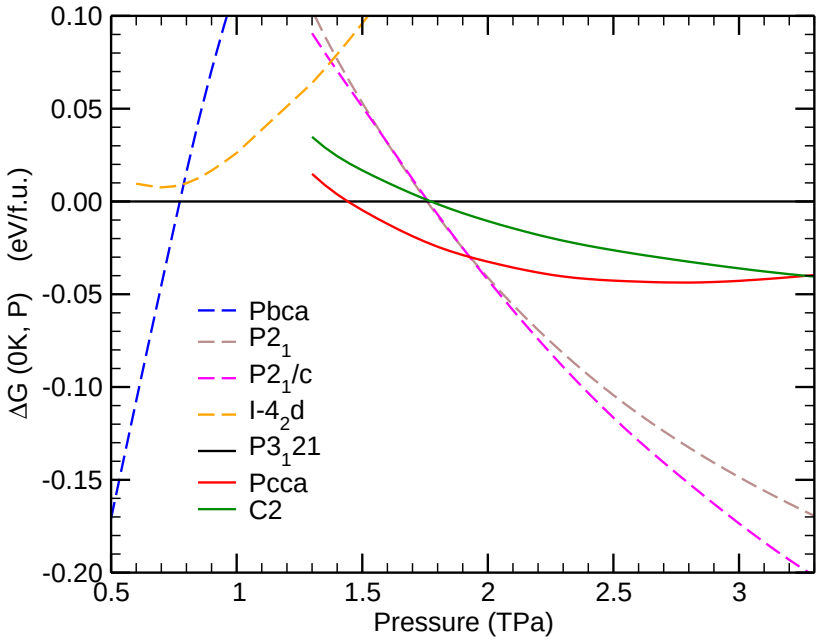
Table 1: Space group symmetries, calculated stability ranges, and numbers of fu per primitive unit cell for phases of H_2O. Nuclear vibrational motion is not included.

Space group	Stability range (TPa)	No. fu	Source
Ice X	<0.30	2	Experiment
$Pbcm$	0.30–0.71	4	DFT: Benoit *et al.*
$Pbca$	0.71–0.78	8	DFT: Militzer *et al.*
$P3_121$	0.78–2.01	12	DFT: This work
$Pcca$	2.01–2.24	12	DFT: This work
$C2$	2.24–2.36	12	DFT: This work
$P2_1$	2.36–2.75	4	DFT: McMahon/Wang/Ji *et al.*
$P2_1/c$	2.75–6.06	8	DFT: Ji *et al.*
$C2/m$	6.06–24.0	2	DFT: McMahon *et al.*
$I4/mmm$	>24.0	4	DFT: This work

