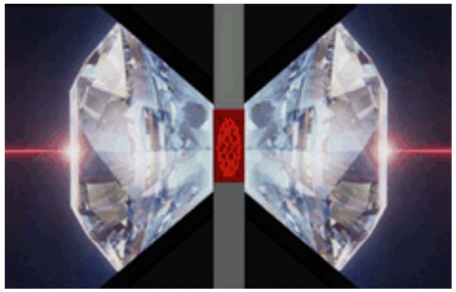
Solid Hydrogen at High Pressure

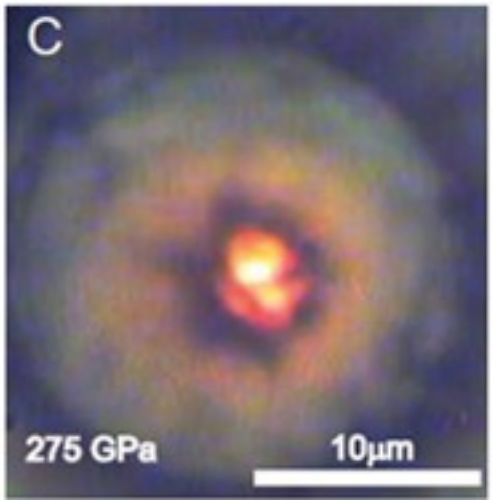
Raman Spectra from Molecular Dynamics

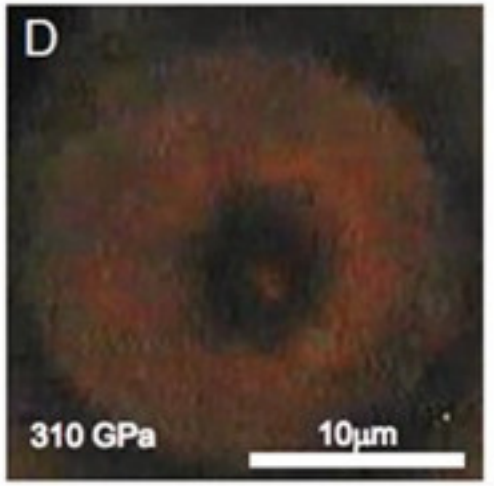
CSEC, SUPA, School of Physics and Astronomy, The University of Edinburgh, UK

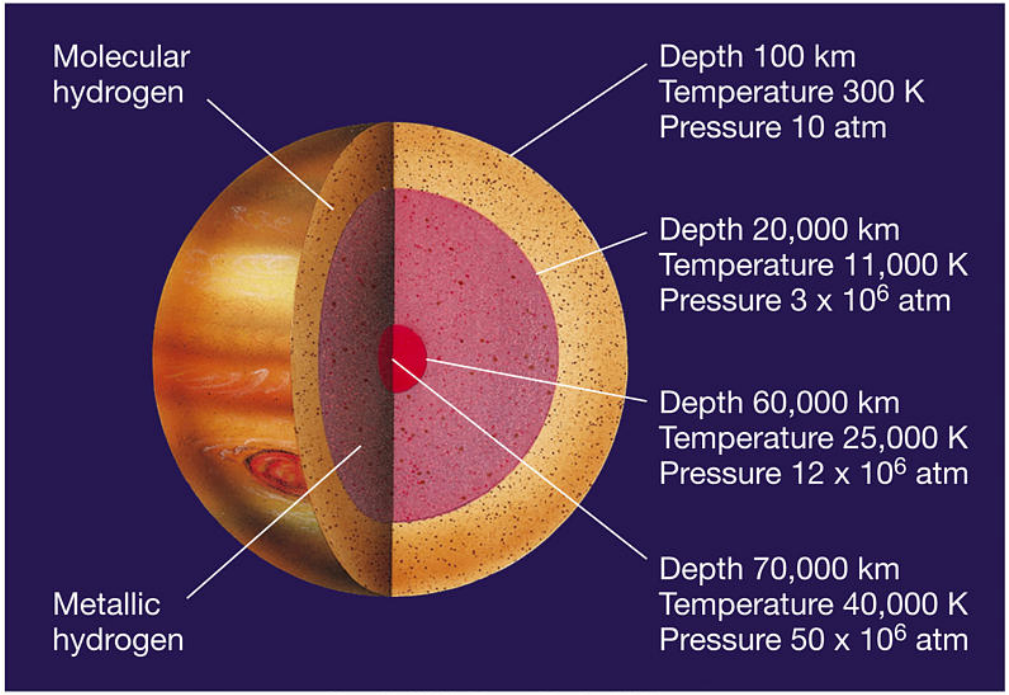
Two ways to make (metallic?) high pressure hydrogen

