In Exploration of Solid Metallic Hydrogen

Sam Azadi and Matthew Foulkes

QMC Workshop
Towler Institute
August 2012

Beginning of the story 1935:

DECEMBER, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

On the Possibility of a Metallic Modification of Hydrogen

E. WIGNER AND H. B. HUNTINGTON, *Princeton University*

(Received October 14, 1935)

At very high pressure solid molecular hydrogen would dissociate and form an atomic solid that is metallic

Metallic Solid Hydrogen

1968:

VOLUME 21, NUMBER 26 PHYSICAL REVIEW LETTERS 23 DECEMBER 1968

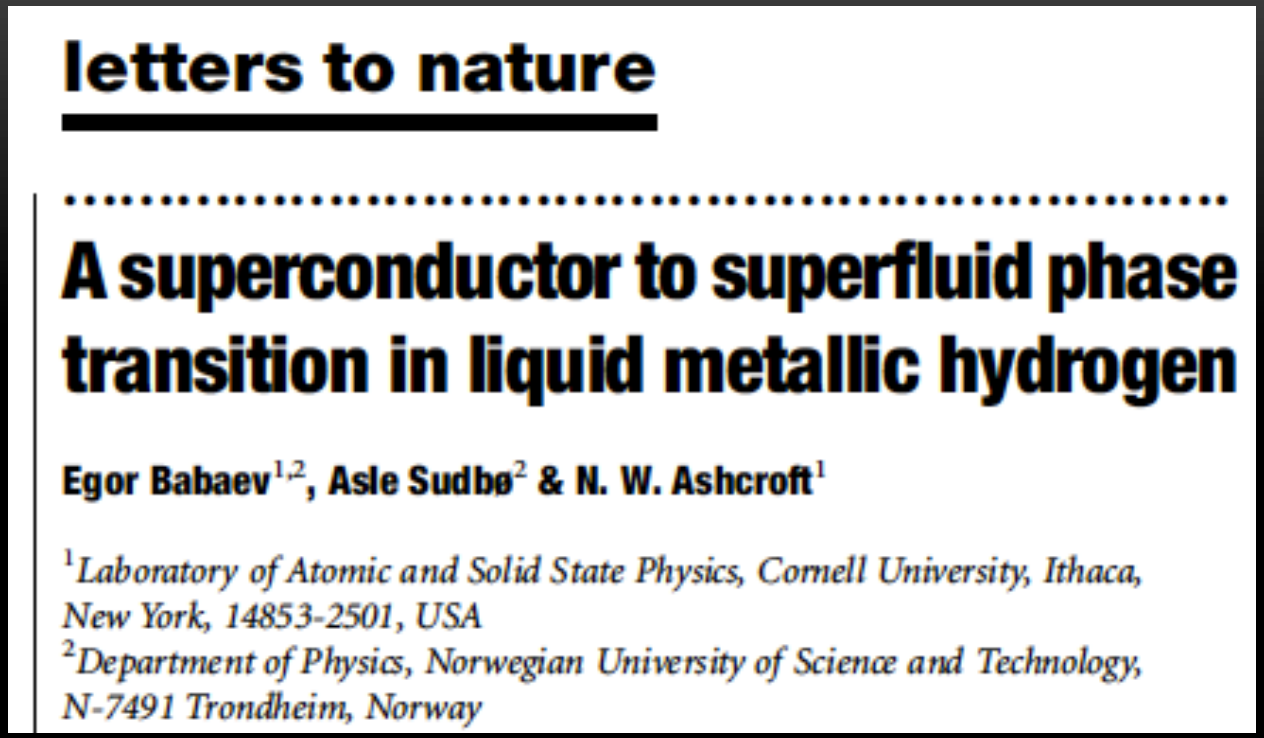
METALLIC HYDROGEN: A HIGH-TEMPERATURE SUPERCONDUCTOR?

N. W. Ashcroft
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
(Received 3 May 1968)

Application of the BCS theory to the proposed metallic modification of hydrogen suggests that it will be a high-temperature superconductor. This prediction has interesting astrophysical consequences, as well as implications for the possible development of a superconductor for use at elevated temperatures.

High-Temperature Superconductivity

2004:



letters to nature

A superconductor to superfluid phase transition in liquid metallic hydrogen

Egor Babaev[1,2], Asle Sudbø[2] & N. W. Ashcroft[1]

[1]Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York, 14853-2501, USA
[2]Department of Physics, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

at high (but experimentally accessible) pressures, compressed hydrogen will adopt a liquid state, even at low temperatures. In reaching this phase, hydrogen is also projected to pass through an insulator-to-metal transition. This raises the possibility of new state of matter: a near ground-state liquid metal, and its ordered states in the quantum domain.

Three phases predicted by experiment:

Phase I (P < 110 Gpa): freely rotating H_2 molecules whose centers of mass are arranged in an *hcp* structure.

Phase II (110 < P < 150 GPa): Also known as the broken symmetry phase. DFT calculations predict orthorhombic $Cmc2_1$, $Pca2_1$, and $P2_1/C$ structures.

Phase III (P > 150 Gpa): At 150 GPa, a large low-temperature discontinuity in the frequency of the Raman and a strong rise in the IR molecular vibrons mark the appearance of Phase III.

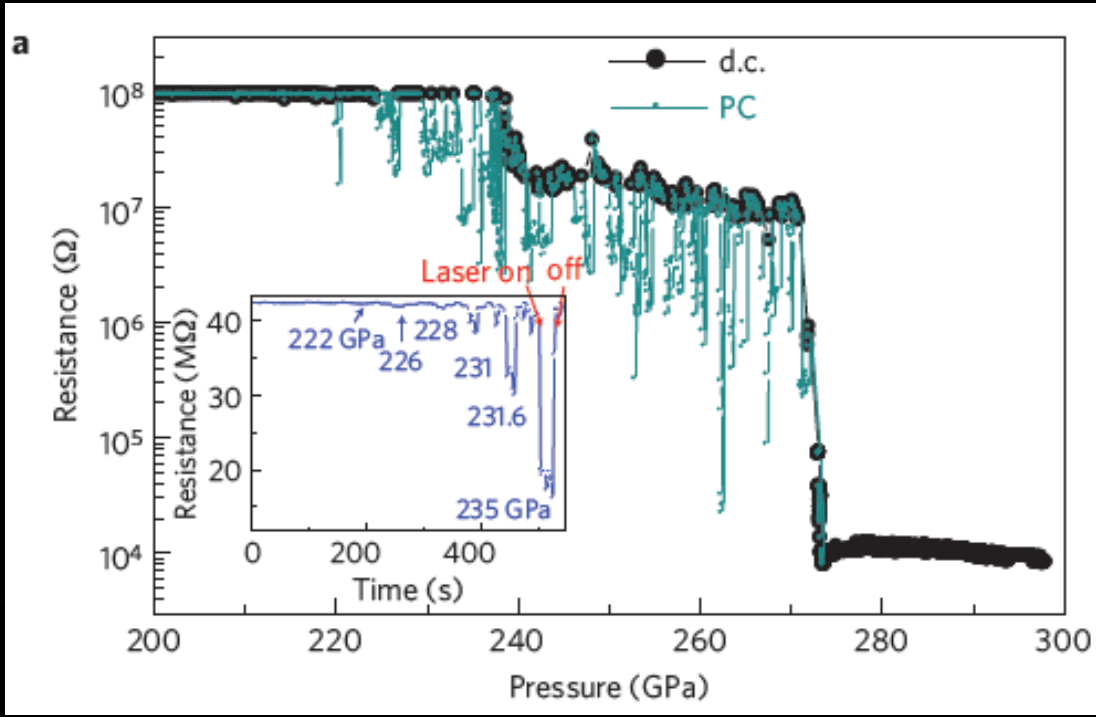
Recent X-ray results suggest *hcp* structure up to 185 Gpa

Phys. Rev. B **82**, 060101(R) (2010)

Recent Experimental Contradiction:

Above 220 Gpa, hydrogen became opaque and electrically conductive. At 260–270 GPa, hydrogen transformed into a metal as the conductance of hydrogen sharply increased and changed little on further pressurizing up to 300 GPa or cooling to at least 30 K; and the sample reflected light well.

