Transitions in Hydrogen Under Pressure

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Hydrogen gas in intergalactic space: $10^{-32}$ atm

Center of Neutron Star: $10^{28}$ atm

Center of Jupiter: $8 \times 10^7$ atm

Center of Earth: $3.6 \times 10^6$ atm.

$10^3$ atm $\approx$ kbar

$10^6$ atm $\approx$ Mbar

10 kbar = 1 GPa

1 Mbar = 100 GPa
Effects of Extreme Pressures on Molecules

\[ P = -\frac{\partial E}{\partial V} \]

\[ P\Delta V \sim eV \]

chemical bond strengths
High-Pressure Technology:
STATIC COMPRESSION
High-Pressure Technology: STATIC AND DYNAMIC COMPRESSION

- Static compression
  - Low temperature
  - High temperature
- Dynamic compression
  - Shock-wave
  - Isentropic
- Combined static/dynamic

National Ignition Facility
I. Introduction
II. Isolated Molecule/Zero Pressure
III. Hydrogen under Pressure
IV. New Phases
V. High Pressures and Temperatures
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1. The aether

Adding to the four elements proposed by Empedocles: Earth, water, air, and fire

“Outside all the other spheres, the heavenly, fifth element, the aether is manifested in the stars and planets, moves in the perfection of circles.”

Aristotle (384-322 BC)
ELEMENT ONE

2. Most abundant element

3. Tests of fundamental theory

\[
\hat{H} = \sum_{i} \hat{T}^{i} + \sum_{j} \hat{T}^{j} + \sum_{k} \sum_{l} \hat{V}^{k,l} + \sum_{m} \sum_{n>m} \hat{V}^{m,n} + \sum_{o} \sum_{p>o} \hat{V}^{o,p}
\]
On the Possibility of a Metallic Modification of Hydrogen

E. Wigner and H. B. Huntington, Princeton University
(Received October 14, 1935)
4. Chemical dichotomy

“Reluctant alkali” or “tenacious halogen”  
[Ashcroft, Physics World (1995)]
5. Quantum system

\[ \hat{H} = \sum_i \hat{T}(i) + \sum_i \hat{T}(j) \]

Fluid ground state
[Brovman et al., JETP (1974)]

‘The Element of Uncertainty’

6. Potential energy material

- High energy density material
  (400 kJ/mole: 35 x TNT)

- High-\(T_c\) superconductor?

- Superconducting/superfluid?
ELEMENT ONE

7. Path to Inertial Confinement Fusion
8. *Driven the development of many high-pressure techniques*

- High compressibility (e.g., deformation of apparatus)
- Reactivity with metals (weaken apparatus, electrical leads)
- Weak x-ray scattering power
- Strong Raman cross-section but variable infrared absorption
- Large neutron cross-section (coherent, incoherent)

**Techniques Used Over Different P-T ranges**

- Optical spectroscopy
- Raman, infrared spectroscopy
- Brillouin scattering
- X-ray diffraction (single xtal, polyxtal)
- X-ray inelastic scattering
- Neutron diffraction
- Neutron inelastic scattering

- Non-linear spectroscopy (e.g., CARS)
- NMR
- Electrical transport
- Ultrasonic
- Shock compression (Hugoniot)
- Isentropic compression
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Hydrogen in condensed phase

1898 – First liquified – 20 K
1899 – First solidified – 14 K

X-ray diffraction

$J=0$
$p$-$H_2$ (hcp)

$V_0 = 23.2 \text{ cm}^3/\text{mol}$
$R(H_2-H_2) = 3.0 \text{ Å}$
$R(H-H) = 0.74 \text{ Å}$

[Keesom et al., Comm. Kamerlingh Onnes Lab (1930)]

The rotational motion of molecules in crystals

By Linus Pauling
Gates Chemical Laboratory, California Institute of Technology
(Received May 7, 1930) [Phys. Rev. (1930)]

$J=1$ ordered state
$o$-$H_2$ (Pa3)

Molecular structure and bonding

**Origin of the chemical bond**
- Valence bond (Heitler-London)
- Molecular orbital (Mulliken)

- Strong covalent bond: 4.53 eV
- 14 bound vibrational states

[Silvera, Rev. Mod. Phys. (1980)]