Enthalpy versus pressure



Without ZP motion

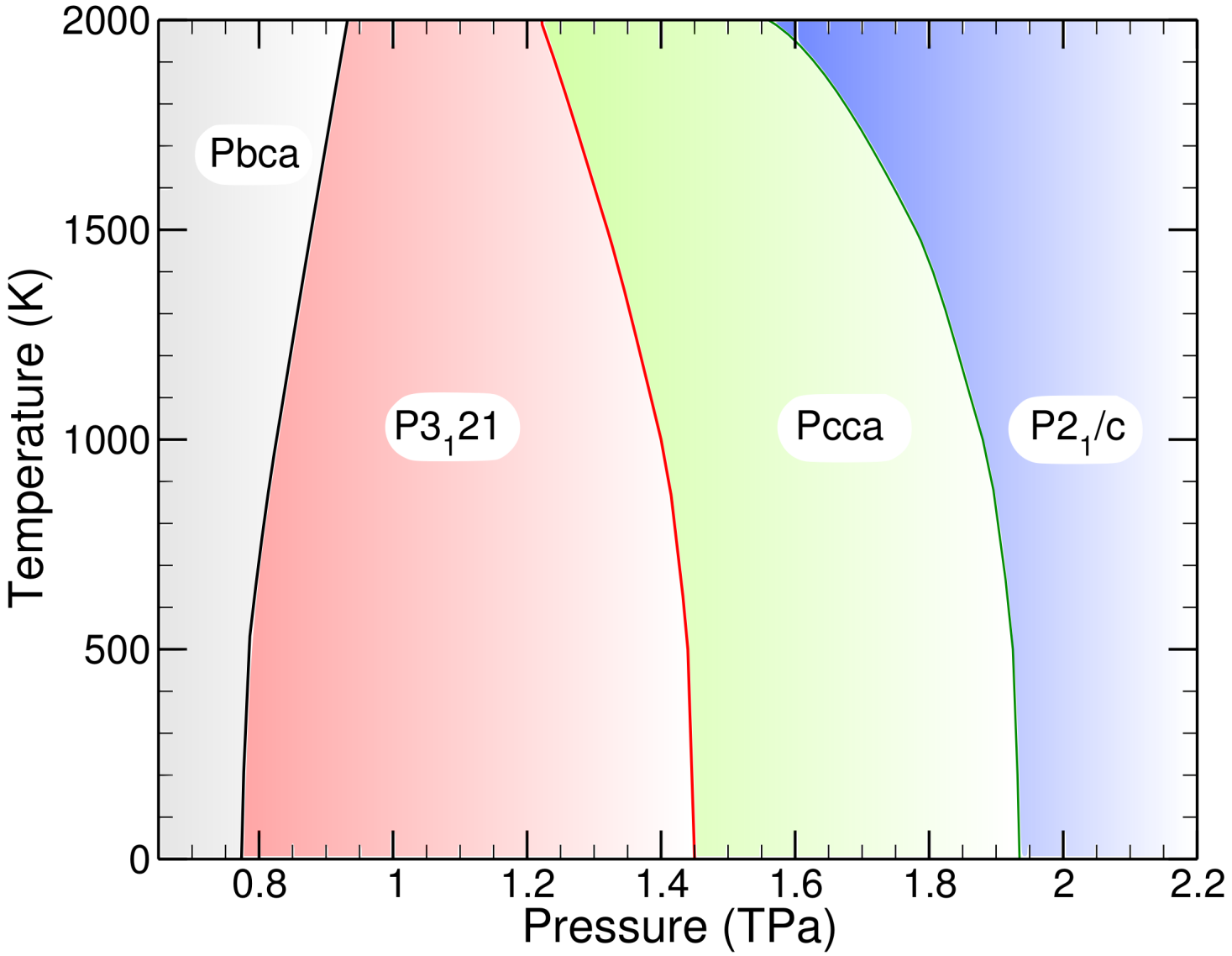


