New Views of Chemical Bonding Under Pressure

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Marker Lecture, Department of Chemistry
Pennsylvania State University, Apr. 8, 2016

CHEMICAL TRANSFORMATIONS

- Temperature

$$A \xrightarrow[\text{heat}]{} B$$

- Pressure

$$A \xrightarrow[\text{pressure}]{} B$$

- Composition

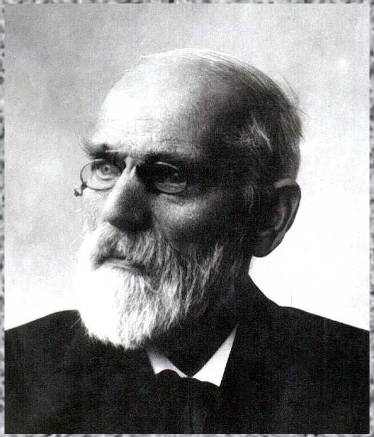
$$A + B \longrightarrow C$$

EFFECTS OF PRESSURE ON GASES

Robert Boyle
1627-1691

$$PV = nRT$$

J. D. van der Waals
1837-1923



$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

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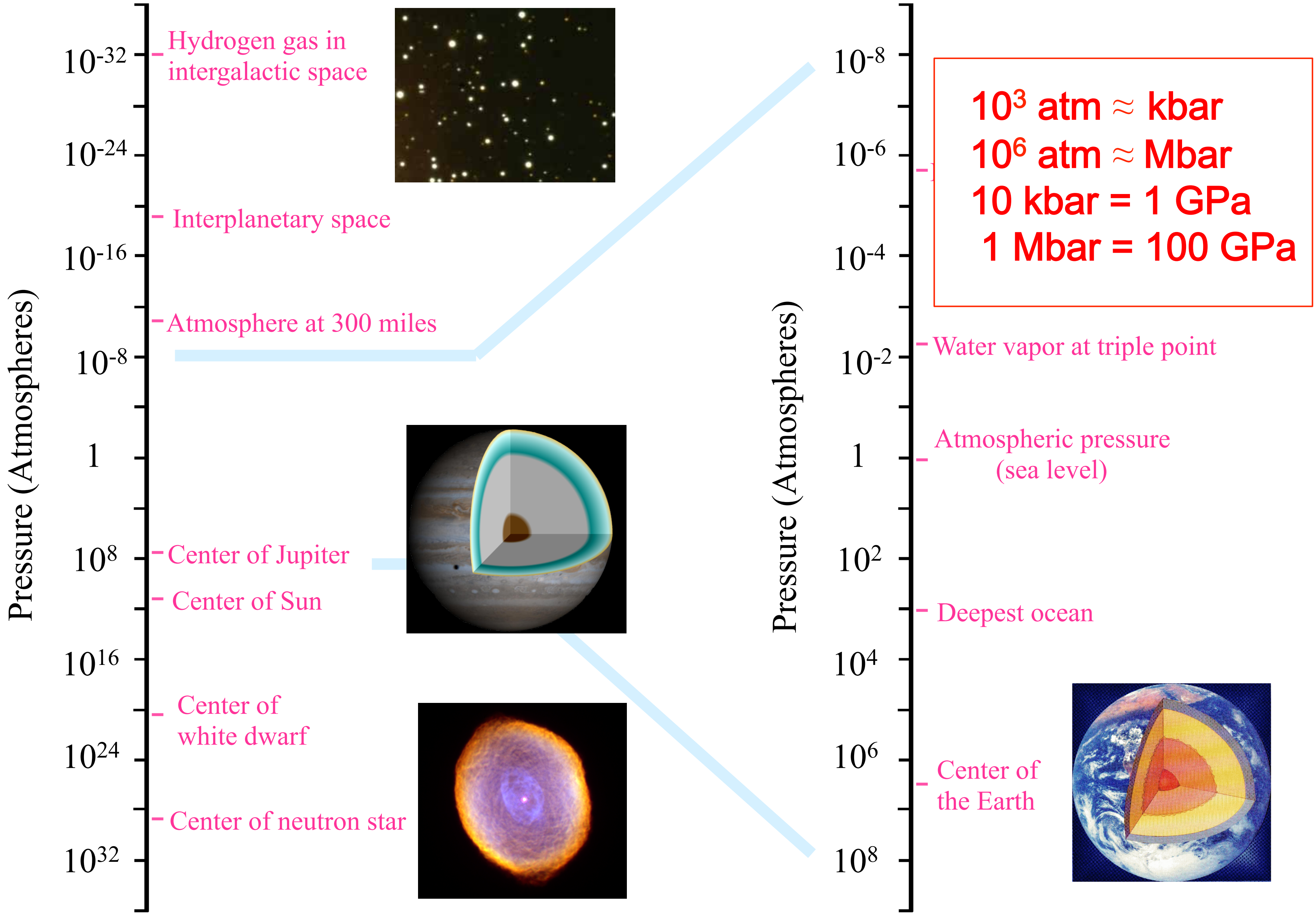
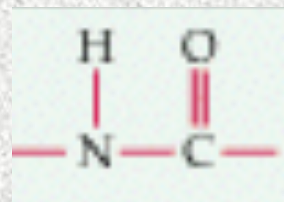
RANGE OF PRESSURE IN THE UNIVERSE

