Hydrogen Under Extreme Pressure

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Complexity in Simplicity

Hydrogen is conceptually the simplest atom and molecule, and in many ways has been the most complex and challenging to theorists to predict properties.

The problem: zero-point motion & energy

The phases and properties with increasing density are rich and fascinating.
At the end of the rainbow is a pot of gold:
metallic hydrogen.

Today, I want to discuss two pathways to the end of the rainbow:

low temperature isotherm and
high temperature, above the melting line.

The Hydrogens at High Pressure

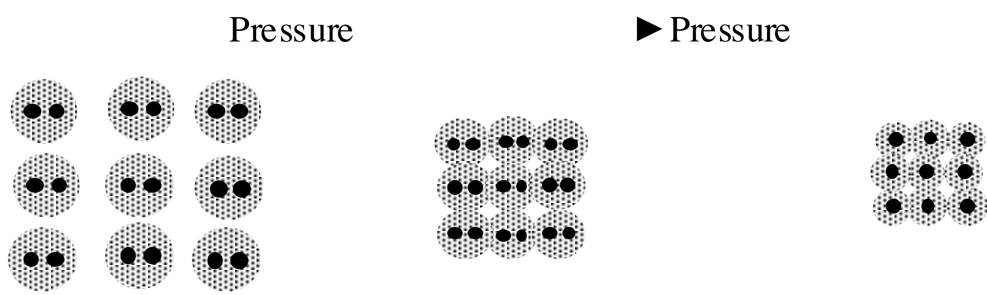
Hydrogens: Hydrogen and its isotopes

D2, HD

	mass	nuclear spin
Hydrogen	2	1/2 fermion
Deuterium	4	1 boson
Hydrogen Deuteride	3	3/2 Maxwell
~~Tritium~~ radioactive	6	1/2 fermion-

The Wigner-Huntington Transition to Atomic Metallic Hydrogen (1935)

Predicted pressure 25 GPa

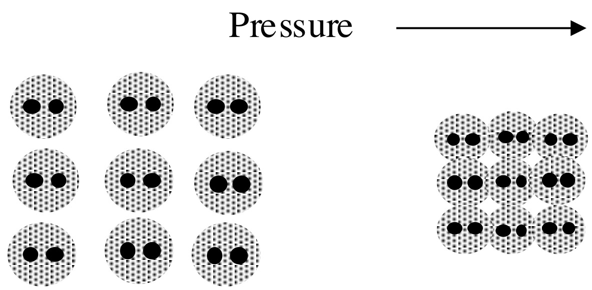


Molecular solid insulator

molecular metal

atomic metal

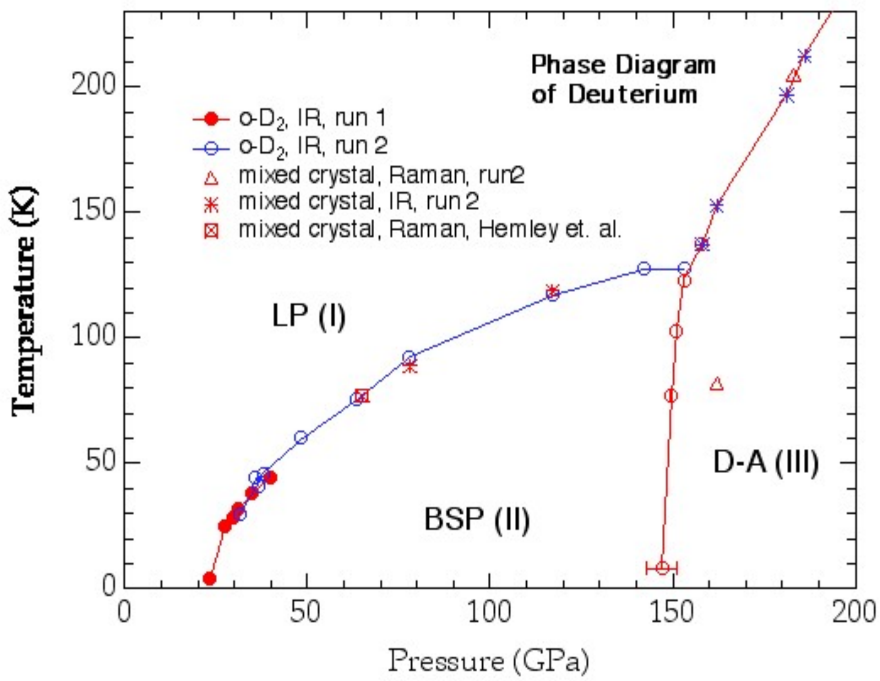
The Known High Pressure Molecular Insulating Phases