Diamond Anvil Cell

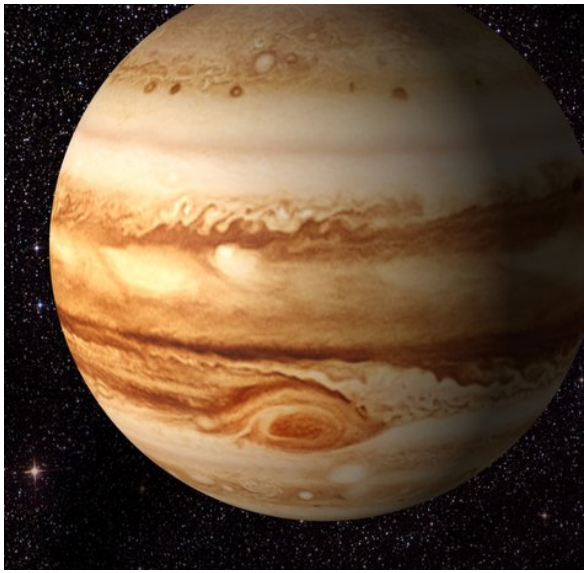








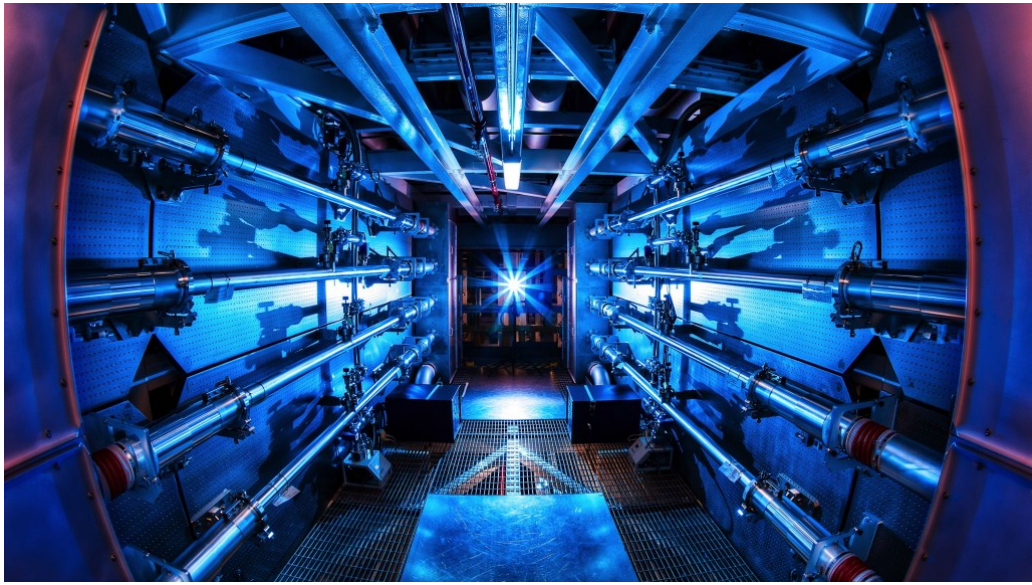
Large Planet

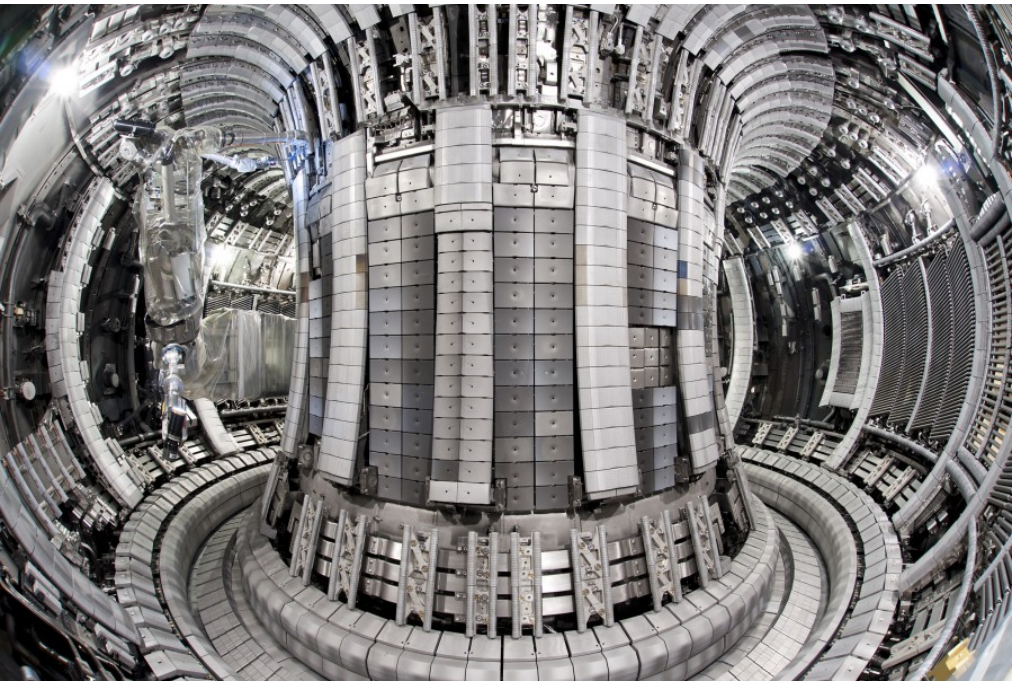


Two ways to make (metallic?) high temperature hydrogen

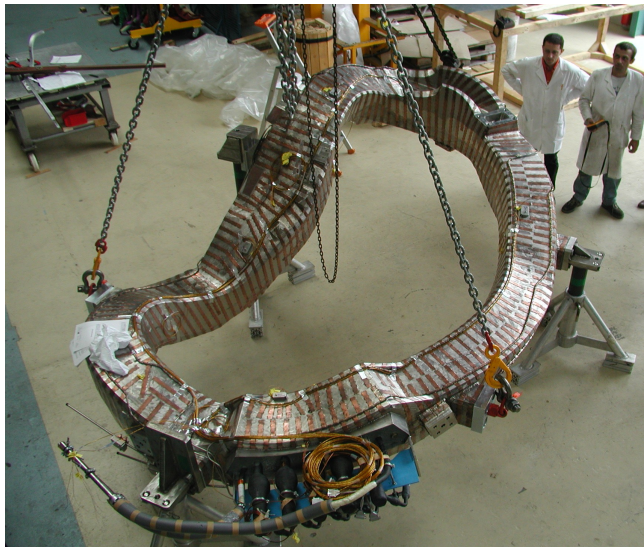
National Ignition Facility

Shock waves
Laser Heating

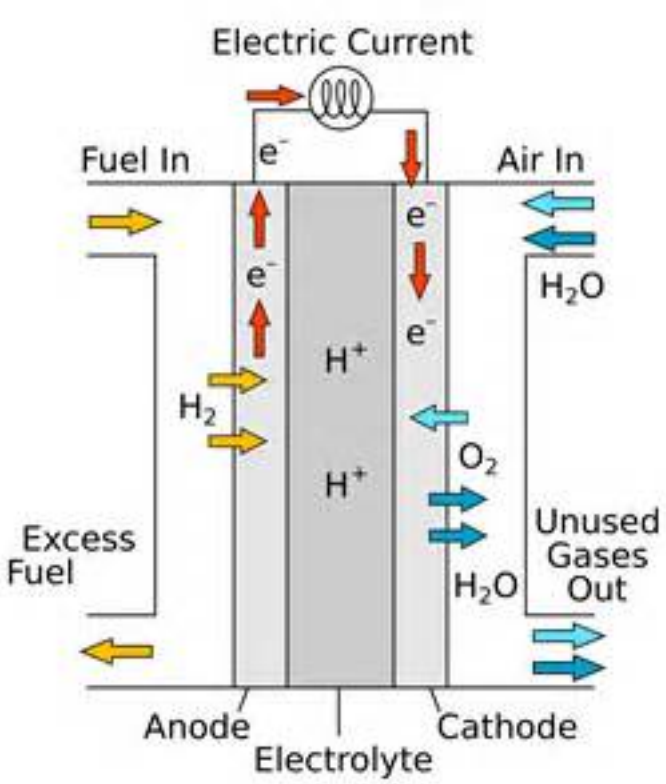




Inertial confinement Fusion
Tokamak Stellarator



Or just as fuel



Hydrogen (protons) flows one way to react with oxygen. Electrons go the other way round a circuit.

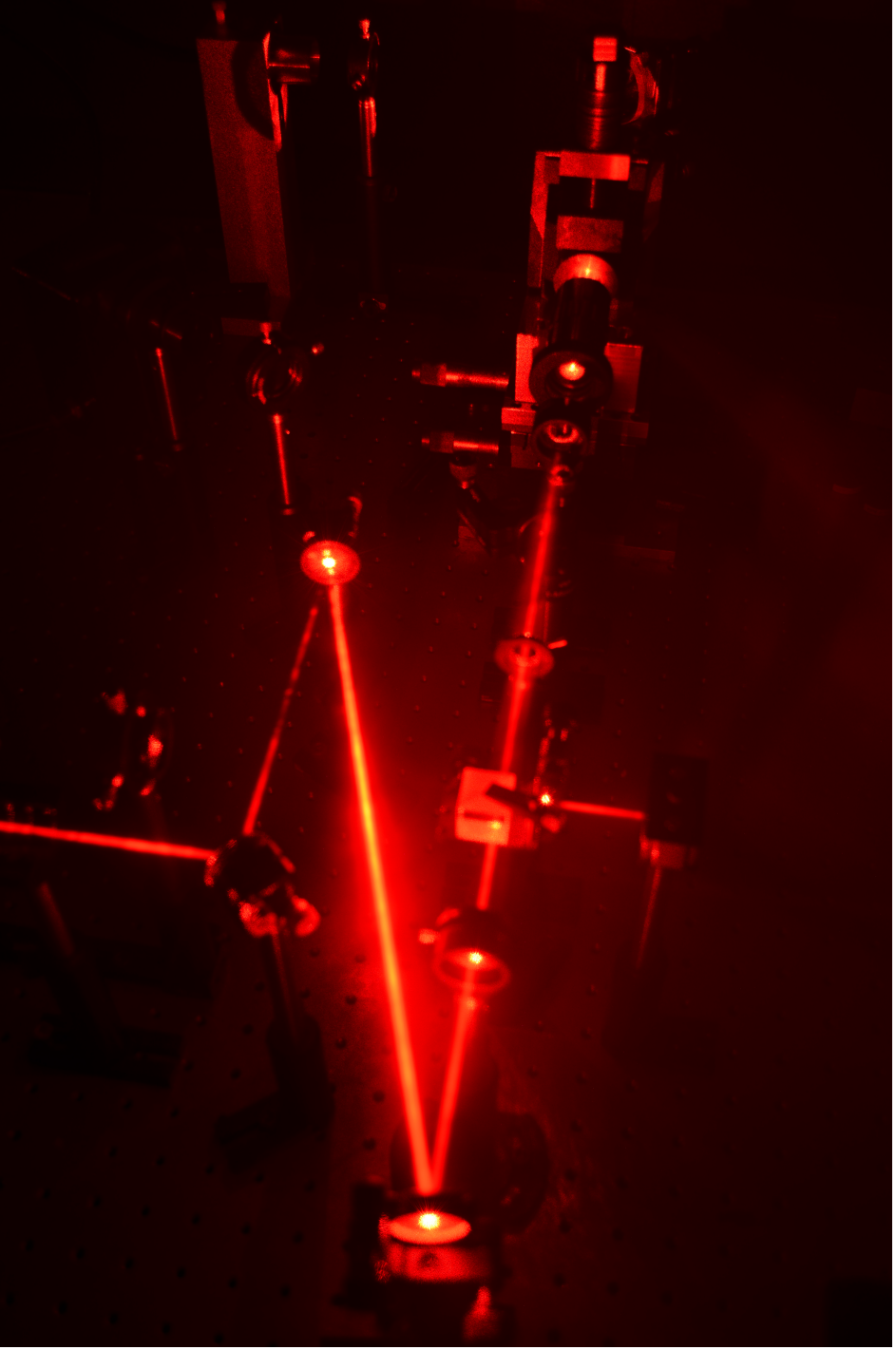
How to study it: Big facilities

X-rays (ESRF, Grenoble)

Very weak scattering from electrons
May not even be on the atoms

Neutrons (SNS, Oak Ridge NL)

Large samples needed
Cannot yet reach high pressures



How to Study it

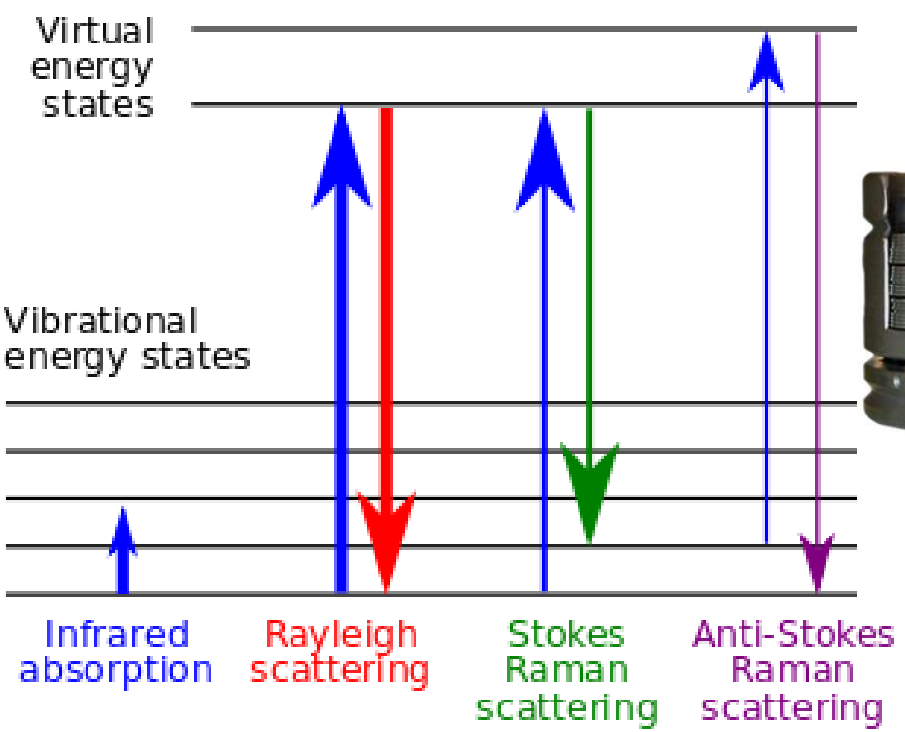
Raman & IR Spectroscopy

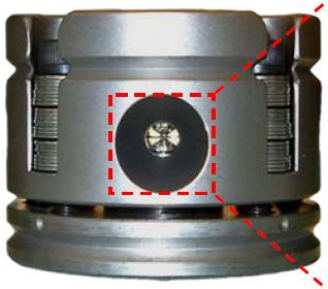
Laser beam in

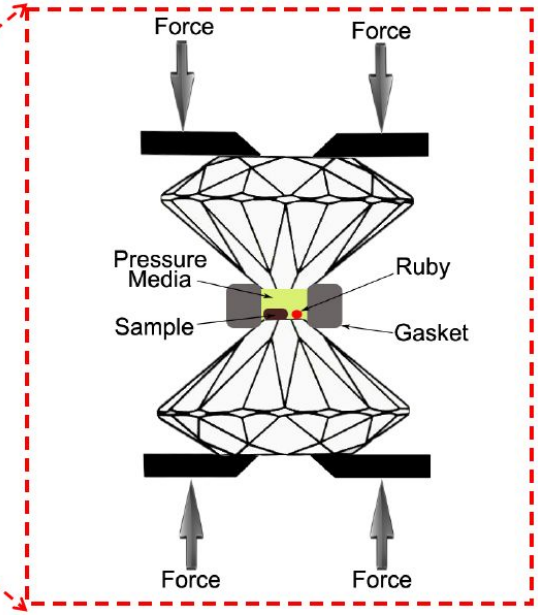
Spins a molecule around/sets up a vibration

Light absorbed (IR) or comes out at different colour. (Raman)