With ZP motion

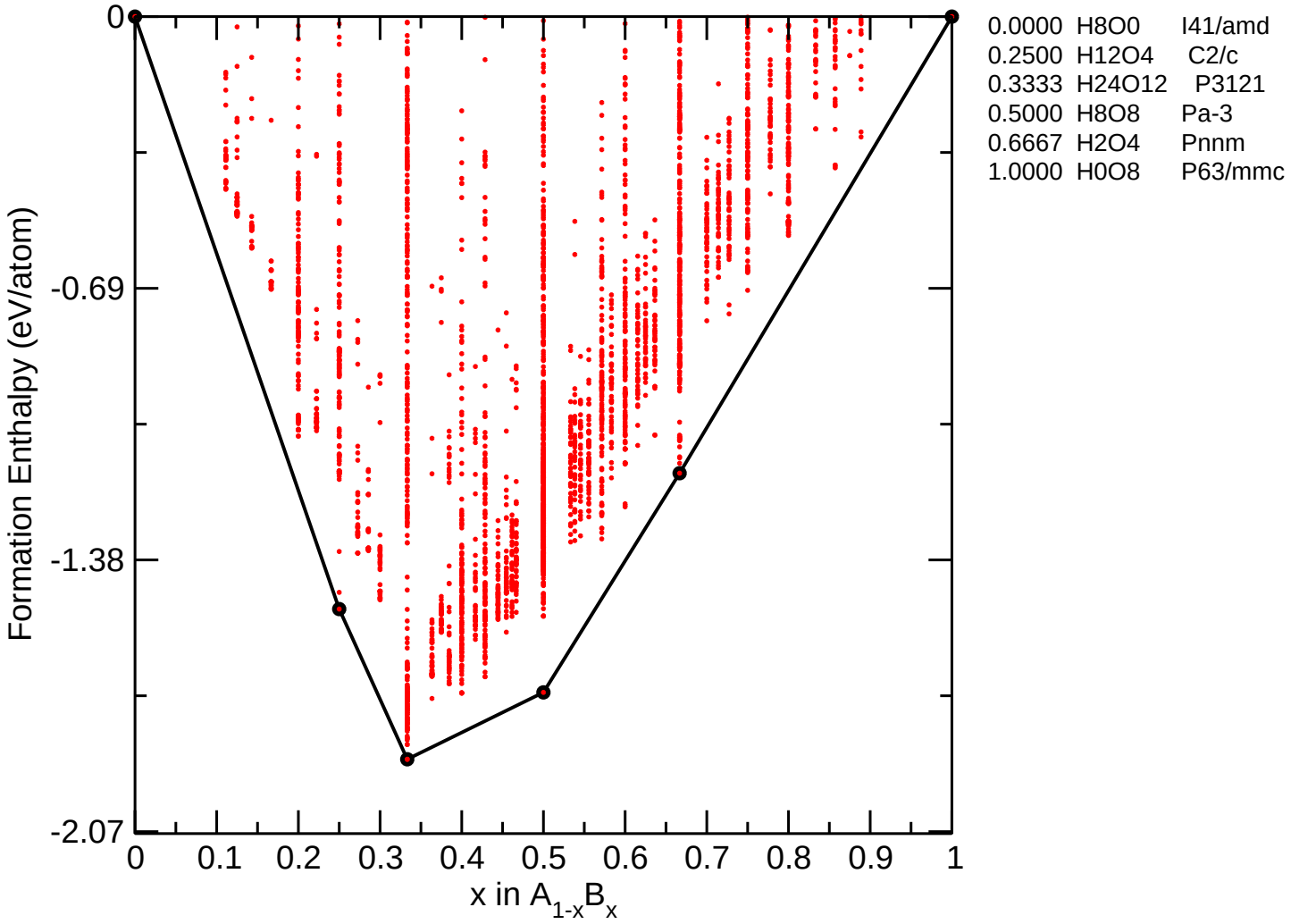
Dashed lines: Previously known structures