Molecular solid insulator

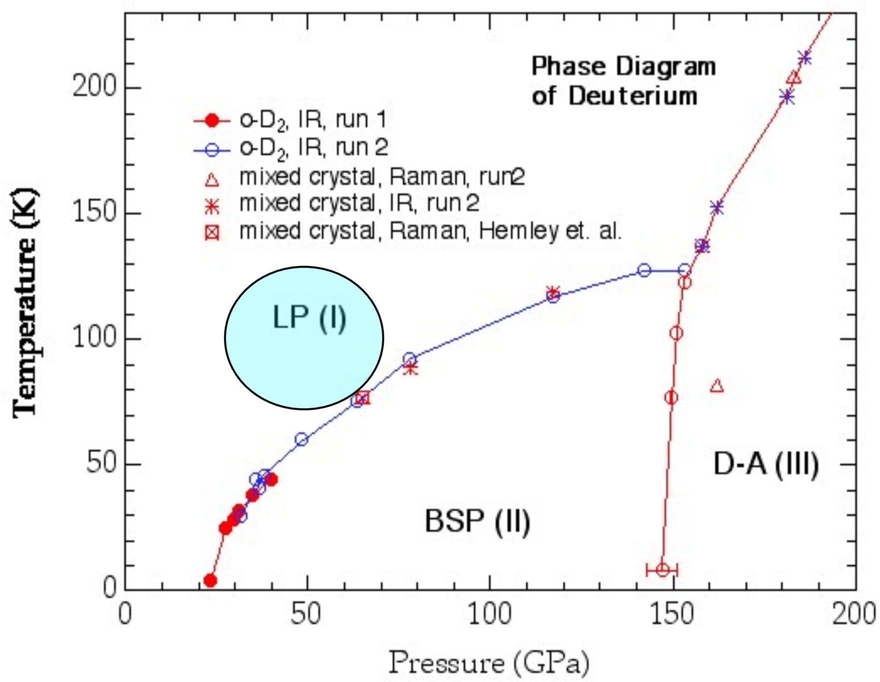
molecular

The Experimentally Visited High Pressure Phases

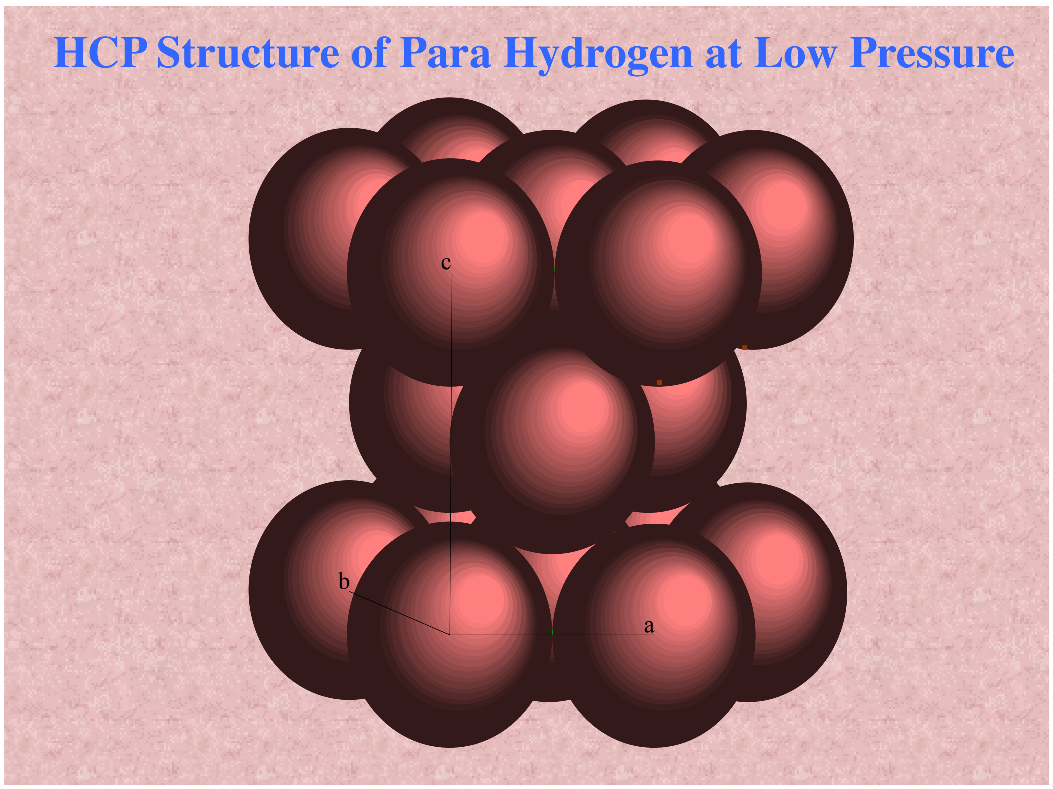


The LP (low pressure) phase in Ortho Deuterium (J=0)

(Hydrogen is similar)



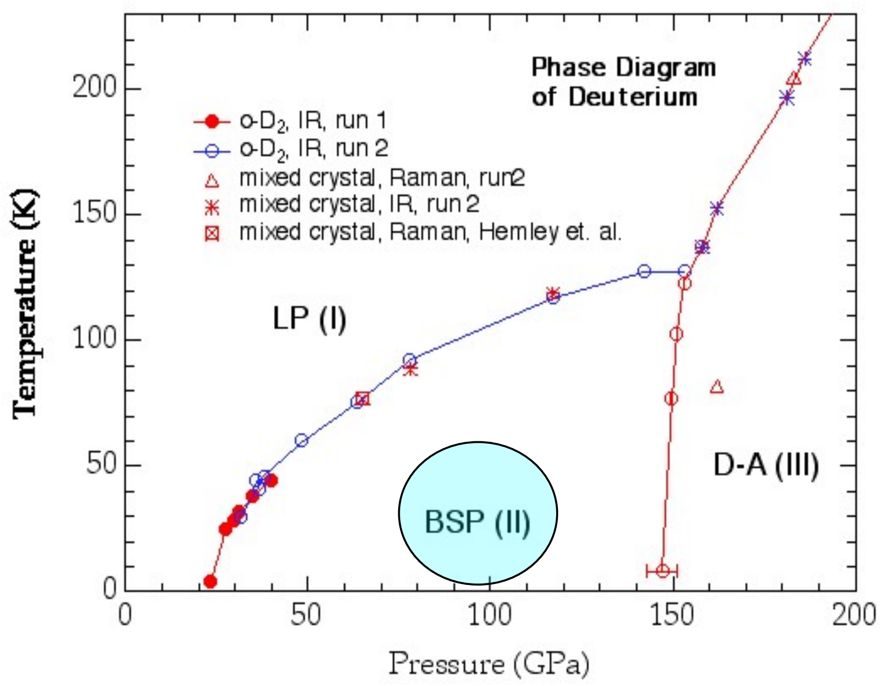
Zero pressure: Both para hydrogen and ortho hydrogen crystallize in an HCP lattice. Para remains HCP to P=0;