Raman Spectroscopy –Diamond Anvils







Raman Spectroscopy – shift in frequency of laser

Only detects zero-momentum modes with high polarizability

Quantum Spectroscopy

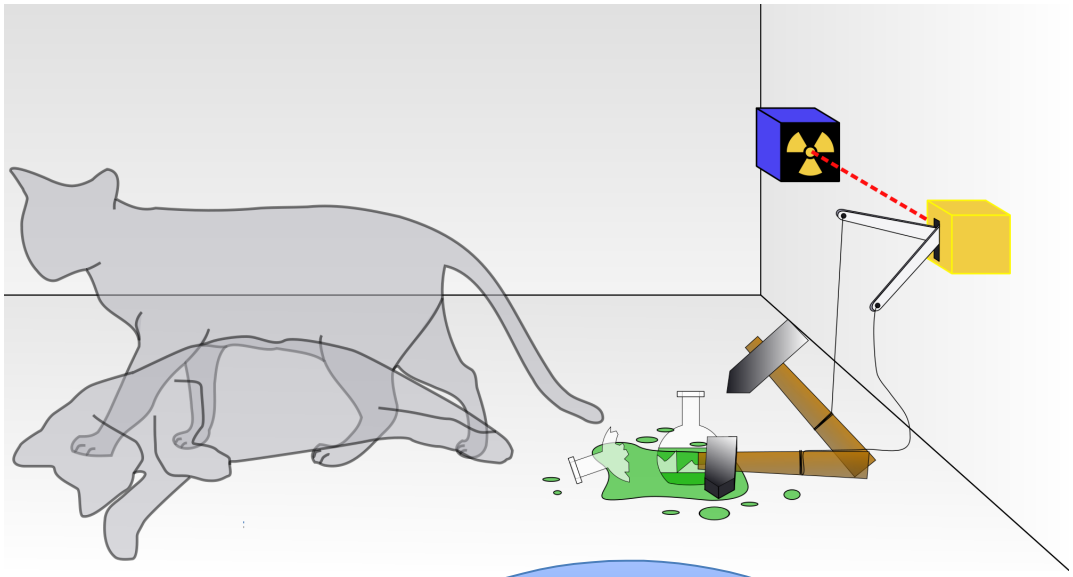
Energy comes in distinct lumps: *quanta*

These lumps of energy come out of the laser beam

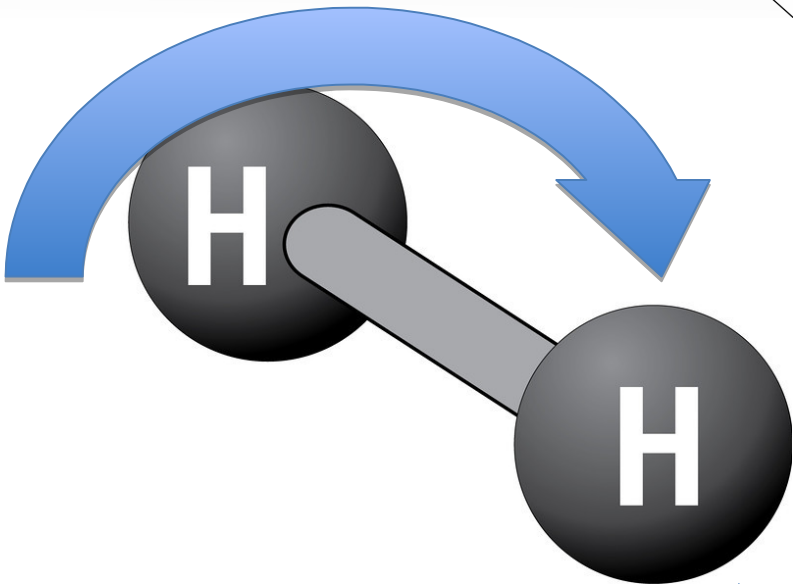
Some *photons (quantum light particles)* have lower energy than input.

The *quanta* are characteristic of the material

Quantum Phase I – nothing is real until measured

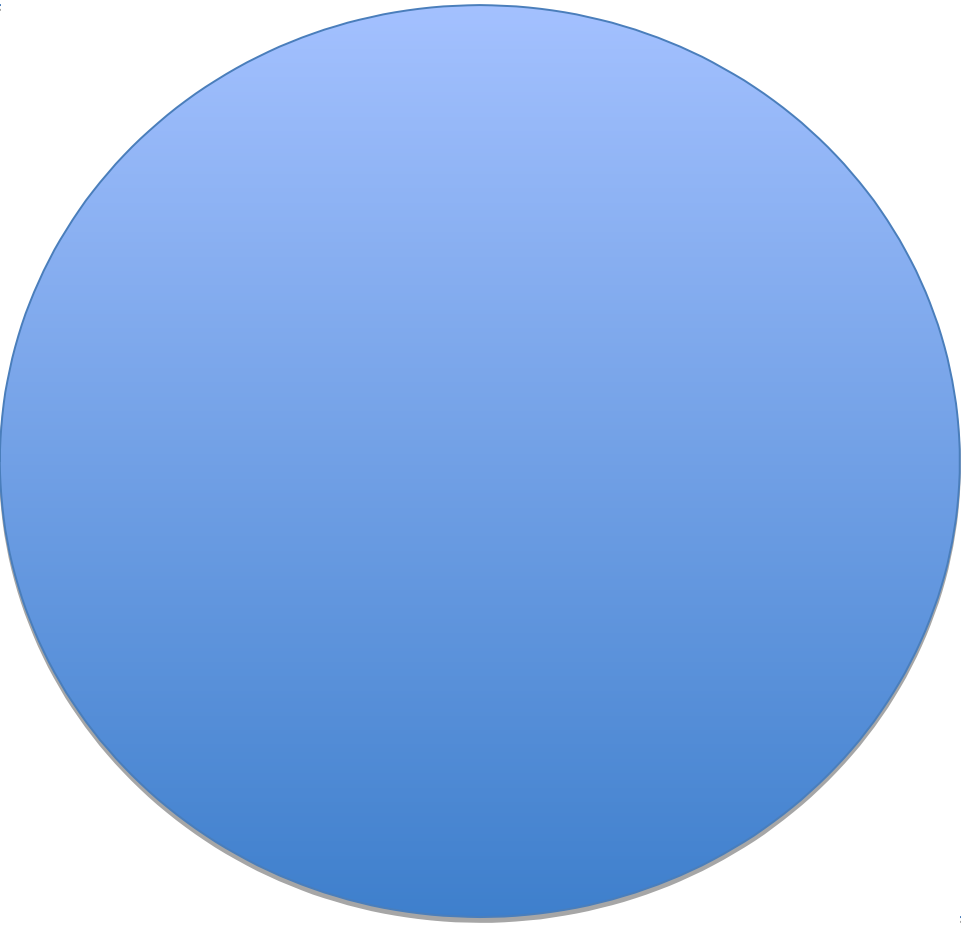


Is the cat dead or alive?



Which way does the hydrogen molecule point?

A picture of H2 molecules



And how to pack them together Phase I

"On the Possibility of a Metallic Modification of Hydrogen"

- Wigner and Huntingdon, 1935, using

Nearly free electron screening…

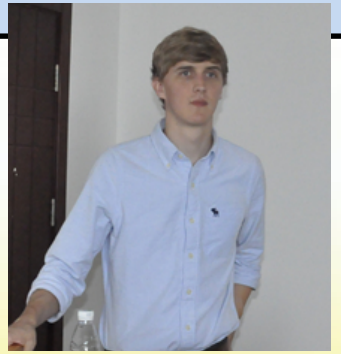
Predicted metal hydrogen around 12-fold compression, in a layered structure.

The body-centered modification of hydrogen cannot be obtained with the present pressures, nor can the other simple metallic lattices. The chances are better, perhaps, for intermediate, layer-like lattices.

25GPa Pressure, which is what the paper is now cited for, mentioned as an afterthought in the paper (actually says 25GPa to infinity)– no density units.

We are now approaching 12-fold compression

Prizewinning Edinburgh students



form stable at *any* pressure. One calculates easily, that even under the assumption of the most advantageous compressibility at high pressures, the pressure necessary for the transformation is 250,000 atmos., which is outside the scope of the present technique.

DECEMBER, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

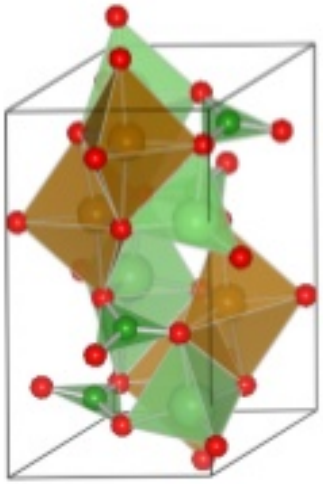
On the Possibility of a Metallic Modification of Hydrogen

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

(Received October 14, 1935)

PPT bingo!

The obligatory Density Functional Theory Slide



+

+

$$i\hbar\frac{d\Psi(\{r_i\};t)}{dt} = \hat{H}\Psi(\{r_i\};t)$$

$$H = \sum_{i=1}^{N_e}\nabla_i^2 + \sum_{i=1}^{N_e}V_{nuclear}(r_i) + \sum_{i=1}^{N_e}V_{effective}(r_i)$$

DFT is a method to solve for the electronic structure and energetics of arbitrary materials starting from ***first-principles***.

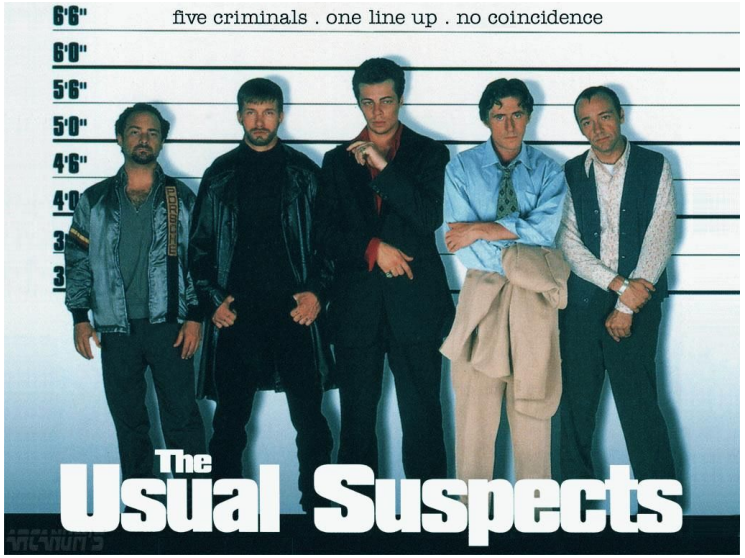
In theory, it is ***exact*** for the ground state. In practice, accuracy depends on many factors, including the type of material, the property to be studied, and whether the simulated crystal is a good approximation of reality.

