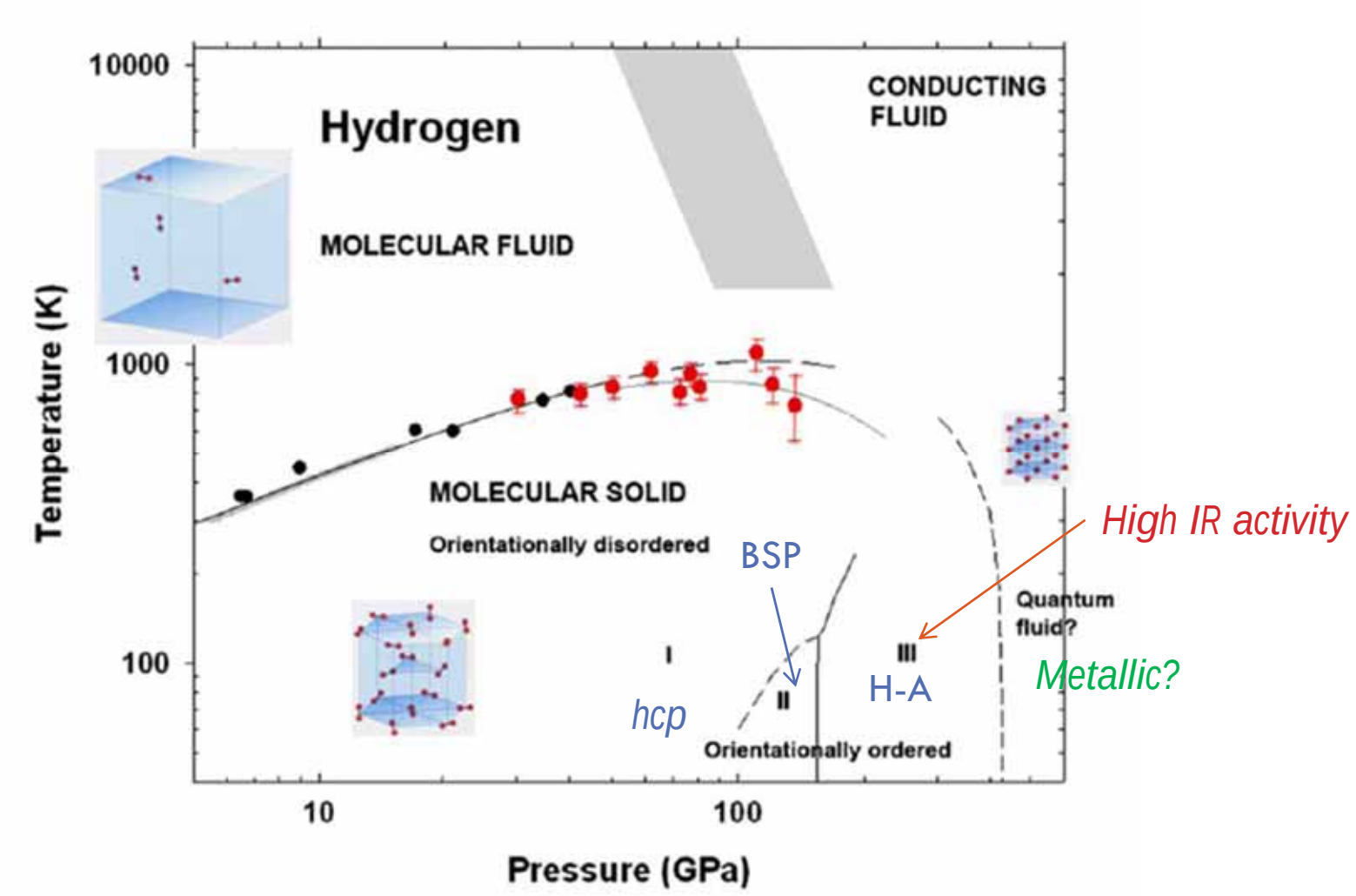
SOLID HYDROGEN UNDER PRESSURE

A fresh look at the H-H distances

Vanessa Labet, Paulina Gonzalez-Morelos, Roald Hoffmann, N. W. Ashcroft

Context



R.J. Hemley, High Pressure Research, 2010, 30, 581-619

Description of the study

LETTERS

Structure of phase III of solid hydrogen

CHRIS J. PICKARD[1]* AND RICHARD J. NEEDS[2]
[1]Scottish Universities Physics Alliance, School of Physics and Astronomy, University of St Andrews, St Andrews, Fife KY16 9SS, UK
[2]Theory of Condensed Matter Group, Cavendish Laboratory, Cambridge CB3 0HE, UK
*e-mail: cjp10@st-andrews.ac.uk

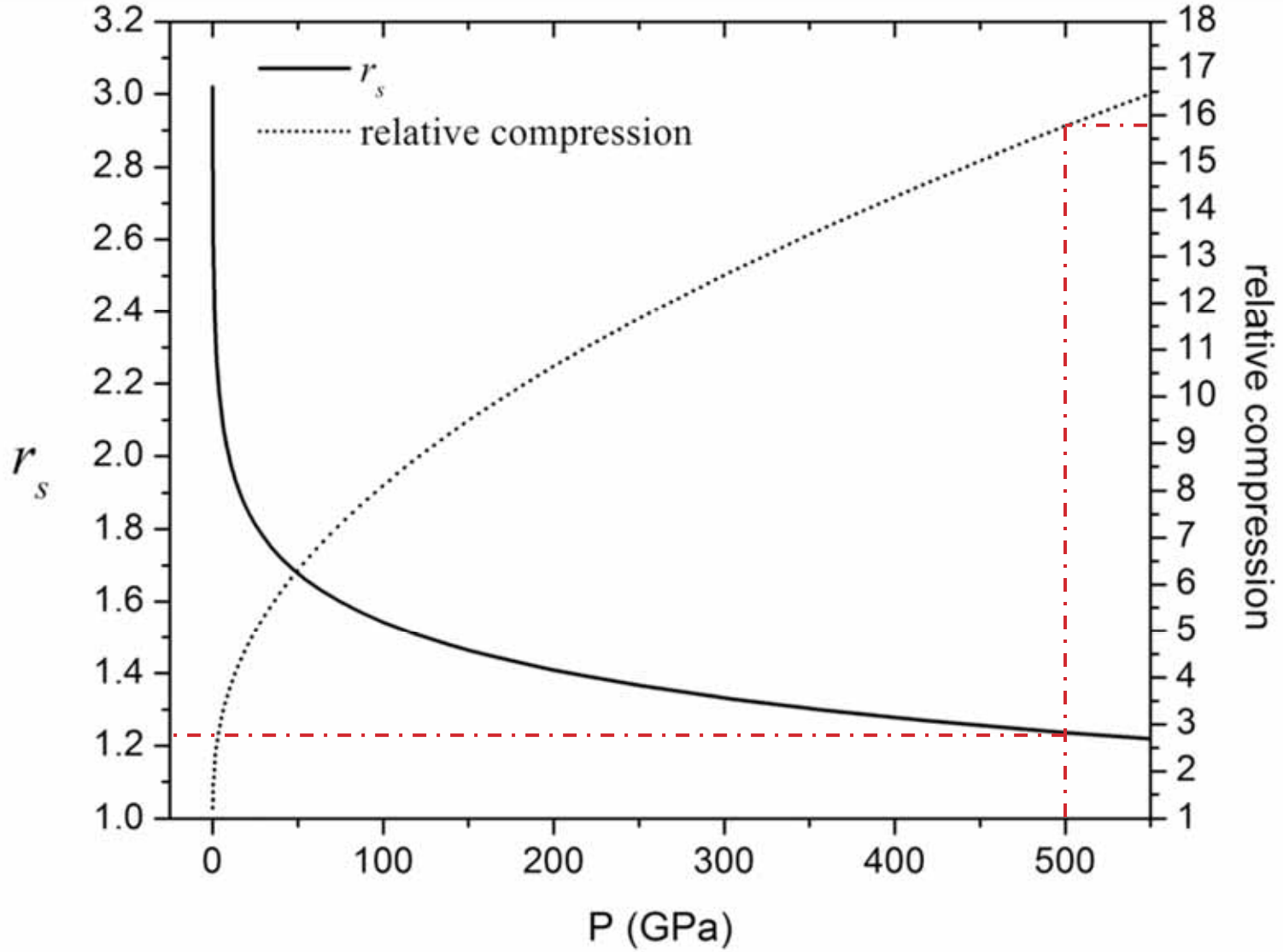
C. J. Pickard & R. J. Needs, Nature Physics, 2007, 3, 473.

A LABORATORY FOR LEARNING MORE ABOUT HYDROGEN UNDER PRESSURE

- Calculations have been repeated (good agreement with the original study)
  DFT/PAW-PBE – R_{cutoff}=0.8 a_0
  *E_{cutoff}: 2,000eV – k-points resolution: 2π*0.02 $Å^{-1}$*

- Structures optimized at several pressures to be able to study the evolution of the H-H distances under pressure

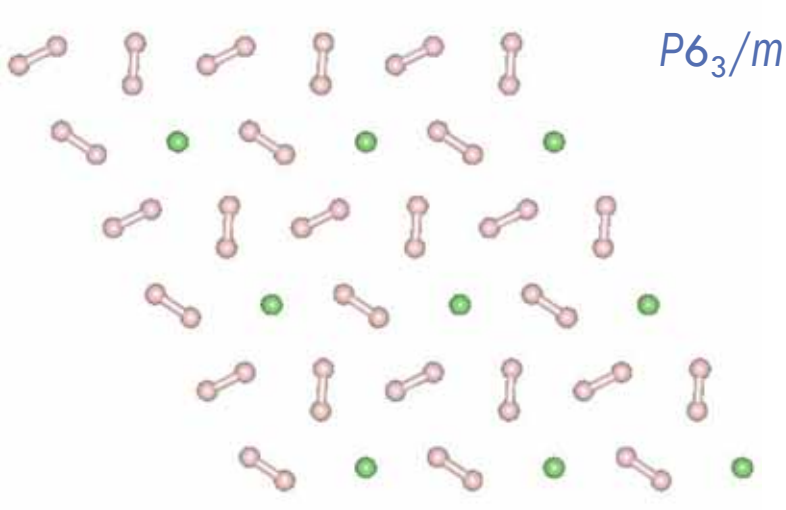
Equation of State



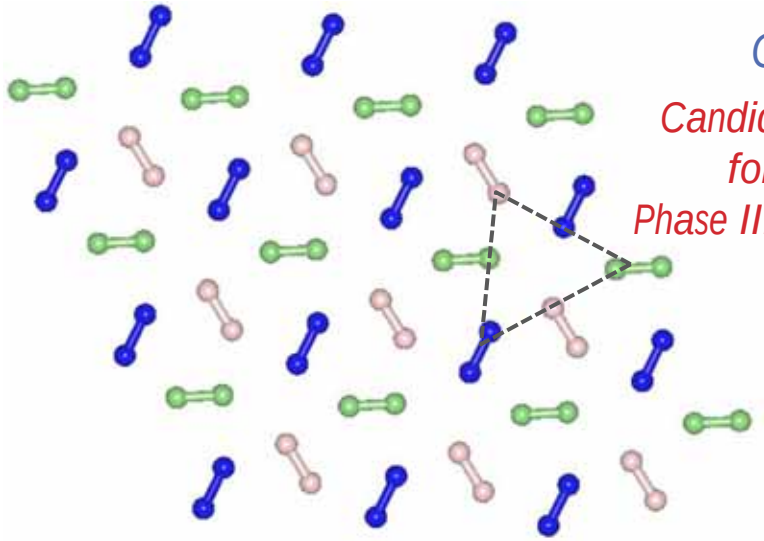
L. Caillabet, S. Mazevet, P. Loubeyre, Phys. Rev. B, accepted