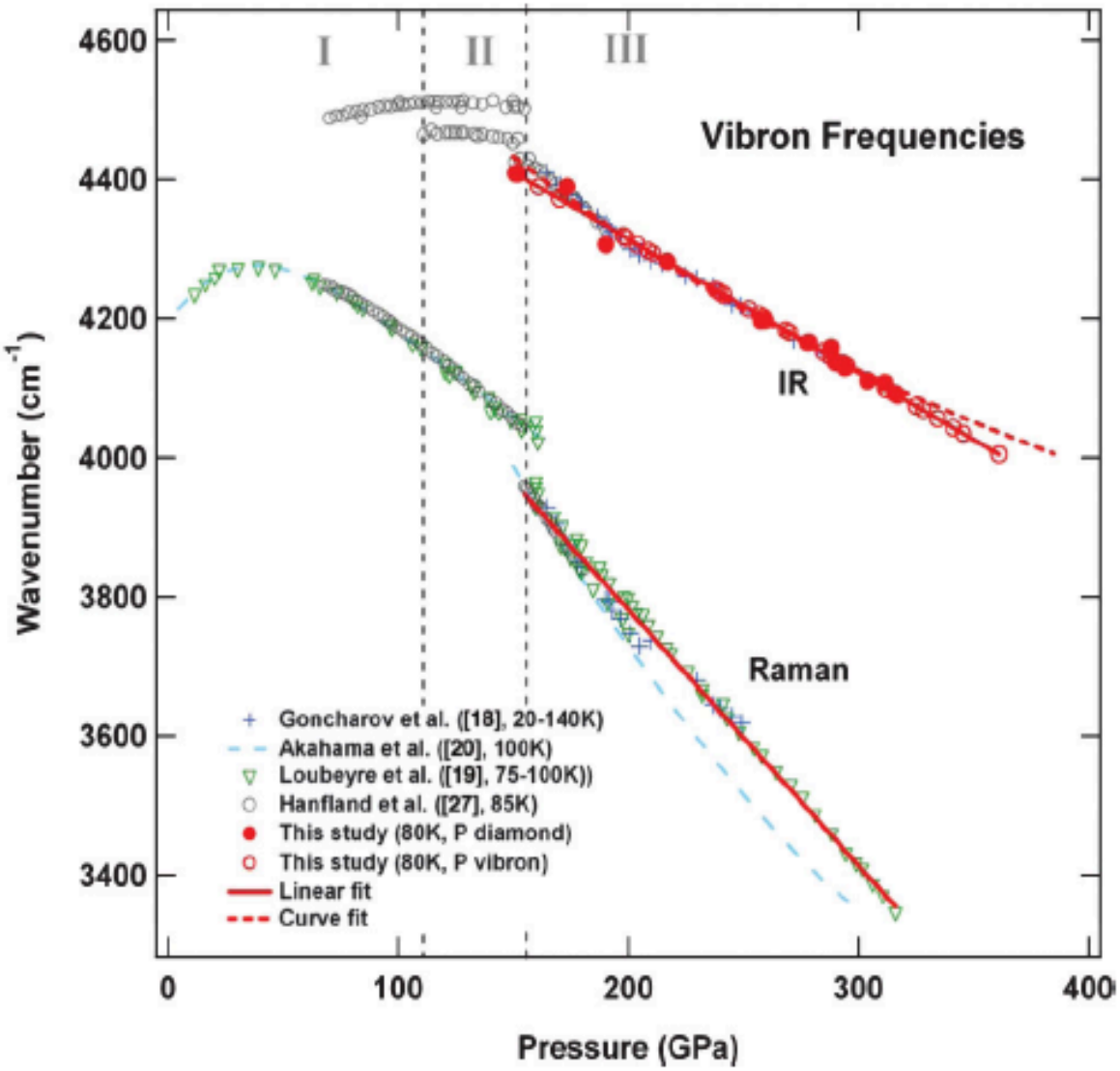
The metallic phase transformed back at 295 K into molecular hydrogen at 200 GPa. This significant hysteresis indicates that the transformation of molecular hydrogen into a metal is accompanied by a first-order structural transition presumably into a montomic liquid state.



Eremets, Nature December 2011

The persistence of the strong infrared absorption of the vibron characteristic of phase III indicates the stability of the paired state of hydrogen. There is no evidence for the predicted Metallic state (up to 360 Gpa) over these conditions, in contrast to recent reports, but electronic properties consistent with semimetallic behavior are observed.

Our measurements show no evidence for the optical conductivity expected for a metal over the entire range of temperatures to the highest pressures explored, and no signatures of an atomic liquid are observed.



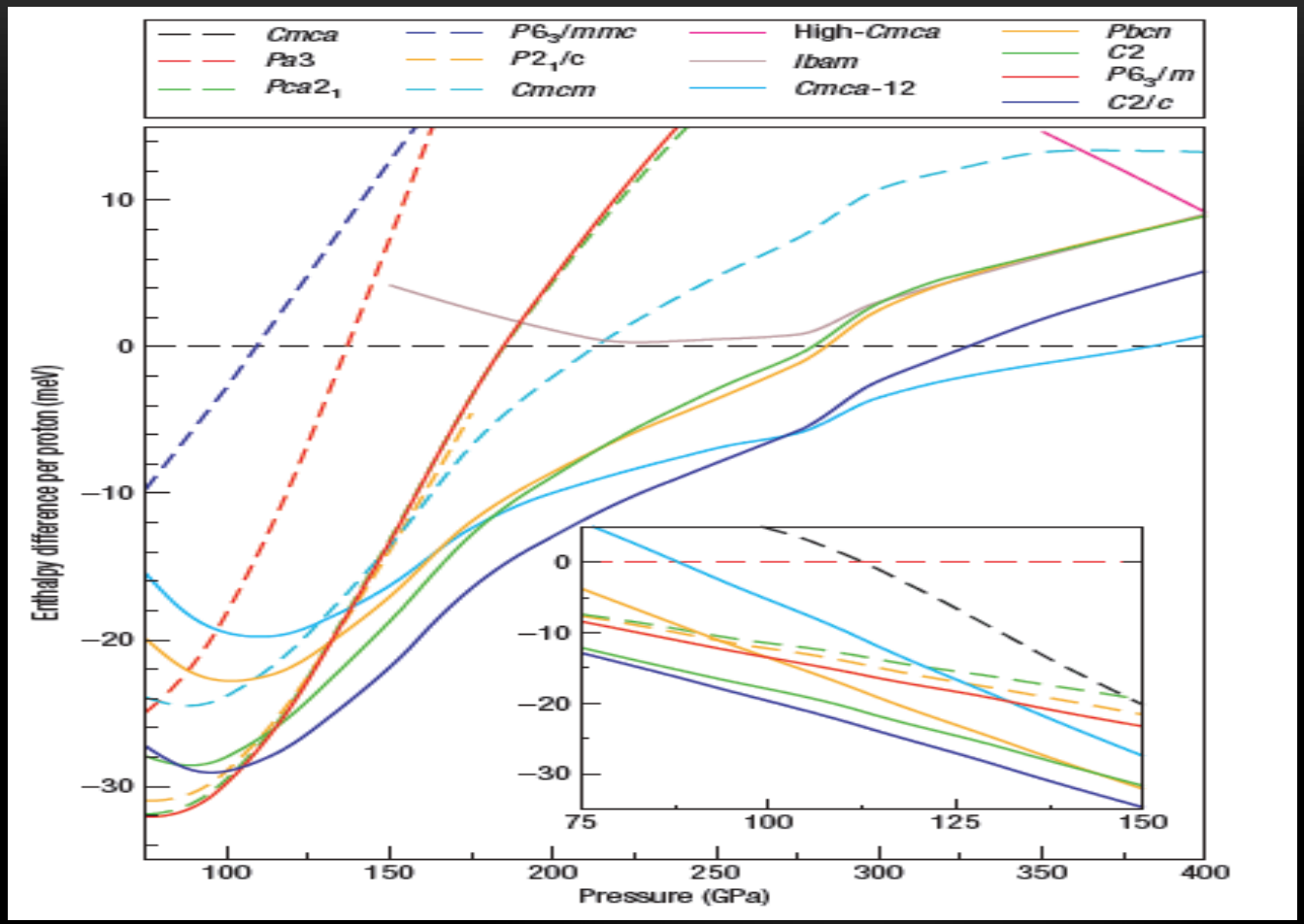
Hemley group, PRL, April 2012

Problems:

The phase diagram of hydrogen is poorly understood. Determining the stable structures of solid (?!) hydrogen is a tremendous experimental challenge, because hydrogen atoms scatter X-rays only weakly, leading to low-resolution diffraction patterns.