DFT resulted in the ***1999 Nobel Prize*** for chemistry (W. Kohn). It is responsible for 2 of the top 10 cited papers of all time, across all sciences.

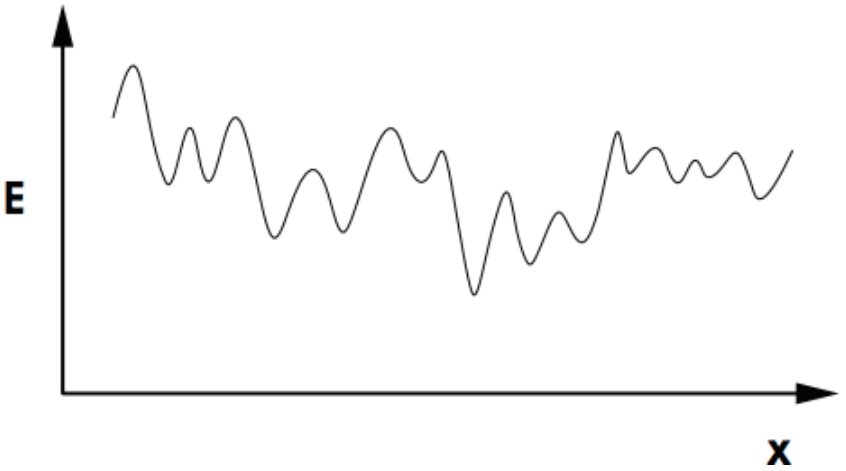
Structure Search – How hard can it be?

There are 219 distinct space groups.

Each allows *n* atoms, on many distinct positions



Find a minimum in Rough energy landscape In *3n* dimensions



No general method exists. Since 2007 use AIRSS –
random searching + massive computation.

Experiment alone cannot determine H2 crystal structure
Enter theory: Structure Search

- Put some atoms in random positions in a periodically repeating cell
- Calculate energy according to Quantum Mechanics (DFT)
- Relax positions to local minimum
- Surprisingly few structures are found

- Calculate the properties they would have: lowest free energy wins!

These calculations can take weeks: Even using the UK's top supercomputer at EPCC

Problem: Zero point energy

$$E = (n + 1/2)\hbar\omega$$

$$\omega = \sqrt{k/m}$$

Covalent bond – k large

Light atom – m small

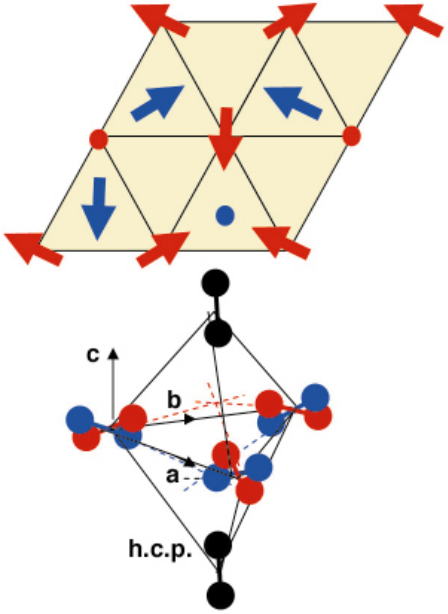
ZPE is about 0.1eV/atom (1200K)

Enthalpy differences between structures are about 0.01eV/atoms

Structure search without ZPE: only provides candidates.

Try not to pick the muppet.

Solid hydrogen



Below 20K or above 20GPa

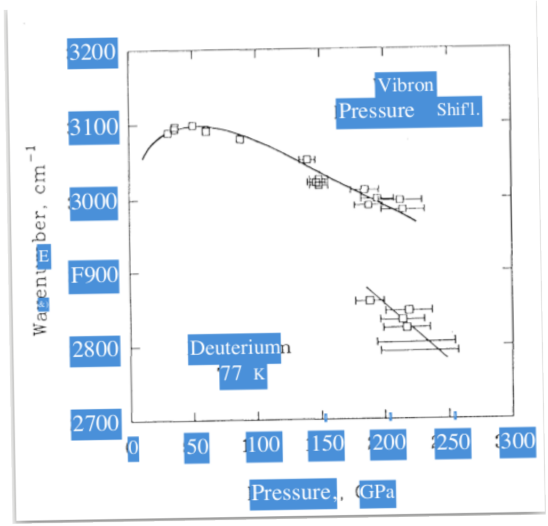
Phase I Spherical objects: close packing

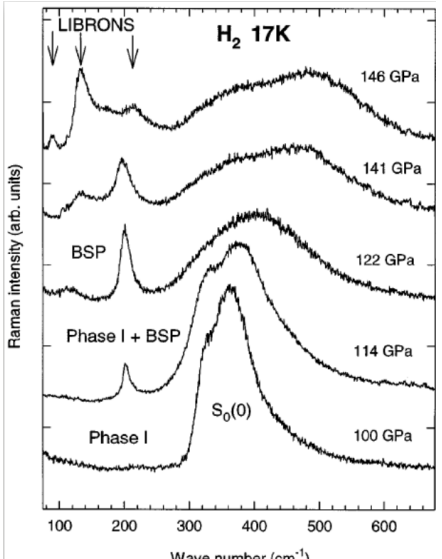
Phase II “Broken symmetry” phase

Rotors stop rotating…

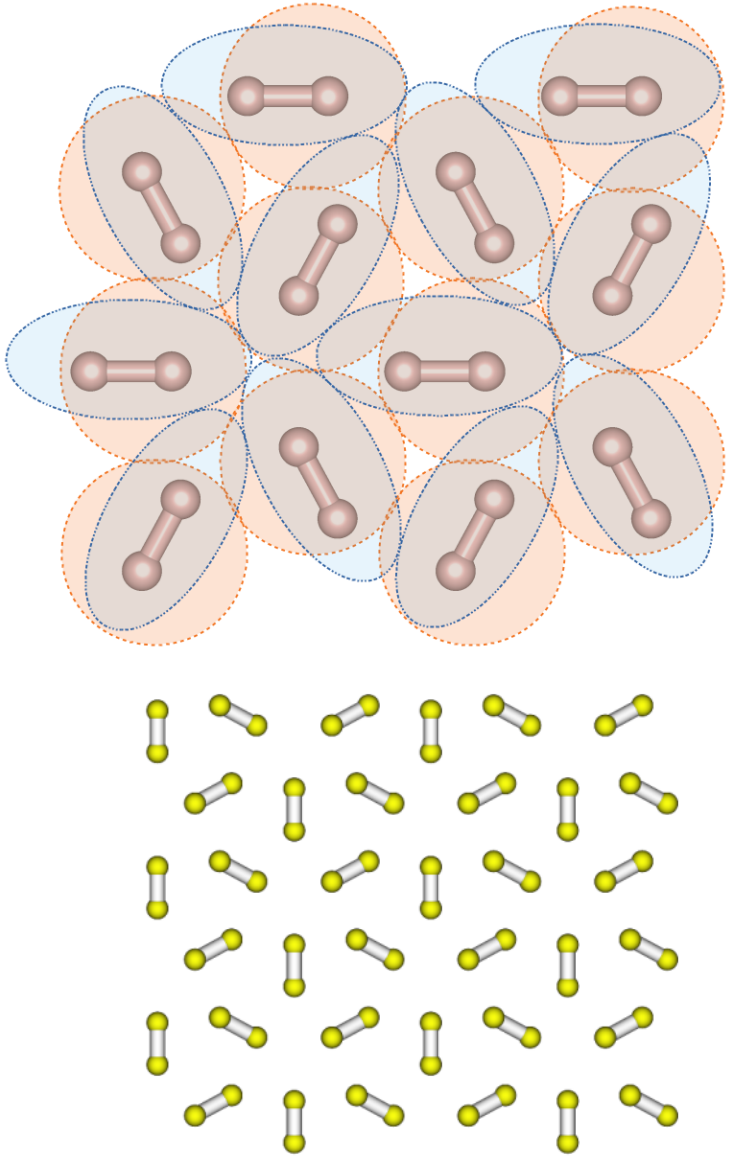
Discontinuities in vibrational frequency