Pickard and Needs "molecular "structures

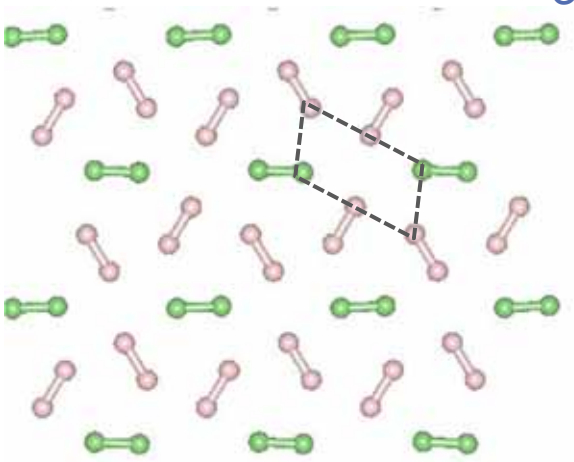
P<490GPa



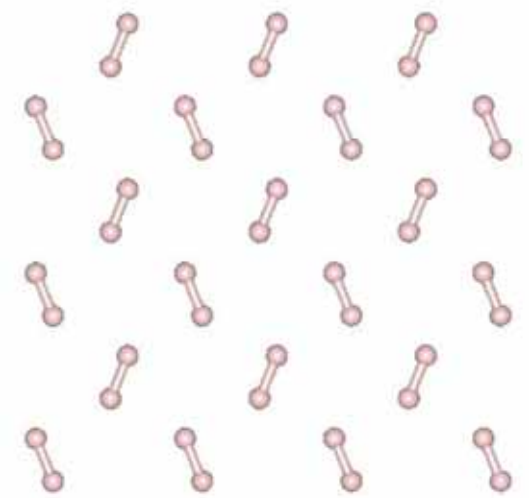
P<105GPa



105GPa<P<270GPa



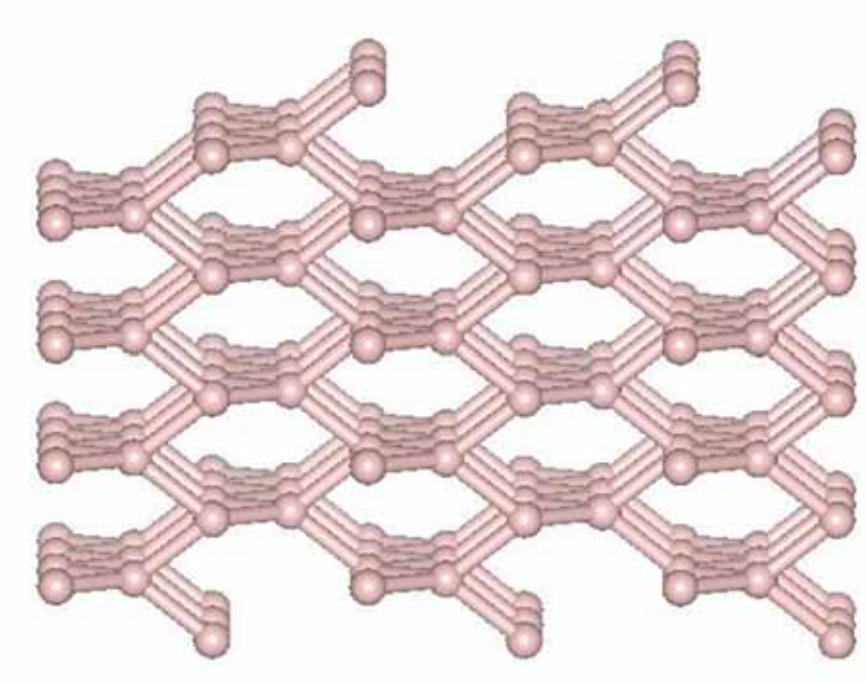
270GPa<P<385GPa



385GPa<P<490GPa

Pickard and Needs monatomic structure

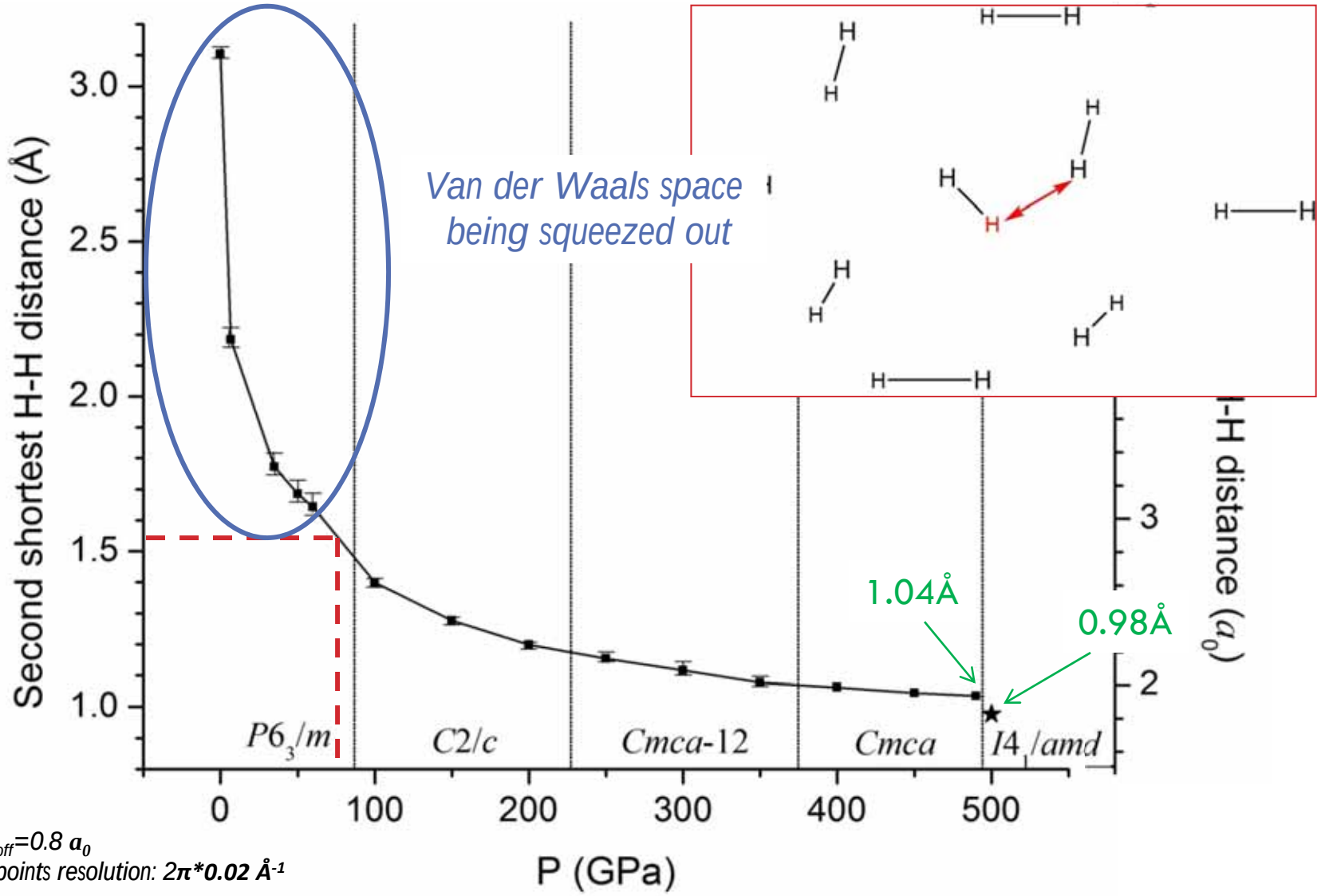
P>490GPa



$I4_1/amd$

- H atoms 4-coordinated
- 6-membered rings

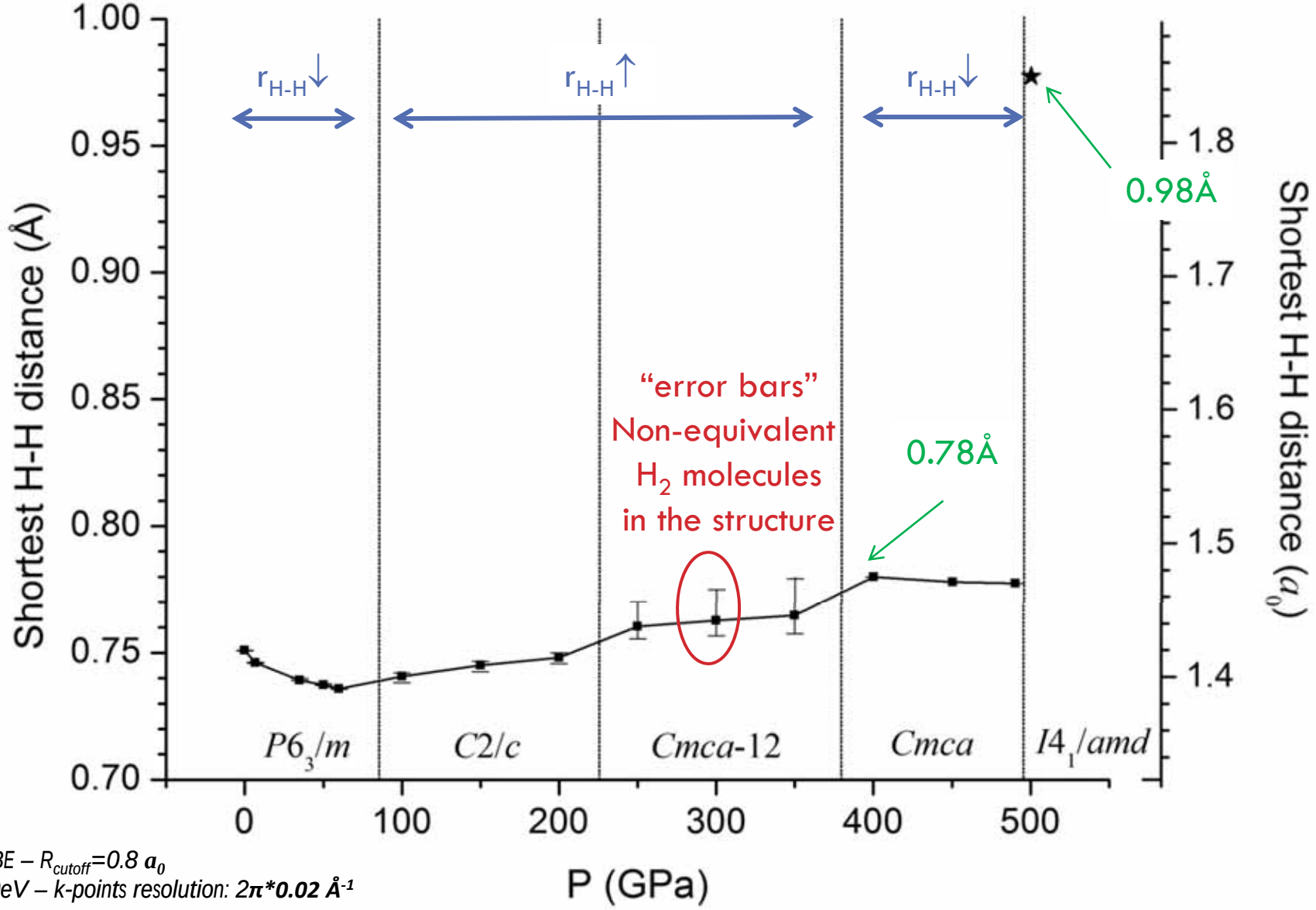
Intermolecular distance



DFT/PAW-PBE – R_{cutoff}=0.8 $\boldsymbol{a_0}$
E_{cutoff}: 2,000eV – k-points resolution: $\boldsymbol{2\pi * 0.02\ Å^{-1}}$

W. Grochala, R. Hoffmann, J. Feng, N.W. Ashcroft, Angew. Chem. Int. Ed., 2007, 46, 3620

Intramolecular distance



DFT/PAW-PBE – R_{cutoff}=0.8 a_0
*E_{cutoff}: 2,000eV – k-points resolution: 2π*0.02 Å^{-1}*

Experimental probes of the H_2 bond length and strength

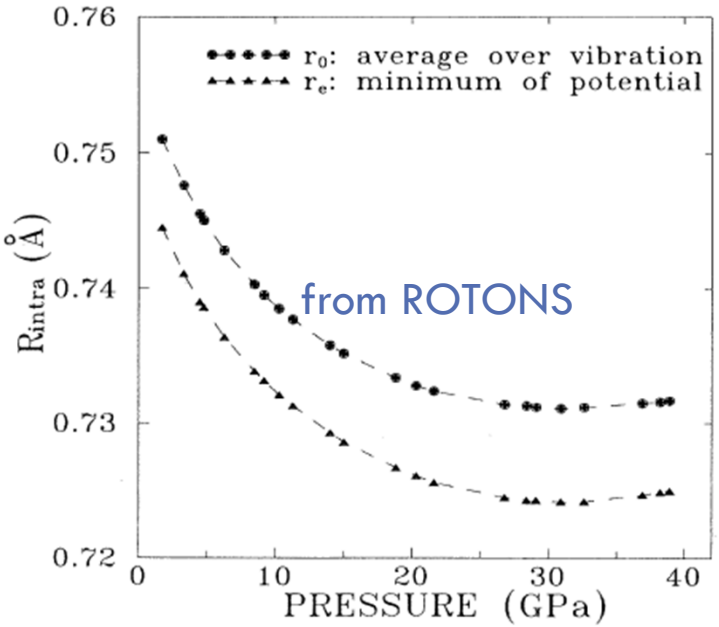


FIG. 2. Spectroscopic determination of the intramolecular distance of H_2 in p-H_2 solid at 5 K. The dots identify the minimum of the intramolecular potential and the triangles the mean value of the lowest vibrational state.