Para molecules have spherical quantum mechanical distributions;

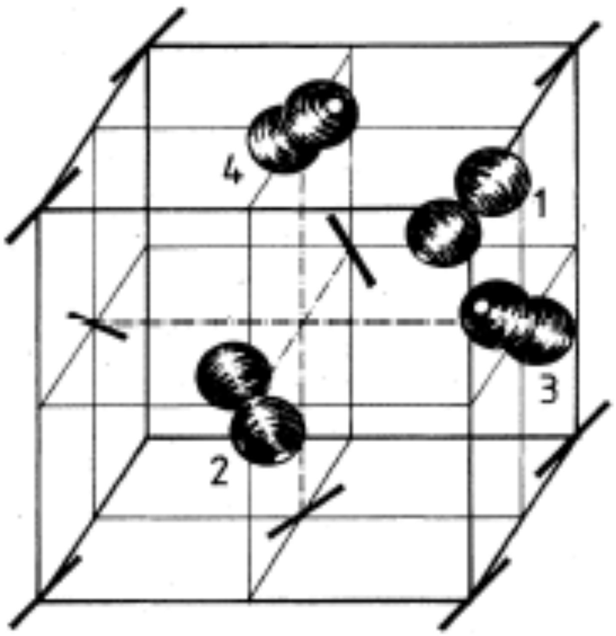
They are not orientationally disordered, but in a "symmetric many-body state"

The BSP in Ortho Deuterium (J=0)
(Hydrogen is similar)



The BSP phase is of orientational order.
Originally predicted to be Pa3, but identified as P3-bar (in deuterium) by Goncharenko and Loubeyre (neutron scattering)

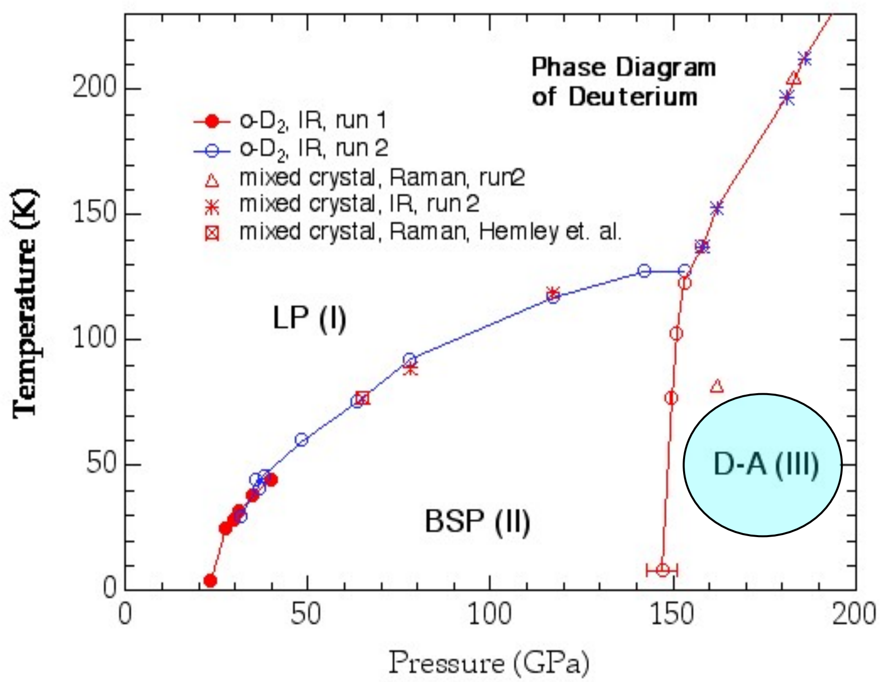
Pa3 structure from Raman Scattering spectra of librons at zero pressure.



P3-bar is similar but more complicated-not on fcc but hexagonal underlying structure of molecular centers.

Above T_C the molecules are orientationally disordered.

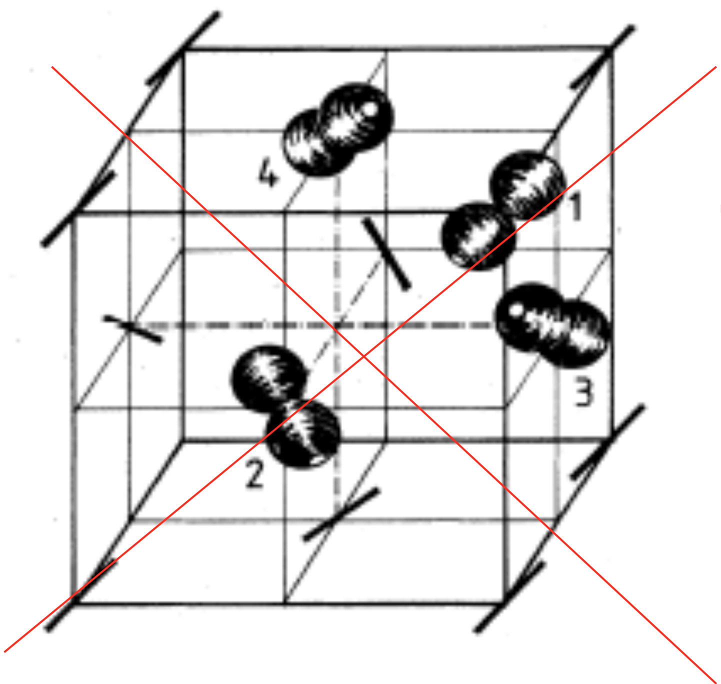
The A-phase in Ortho Deuterium (J=0)
(para-Hydrogen and HD are similar)



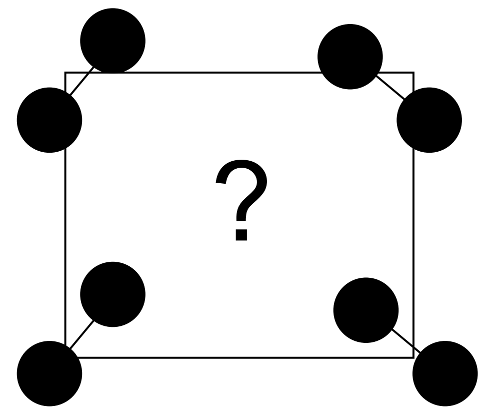
The A-phases: molecules are orientationally ordered but not in well defined spherical harmonic quantum states.