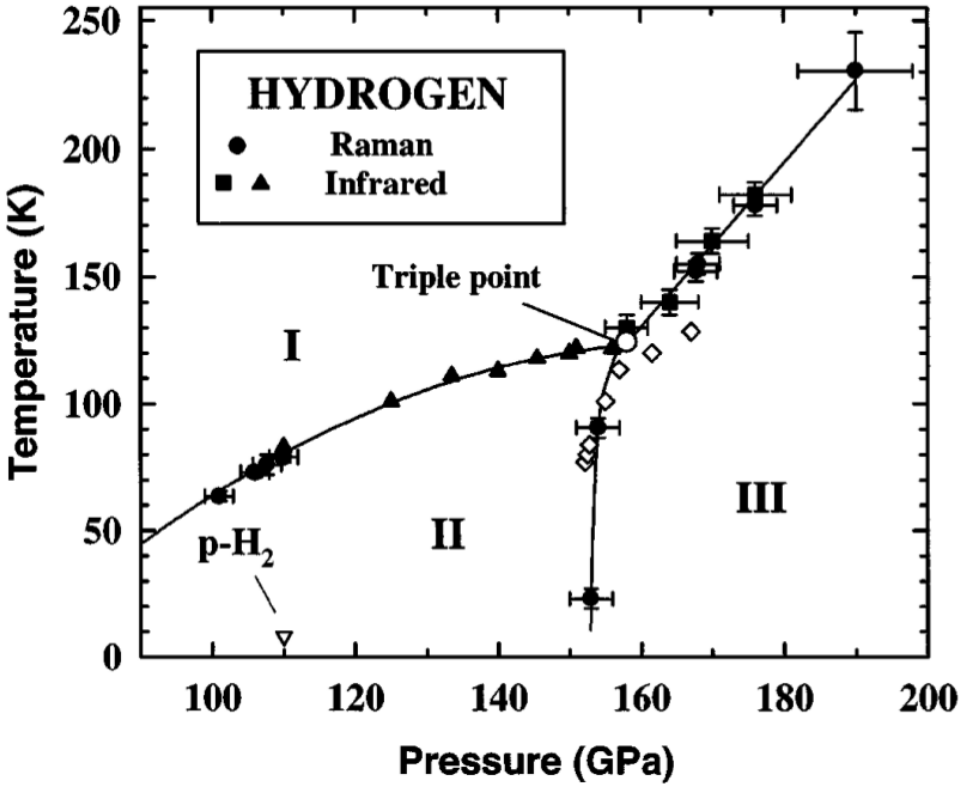
X-ray still looks like hcp





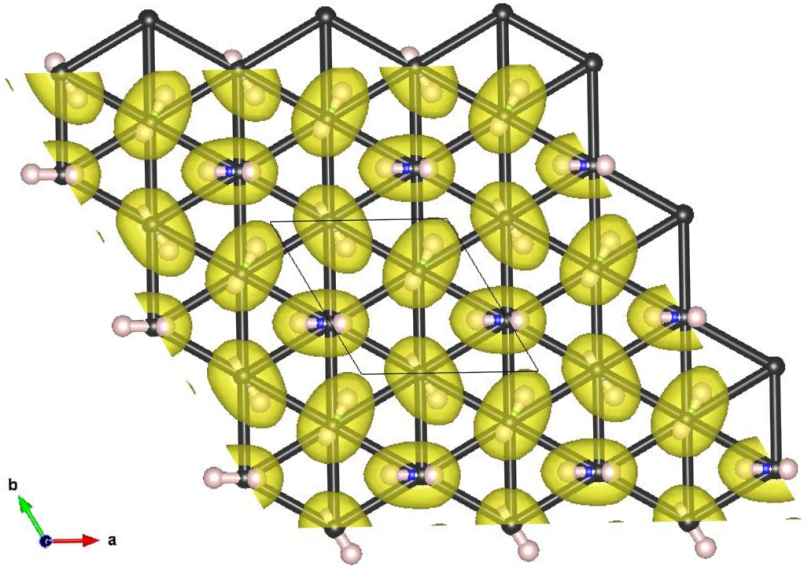
A New Phase III at 150GPa



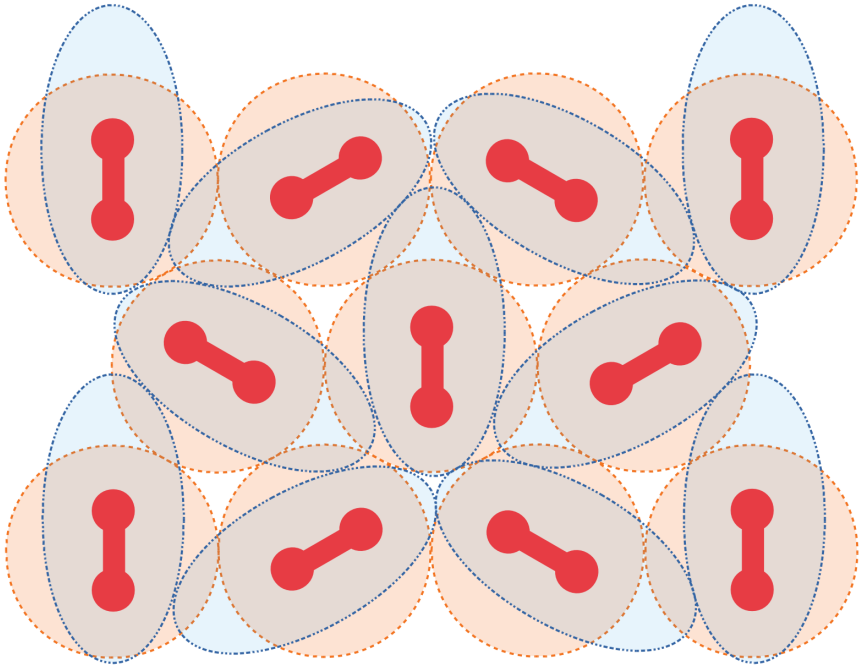


Heroic synchrotron X-ray
(read – terrible data quality)
Still looks like hcp

Phase III Where are the atoms & electrons?



Close-packing of Molecules. Electron distribution still centred on covalent bonds



Atoms only – appear to be forming hexagonal rings. “Graphene layer”

Experiment: Very strong IR signal, suggests molecules have acquired a dipole moment. X-ray looks slighly distorted hcp

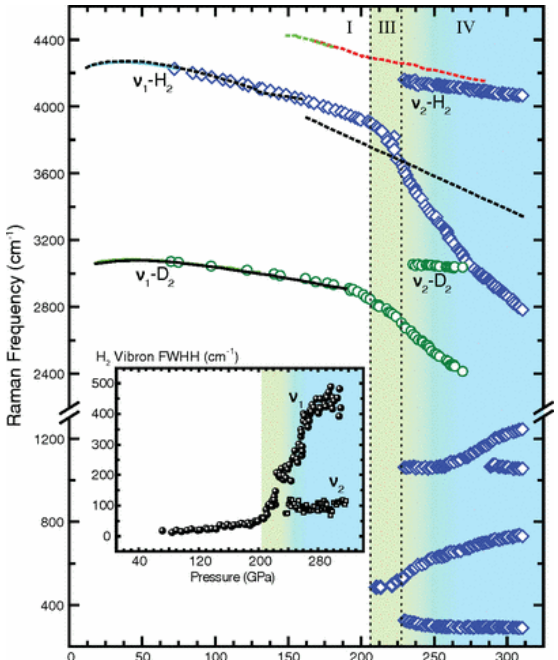
Structure: Still unknown, likely candidates from AIRSS by Pickard et al.
Not a metal, but electrons escaping from the covalent bond

2012 CSEC finds Phase IV at 220GPa/300K

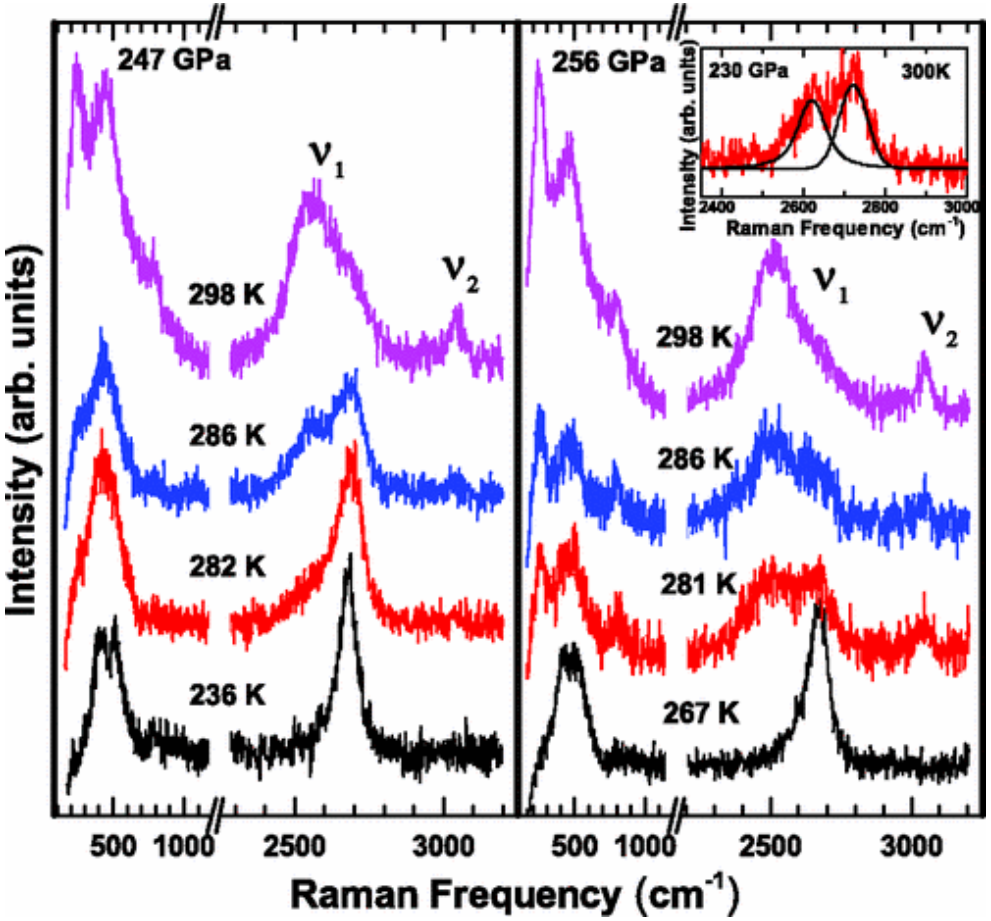
Observed by Eremets in 2011, but claimed as “conductive hydrogen”.

Characterised by two vibrons: two types of molecule.

Structure type predicted by Pickard & Needs in 2007 (Supplemental material)