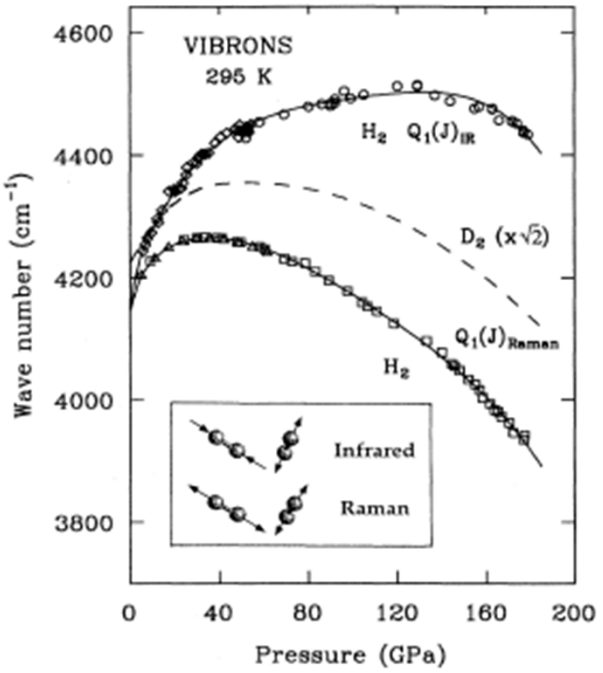
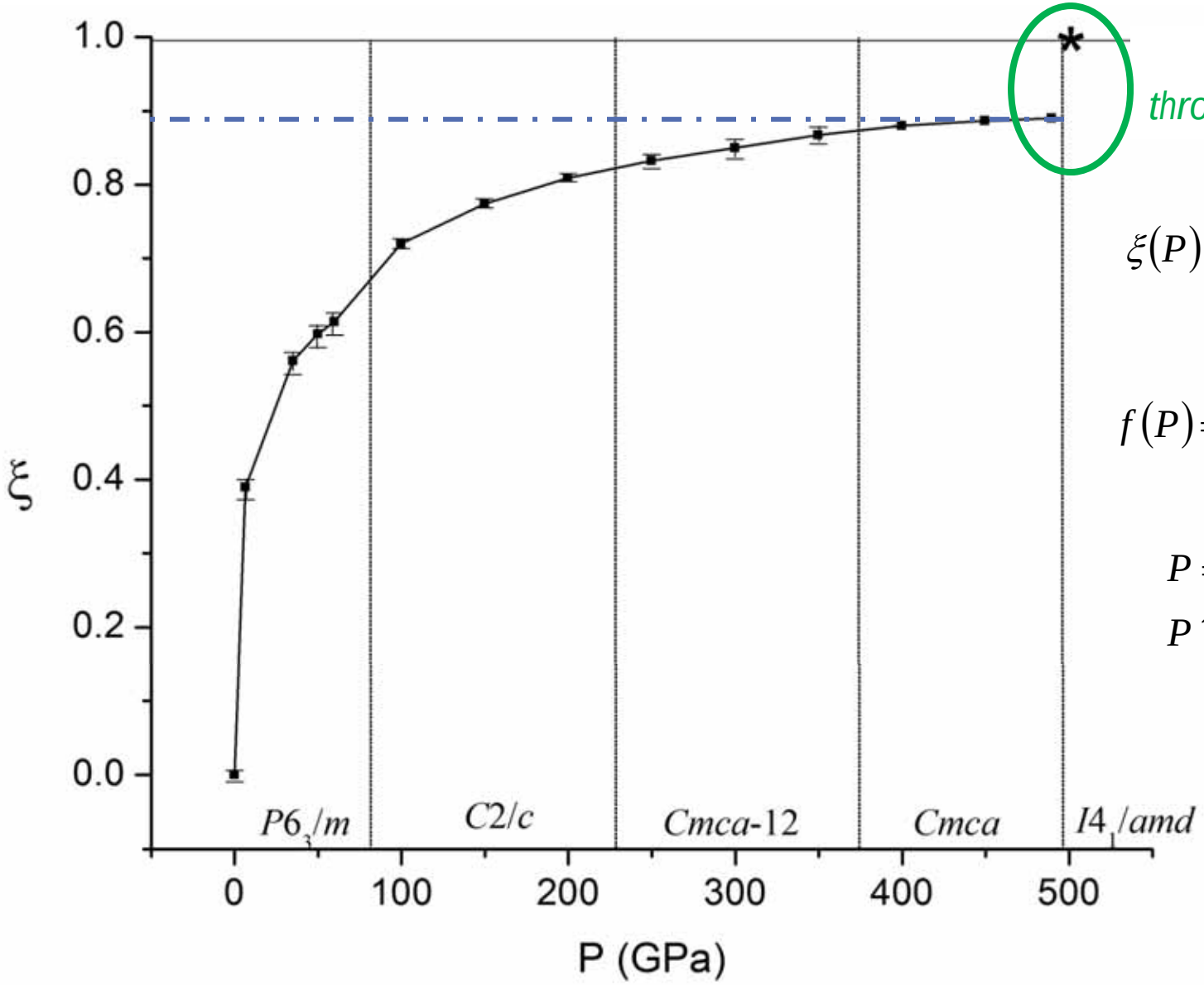


FIG. 7. Pressure dependence of the fundamental transitions of the Raman $[Q_1(J)_{Raman}]$ and infrared $[Q_1(J)_{IR}]$ vibrons at 295 K. The Raman and IR vibrons correspond to the in-phase and out-of-phase combination of the two internal stretching modes, respectively, as shown in the inset for an assumed structure (e.g., hcp) with two molecules per unit cell. The Raman data are from Sharma *et al.* [1980(a)], Hemley and Mao [1990(a)], and Hemley, Hanfland, Eggert, and Mao (1994). The infrared data are from Mao *et al.* (1984) (low pressure) and Hanfland *et al.* (1992) (high pressure). The dashed curve summarizes the results for the Raman vibron of deuterium [Sharma *et al.*, 1980(b); Hemley, Hanfland, Eggert, and Mao, 1994], where the frequency has been scaled by $\sqrt{2}$.

P. Loubeyre, M. Jean-Louis and I.F. Silvera, Phys. Rev. B, 1991, 43, 10191

H. Mao & R.J. Hemley, Rev. Mod. Phys., 1994, 66, 671

Degree of equalization



Brutal dissociation through a phase transition?

$$\xi(P) = 1 - \frac{f(P)}{f(P = 1\text{atm})}$$

$$f(P) = R_{H_2-H_2}(P) - r_{H-H}(P)$$

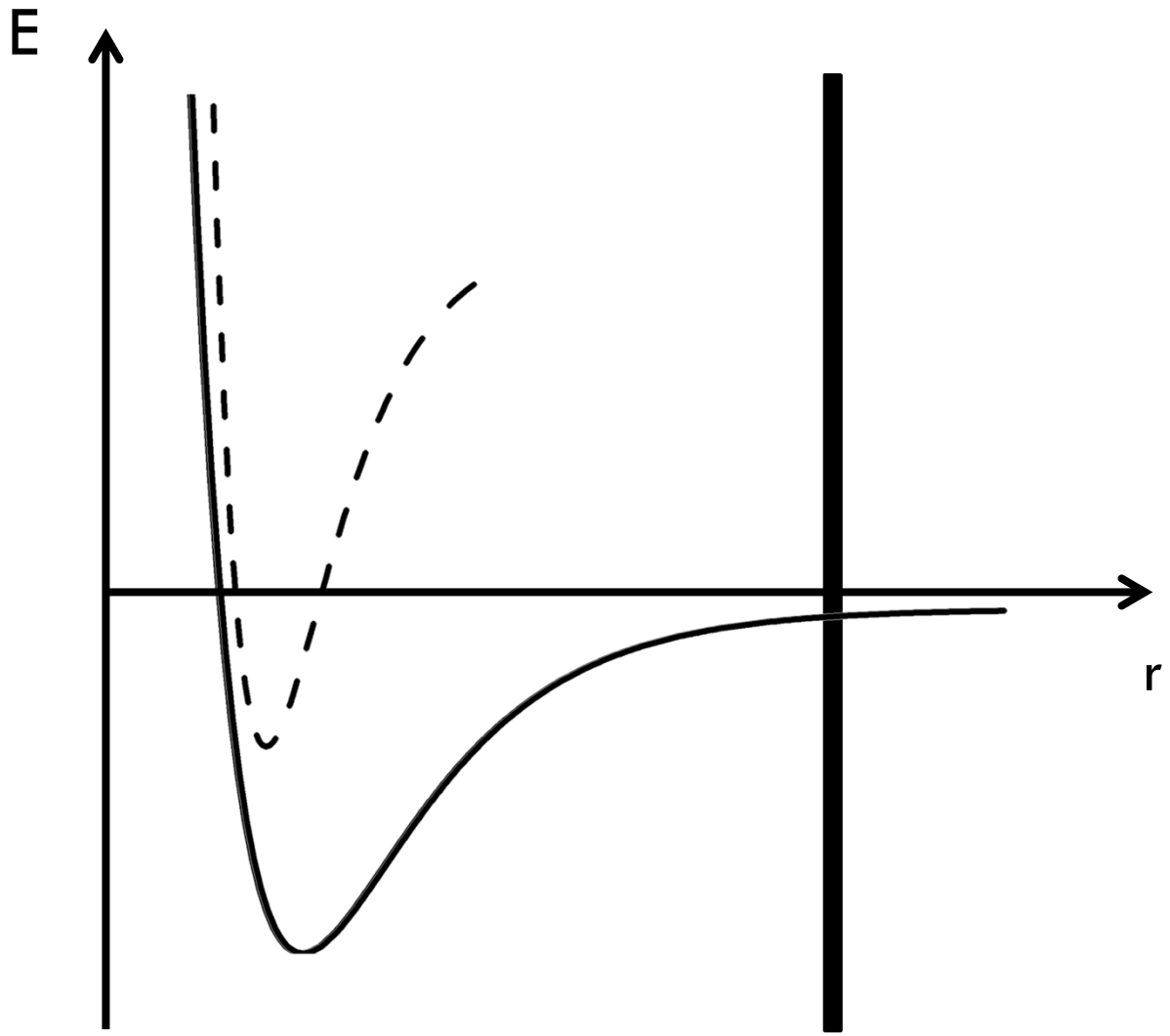
$$P = 1\text{atm} \Rightarrow \xi(\text{P}) = 0$$

$$P \uparrow \Rightarrow \xi(P) \to 1$$

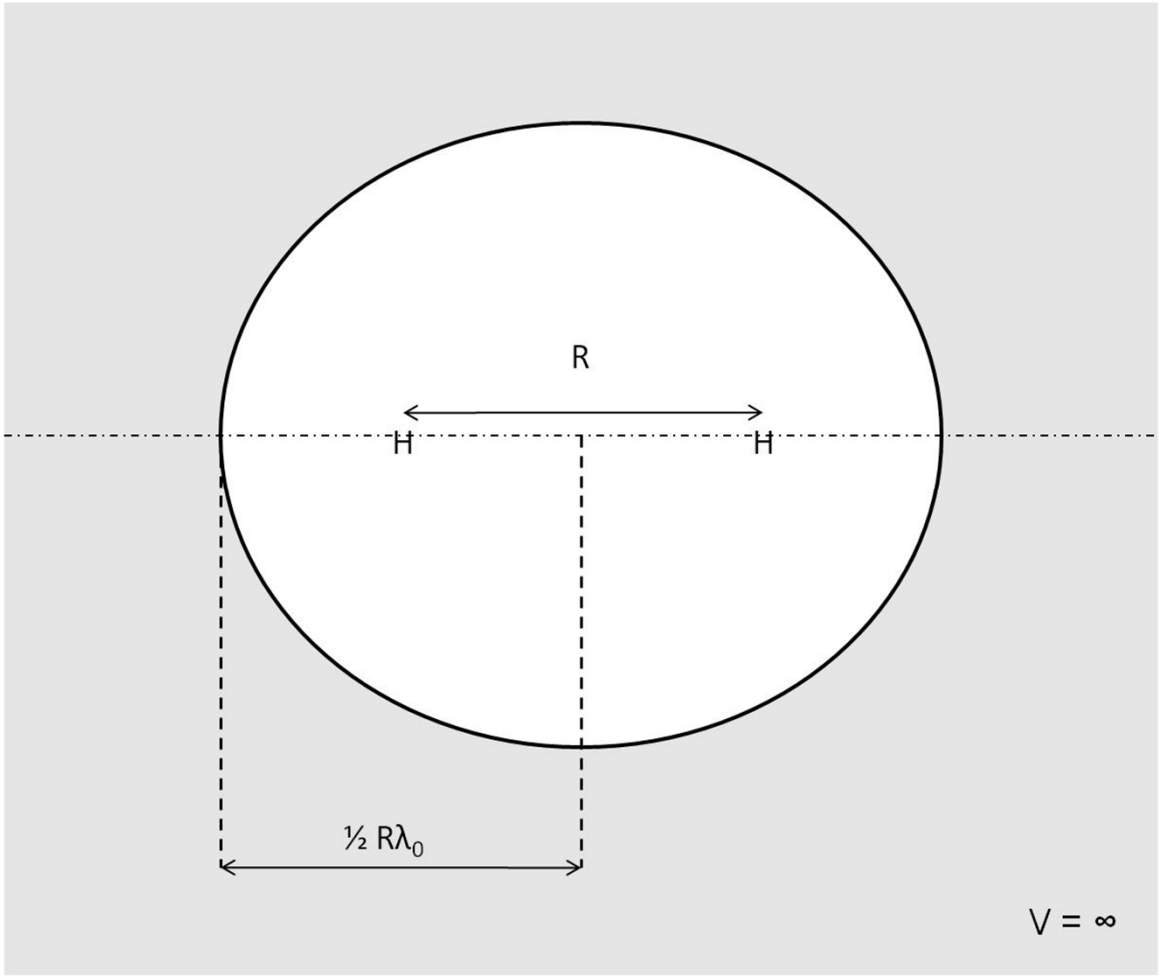
Conclusions 1

- Study of the structures proposed by Pickard and Needs as a laboratory for learning more about hydrogen under pressure:
  - As P ↑:
    - The shortest intermolecular H_2-H_2 separation ↓
    - whereas the intramolecular H-H bond length globally ↑ (slightly).
  - But resistance to a perfect equalization of the H-H distances
    - → *possible molecular metallic state of solid hydrogen, before its dissociation.*
  - 3 ≠ regimes for the evolution of the intramolecular H_2 bond length
    - At lower pressures, it decreases slightly with pressure,
    - then the H_2 bond length elongates.
    - And at still higher pressures, it gets shorter again
  - Proposing an equalization function
    - as a useful way to look at the evolution of H---H separations obtained from static calculations.
    - useful tool to compare quantitatively the behavior of hydrogen by itself under pressure and that of hydrides.

Why the H_2 bond should shorten under pressure?



H_2 molecule confined in a hard box



- The H atoms are placed at the foci of a spheroidal "box".
- Outside the box, the potential V is infinite (the wave function is forced to be zero – the electronic density is forced to be completely inside the box).
- For several values of the semi-major axis ($^1/_2\,R\lambda_0$), the H_2 bond length R is optimized.