Molecules are in classical ball and stick states.

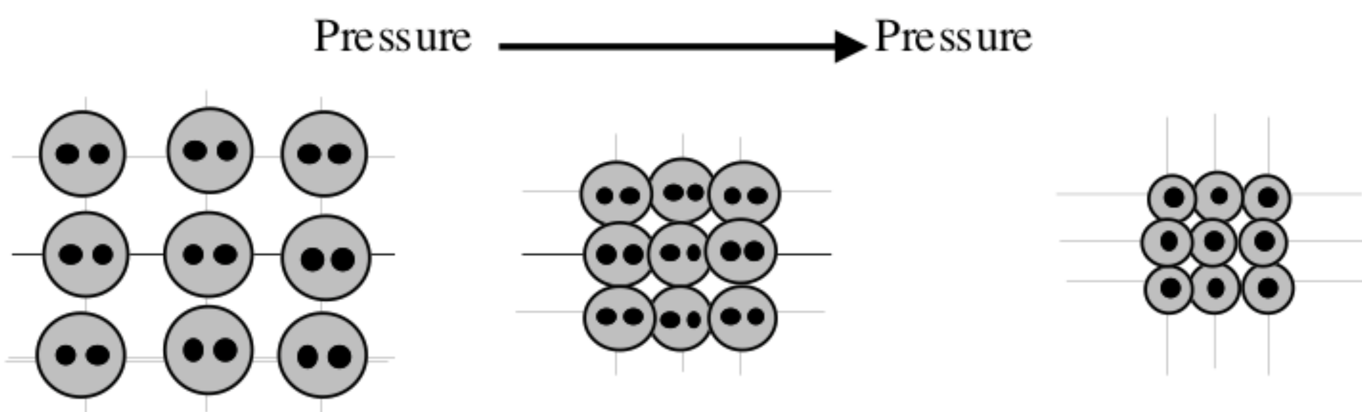
The solid is an insulator, not a metal!



The structure is not known



Solid Metallic Hydrogen



Molecular solid
insulater

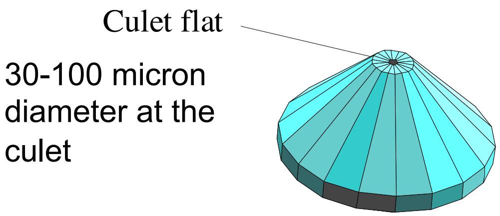
molecular
metal

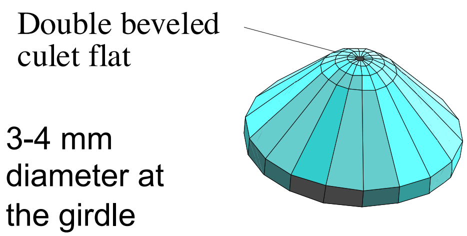
atomic
metal

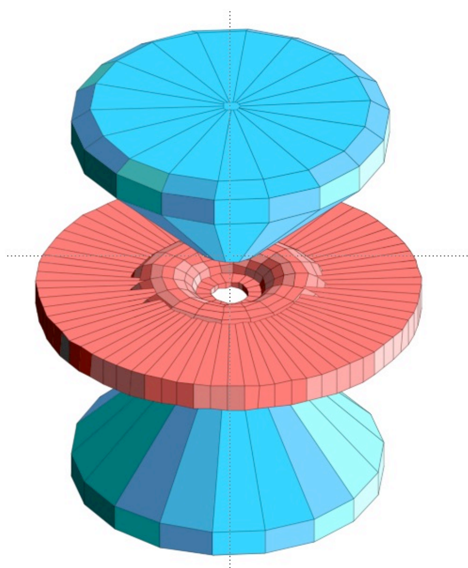
Solid Metallic Hydrogen: Theory, Predictions