Solid lines: Our new structures

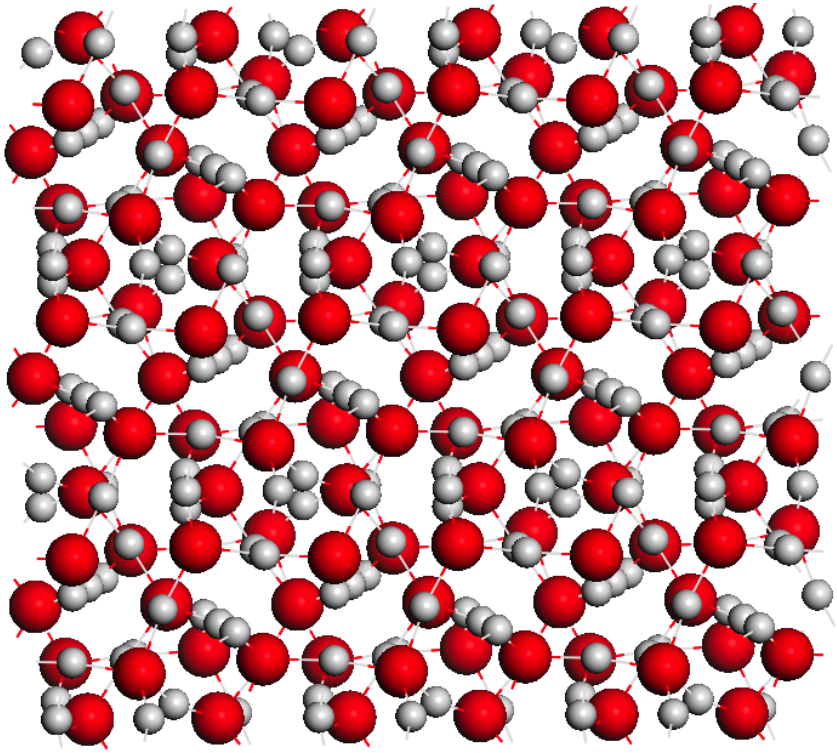
Phase diagram of water ice



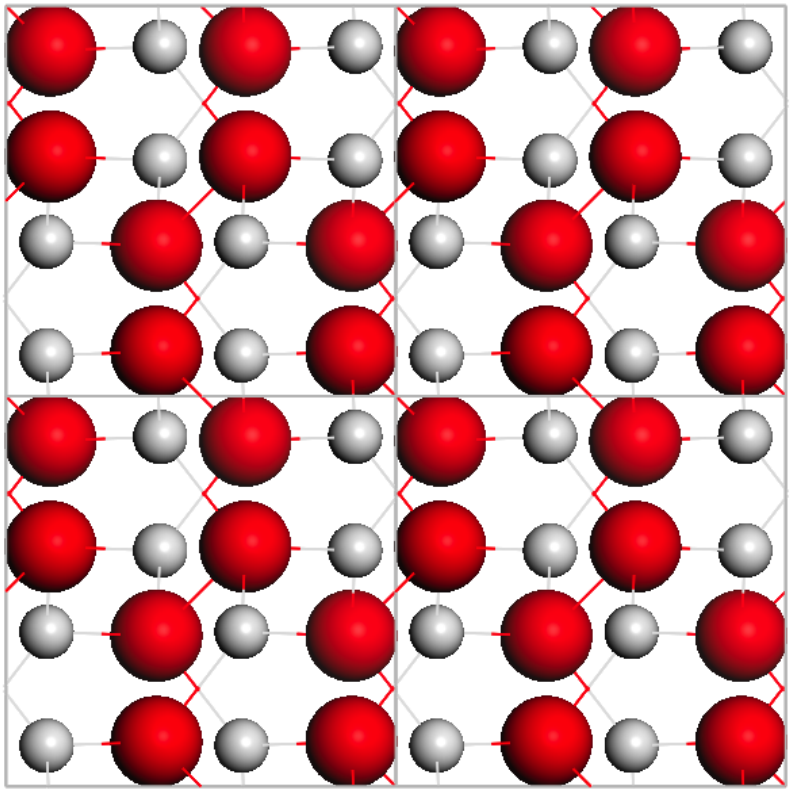
Convex hull diagram at 1 TPa



The $P3_121$ and $Pa\bar{3}$ structures

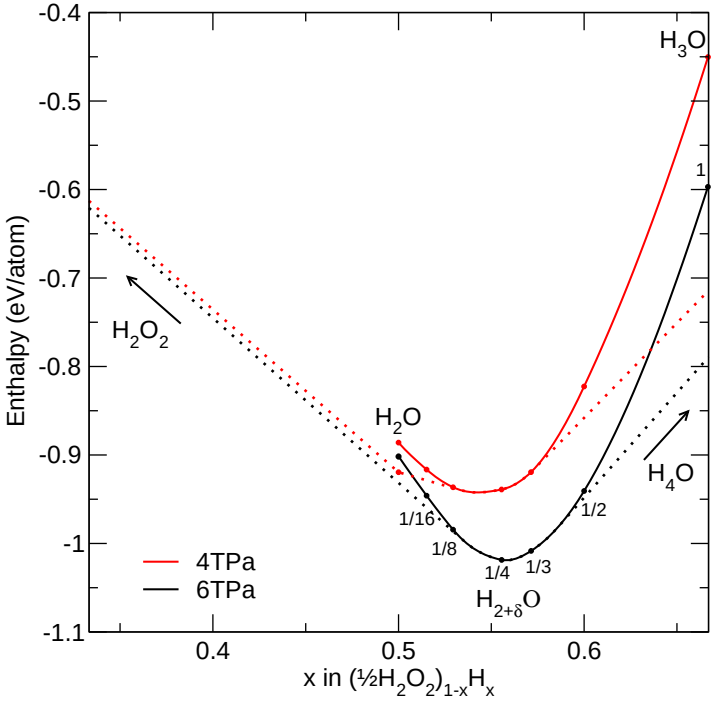


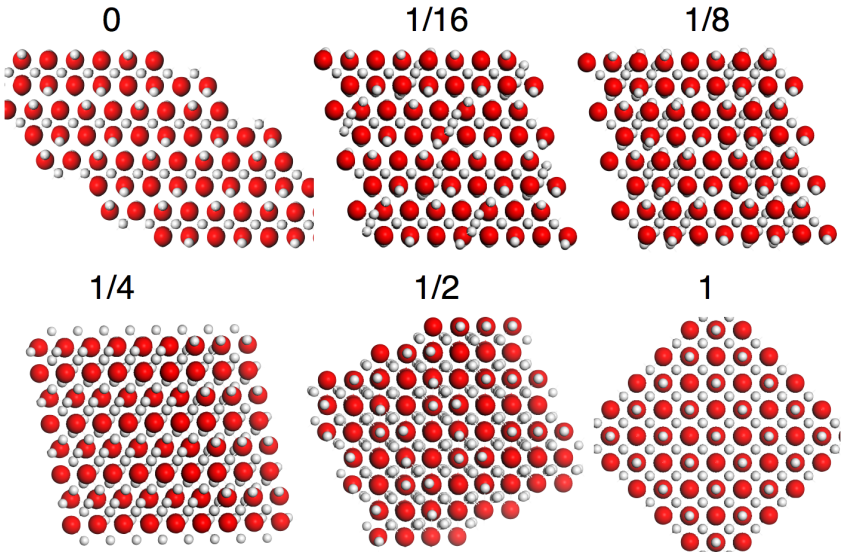
$P3_121$ structure of H_2O at 1 TPa



$Pa\bar{3}$ structure of H_2O_2 at 6 TPa

H_2O becomes unstable above 5 TPa!