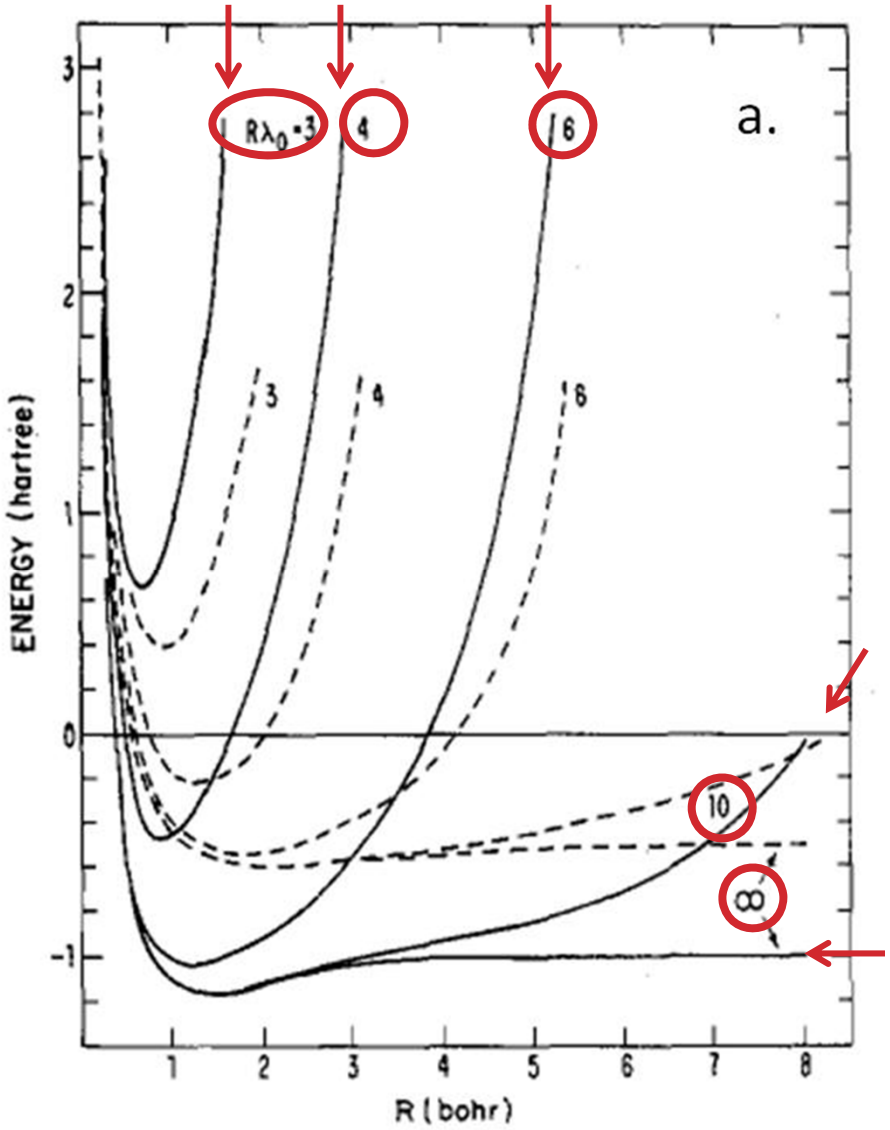
Decreasing the size of the box

↕

Modeling an increase of pressure

R. LeSar, D.R. Herschbach, J. Phys. Chem. 1981, 85, 2798-2804.

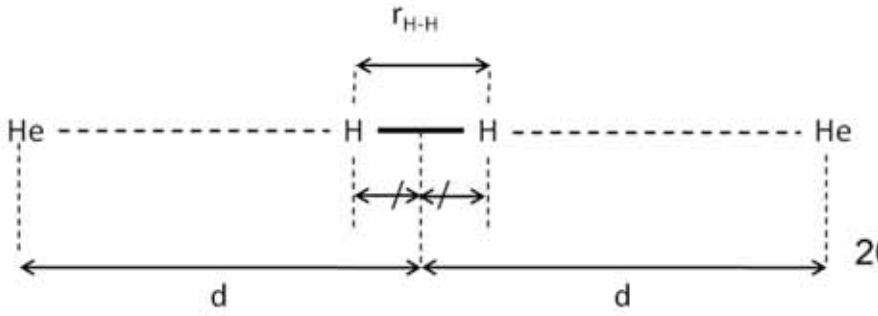
H_2 molecule confined in a hard box



As expected, as the H_2 bond is shortened, the bond is stiffened.

R. LeSar, D.R. Herschbach, J. Phys. Chem. 1981, 85, 2798-2804.

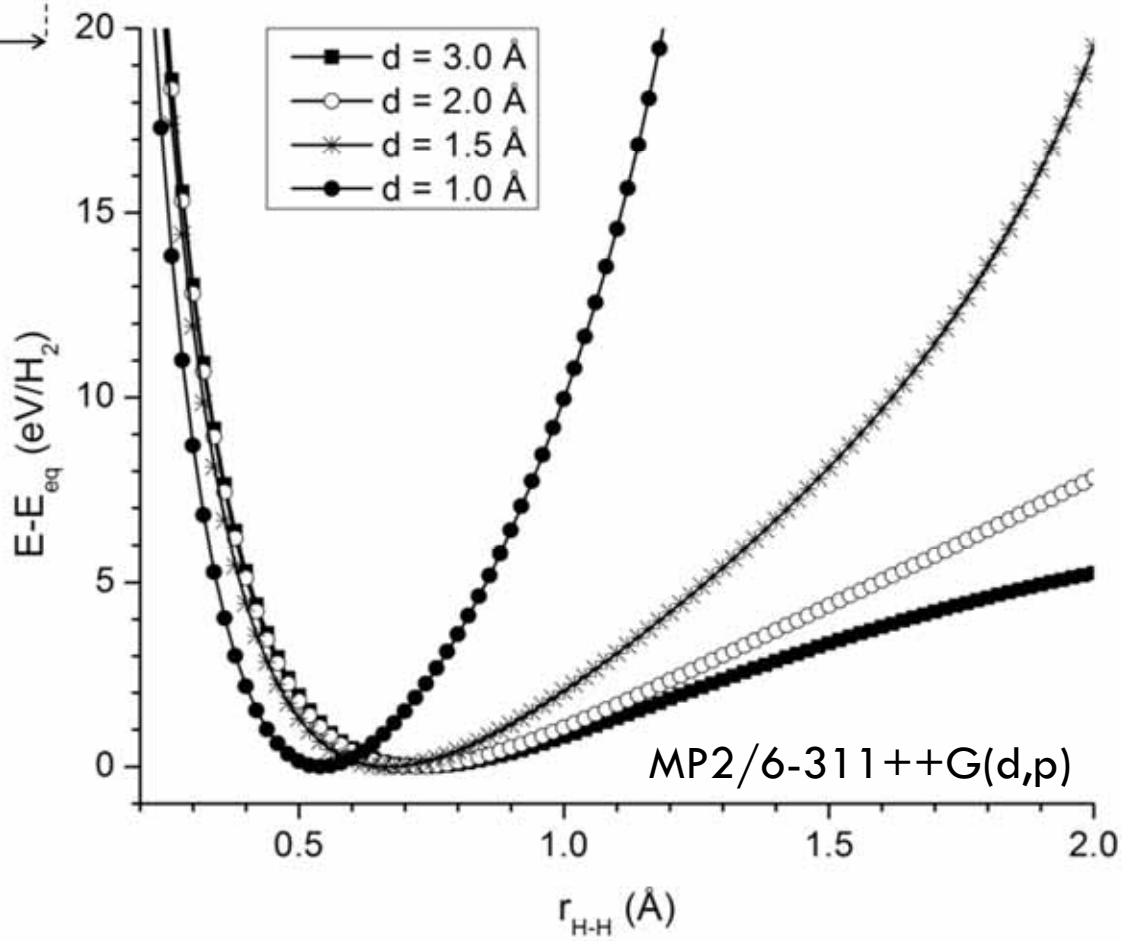
H_2 molecule "confined" in a "softer" box



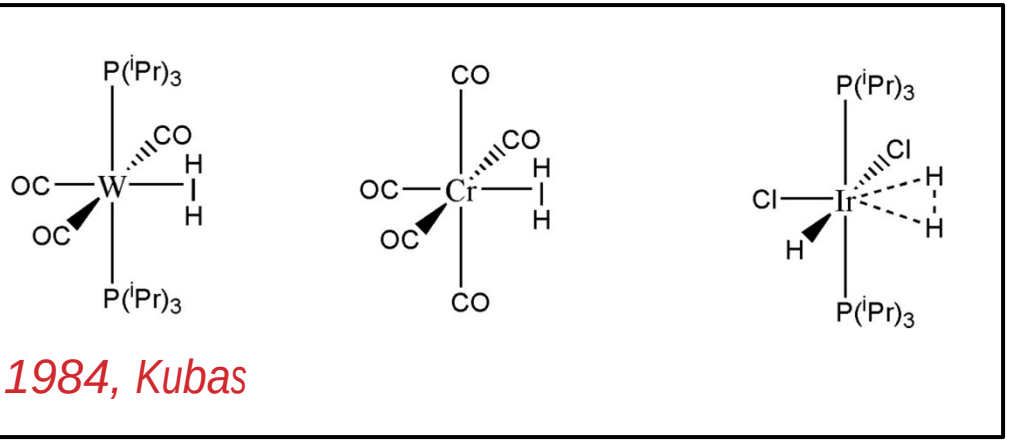
Decreasing d

⇕

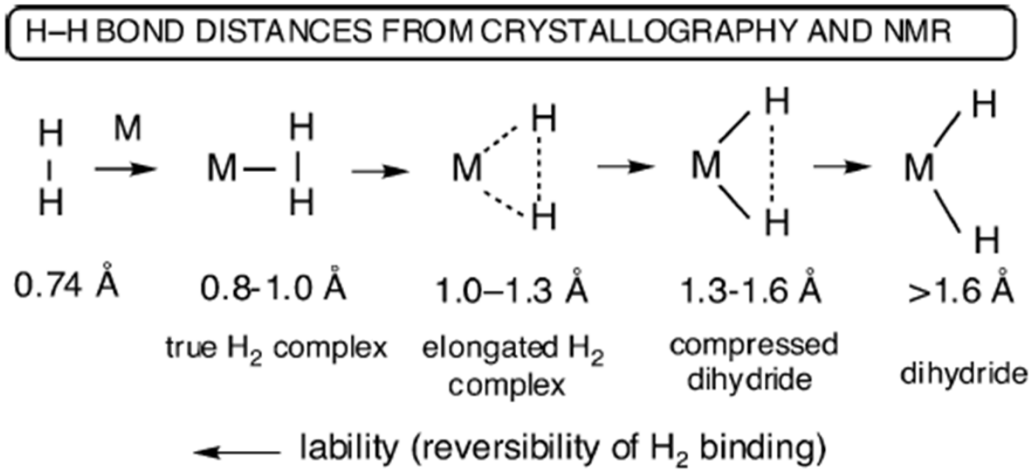
Modeling an increase of pressure



Long H_2 bonds in organometallic chemistry



1984, Kubas



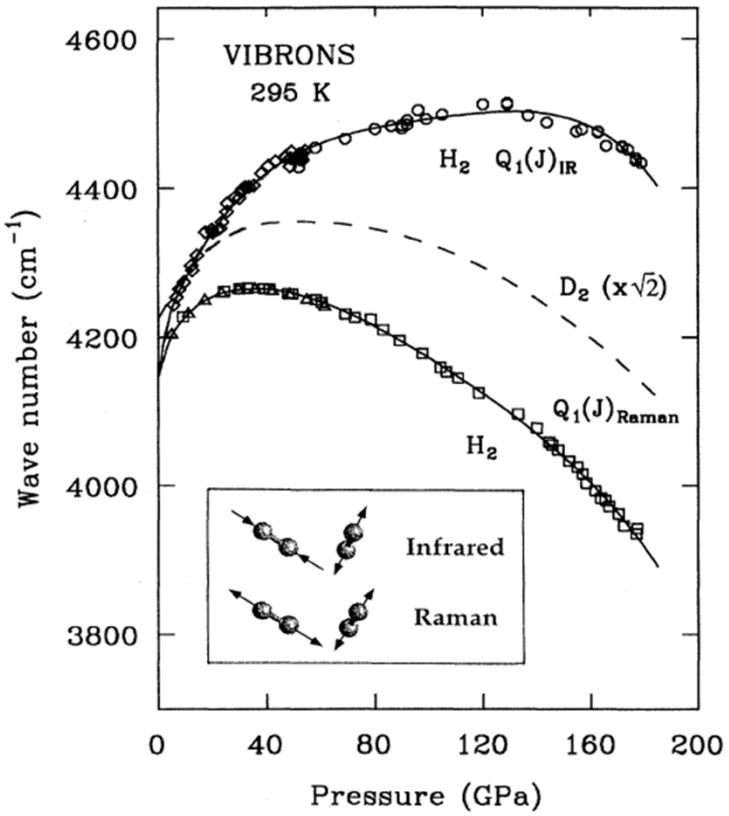
G. J. Kubas, Chem. Rev., 2007, 107, 4152-4205