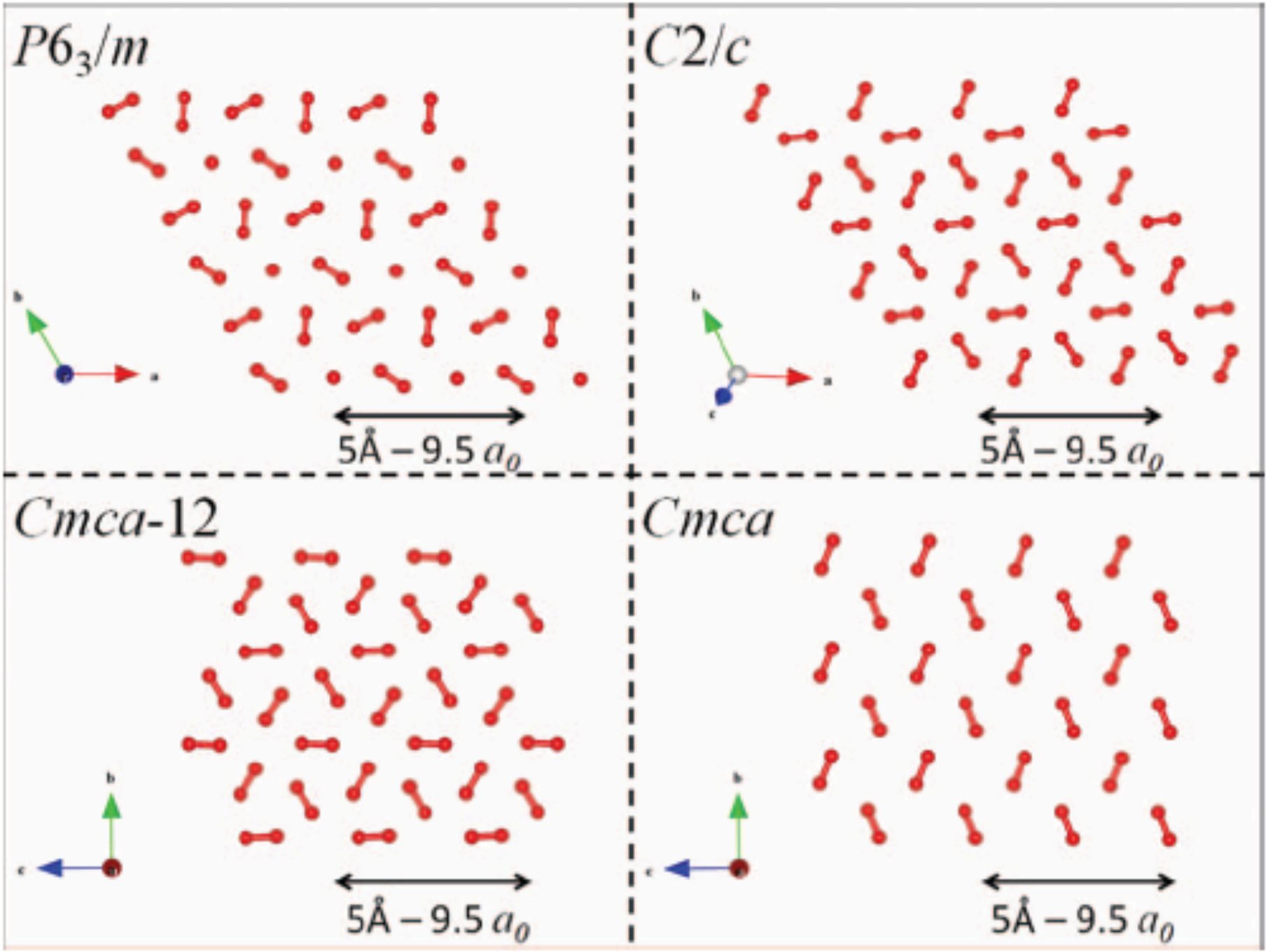
Theoretical studies encounter major difficulties owing to the small energy differences between structures and the importance of the zero-point motion of the protons.

Density Functional Theory (DFT) phase diagram

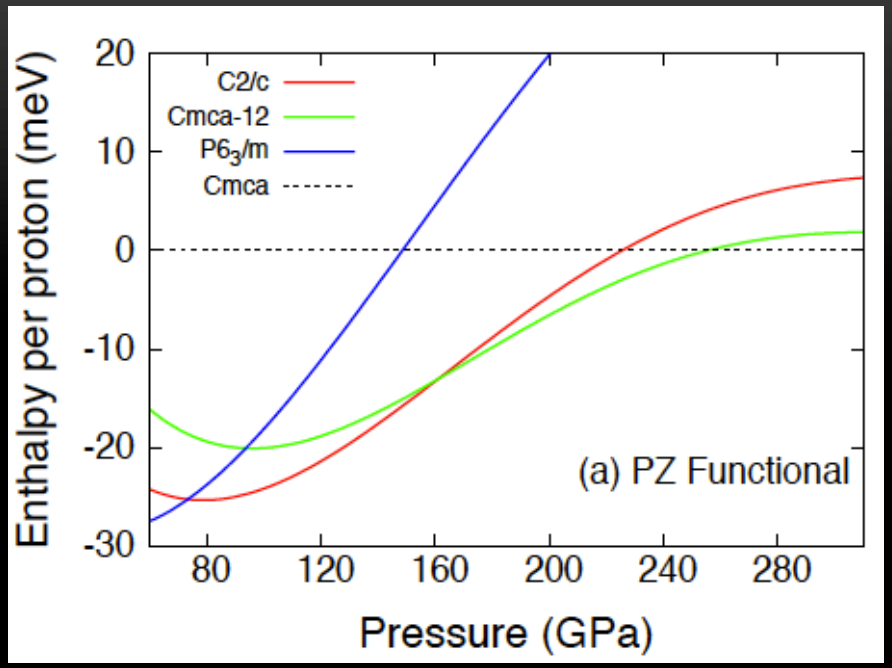


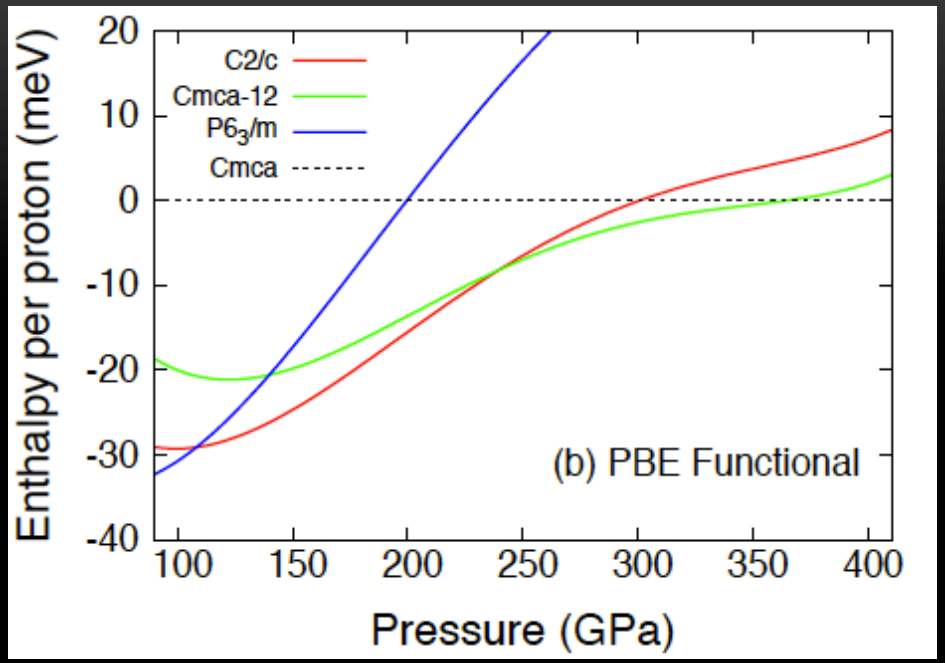
Their approach is to relax many random structures to minima in the enthalpy at fixed pressure