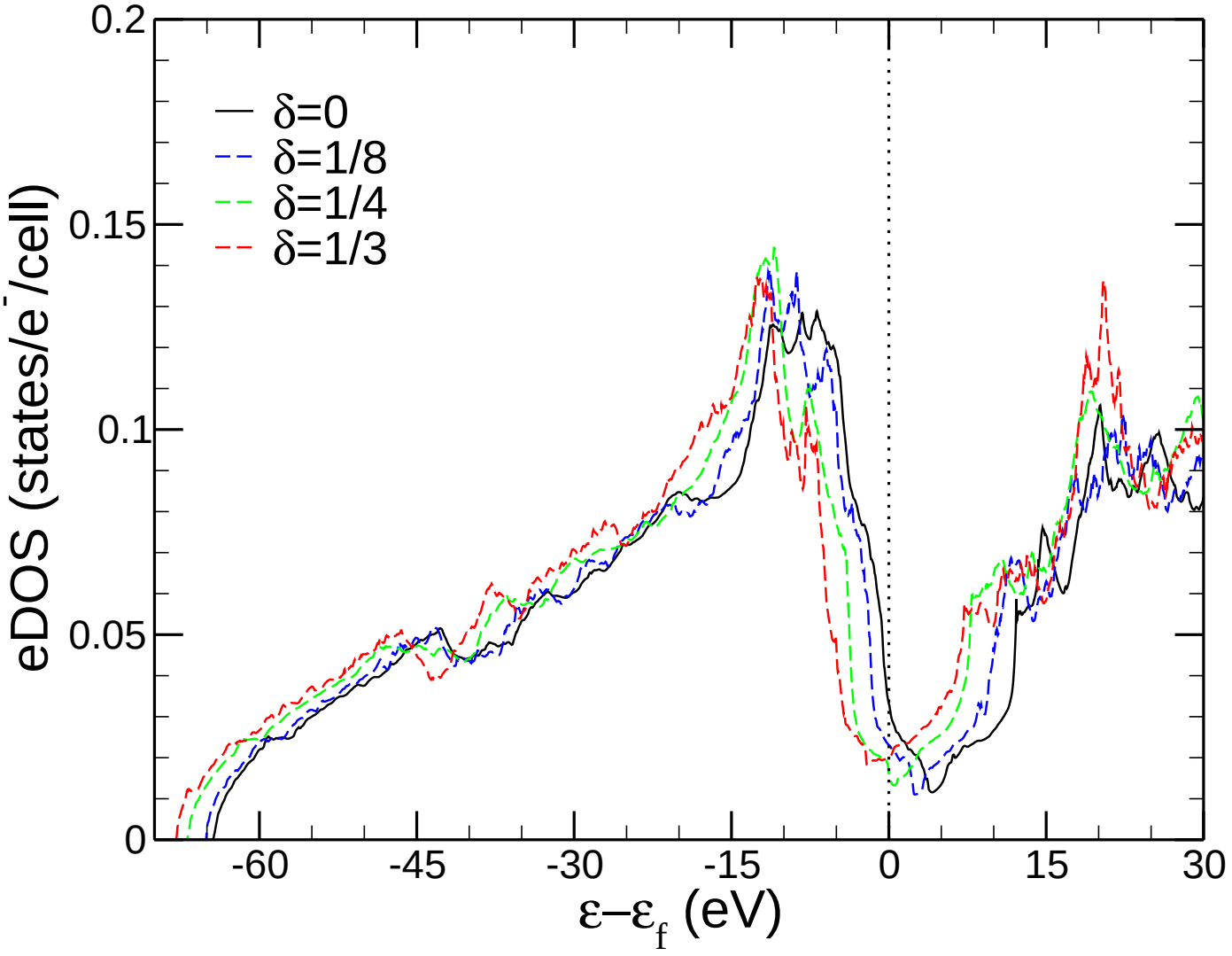


Different values of δ

Structures are stable over a range of H contents - a topotactic transition