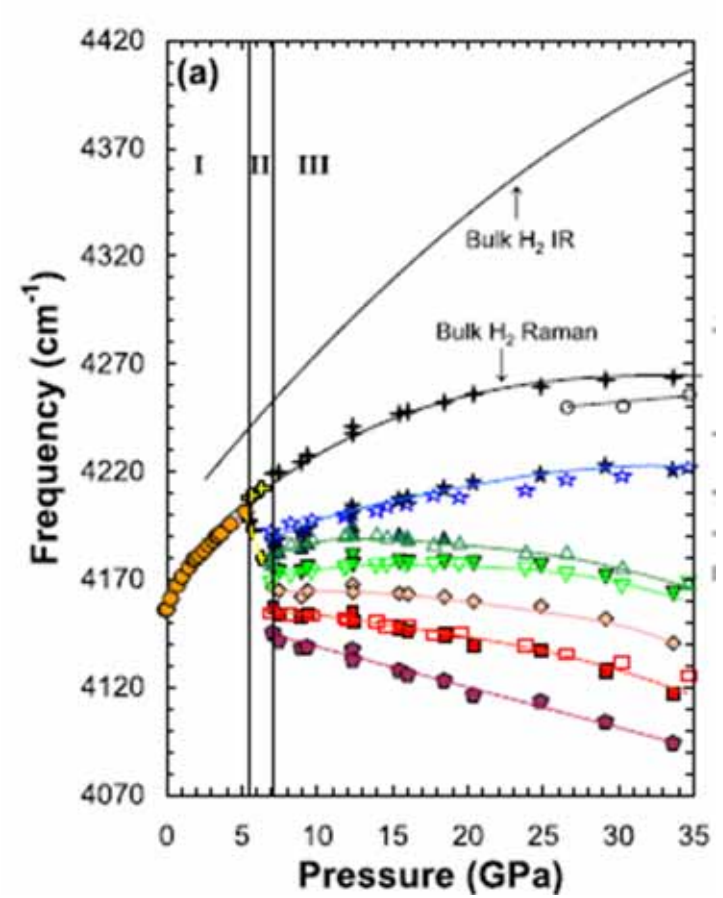
Long …. and weak

complex	ν(HH)	d_{HH}
$CpV(CO)_3(H_2)$	2642	
$CpNb(CO)_3(H_2)$	2600	
$Cr(CO)_5(H_2)$	3030	
$Cr(CO)_3(PCy_3)_2(H_2)$		0.85
$Mo(CO)_5(H_2)$	3080	
$Mo(CO)_3(PCy_3)_2(H_2)$	~2950[c]	0.87
$Mo(CO)(dppe)_2(H_2)$	2650	0.88
$W(CO)_5(H_2)$	2711	
$W(CO)_3(P^iPr_3)_2(H_2)$	2695	0.89
$W(CO)_3(PCy_3)_2(H_2)$	2690	0.89
$W(CO)_3(PCyp_3)_2(H_2)$[d]		
$Fe(CO)(NO)_2(H_2)$	2973	
$Co(CO)_2(NO)(H_2)$	{3100, 2976}[e]	
$FeH_2(H_2)(PEtPh_2)_3$	2380	0.82
$RuH_2(H_2)_2(P^iPr_3)_2$	2568	0.92
$Tp^*RuH(H_2)_2$	2361	0.90
$Tp^*RuH(H_2)(THT)$	2250	0.89
$[Os(NH_3)_5(H_2)]^{2+}$	2231[b]	[1.34][g]
$[CpRu(dppm)(H_2)]^+$	2082[b]	[1.10][h]
$Tp^*RhH_2(H_2)$	2238	0.94[i]
$Pd(H_2)$ (matrix)	2971	0.85[i]
$Ni(510)-(H_2)$[j]	3205	

G. J. Kubas, Chem. Rev., 2007, 107, 4152-4205

Weaker than in solid hydrogen

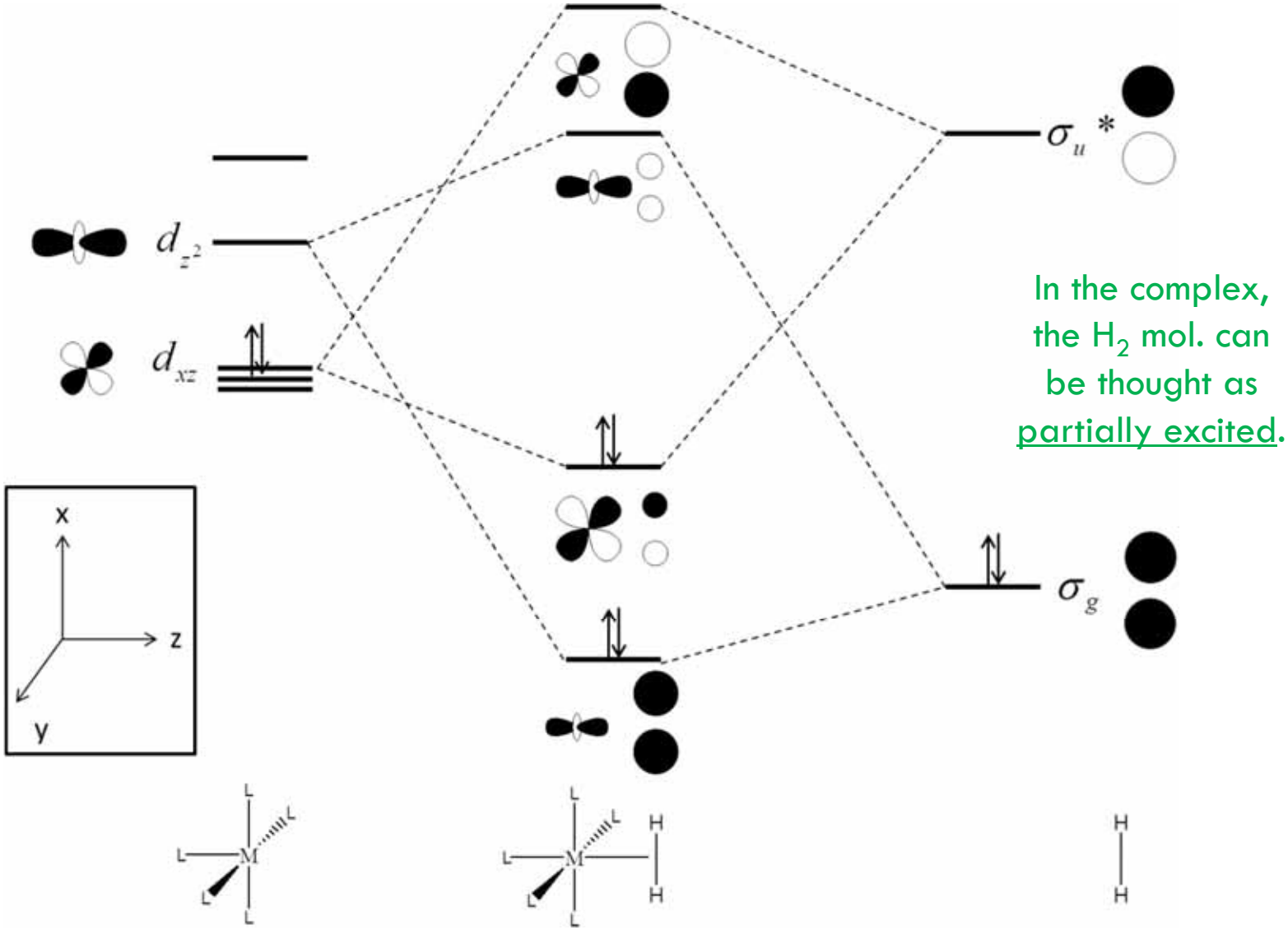




H. Mao & R.J. Hemley, Rev. Mod. Phys., 1994, 66, 671

T.A. Strobel et al., PRL, 2009,103, 065701

… because of donation/backdonation

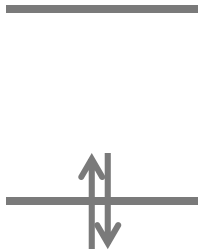


In the complex, the H_2 mol. can be thought as partially excited.

J.-Y. Saillard and R. Hoffmann, J. Am. Chem. Soc. 1984, 106, 2006-2026

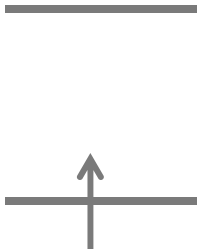
Why the H_2 bond should lengthen under pressure?

H_2 ($^1\sum_g$): 0.741 Å



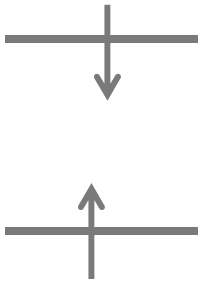
Bond order:
1

H_2^+ ($^2\sum_g^+$): 1.052 Å



Bond order:
½

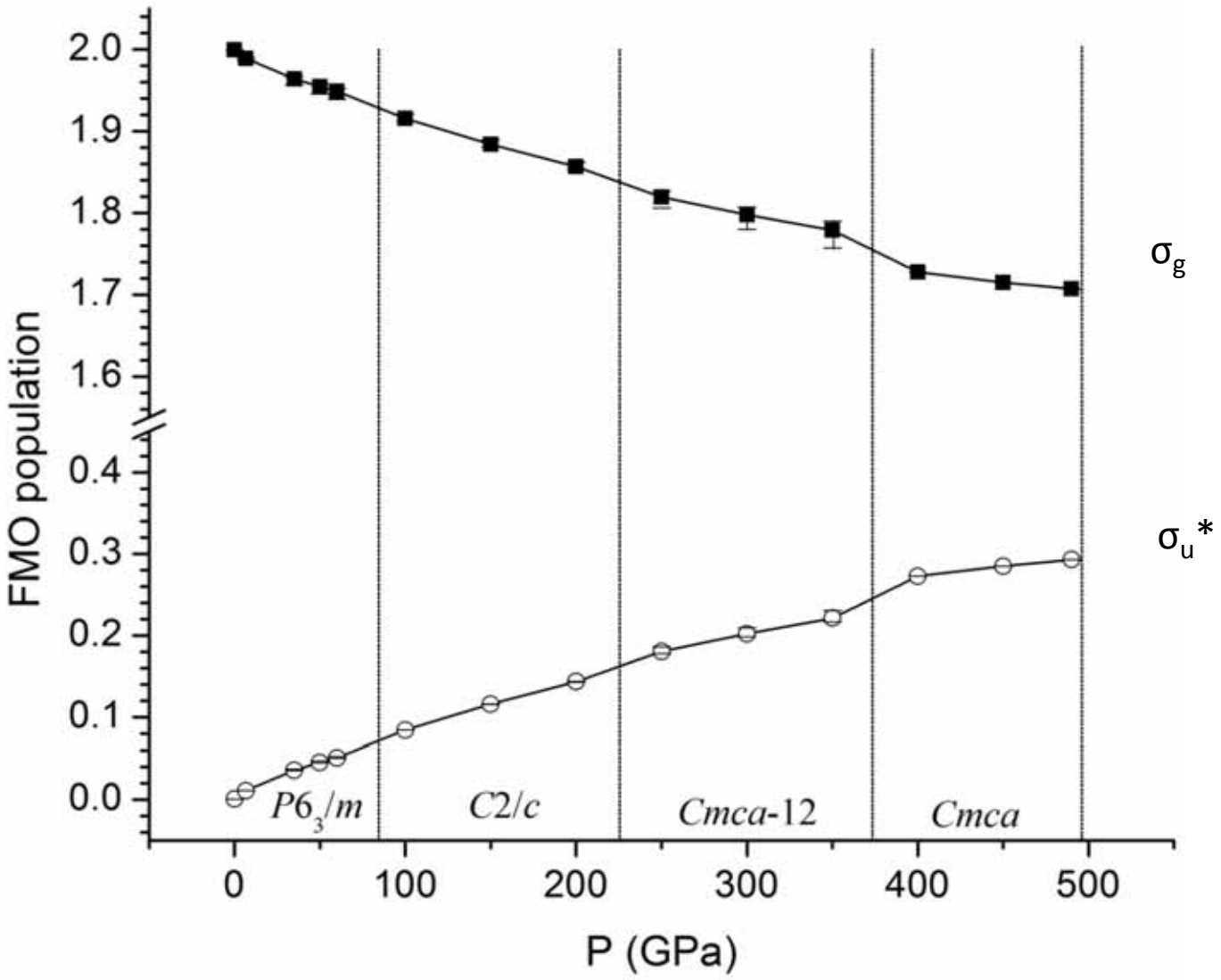
H_2* ($^1\sum_u^+$):1.293 Å



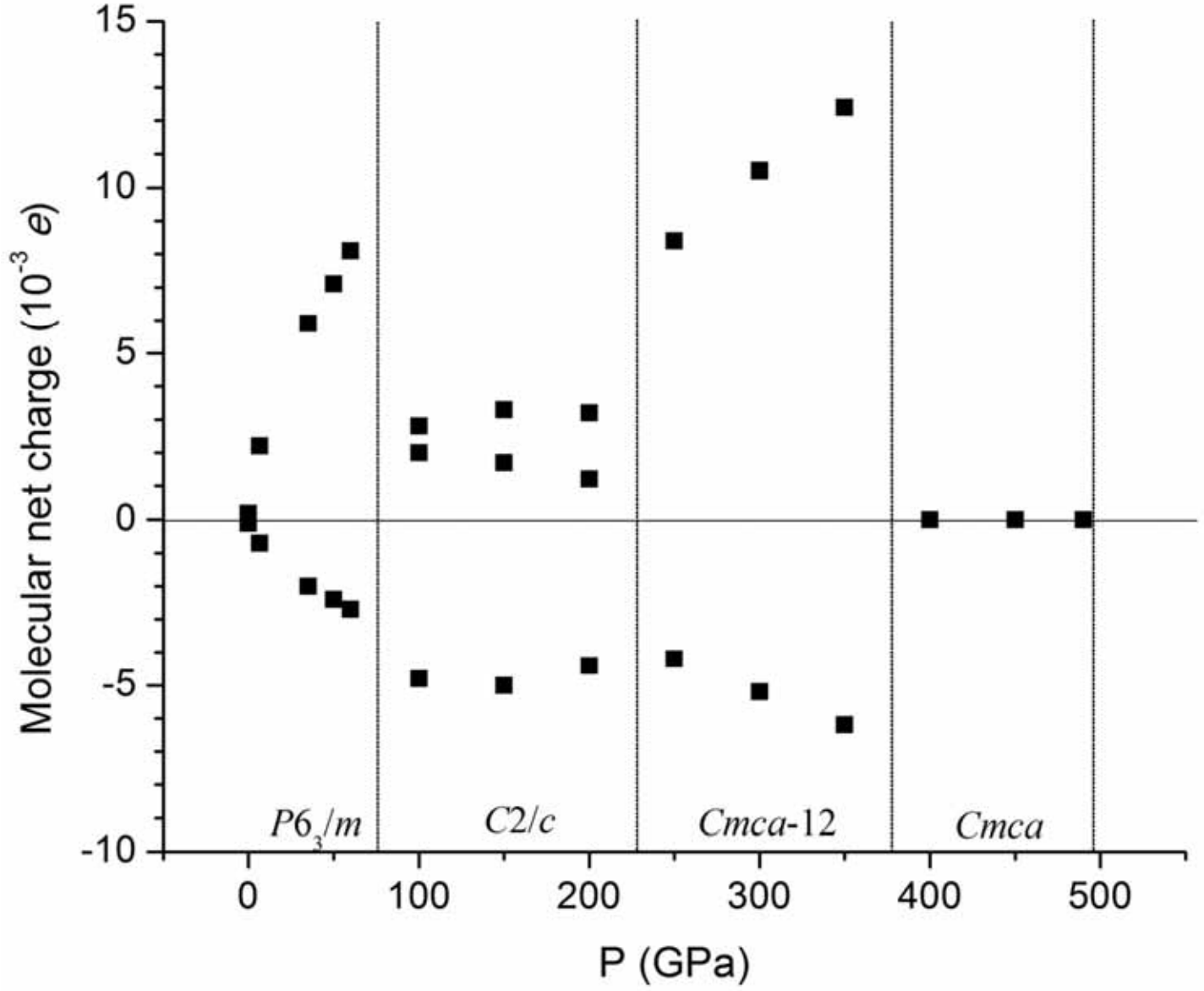
Bond order:
0

Fragment MO population

Fragment MO analysis with the extended Hückel method (YAeHMOP)