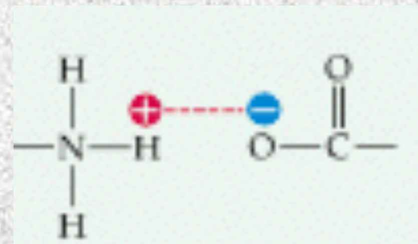


Types of Chemical Bonds

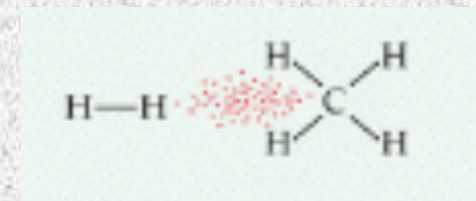
a. Covalent $A - B$



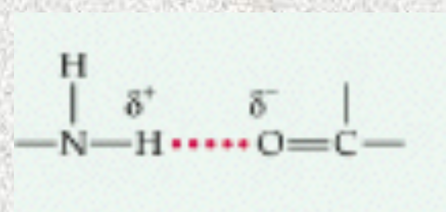
b. Ionic $A^{+}\ B^{-}$



c. van der Waals $A \cdots B$



d. H-bonds $A \cdots H$



e. Metallic $A \approx A$

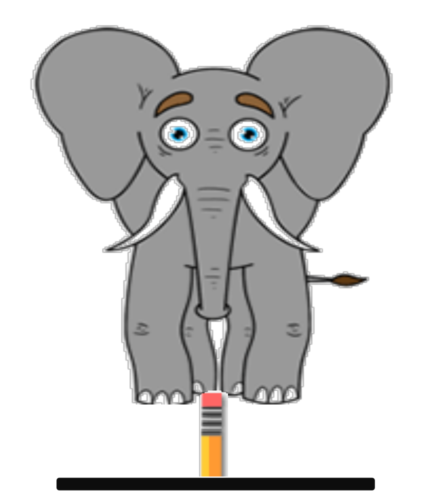
M ··· M ··· M

High-Pressure Chemistry

DOI: 10.1002/anie.200602485

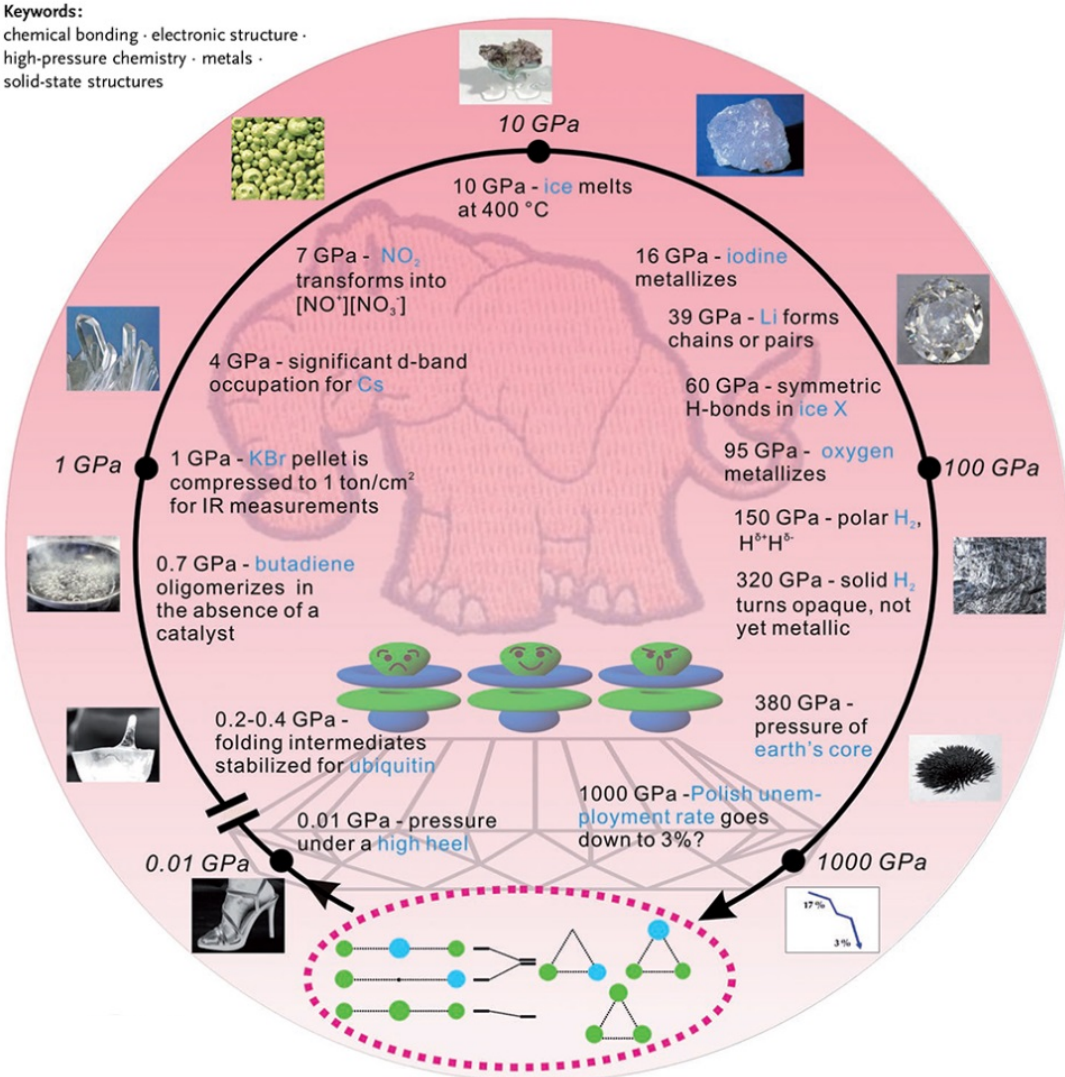
The Chemical Imagination at Work in *Very* Tight Places

Wojciech Grochala, Roald Hoffmann,* Ji Feng,* and Neil W. Ashcroft**



1 GPa =
1 Elephant per pencil =10,000 atm

Keywords:
chemical bonding · electronic structure · high-pressure chemistry · metals · solid-state structures



Angewandte Chemie
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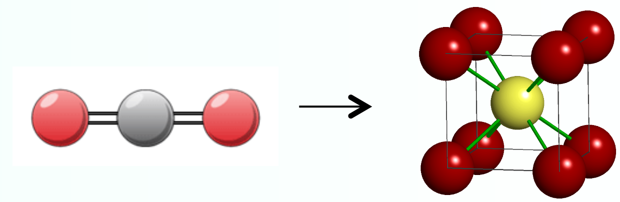
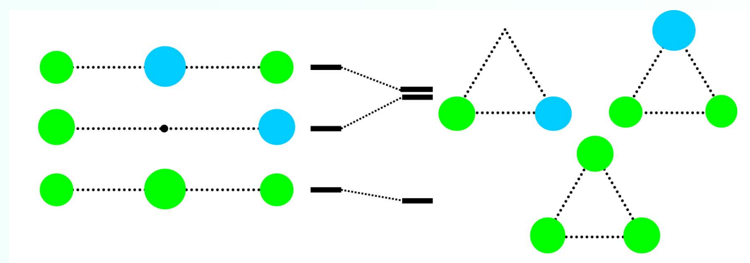
Intuition and Expectations