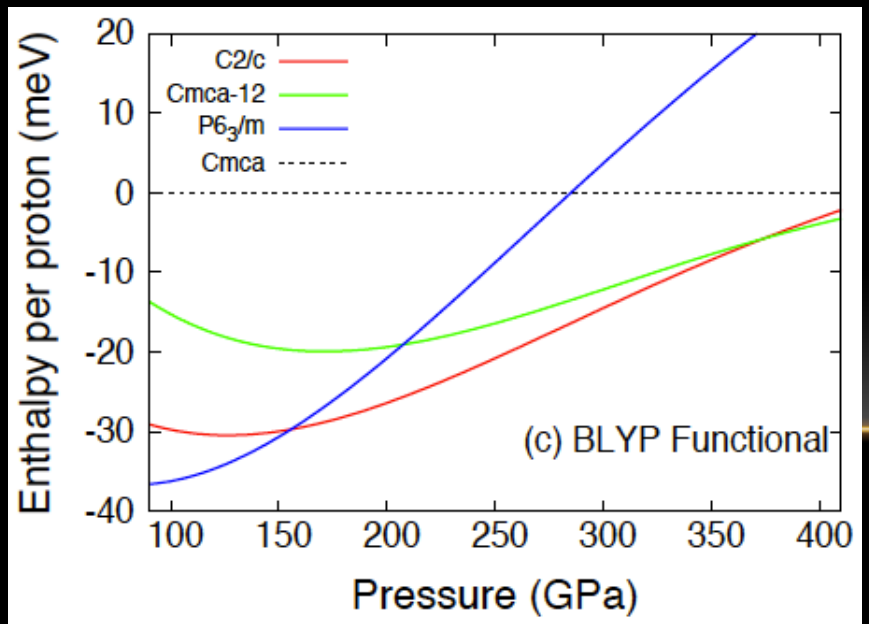
Nature **3**, 473 (2007)


$P6_3/m$
5Å – 9.5 a_0
$C2/c$
5Å – 9.5 a_0
$Cmca$-12
5Å – 9.5 a_0
$Cmca$
5Å – 9.5 a_0

Can we trust DFT phase diagram ?

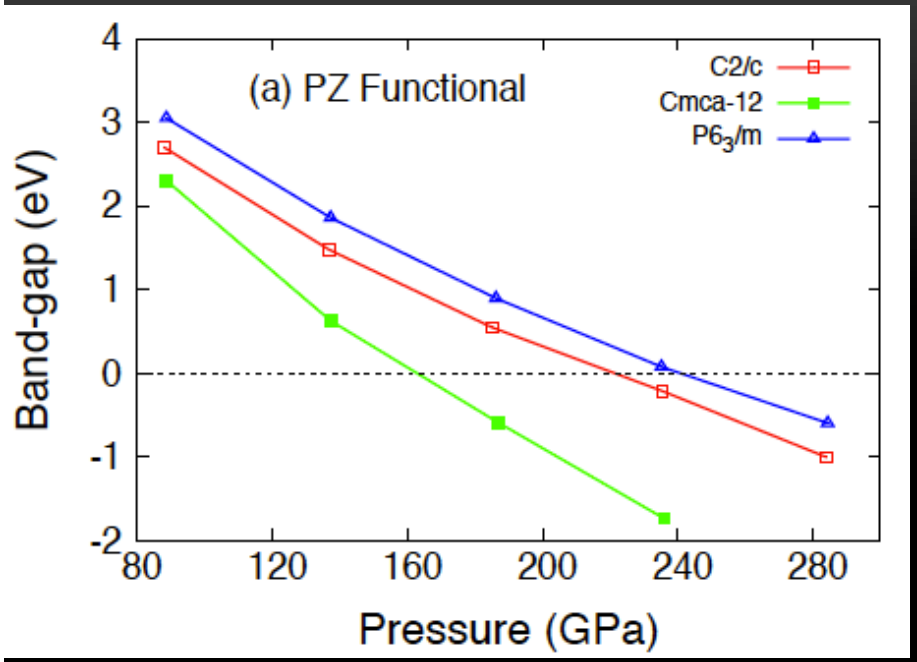


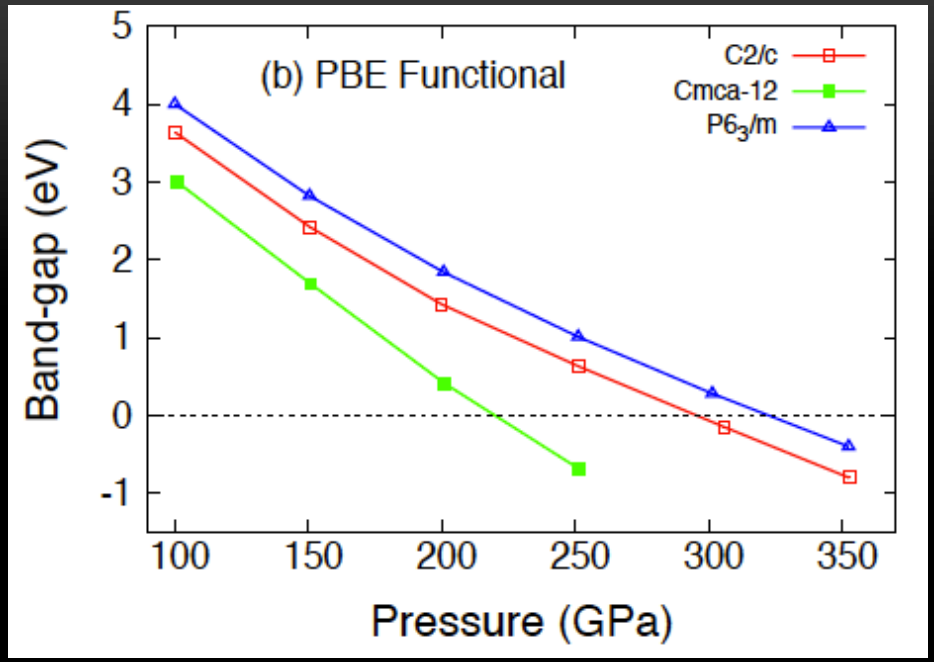


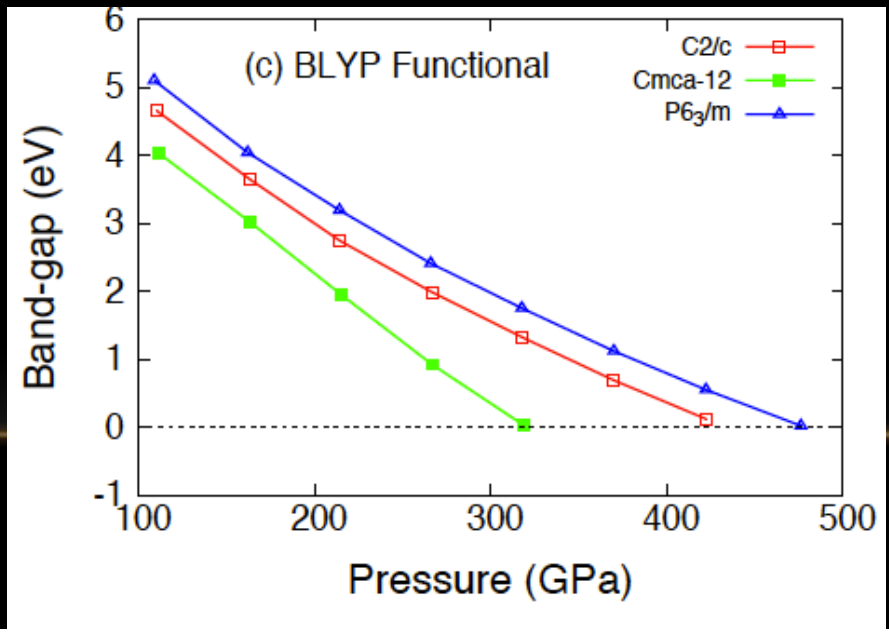


At least DFT shows three structure transitions !