Intermolecular charge transfer

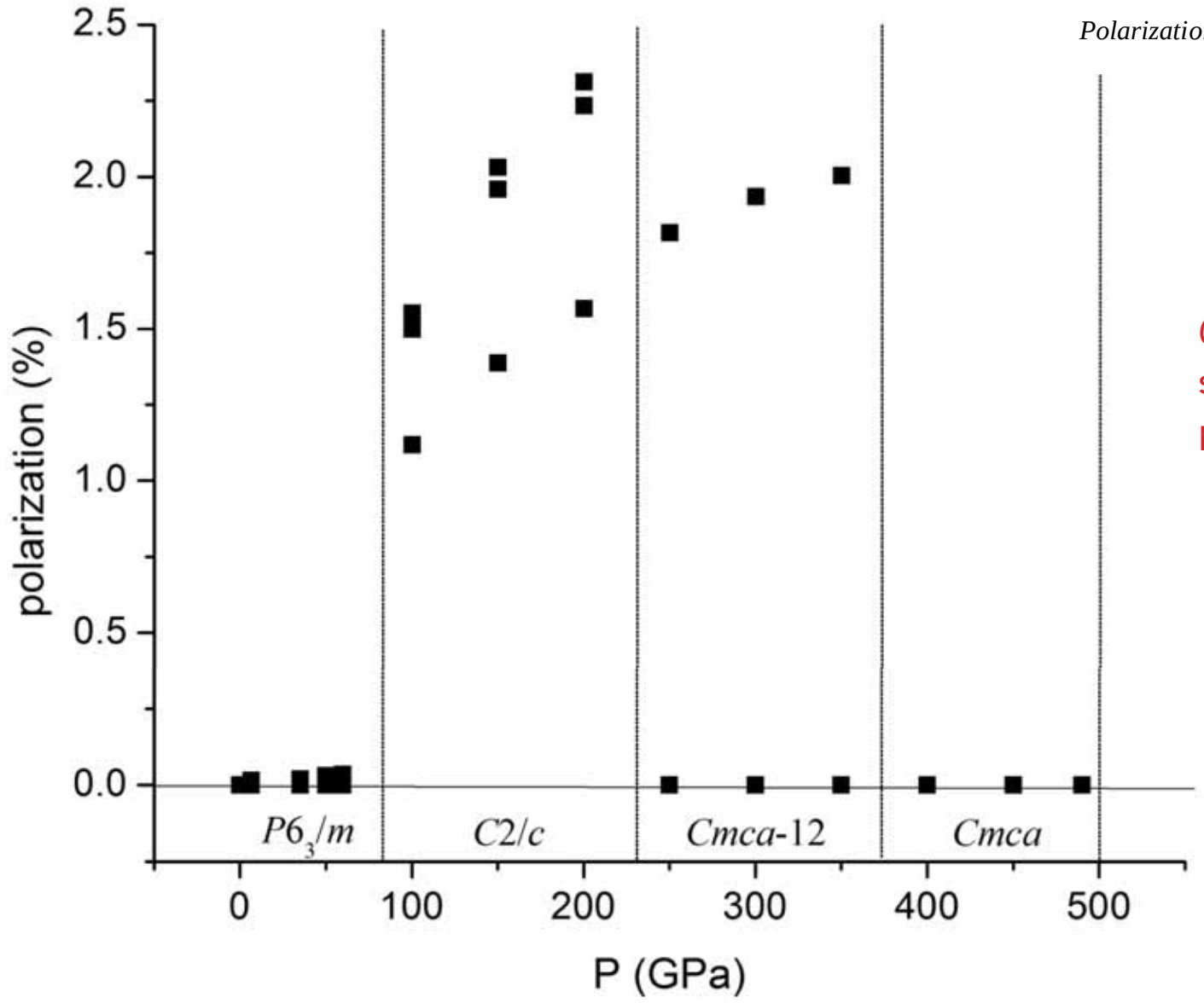


H_2 molecules almost neutral

→ Effectively partially excited molecules

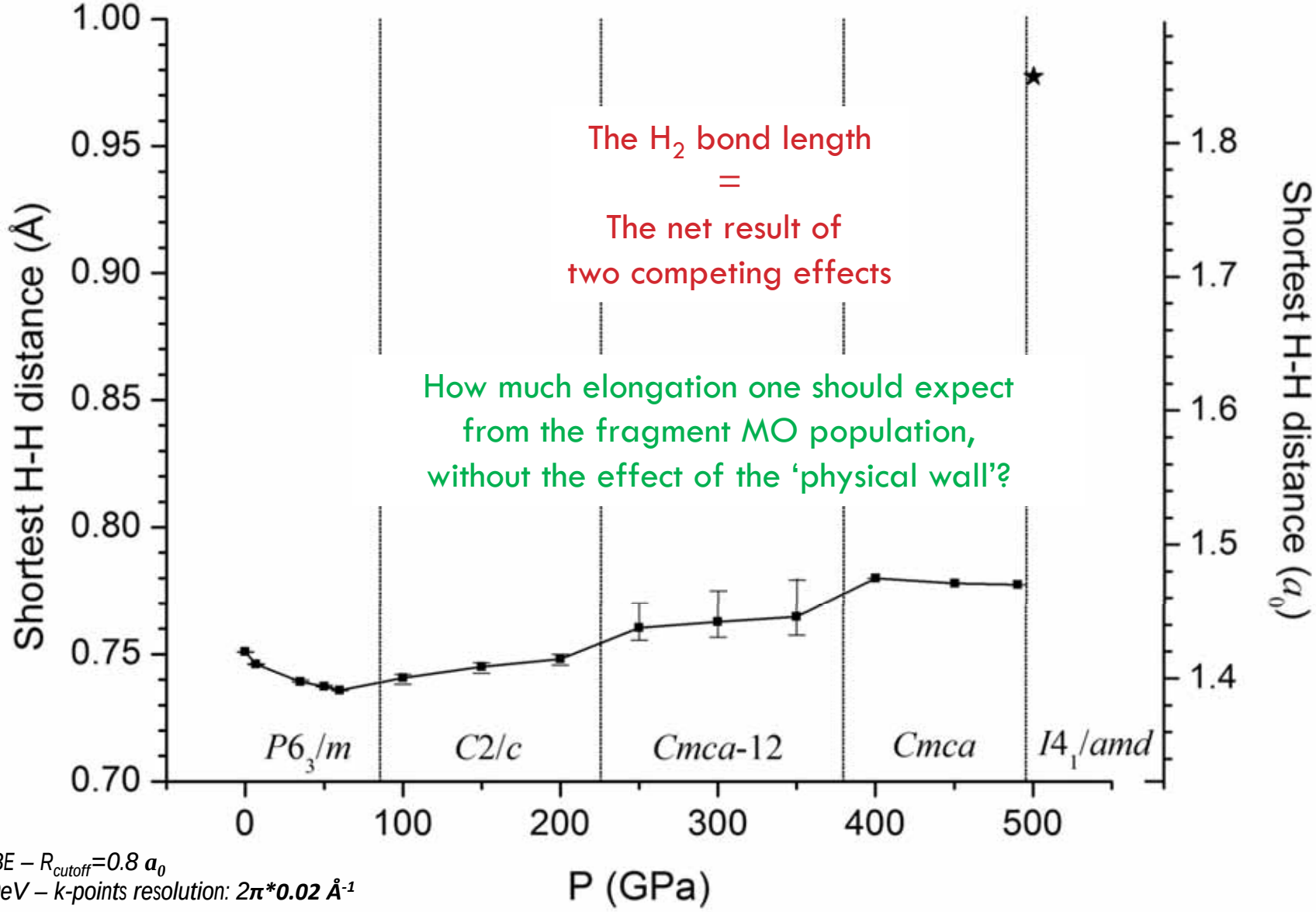
Polarization

$$Polarization\,(\%) = \frac{\left|(1-q(H_A))-(1-q(H_B))\right|}{2-q(H_A-H_B)} \times 100$$



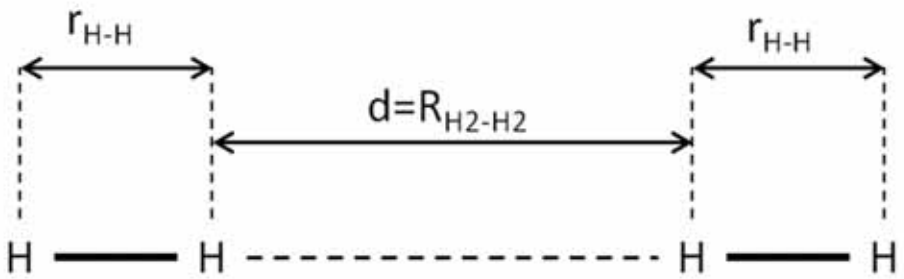
*C*2/*c* and *Cmca*-12 structures involved quite polarized H_2 molecules

Intramolecular distance

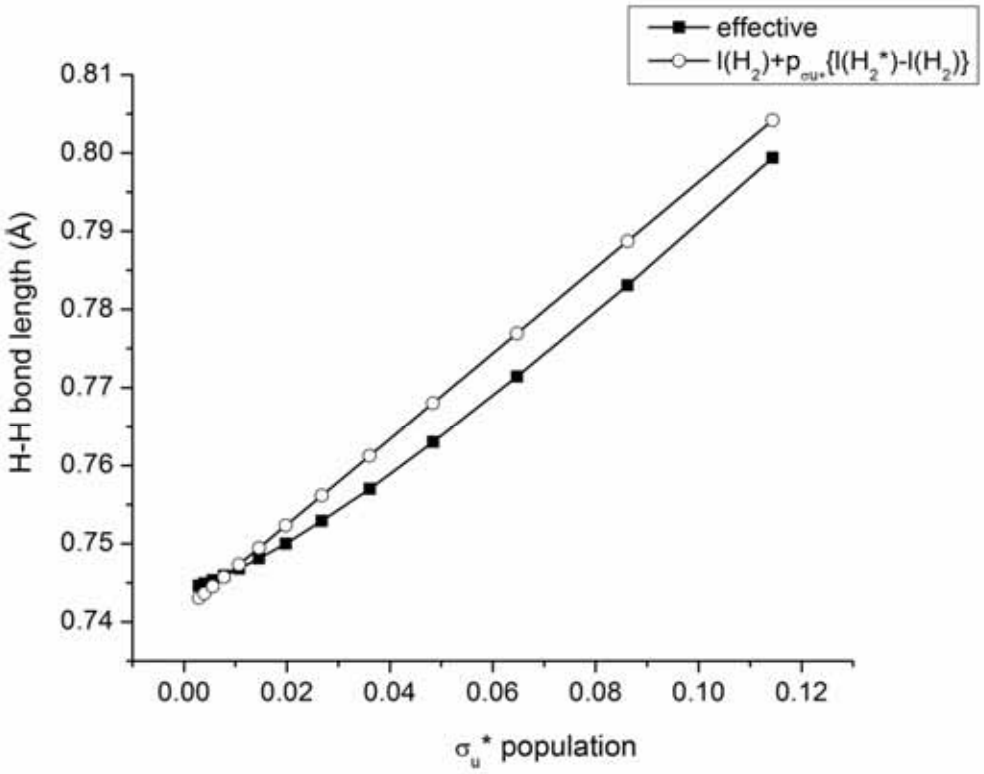


DFT/PAW-PBE – R_{cutoff}=0.8 a_0
*E_{cutoff}: 2,000eV – k-points resolution: 2π*0.02 Å^{-1}*