- **Close packing**

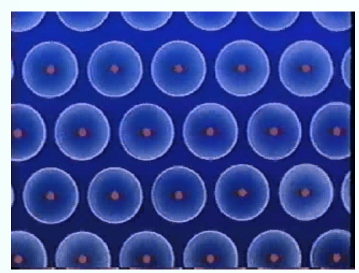
- **Increasing coordination**

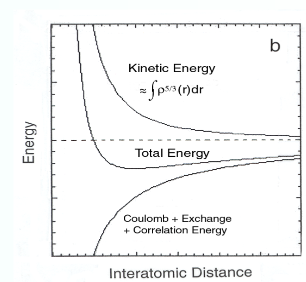


- **Orbital mixing**



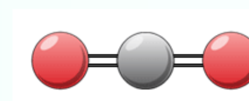
- **Ultimately metallic**

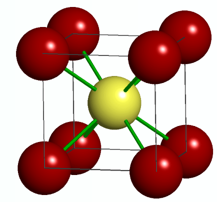


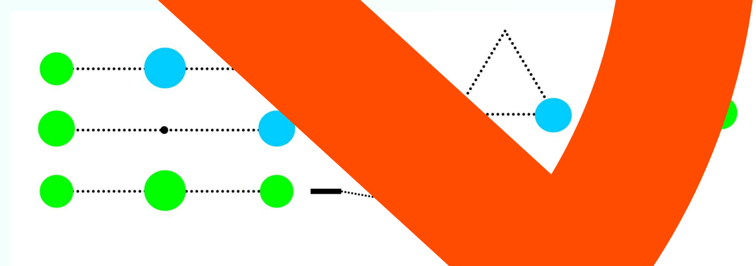


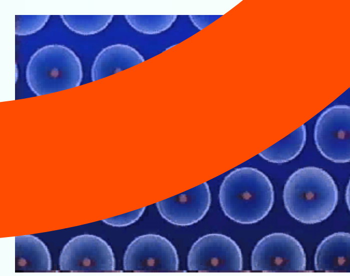
Intuition and Expectations

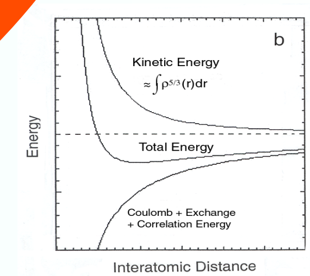
- Close p
- Incre ng coordi n
- Orbita ixing
- Ultimately