DFT band-gap:


(a) PZ Functional
C2/c
Cmca-12
P6$_3$/m
Band-gap (eV)
Pressure (GPa)
4
3
2
1
0
-1
-2
80
120
160
200
240
280

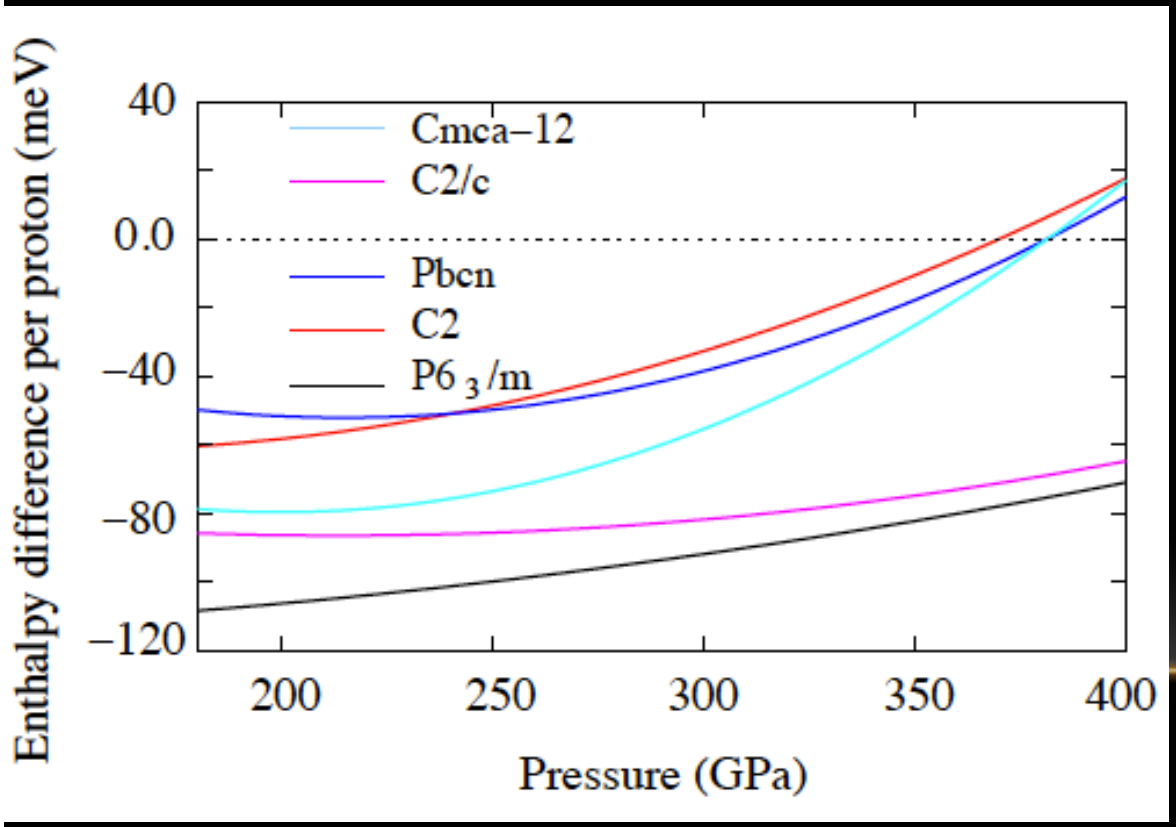

(b) PBE Functional
C2/c
Cmca-12
P6$_3$/m
Band-gap (eV)
Pressure (GPa)
5
4
3
2
1
0
-1
100
150
200
250
300
350


(c) BLYP Functional
C2/c
Cmca-12
P6$_3$/m
Band-gap (eV)
Pressure (GPa)
6
5
4
3
2
1
0
-1
100
200
300
400
500

Hybrid DFT phase diagram:

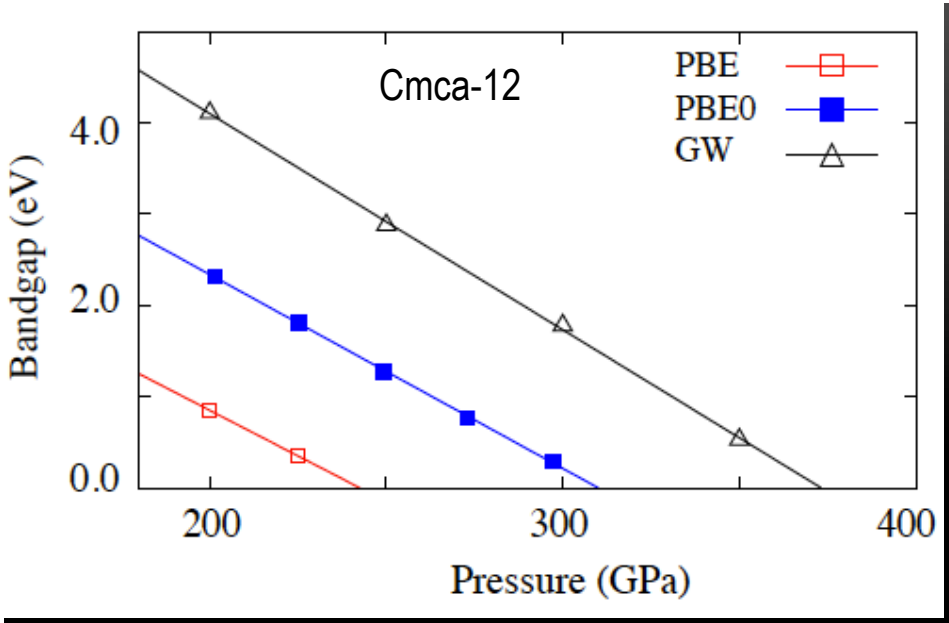
Hybrid DFT: DFT + small fraction of Hartree-Fock exchange

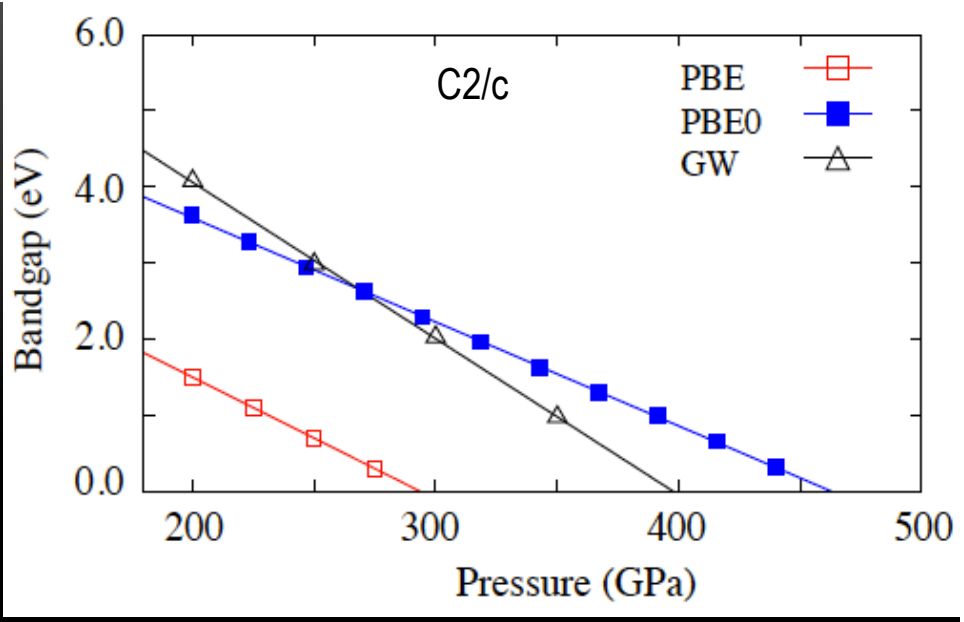
Typically yields much improved band gap that are often
in close agreement with experiment