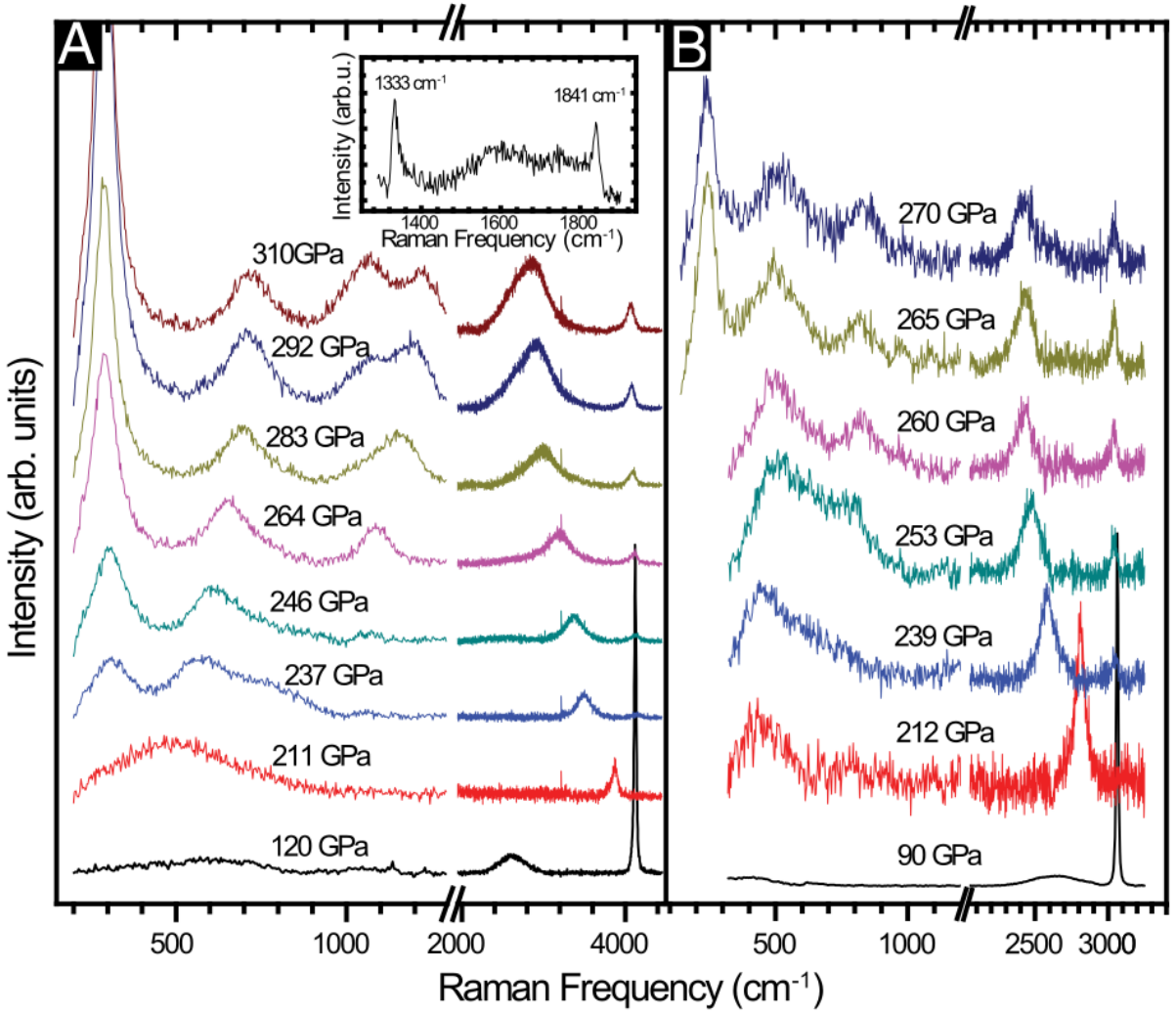


Howie, Gregoryanz et al



Great science - two terrible titles:
Mixed atomic and molecular phase.
Proton tunnelling in hydrgoen and deuterium

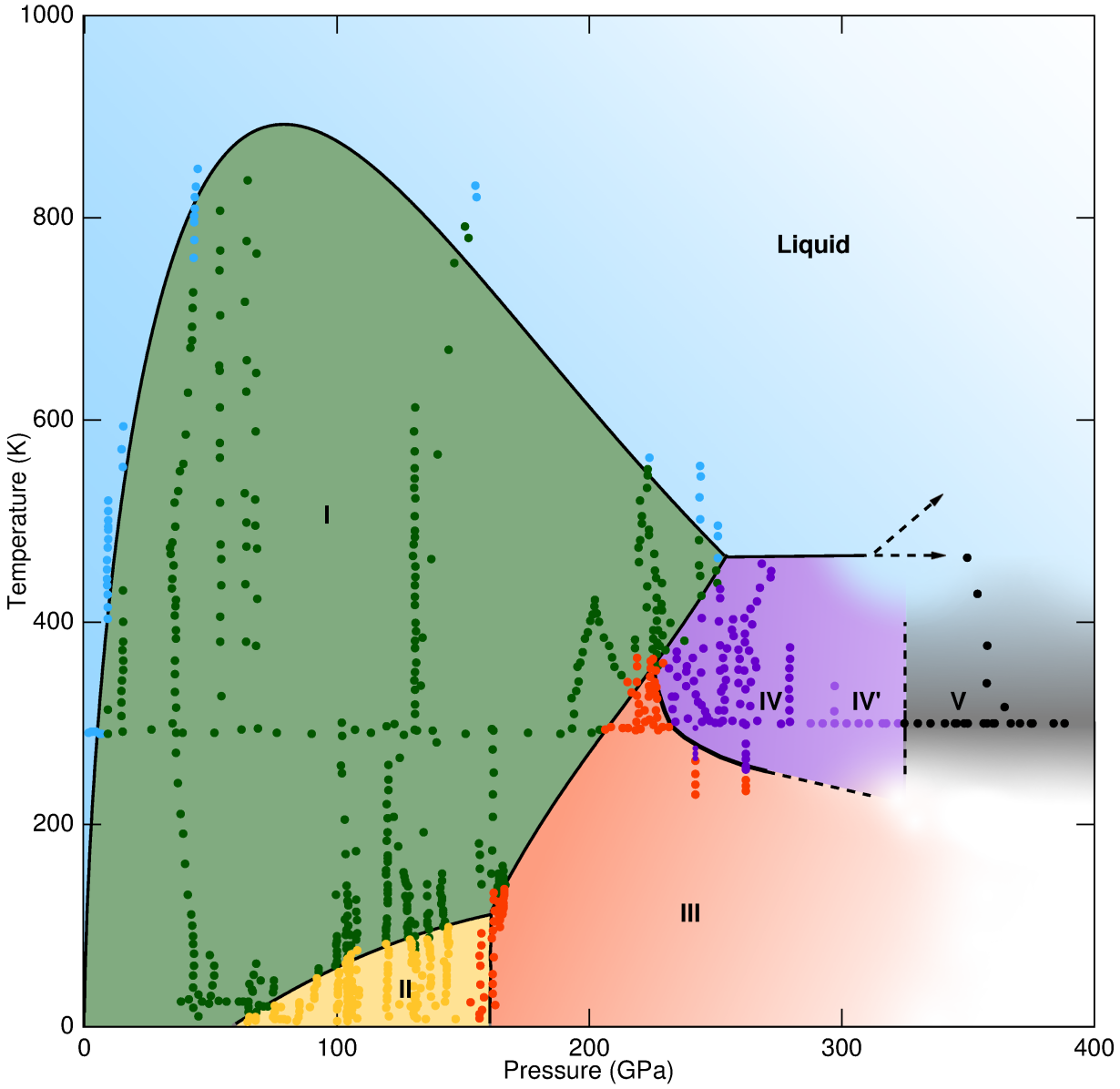
2015 – Edinburgh claims a New Phase V



A: Hydrogen
B: Deuterium

Phil Dalladay Simpson
Howie, Gregoryanz

Melting Curve



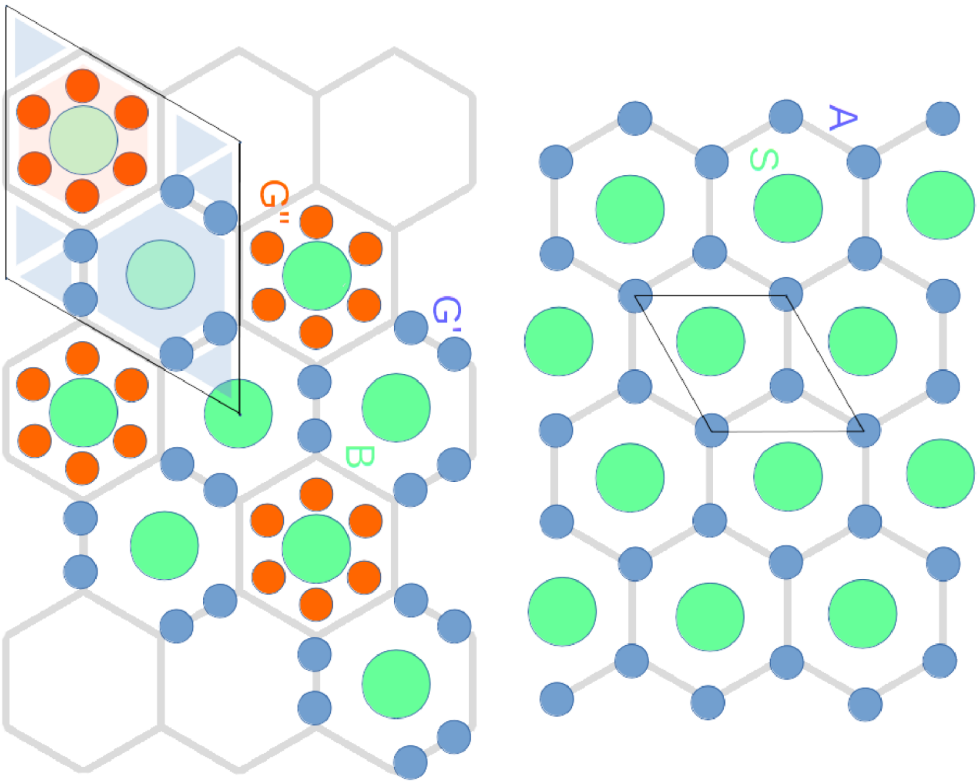
Predicted that H2 would become a liquid at zero-T on account of ZPE. (Ashcroft)

Calculated to have a maximum using DFT and classical protons (Bonev & Galli)

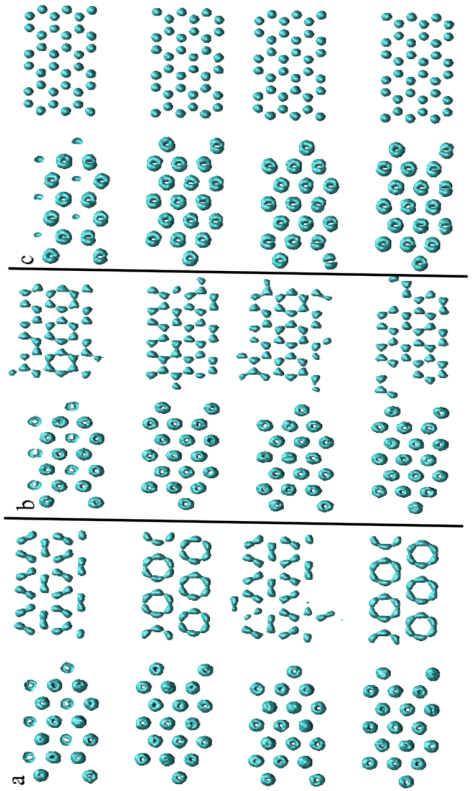
Measured to have a maximum (Howie & Gregoryanz)

Calculated to have a minimum at 300GPa Using DFT and classical protons (Geng)

Theory of “mixed” phases IV & V



This structure is the most efficient way to pack spheres of two different sizes.



Time Averaged positions

Half the molecules are continually reorientating (green).