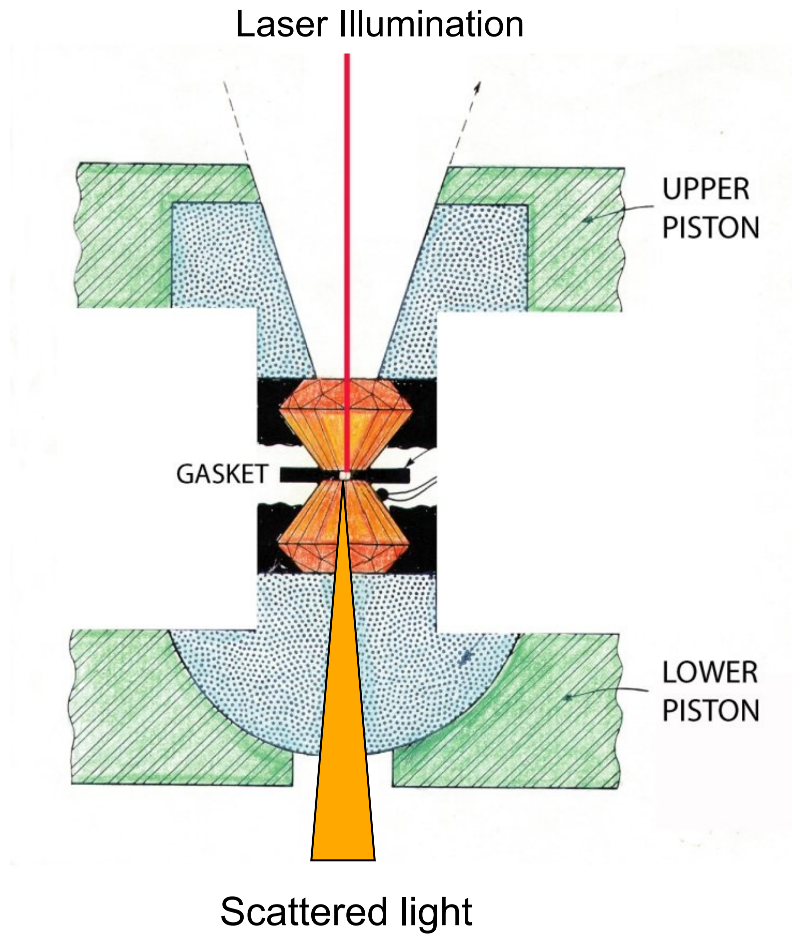
- **Metal Insulator Transition in Solid Hydrogen--0.25 megabar**
  Wigner, Huntington, 1935
- **High Temperature Superconductivity in Atomic Metallic Hydrogen**
  Ashcroft , 1968
- **Molecular metal at high pressure**
  Harris, Monkhorst, 1971
- **Metastability, liquid at T=0 K**
  Brovman, Kagan, Kholas, 1972-- Salpeter-perhaps unstable to recombination
- **Calculations of the critical pressure for metallization-- 1 to 20 megabar**
  A few dozen published and unpublished calculations by a large number of researchers 1950's to present day-- Difficulty with ZPM, fermion node problem, assumed structures
- **Negative slope in the melting curve; new phase lines in the melt; possible liquid at T=0 K**
  Scandolo, 2003; Bonev et al, 2004; Ashcroft et al-- quantum-classical MD calculation
- **Two component Superconductivity &Superfluidity in high-pressure liquid hydrogen**
  Babaev, Sudbe, Ashcroft-- electron-proton coupling challenge

16 FACETED DIAMOND ANVILS









Highest pressures in solid hydrogen in a DAC ~350 GPa--Not yet metallic!

(Ruoff group; Loubeyre Group)

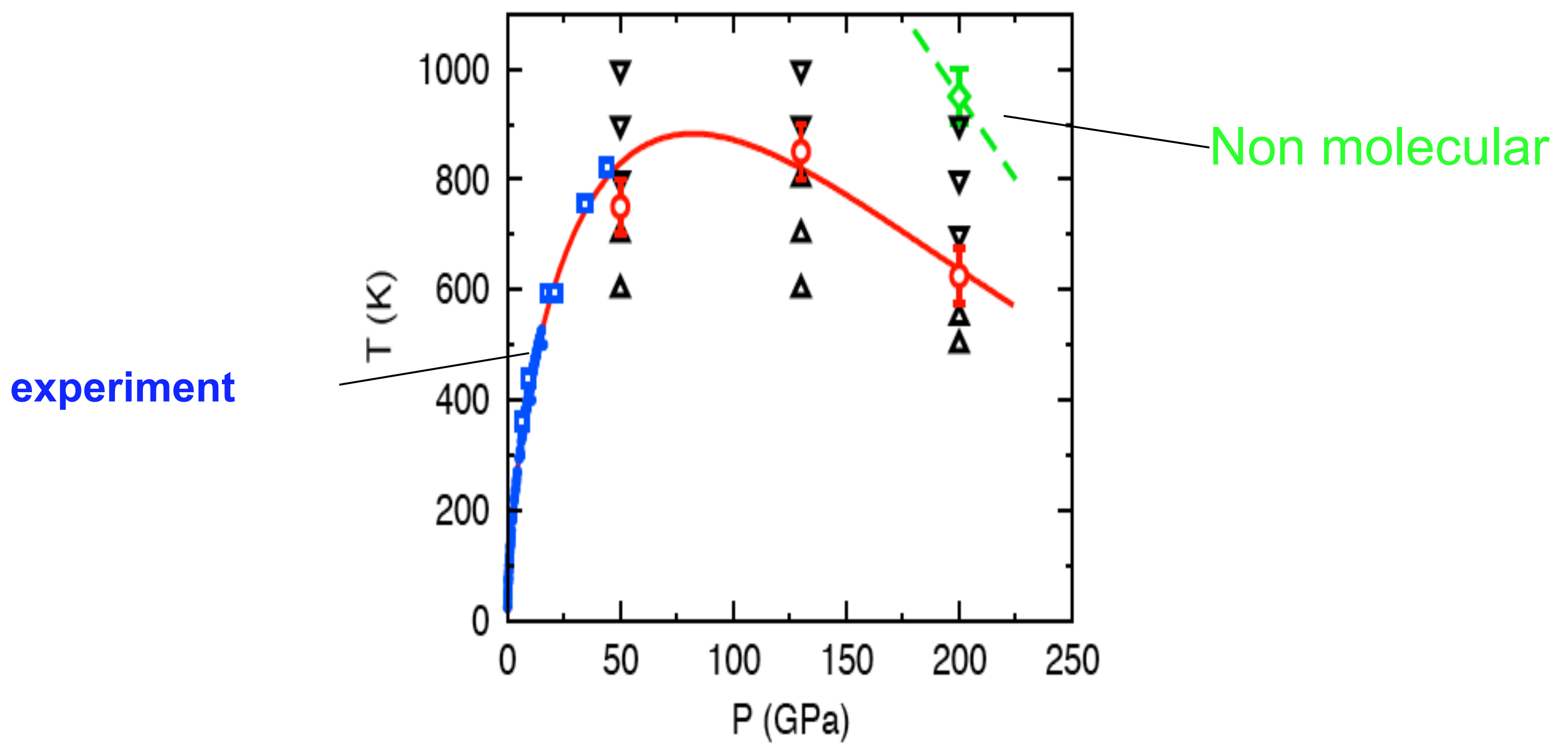
Highest Pressures are achieved with small culet flat diameters