Intramolecular and intermolecular interactions

**INTRAMOLECULAR POTENTIAL**  
(pure; i.e., isolated molecule)

- Strong Raman cross-section
- No dipole-allowed IR absorption

**INTERMOLECULAR POTENTIAL**  
(effective potential in condensed phase)

- Binding energy 3.0 meV (35 K)
- Interactions: *Isotopic* + *Anisotropic*
  - Leading anisotropic term is electric quadrupole-quadrupole (EQQ) interaction (odd J)

[Silvera, Rev. Mod. Phys. (1980)]  
Carnegie Institution
Ortho-para distinction

**BJ \((J+1)\)**

Rotational levels of free Hydrogen molecule

<table>
<thead>
<tr>
<th>(J)</th>
<th>((2J+1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>(11)</td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(7)</td>
</tr>
<tr>
<td>2</td>
<td>509.9 K</td>
</tr>
<tr>
<td>1</td>
<td>170.5 K</td>
</tr>
</tbody>
</table>

Species

- \(H_2\): even, \(p-H_2\)
- \(D_2\): odd, \(p-D_2\)
- \(H_2\): odd, \(o-H_2\)
- \(D_2\): even, \(o-D_2\)

Coupling of nuclear spin \(I_N\) and rotational states \(J\) in total molecular spin \(I_{mol}\)

<table>
<thead>
<tr>
<th>(I_N)</th>
<th>(I_{mol})</th>
<th>(J)</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{1}{2})</td>
<td>0</td>
<td>even</td>
<td>(p-H_2)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>odd</td>
<td>(o-H_2)</td>
</tr>
<tr>
<td>1</td>
<td>0,2</td>
<td>even</td>
<td>(o-D_2)</td>
</tr>
</tbody>
</table>

[Silvera, *Rev. Mod. Phys.* (1980)]
Vibrational excitations

$O, P, Q, R, S \ldots \Delta J = -2, -1, 0, -1, 0, -2$

Rotons

$L_0(J)$

Lattice Modes

Vibrons

$Q_{\Delta v}(J); \text{ e.g., } Q_1(1)$

PRESSURE EFFECTS

- Rotational ordering
  - breakdown of $J$
- Molecular stability
  - lattice mode = vibron?
- Molecular interactions
  - molecular coupling?
H$_2$ excited electronic states

UV Absorption (zero pressure)

[Inoue et al. Solid State Comm. (1979)]

I.P.


Refractive Index of the Hydrogen Molecule

M. KARPLUS
Department of Chemistry and Watson Laboratory, Columbia University, New York, New York
(Received 13 March 1964)

\[
\epsilon_2(\omega) = \frac{e^2}{\pi m^2 \omega^2} \sum_{\nu, c} \int_{B_2} dk |e \cdot M_{\nu c}(k)|^2 \delta(E_c(k) - E_{\nu}(k) - \hbar \omega),
\]

\[
e \cdot M_{\nu c}(k) = \langle \psi_{\nu k} | e \cdot p | \psi_{\nu k} \rangle
\]

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Room-Temperature Compression of Hydrogen Gas

Freezing at Room Temperature
5.4 GPa

[Mao and Bell, Science (1979)]
High-pressure measurements of the Raman vibron

Evidence for bond weakening?

Effect of compression on vibron frequencies

Compression
Frequency Increase

Orbital interactions
Frequency Decrease

Enhancement of vibrational coupling: combining Raman and IR spectroscopy

\[ H_{JK} = \sum_m W'_m |m\rangle \langle m| - \frac{1}{2} \sum_{m,n \neq m} \epsilon'_{m,n} |m\rangle \langle n| \]

\[ 6\epsilon' = 3 \text{ cm}^{-1} \quad \text{(zero pressure)} \]

\[ 520 \text{ cm}^{-1} \quad \text{(180 GPa)} \]

Crystal structure by high-pressure diffraction

*hexagonal close packed*

Neutron diffraction (to 30 GPa)
[Glazkov et al., JETP Lett. (1986)]

X-ray diffraction (to 200 GPa)

- Monotonic decline in c/a
- No measurable isotope effect
- High compressibility shifts $P_{\text{met}} > 400$ GPa

\[
\int VdP \text{ compared to theory}
\]
Higher pressure transition: phase III

**Raman Vibron**

- I: solid $H_2$ at 75K
- II: solid $H_2$ in helium at 100K
- III: solid $H_2$ at 100K