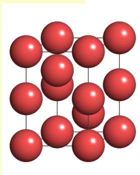




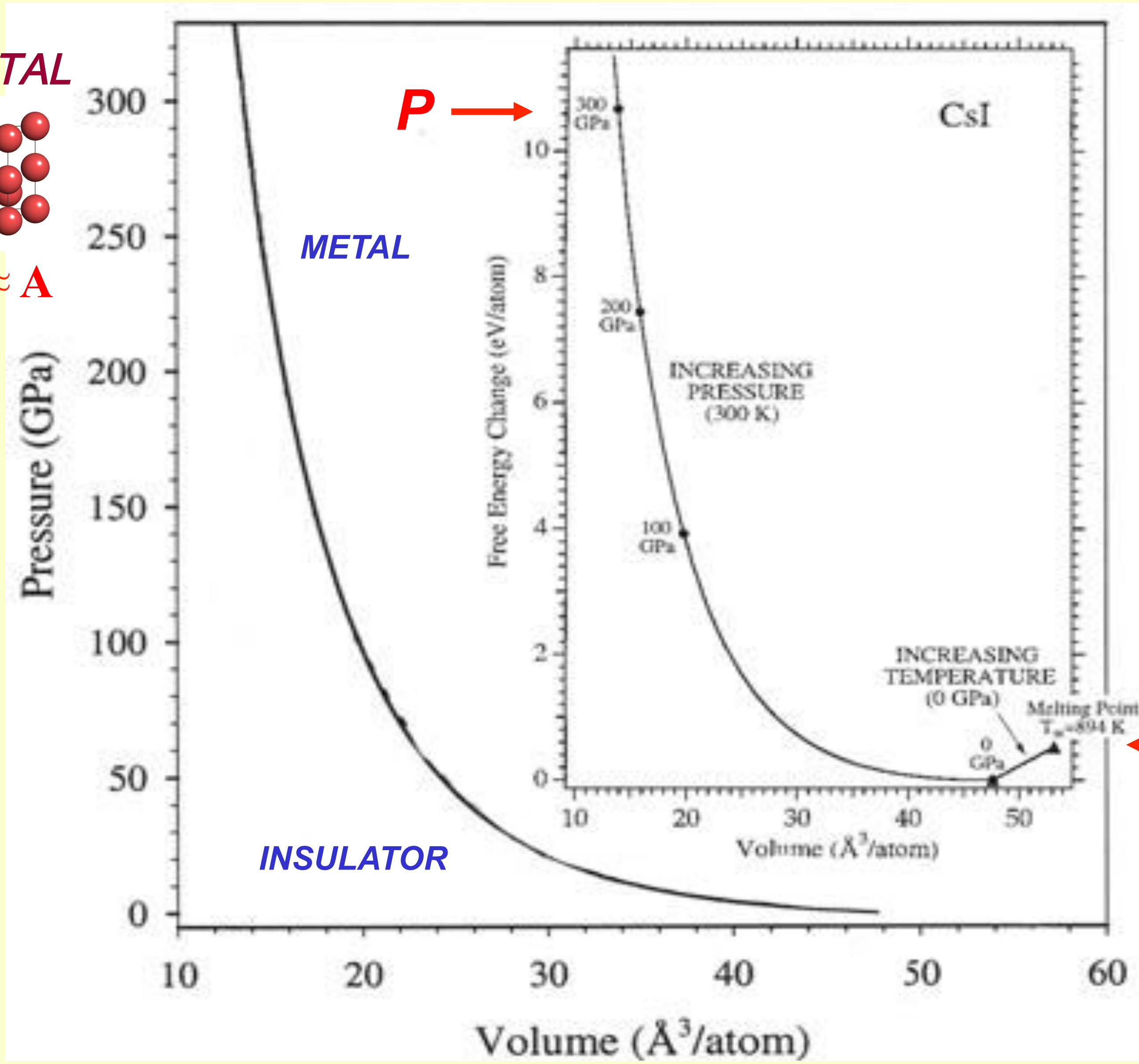


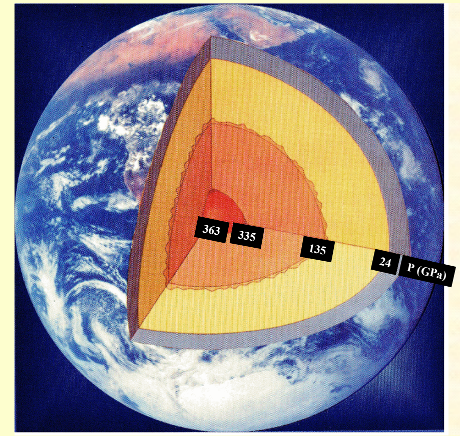
Free Energies and Extreme Conditions

METAL

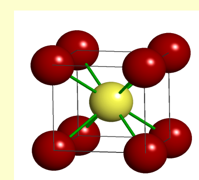