To reach 5 megabars:

Sample sizes-diameters- in a DAC ~5-30 microns

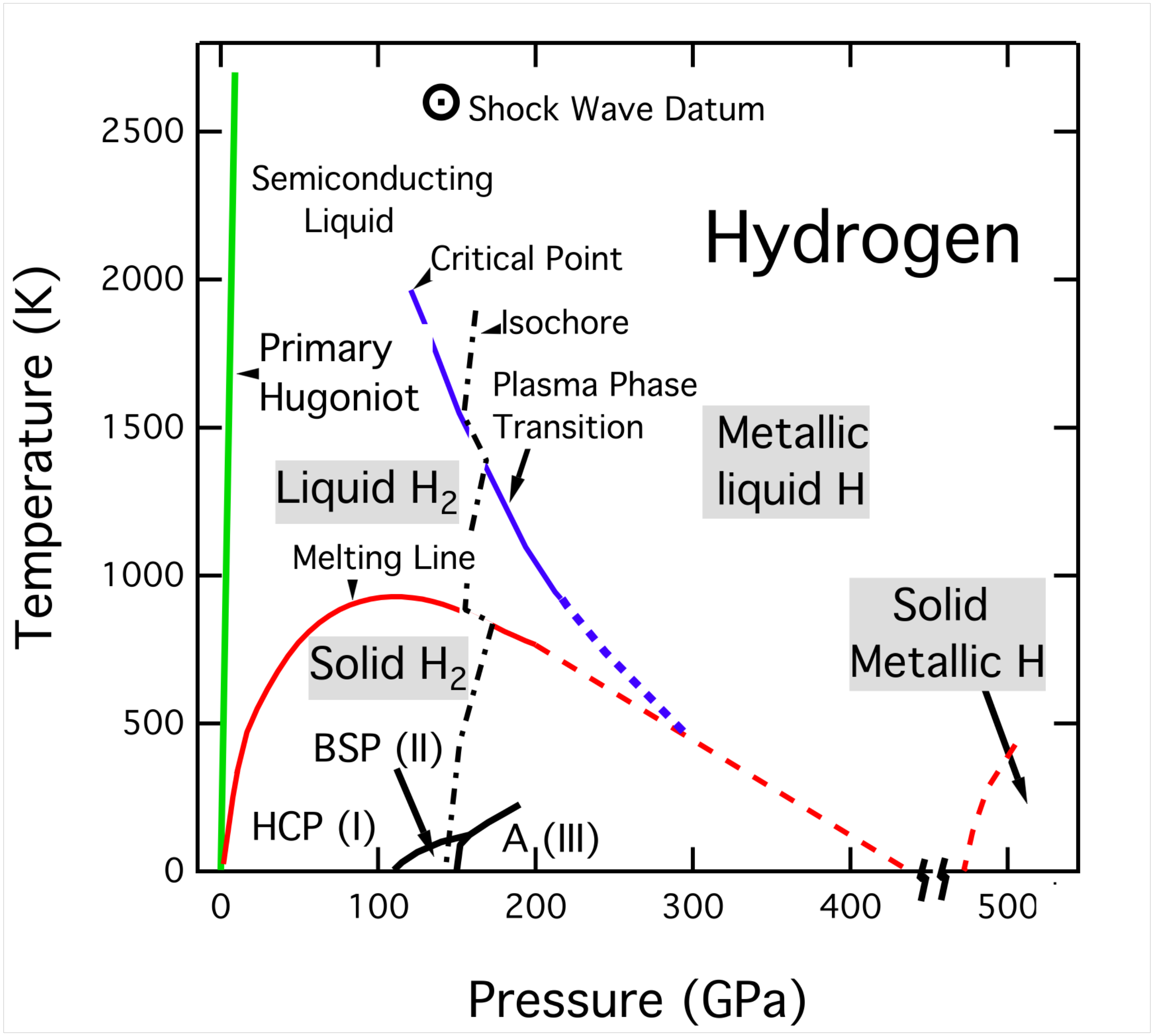
The melting line of hydrogen and the states at very high pressures

Melting line prediction from Molecular Dynamics Calculation



The predicted high pressure melt line of hydrogen. Above the dashed line molecules are predicted to dissociate.

S. A. Bonev, E. Schwegler, T. Ogitsu, and G. Galli, Nature 431, 669 (2004).



Shock Wave Datum
Semiconducting Liquid
Hydrogen
Critical Point
Isochore
Primary Hugoniot
Plasma Phase Transition
Metallic liquid H
Liquid H2
Melting Line
Solid H2
Solid Metallic H
BSP (II)
HCP (I)
A (III)
Temperature (K)
Pressure (GPa)
0
500
1000
1500
2000
2500
0
100
200
300
400
500

Will high pressure hydrogen be an atomic metallic liquid at T=0 K?

Babaev,Sudbe, & Ashcroft predict possible

- Superconducting electrons
- Superconducting protons
- Superfluid properties.

Possible limitations for study of the high temperature melting line.