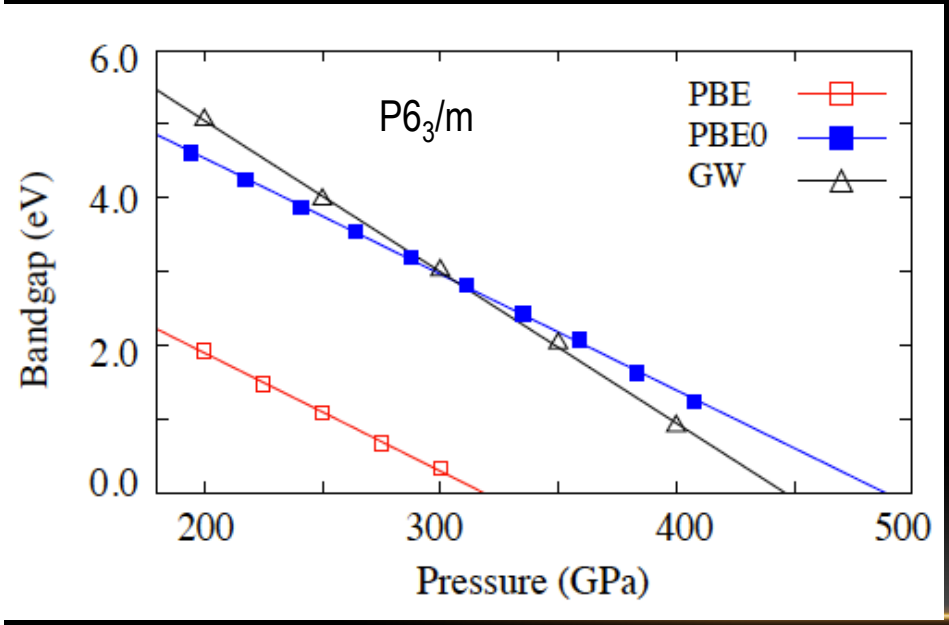


Oops ! No Metallization,
No structure transition !

The lower the energy
The wider the band-gap
Hemley, PRL **67** 1138 (1991)







Hybrid functional metallization pressures are larger than GW ones ~ 50 GPa

GW predicts metallization should happen before 400 Gpa

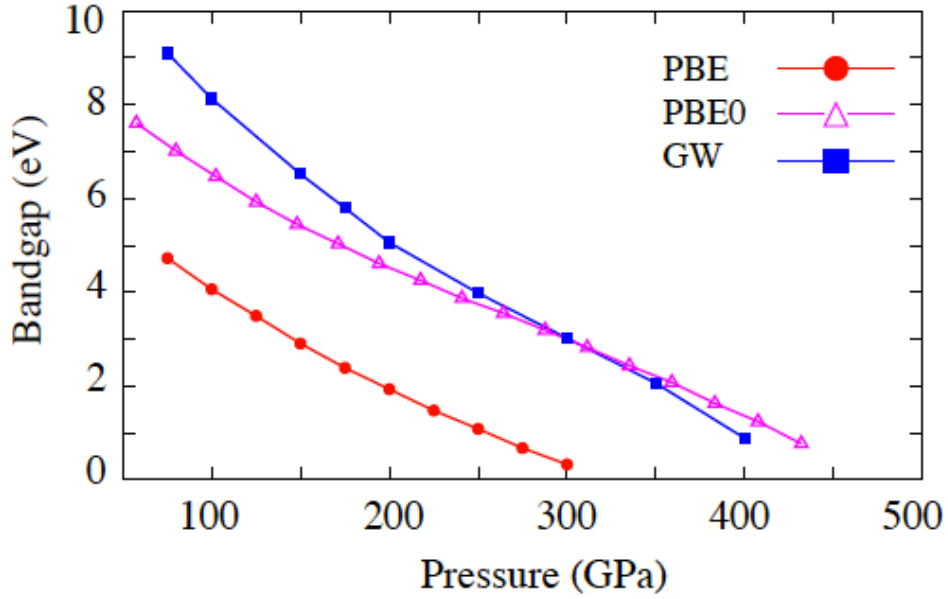


FIG. 4: (Colors online) Band-gap of $P6_3/m$ hydrogen crystal structure as functions of pressure in the range of phase I,II, and III obtained by PBE,PBE0 and GW calculations.

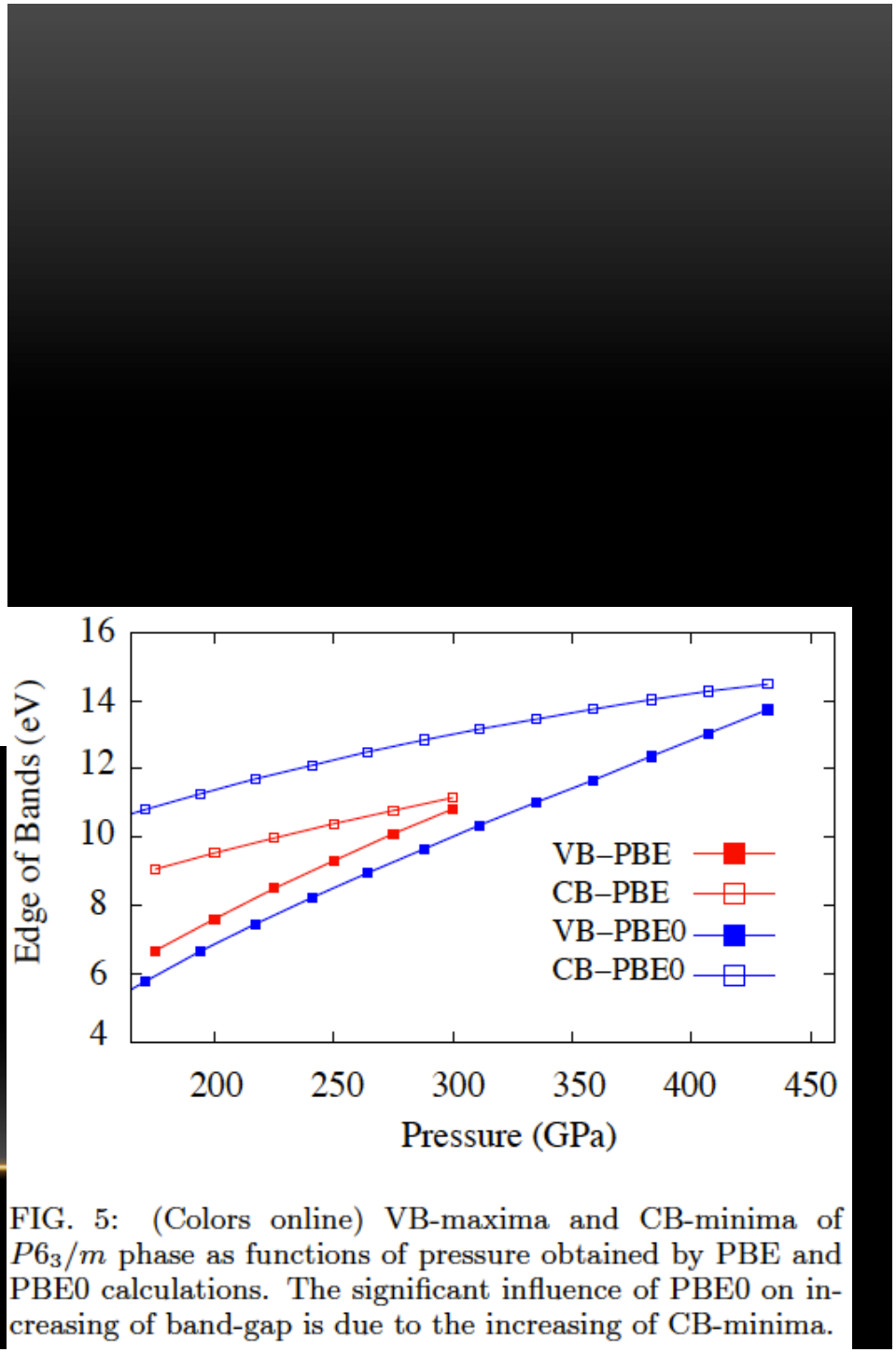


FIG. 5: (Colors online) VB-maxima and CB-minima of $P6_3/m$ phase as functions of pressure obtained by PBE and PBE0 calculations. The significant influence of PBE0 on increasing of band-gap is due to the increasing of CB-minima.