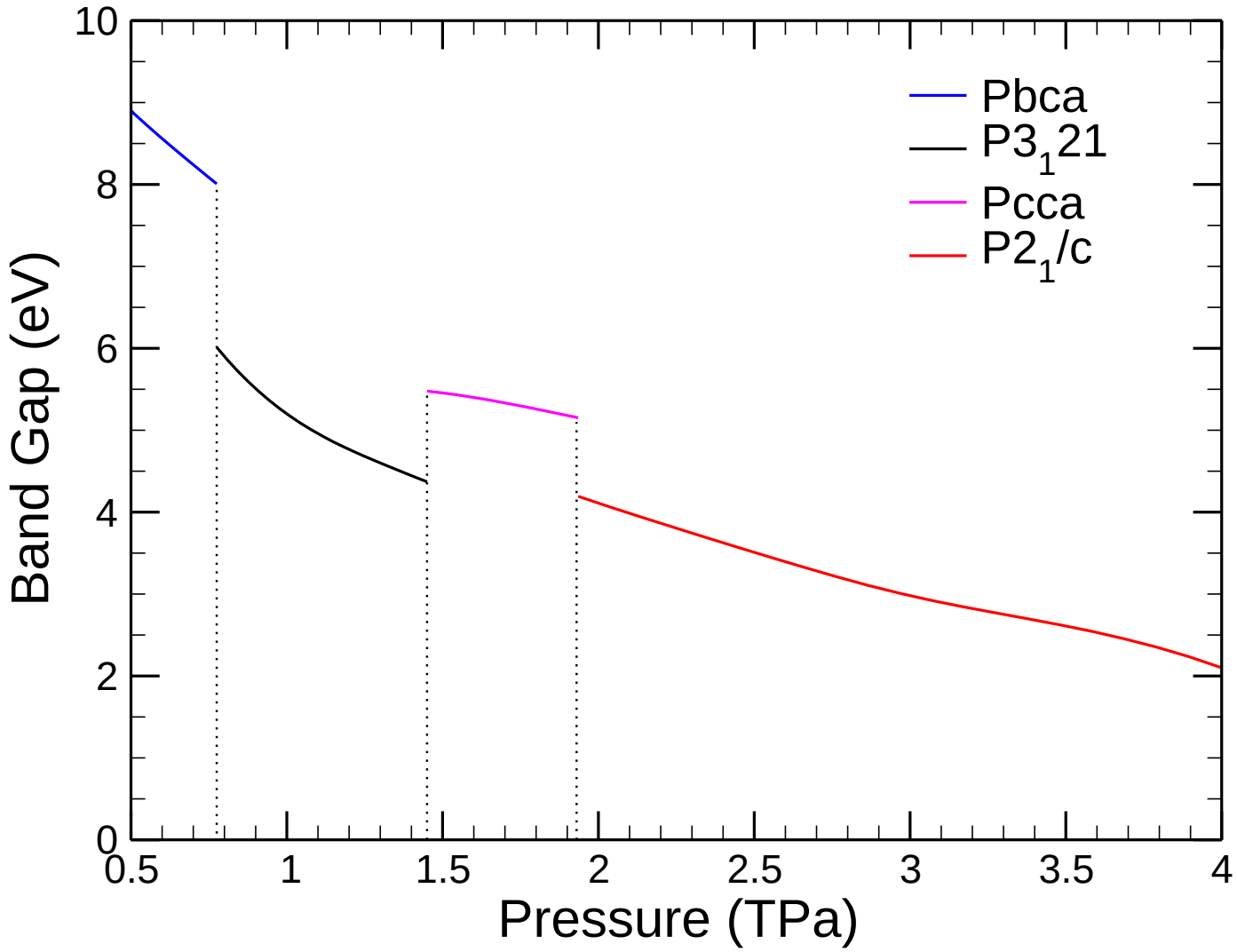
See R.D. Shannon and R.C. Rossi, Nature (London) 202, 1000 (1964)