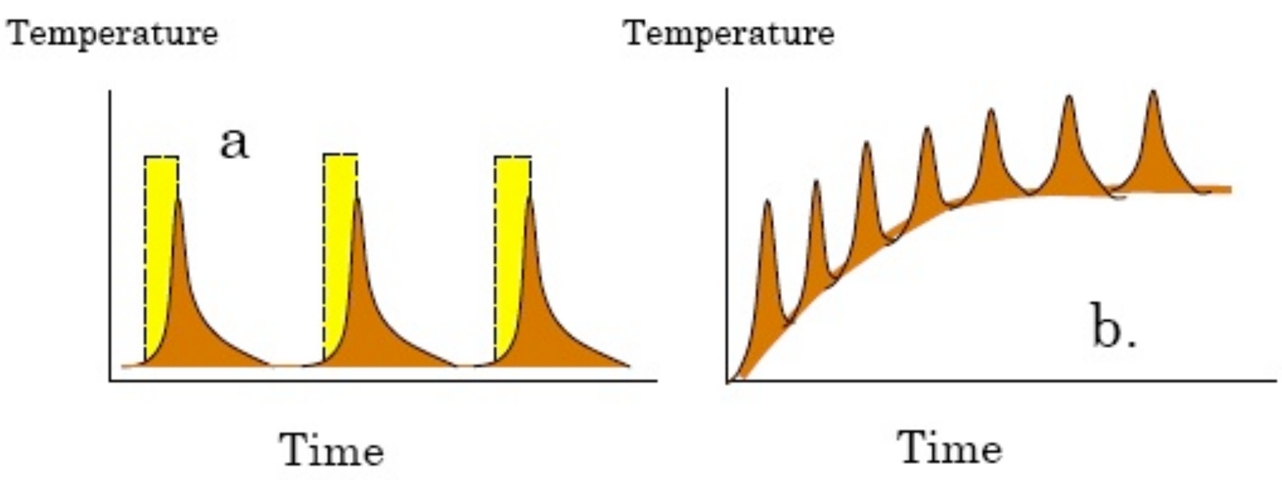
At high temperatures hydrogen diffuses into the diamonds which embrittle and fail.

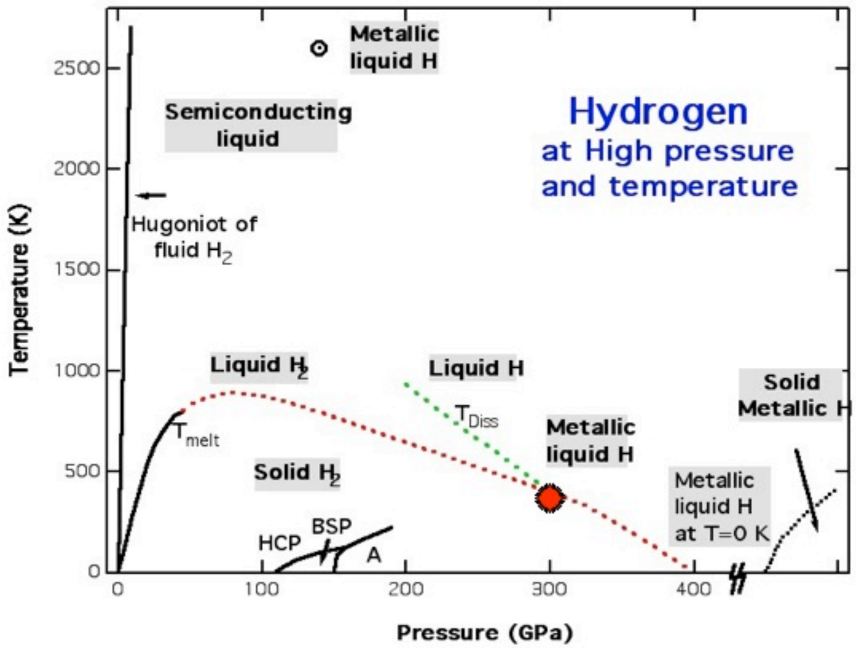
Solution: pulsed laser heating.

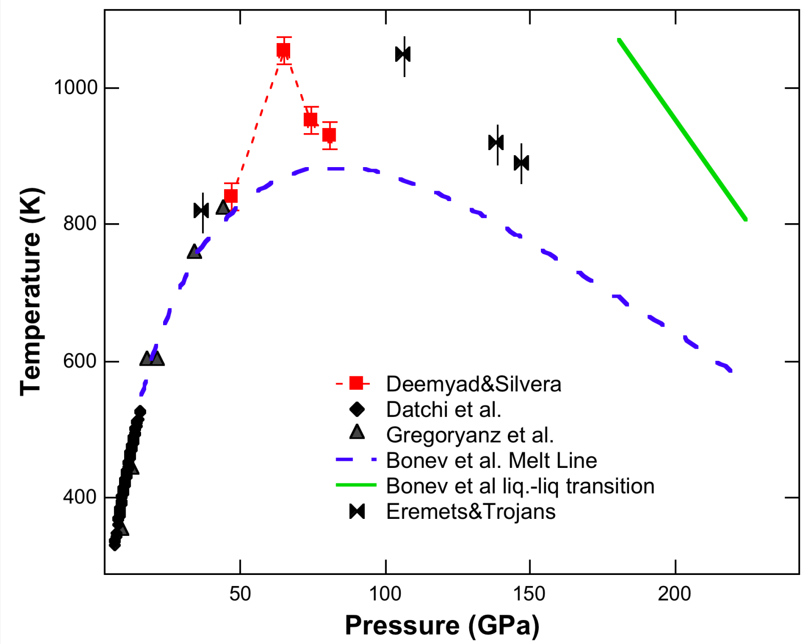
Pulsed laser heating

Sufficient time to heat to local equilibrium;

Insufficient time for diffusion.