QMC phase diagram:

Contrary to standard DFT methods, QMC calculations have to be performed on a super-cell. Therefore, finite-size (FS) effects can be a relevant source of error in QMC calculations.

One-body term (independent particle source), arises from the kinetic and Hartree term

Two-body term, related to the FS effects of exchange and correlation

Hold on! How DFT functionals change QMC energy ?

TABLE I. VMC and DMC energies of the $P6_3/m$ phase using PBE and PBE0 single particle orbitals. Energies and pressures are in eV per proton and GPa, respectively.

Pressure	PBE-VMC	PBE0-VMC	PBE-DMC	PBE0-DMC
100	-15.1335(4)	-15.1397(4)	-15.2327(3)	-15.2338(3)
200	-14.5898(4)	-14.5979(4)	-14.6856(3)	-14.6867(3)
300	-14.0473(4)	-14.0524(4)	-14.2184(3)	-14.2193(3)

This demonstrates that, in the case of solid molecular hydrogen, DMC energies calculated using PBE and PBE0 orbitals differ negligibly, even though the change of functional has a large effect on the DFT phase diagram. This contrasts with the case of 3d transition metal compounds [Phys. Rev. B **82** 115108 (2010)] , where changing the functional does affect the DMC results.

QMC+DFT to calculate FS correction:

DMC -TABC: *Twist averaging* means taking the average of expectation values over all simulation-cell Bloch vectors $\mathbf{k}_s$ in the first Brillouin zone of the simulation cell, i.e., over all offsets to the grid of **k** vectors

KZK functional: the exchange and correlation energy functional is replaced by the LDA functional parameterized for a finite system, which keeps an explicit dependence on the number of particles (Phys. Rev. Lett. 100, 126404 (2008))

Static Phase Diagram:

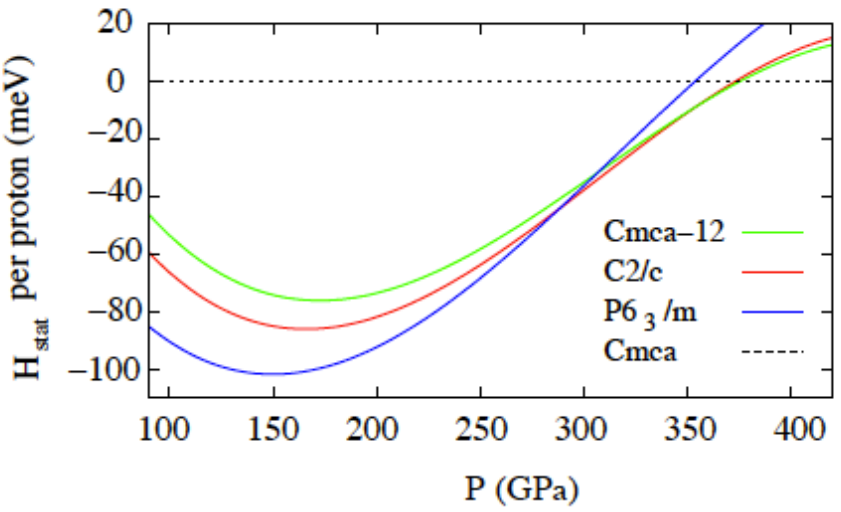
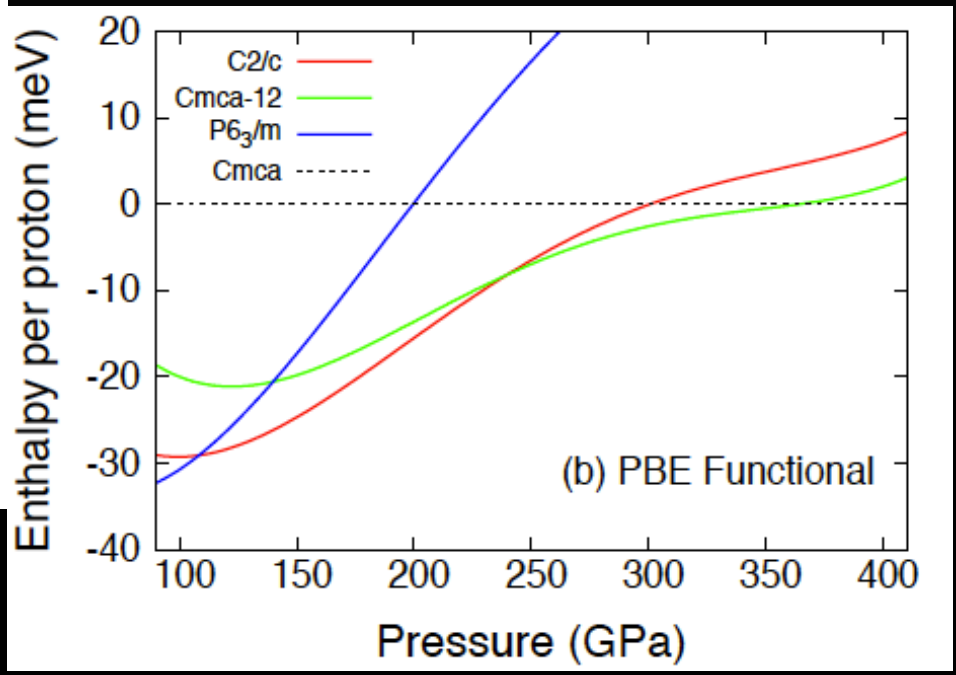
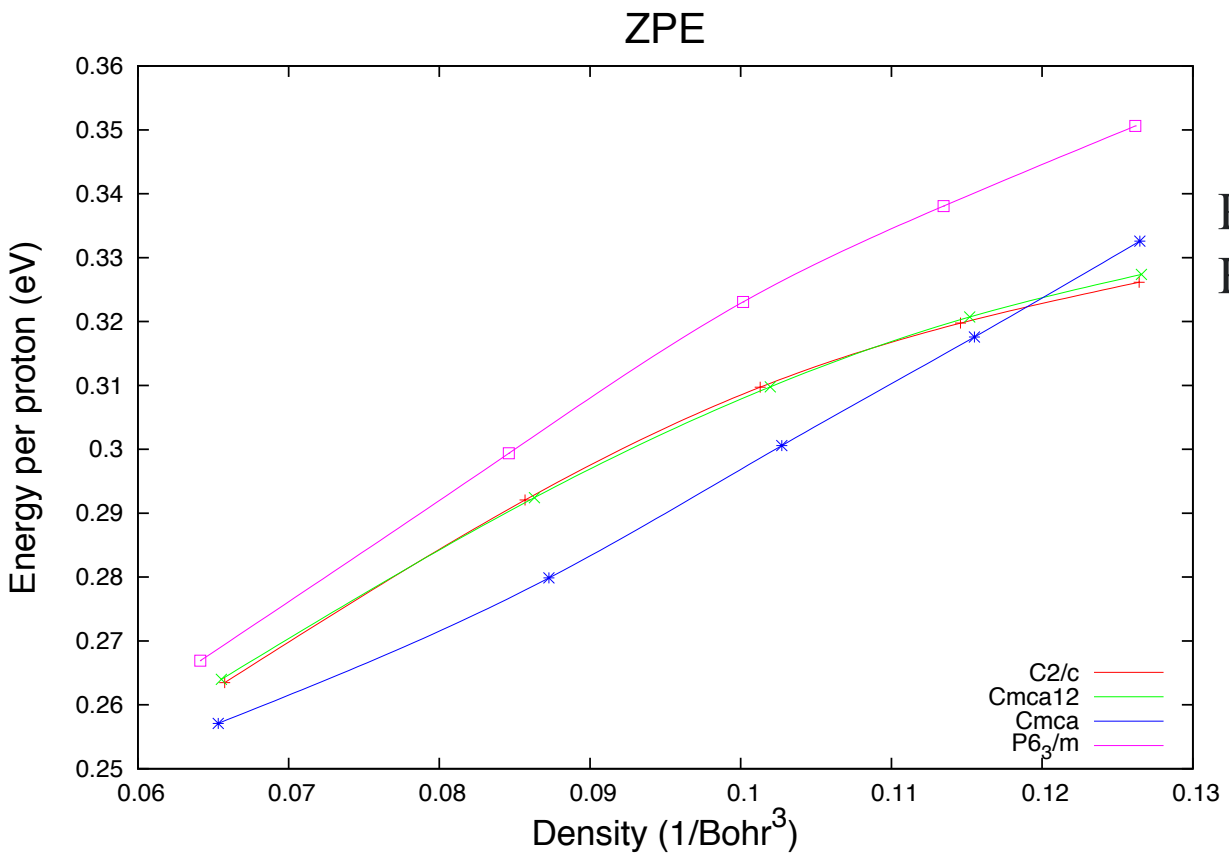


FIG. 1. (color online). Enthalpy as a function of pressure calculated using the DMC-TABC method in the static approximation.