Relative stability of the δ phases



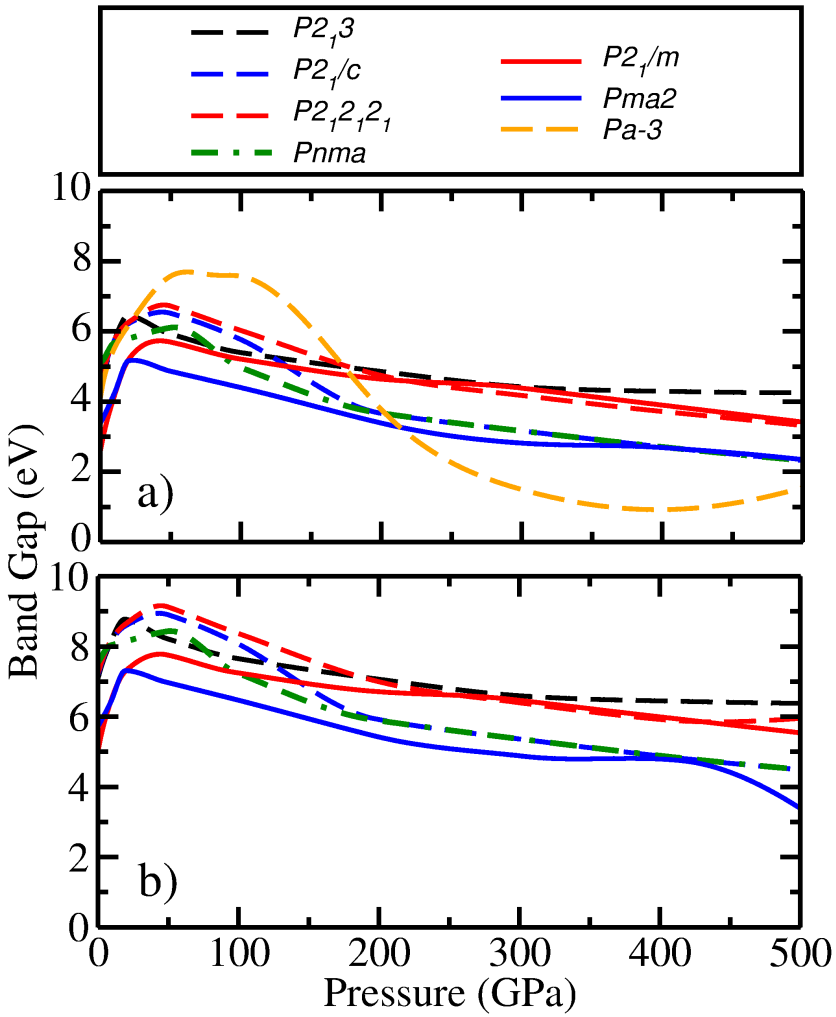
$$\mathrm{H_2O} \rightarrow \frac{\delta}{1+\delta}\frac{1}{2}\,\mathrm{H_2O_2} + \frac{1}{1+\delta}\,\mathrm{H_{2+\delta}O},$$

Band gap versus pressure



Band gap increases with pressure at low pressures (increasing Stark shift)
Band gap decreases with pressure at high pressures

Band gap versus pressure in ammonia



a) PBE GGA functional b) PBE0 hybrid functional

Conclusions

- H_2O decomposes into H_2O_2 and a hydrogen-rich phase at pressures of a little over 5 TPa

- H_2O is not a stable compound at the highest pressures at which it has been suggested to occur within Jupiter

- The hydrogen-rich phase is stable over a wide range of hydrogen contents, and it might play a role in the erosion of the icy component of the cores of gas giants as H_2O comes into contact with hydrogen

- Metallization of H_2O is predicted at just over 6 TPa, and therefore H_2O does not have a thermodynamically stable low-temperature metallic form

- We have found a new and rich mineralogy of complicated water ice phases that are more stable in the pressure range 0.8–2 TPa than any predicted previously