**Infrared Vibron**

- *H$_2$*: Infrared Absorption
- 85 K

Wavenumbers (cm$^{-1}$):

- 4300
- 4400
- 4500
- 4600
- 4700

Absorbance:

- 0.5

Pressures (GPa):

- 0
- 50
- 100
- 150
- 200
- 250


Infrared spectroscopy of phase III: charge transfer instead of metallization

Predicted Drude models

[Hemley et al. Phys. Rev. Lett. (1996); see also, Chen et al. ibid (1996)]

Vibrational spectroscopy of phase III: low to high frequency excitations

**RAMAN**

![Raman spectrum of hydrogen at 140 K and 250 GPa](image)

- Librons and Phonons
- Diamond Anvils
- Vibron

**INFRARED**

![Infrared spectra of hydrogen at different pressures](image)

- Combination bands
- Vibron
- Absorbance

- J no longer a good quantum number
- Vibron softening/orient. ordering
- Molecules persist to >320 GPa


[Loubeyre et al., Nature (2002)]

[Souza et al., PNAS (2001)]
$P-T$ phase diagram of the solid hydrogens from vibrational spectroscopy to 200 GPa

Relationship to metallization?

THEORETICALLY PREDICTED BAND GAPS

$\rho/\rho_0 = 9$


$\rho/\rho_0 = 9$
Theory challenge for phase III: preventing band overlap with the correct crystal structure

Molecular orientation and band overlap


Dielectric Properties

Refractive Index and Oscillator Models

\[ I(\nu) = A \sin\left\{ 4\pi B[1 + (\nu - \nu_0)C]\nu + D \right\} \]

\[ C = (1/n_0)(dn/d\nu)_{\nu_0} \]

\[ n^2 - 1 = E_d E_0 / (E_0^2 - \hbar^2 \omega^2) \]

[Hemley et al., Nature (1991)]

- Oscillator model fits to \( \varepsilon(\omega) \)
- Constrains the direct band gap not indirect gaps
- Direct measurements?
Visible absorption at ~300 GPa

- Optical absorption
- Variable sample thickness/diamond absorption
- Direct gap, not indirect gap
Early Electrical Transport Measurements

[Image of a diagram showing the setup of the experiment with labels for Alumina layer, Platinum electrodes, and Metallic gasket.]

40 µm

HYDROGEN SAMPLE

[Image of a hydrogen sample under a microscope with a scale.]  

[Graph showing resistance vs. pressure with markers for S, CsI, Xe, and B.]

[H₂ (80 K)]

Early Electrical Transport Measurements [Eremets et al., Frontiers in High-Pressure Science (2002)]
X-Ray Raman of dense hydrogen: direct measurements of the band gap

0 10 20 30 40 50 60 70 80
Normalized Intensity

2 x 2.5 mm
diamonds

1.8 GPa
4.5 GPa
7 GPa
11 GPa

Energy Loss (eV)

0.0 0.5 1.0 1.5 2.0
Log(I/I₀)

2 mm Be

REE L TransE K α K α

Supporting seats

X-RAY

ELECTRONIC STATE (K-edge, Band Gap)

OPTICAL

VIBRATIONAL STATE
GROUND STATE
X-Ray Raman of dense hydrogen: direct measurements of the band gap

Direct Absorption (zero pressure)

Excitons
Band Gap

[Inoue et al. (1979)]
X-Ray Raman of dense hydrogen: direct measurements of the band gap

Estimated $H_2$ Band Gap

[Estimated $H_2$ Band Gap: Loubeyre et al. (2002)]

Normalized Intensity

Excitons, Band Gap

Density (mole/cm$^3$)

Energy (eV)

Normalized Intensity

Energy Loss (eV)

1.8 GPa
4.5 GPa
7 GPa
11 GPa
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Evidence for new transitions

Electrical Conductivity Onset

Raman Evidence for New Phase

H$_2$

D$_2$


[Howie et al., *Phys. Rev. Lett.* (2012)]
Synchrotron infrared spectroscopy of phase IV

(a) 268 GPa Isobaric Infrared

(b) 295 K Isothermal

(c) 280 GPa, 295 K

Absorbance

Wavenumber (cm$^{-1}$)

Pressure shifts and phase transitions

Vibron Frequencies

[Pressure (GPa)]

Wavenumber (cm⁻¹)