The other molecules occupy 1/3rd of the edges (blue)
Or as trimers occupy 1/3 of the cells (red)
Or as atoms occupy all the vertices.
https://www.youtube.com/watch?v=x5WpbRCoHfU

Non – metallic phases of hydrogen

Three types of “hydrogen”

Free rotor (large, high entropy)

Rodlike (low volume)

Dissociated (lower volume),

interacting only by covalent bonds or quadrupole moments in Phase II

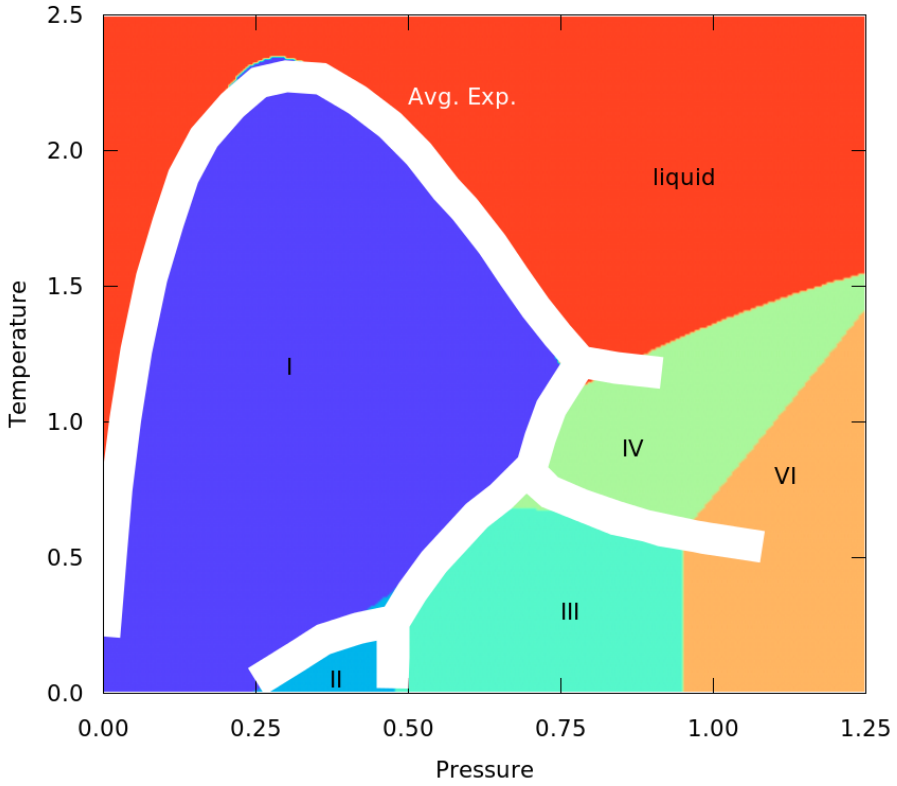
Phase I – Free rotors, hcp

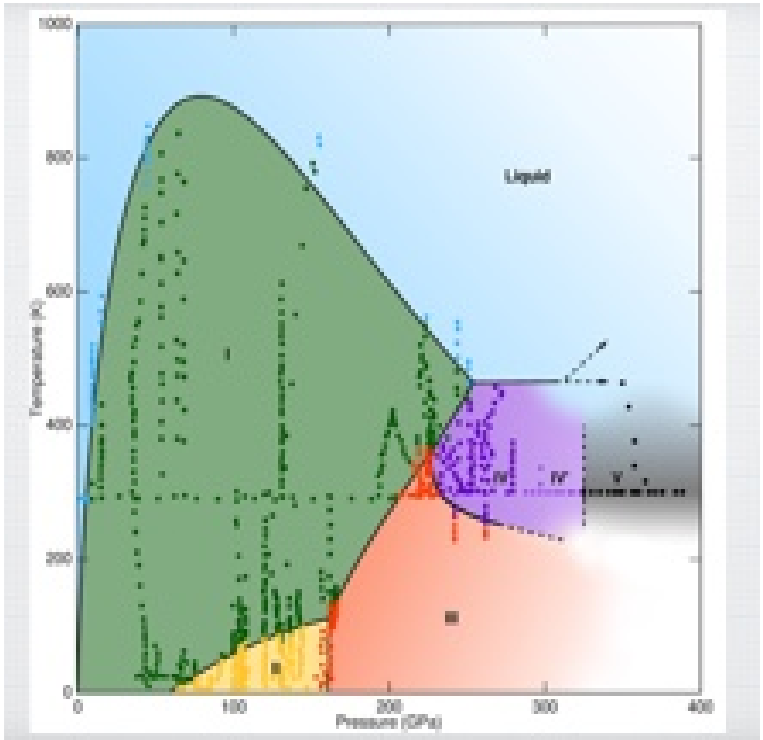
Phase II – rods + quadrupole moment

Phase III – rods, efficiently packed

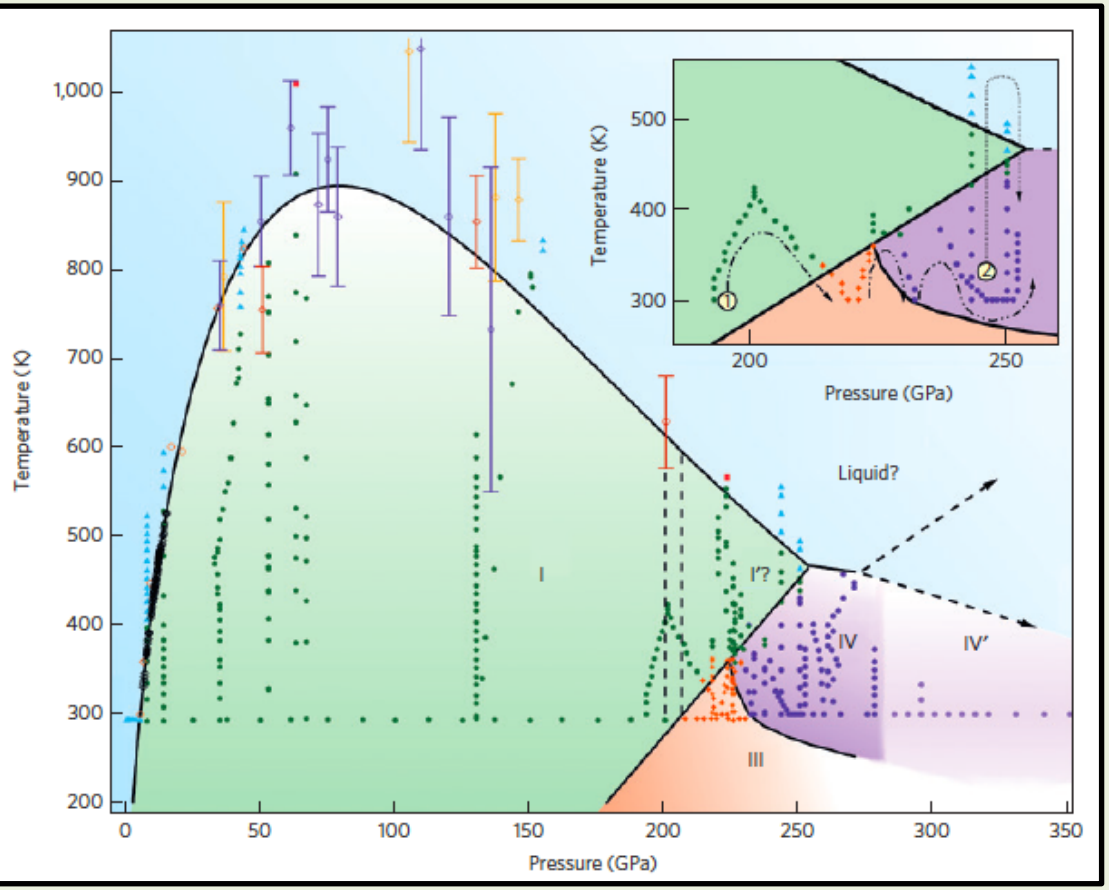
Phase IV – rotors & rods, efficiently packed

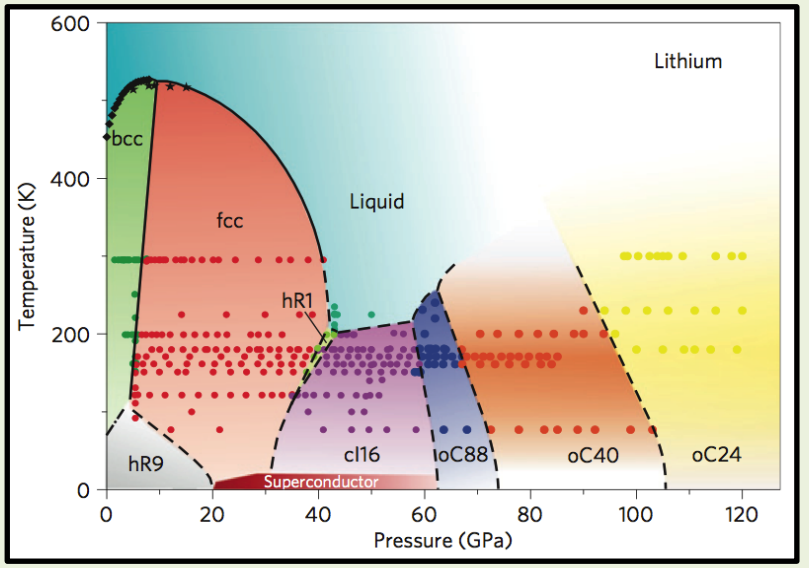
Liquids – mixture of all 3 types.



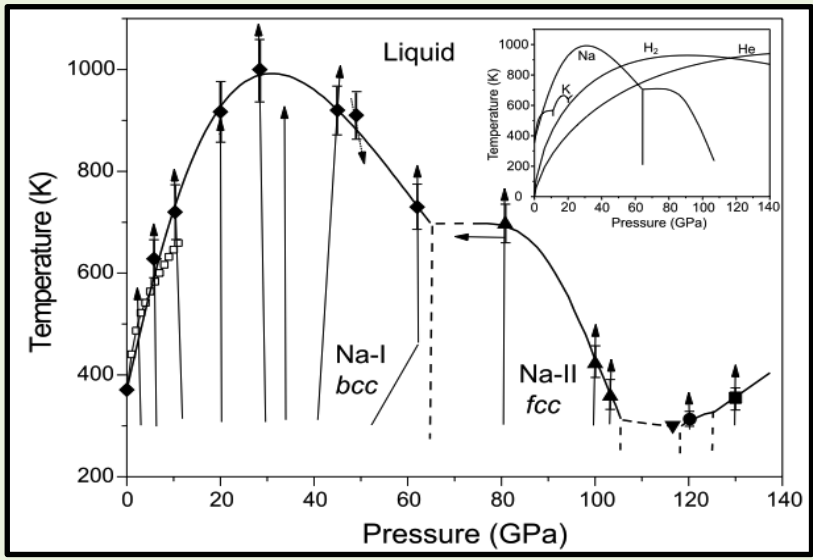


Is hydrogen an alkali metal?





Li – Guillaume et al.



Na – Gregoryanz et al.