Our *GW* results show that the band gaps of the P63/m, C2/c, and Cmca-12 structures vanish at the static pressures of 446, 398, and 373 GPa, respectively.

Zero Point Energy (ZPE) :



Protons ZPE is estimated using Harmonic approximation

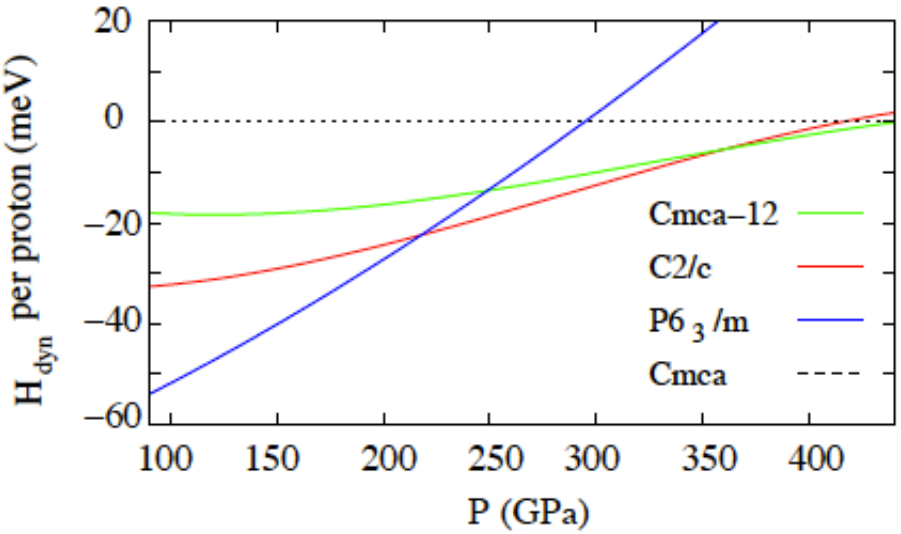


FIG. 2. (Colours online) Dynamic enthalpy obtained by DMC-TABC calculation including proton ZPE as a function of pressure calculated by DFT method

Semimetalic ?!

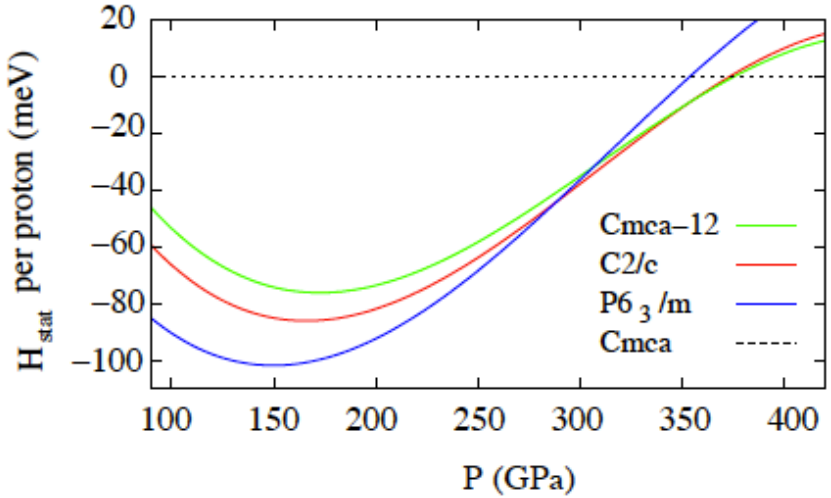
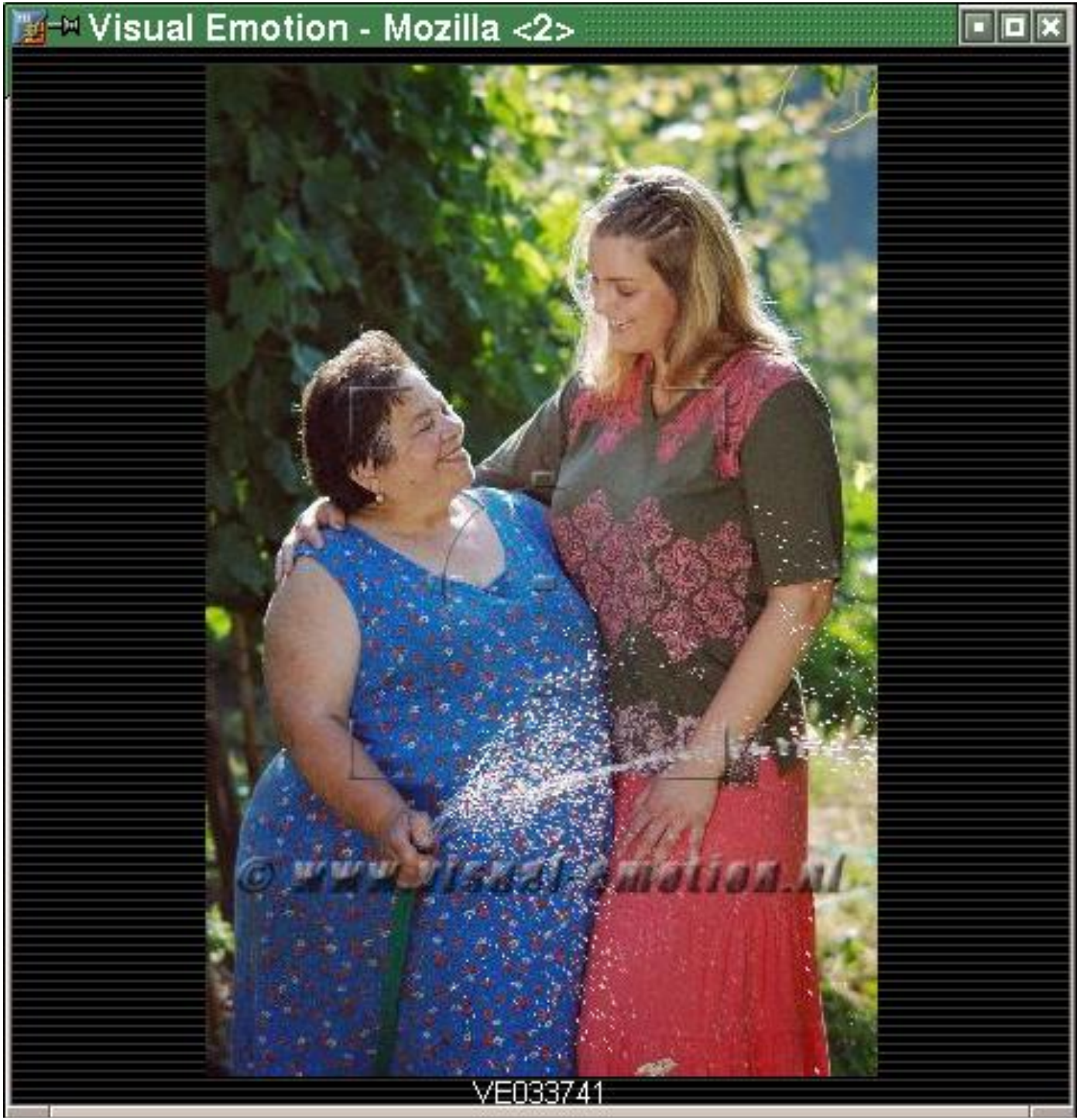


FIG. 1. (color online). Enthalpy as a function of pressure calculated using the DMC-TABC method in the static approximation.

Summary:

?!



TTI Fashion Shoot !
Thank you