Correlation MO pop. – H_2 bond length

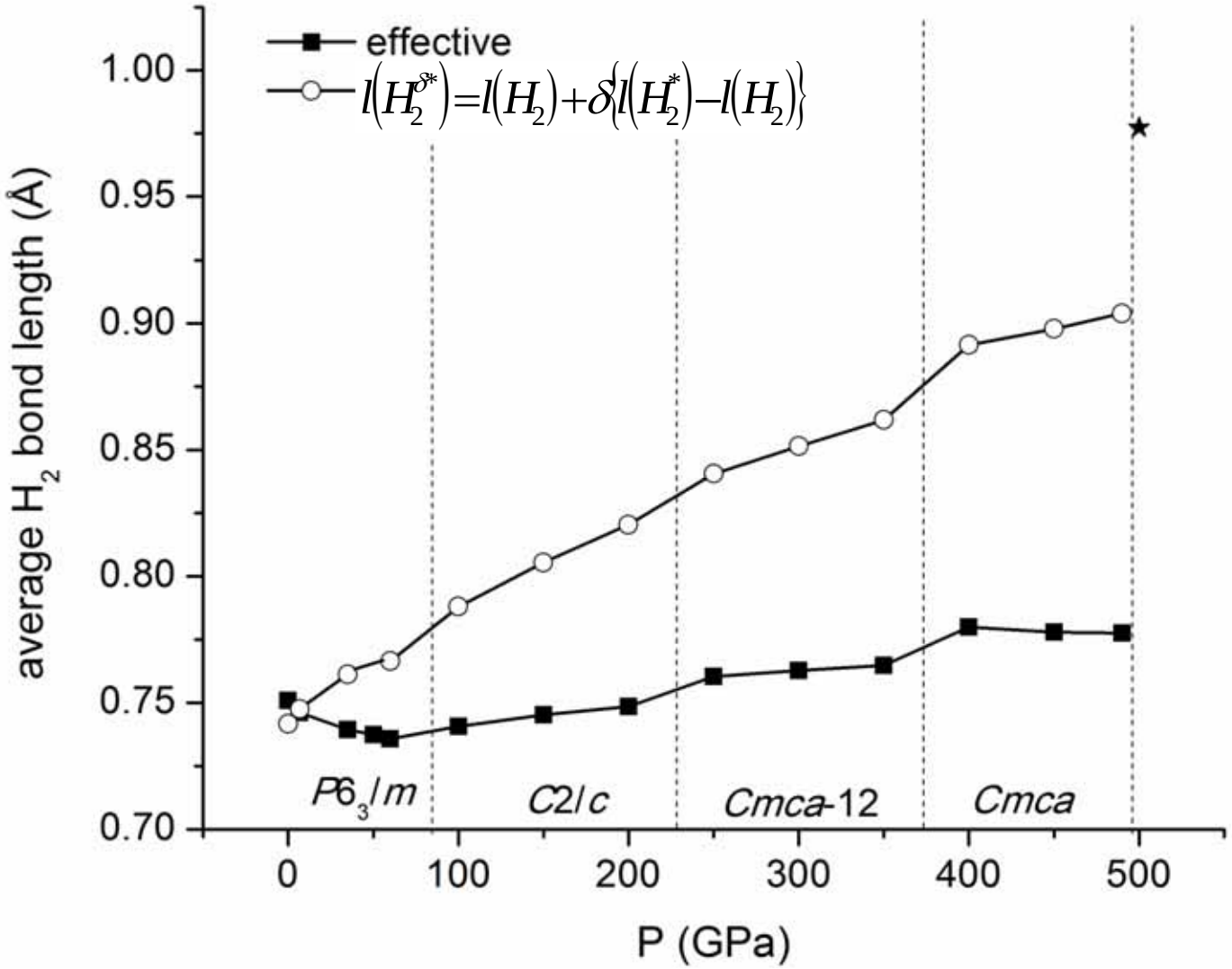


1. d imposed
2. r_{H-H} optimized
3. Fragment analysis with the extended Hückel method



Two co-existing effects

Correlation between H_2 bond and FMO population

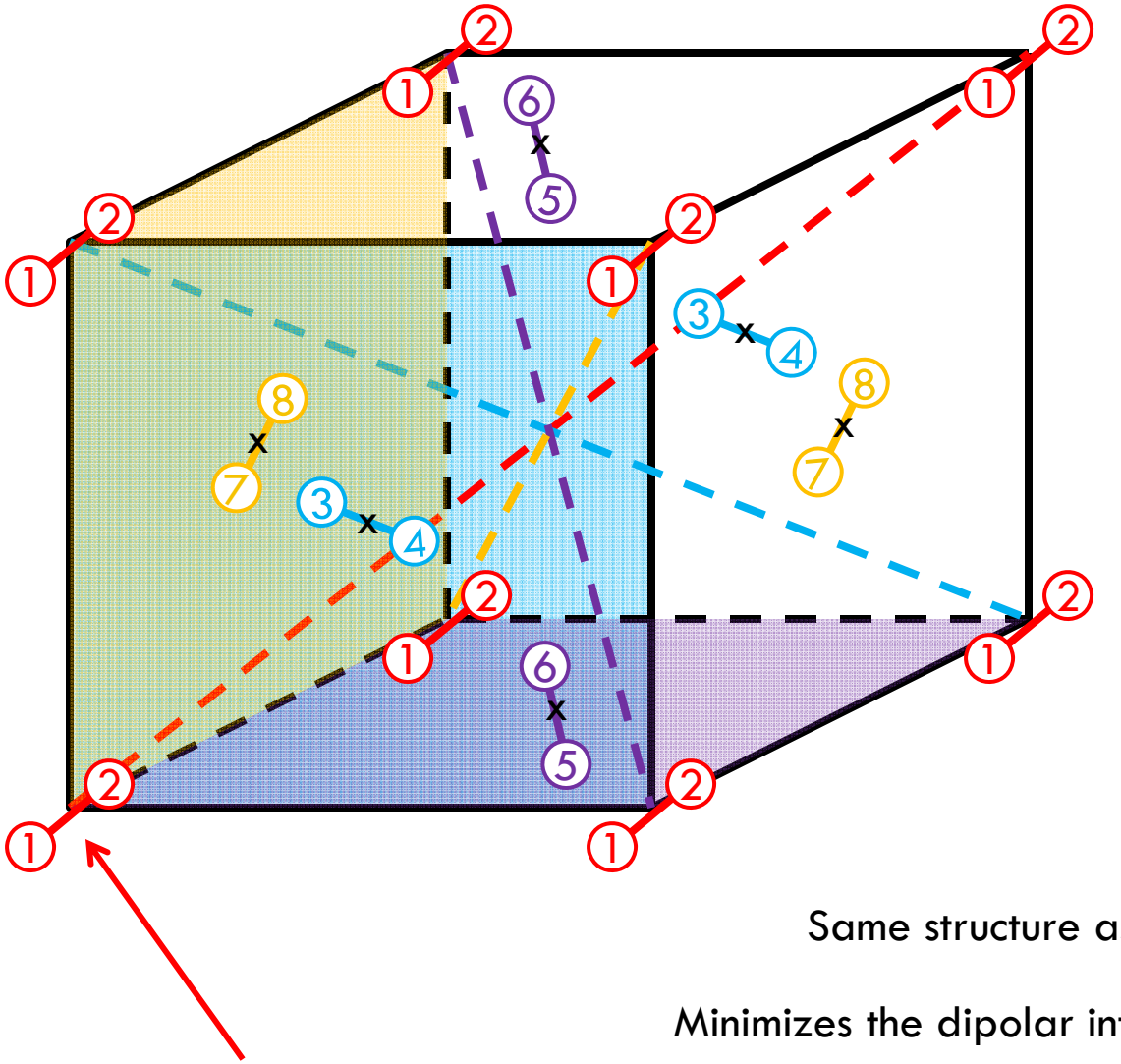


H_2 bonds are shorter than expected!

Conclusions 2

- 2 models for what happens to the intramolecular H-H separation as pressure ↑.
  - A "physical" effect: spatial confinement
    - Shortening and stiffening of the H-H bond
  - A "chemical" effect: orbital interaction
    - Lengthening and weakening of the H-H bond.
- Analysis of the structures proposed by Pickard and Needs:
  - As P ↑, σ_g fragment MOs pop. ↓, σ_u^* fragment MOs pop. ↑
  - H_2 mol. partially excited – almost no intermolecular charge transfer but H-H bonds slightly polarized.
  - The H-H bonds are much shorter than they should be.
    - *→ 2 effects coexist and compete under pressure.*

$Pa\bar{3}$



1:	-δ	-δ	-δ
2:	δ	δ	δ
3:	-δ	½ + δ	½ - δ
4:	δ	½ - δ	½ + δ
5:	½ - δ	-δ	½ + δ
6:	½ + δ	δ	½ - δ
7:	½ + δ	½ - δ	-δ
8:	½ - δ	½ + δ	δ

Same structure as α-dinitrogen

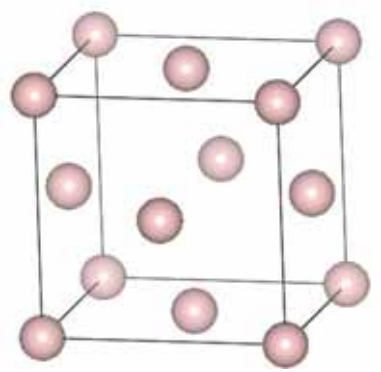
Minimizes the dipolar interaction energy

2 limit cases

$$\delta = 0$$

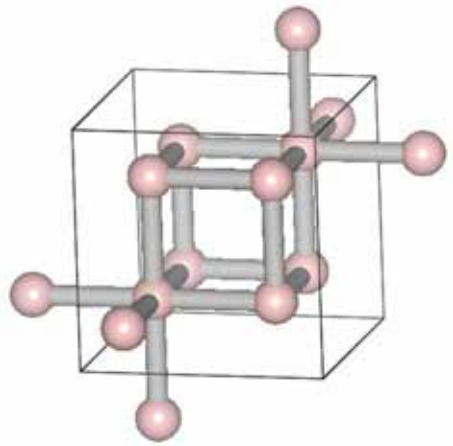
Face-centered cubic lattice

(💣 2 atoms superimposed)