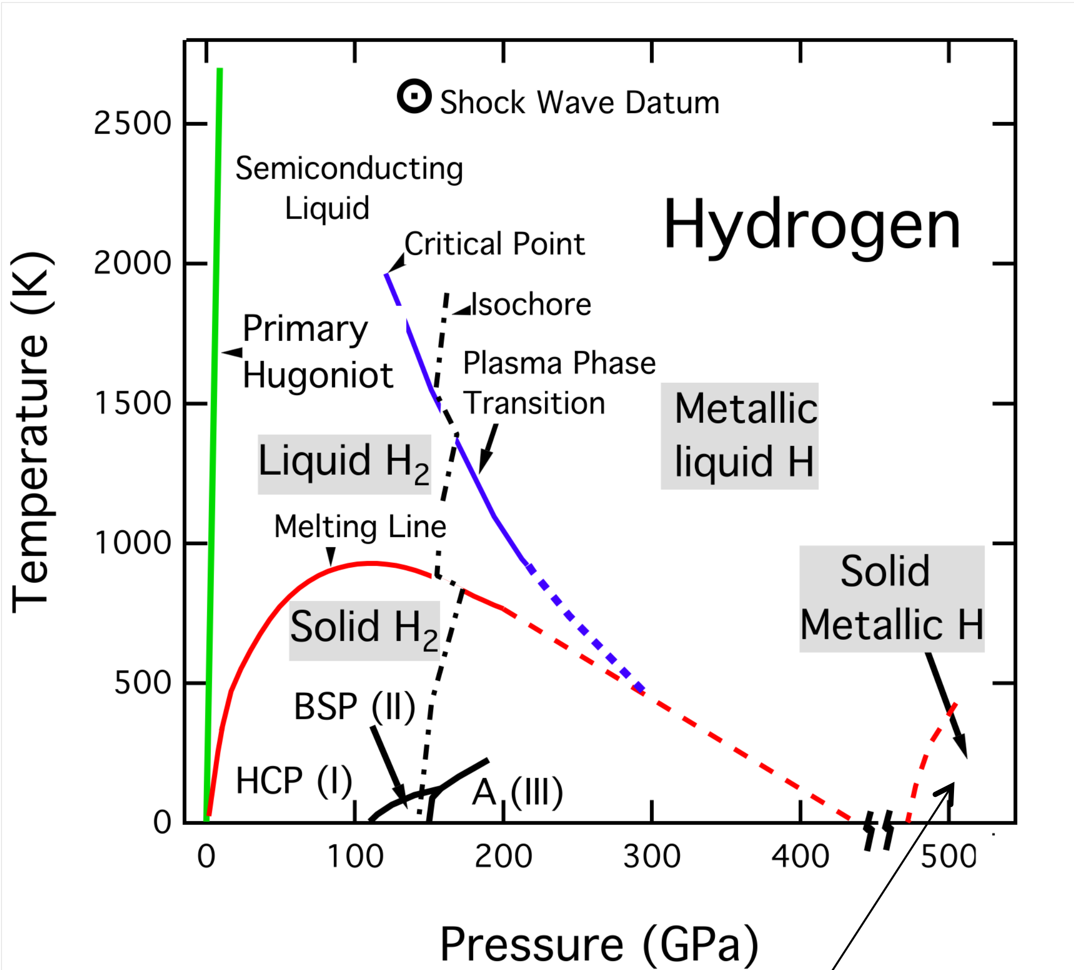






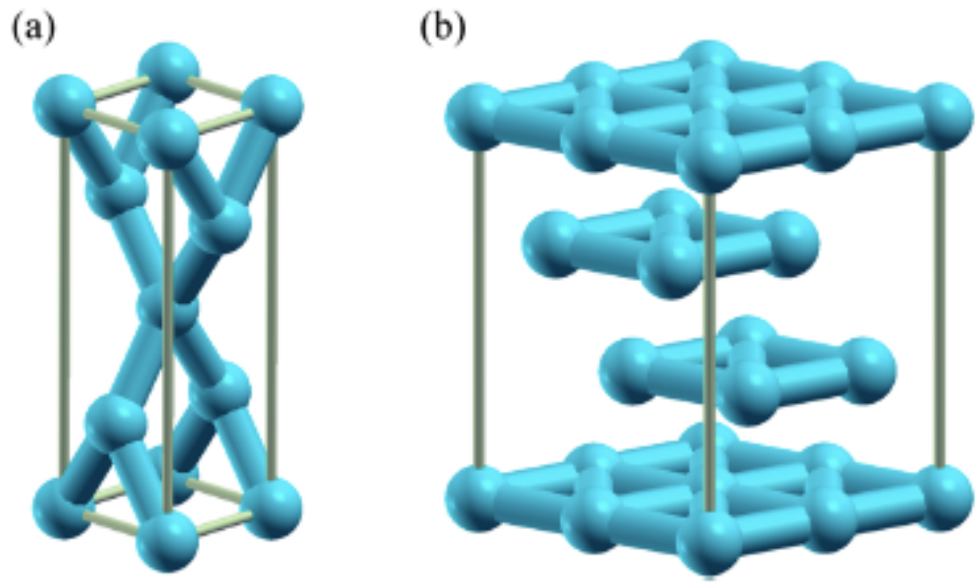
Recent work of Attaccalite and Sorella (filled circle) confirms the extrapolation to 400 K.

Eremets and Trojan have extended the range of the melting line.



Predictions of structures of atomic metallic hydrogen solids using random structure search:

McMahon&Ceperley, PRL 106, 165302, 2011



Structures of the ground-state phases of atomic metallic hydrogen.

(a) Unit cell of $I4_1/amd$ (c=a > 1) at ~500 GPa.
(b) 2 x2 x1 supercell of R-3m at 1 TPa. Fictitious bonds have been drawn for clarity.

The Hydrogens at High Pressure

Unanswered Questions:

Crystal structure of high pressure

molecular phases

Molecular or atomic

Insulating or metallic

Liquid at high pressure and T=0 K

Crystal structure of atomic metallic phases

Superconducting or normal metal

Superfluidity

Challenges to be met by the new ERL x-ray source:

Assuming samples pressurized in DACs and sample sizes very small

Static Measurements

- Structure of BSP for H2, HD
- Structure of the A-phases
- Structure of metallic hydrogen

Dynamic measurements

Synchronize x-ray pulse to laser heating pulse:

Determine high Pressure-high Temperature

- Structural Phases
- Melting
- Molecular-atomic dissociation line
- Metallic? Superfluid?

The End