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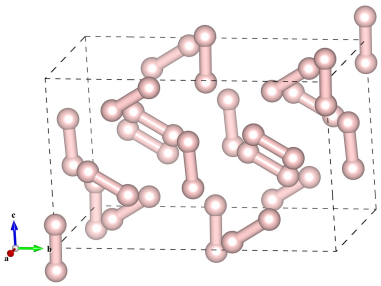
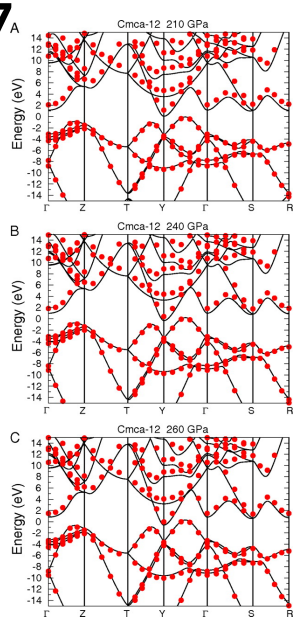
We are now approaching 12-fold compression

Predictions of Metallic Hydrogen

- Lots of structure search work since 2007 three scenarios.





1/ Molecular metal (Cmca)

2/ 2D metal layers (c/f Phase IV)

3/ Atomic metal (I4amd)

Predicted Properties of Metallic Hydrogen

Room Temperature Superconductor.

Quantum liquid to zero temperature.

Hydrogen storage material.

Super rocket fuel.

Protection against vampires.

Room* Temperature superconductor

In 2015, Mikhail Eremets found superconductivity at 200K in hydrogen sulphide.

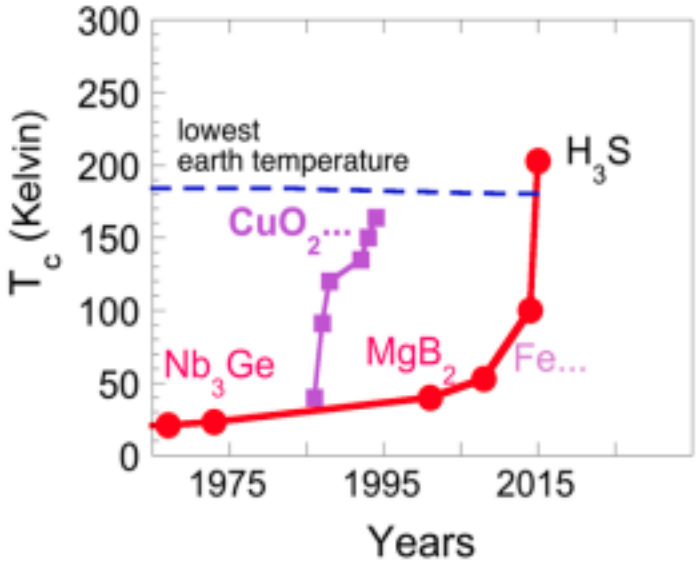
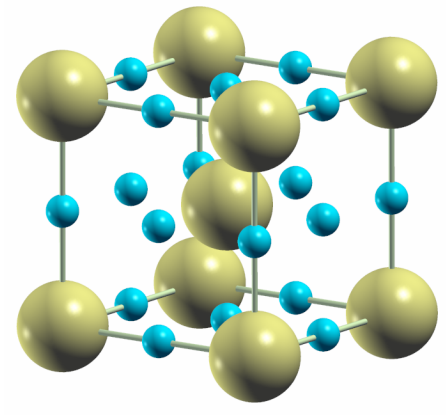


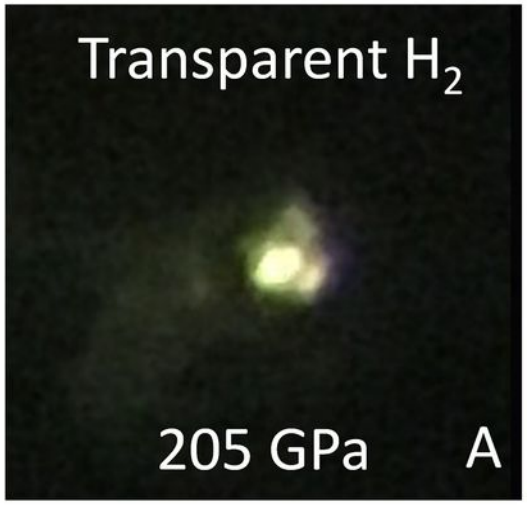
FIG. 1: (Color online) Records for the highest superconducting critical temperature found in: cuprates (1994), made of CuO_2 layers intercalated by spacer layers, in MgB_2 (2001), in iron based superconductors (2008), made of Fe layers in-

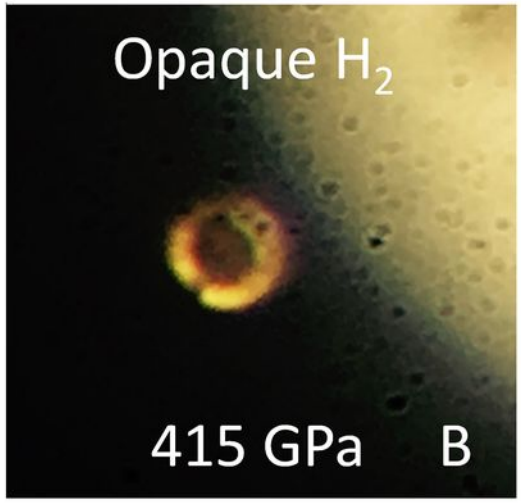


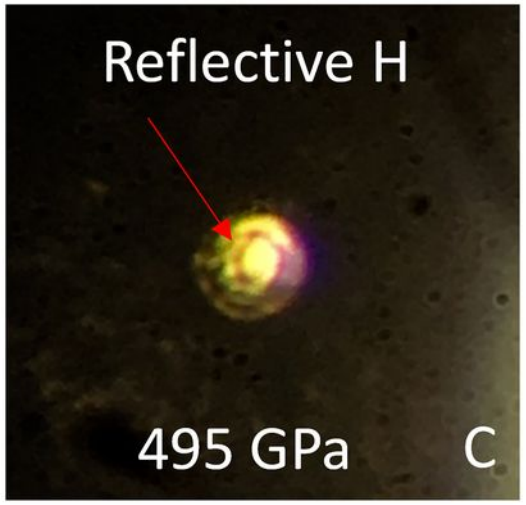
Probable crystal structure H3S

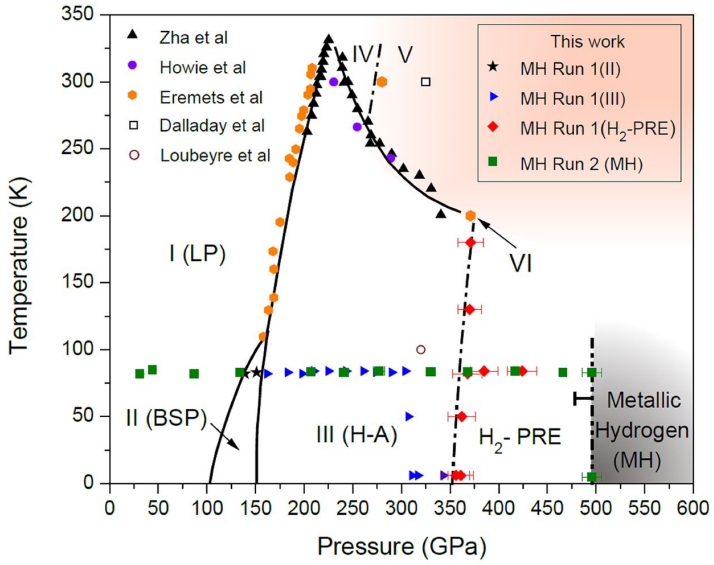
Just like Hydrogen..
Low mass – strong bond network.
High zero-point energy phonons
Strong binding of electrons into Cooper Pairs

iPhone Photographs of hydrogen at different stages of compression.







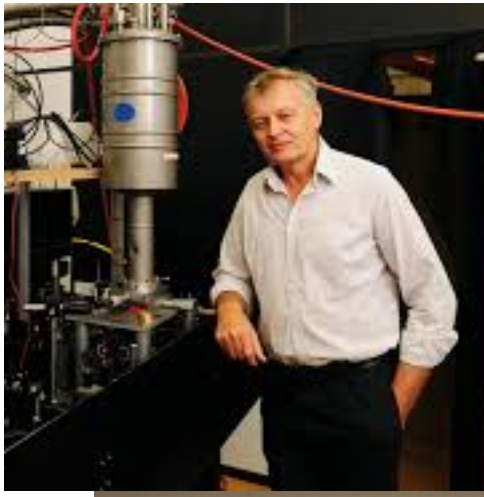


Ranga P. Dias, and Isaac F. Silvera Science 2017;science.aal1579

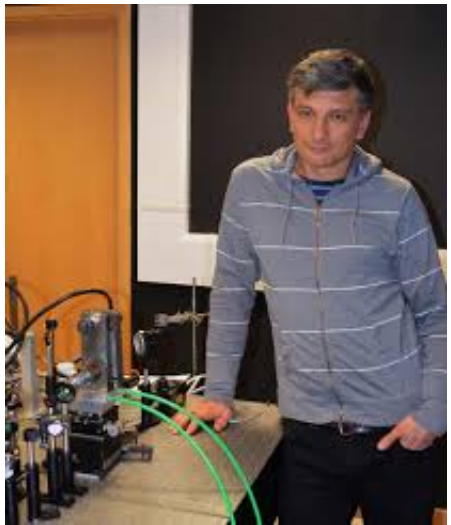
Published by AAAS

"It took weeks for the excitement to die down" Ike Silvera & Ranga Dias (Harvard)

"If it's true it would be fantastic,"
Reinhard Boehler (Carnegie Institute)



"From our point of view it's not convincing,"
Mikhail Eremets (MaxPlanck Institute)



"The word garbage cannot really describe it,"
Eugene Gregoryanz (CSEC),

...they want to rebuild the electricity network with rocket fuel - what could possibly go wrong? Andreas Hermann, (Edinburgh)

Philosophical objections to Silvera's paper

Method was designed to create metallic hydrogen, not to prove it.

Minimal data – no spectroscopy, conductivity, magnetisation

Absurd, irrelevant claims about rocket fuel, trains and power network

Comparison with long superceded theory (Drude model reflection, Born stability) – 81 times more free electrons than silver.

No top experimentalists refereed the paper

Plus a host of technical objections from competitors

Metastable hydrogen: how hard can it be?