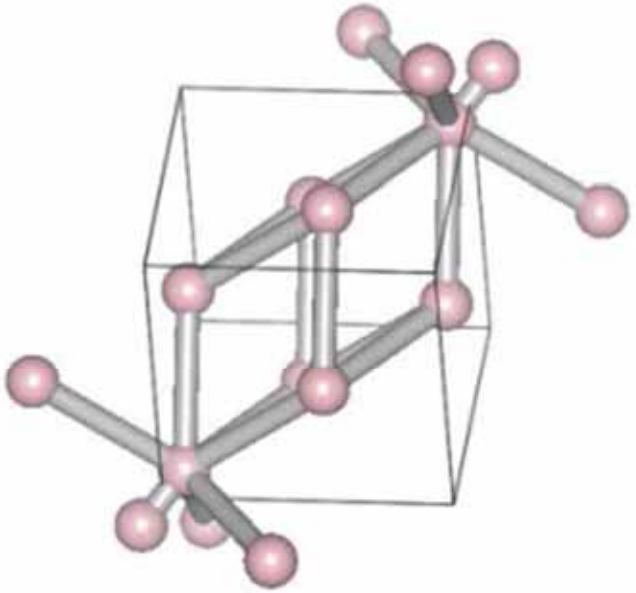


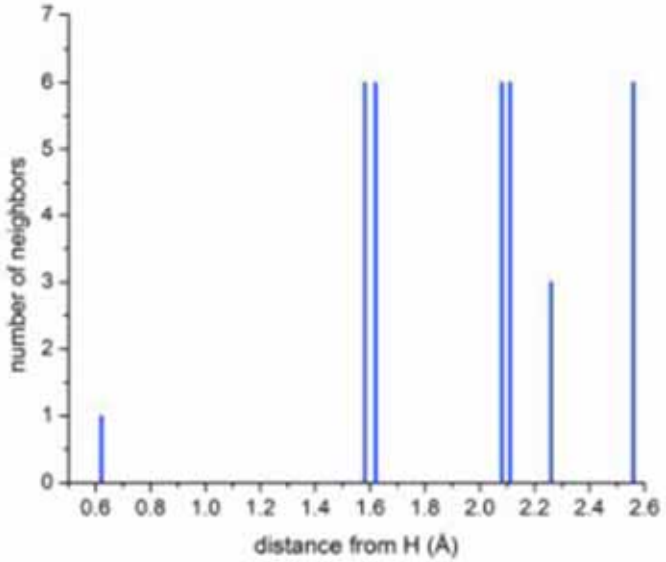
$$\delta = \frac{1}{4}$$

Simple Cubic Lattice

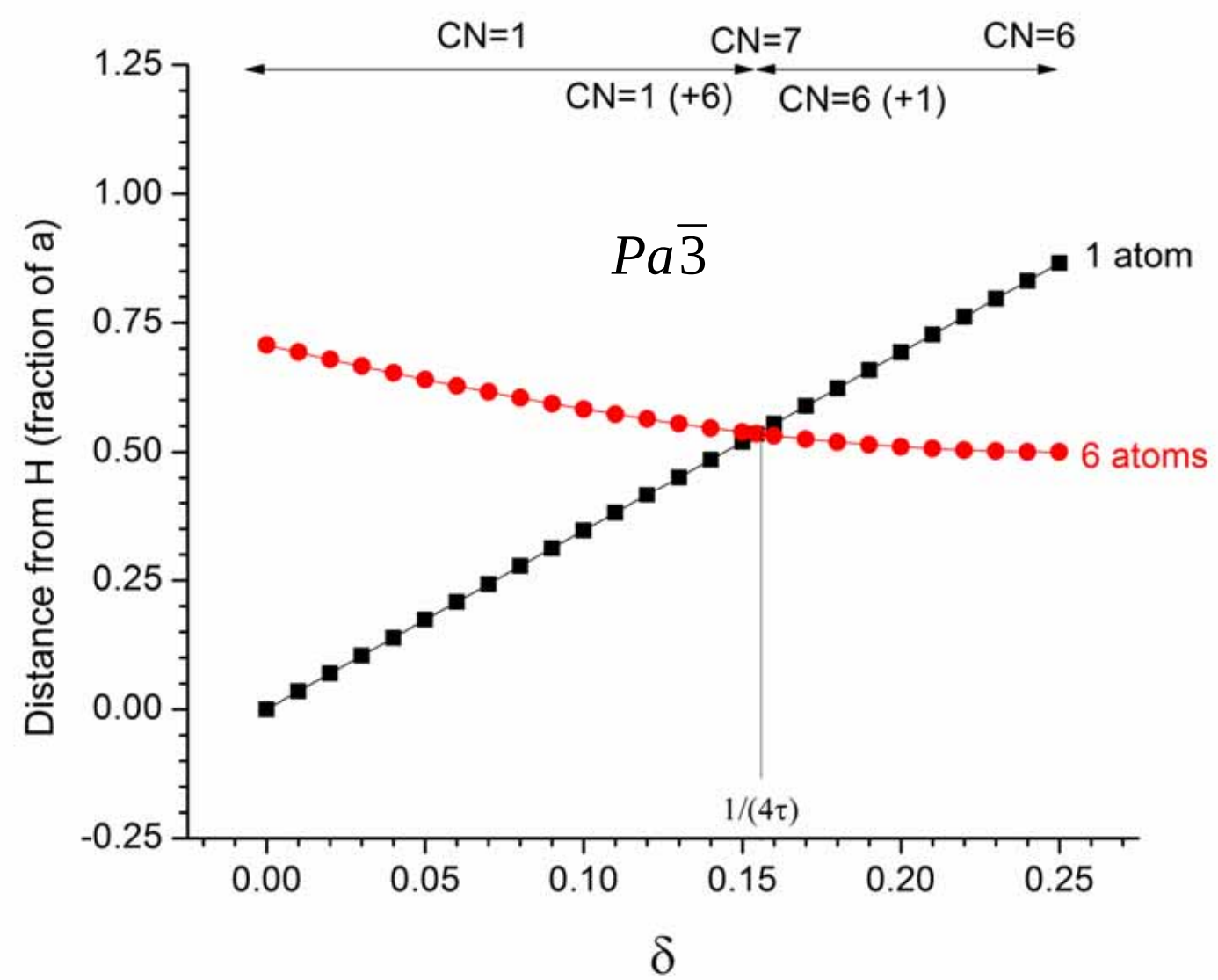


$Pa\bar{3}$: molecular → monatomic



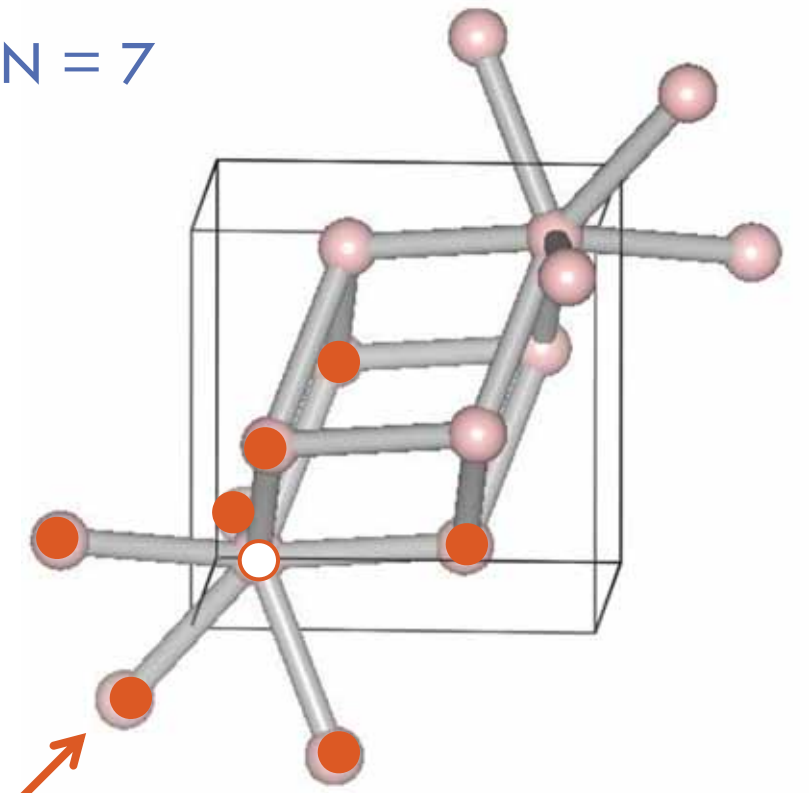


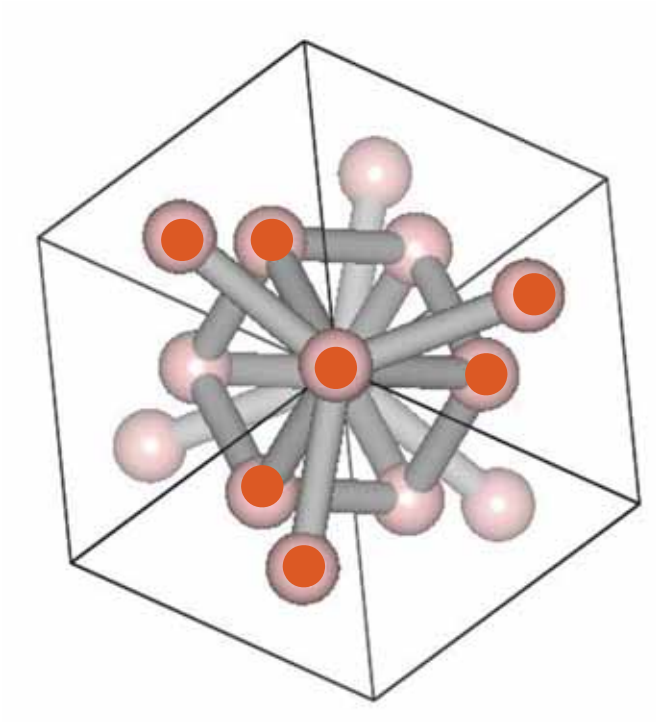
Coordination Number

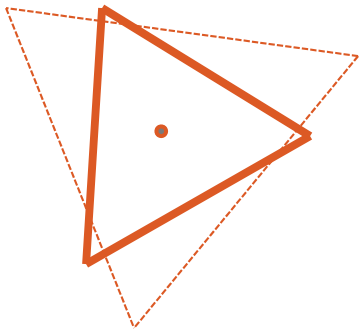


Which structure at ξ=1? – $Pa\bar{3}$

CN = 7



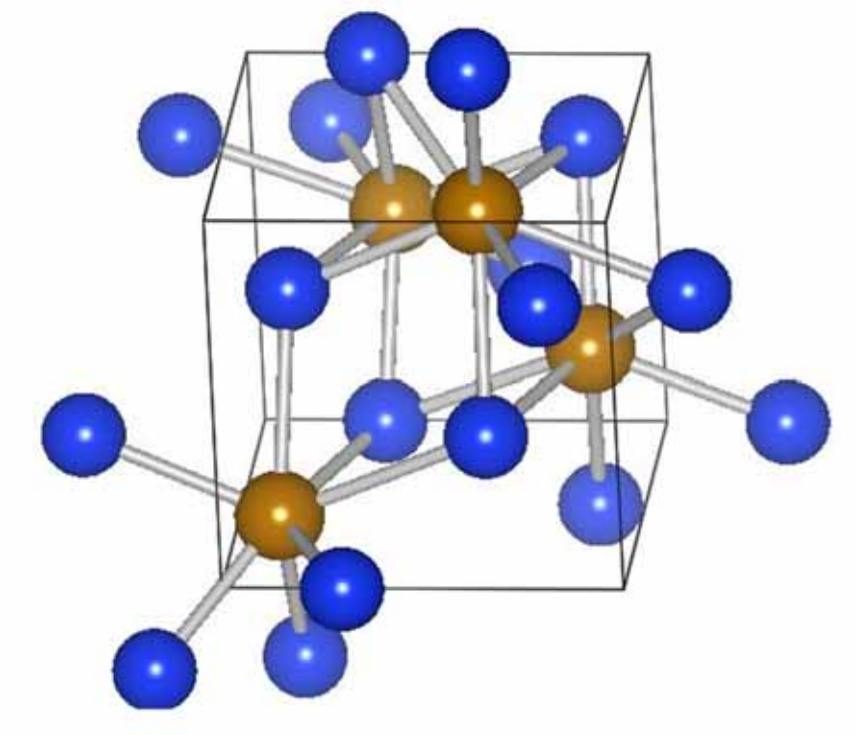




Intermediate between :

- Capped octahedron
- Capped trigonal prism

Which structure ξ=1? – $Pa\bar{3}$



FeSi

Binary system

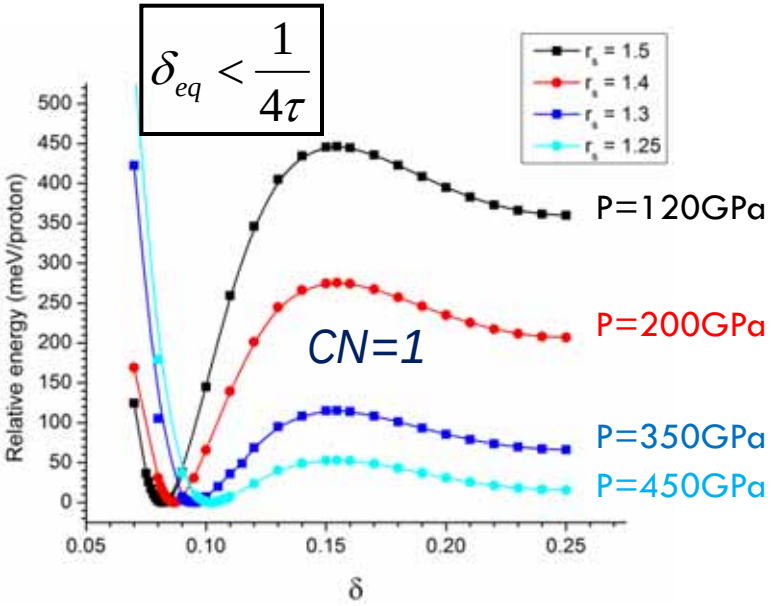
$$Pa\bar{3} \rightarrow P2_13$$

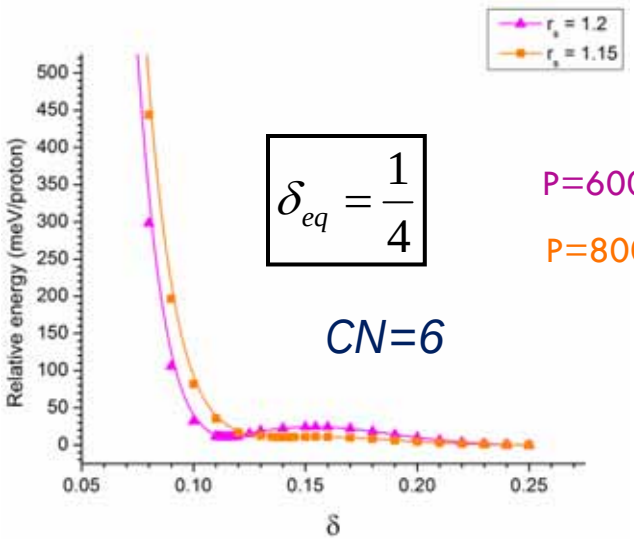
$$\delta_{Fe} = 0.1365$$

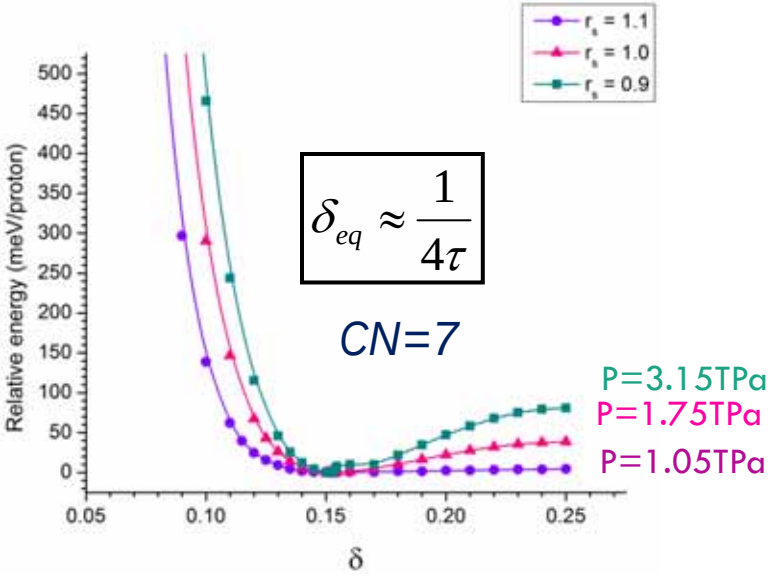
$$\delta_{Si} = 0.1574$$

$$\delta_{ideal} = 0.1545$$

Potential energy profiles - $Pa\bar{3}$







- As expected, the coordination number increases as the density increases (1→6→7).

- Around r_s=1.1 – 1.2, change δ costs very little energy → "plastic" state?

DFT/PAW-PBE – R_{cutoff}=0.8 a_0
E_{cutoff}: 2,000eV – k-points resolution: 2π*0.04 Å^{-1}*

Conclusions 3

- As P ↑:
  - The shortest intermolecular H_2-H_2 separation ↓whereas the intramolecular H-H bond length globally ↑. But resistance to a perfect equalization of the H-H distances.
  - 2 effects coexist and compete: spatial confinement and orbital interaction. The H-H bonds are shorter than they should be.
- As the system approaches equalization, appearance of a plastic state? Has to be studied in more detail, taking into account dynamics.

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