IV

Weakly Interacting H₂

Strongly Interacting H₂


[Wigner & Huntington (1935)]
Hydrogen Phase Diagram

[Zha et al., Phys. Rev. Lett. (2013); PNAS (2014);
see also, Howie et al., Phys. Rev. B (2013)]
Hydrogen Phase Diagram

Phase IV is a graphene-based layer structure

C-graphene

H-graphene

$H_6$ ‘aromatic cluster’


Hückel’s rule:

Aromatic compounds must have $4n + 2$ π electrons, $n = 0, 1, 2, 3...$ to fill a π shell

- $D_{6h}$ to $D_{3h}$
- Both are aromatic

Distortions and relationship to graphene / graphite structures

PEIERLS DISTORTION -> Residual Pairing
Is hydrogen metallic at these $P$-$T$ conditions?

$360 \text{ GPa, } 292 \text{ K}$
Is hydrogen metallic at these $P$-$T$ conditions?

- Transparent to at least 0.1 eV
- Plasma frequency $\omega_p < 0.2$ eV
- Semiconducting or semimetallic?
- Transition to semimetal at 270 GPa (phase VI’?)

\[ \epsilon_1 = n^2 - k^2 = \epsilon_{1B} - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \]

\[ \epsilon_2 = 2nk = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)} \]

**DRUDE MODELS**

[Ermerets & Troyan, Nature Materials (2011)]
A new mechanism for hydrogen metallization

- Borderline of semiconductor-semimetal at 300 GPa
- Parallels to graphite (not alkali metals)
- Higher pressures in solid?

Other structures of dense hydrogen: *Topological semimetals and surface metallization*

**Cmca-4**

- Band structure of a 8L slab
- Charge density of a SS at \( \Gamma \)

Predicted stable < 300 GPa


Metallic SSs also exist

- In other candidate structures including \( Pca_{2} \), \( C2/m \) and \( Cmc_{2} \).

- [Naumov et al. in preparation]
Predicted metallic superfluid

Observability of a Projected New State of Matter: A Metallic Superfluid

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N. W. Ashcroft
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(Received 13 June 2005; published 1 September 2005)
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Juno Mission will let Jupiter tell us

**MISSION GOALS**

- **Internal structure?**
- **Composition (e.g., H\textsubscript{2}O)?**
- **Gravity / magnetic fields?**
- **Origin and evolution?**
- **Size and existence of a core?**
DENSE HYDROGEN: Dynamic (Shock) Compression

ELECTRICAL CONDUCTIVITY

HUGONIOT MEASUREMENTS


High $P$-$T$ Transition in Fluid Hydrogen

- Insulating to Conducting?
- Dissociation: $H_2$ to $H$?
- Pressure differences?
- Relationship to the solid transition?
High $P-T$ Transition in Fluid Hydrogen

176 beams of the NIF Laser were used, with a custom 300 kJ - 35 ns long pulse shape.

**Sample Geometry**

- Cu [70μm]
- D$_2$ [30μm]
- LiF [720μm]
- Al Mirror coating

**Laser Pulse**

![Laser pulse diagram]

**Optical/Velocity (VISAR) Data**

- 1st shock: D$_2$ is transparent
- 2nd shock
- 3rd shock
- 4th shock etc...
- D$_2$ becomes opaque
- D$_2$ becomes reflecting (Metallic)

**Evidence for changes in the hydrogen optical properties during the reverberation compression**

[Jeanloz & Hemley (PIs), *NIF Discovery Science Campaign*]
We direct experiments at the National Ignition Facility to understand the materials in ultra-extreme conditions.

- Conducting transition in fluid of hydrogen at megabar pressures?
- Depth of magnetic field generation in Jupiter?
- Melting curve of iron in exoplanets (>20 Mbar)
CONCLUSIONS AND OUTLOOK

1. Dense hydrogen is a system of unexpected complexity.

2. There is no sign of the ‘Wigner-Huntington metallization’ to 340 GPa in phases III and IV (below 300 K).

3. The structure of phase IV is broadly consistent with the structures predicted theoretically.

4. There is a remarkable parallel between dense hydrogen and graphene that reveals a new mechanism for metallization.

5. New dynamic compression results reveal a transition in fluid starting at 140 GPa.
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Hydrogen

[Guillot et al. (2002)]

Hydrogen