A ≈ A





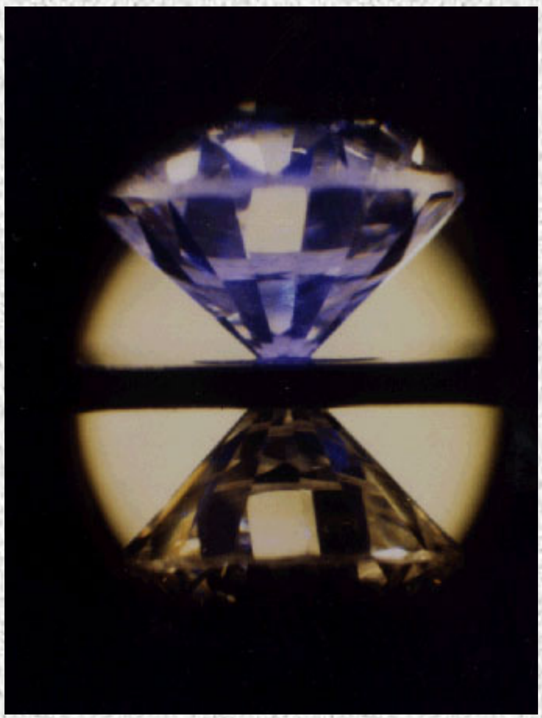
PΔV ~ eV
chemical
bond
strengths

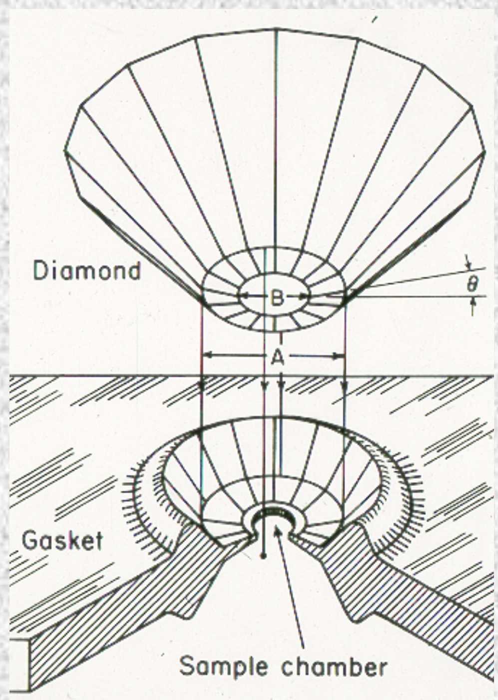


CsI
SALT
A^+B^-

Generating Extreme Pressures in the Laboratory

Static

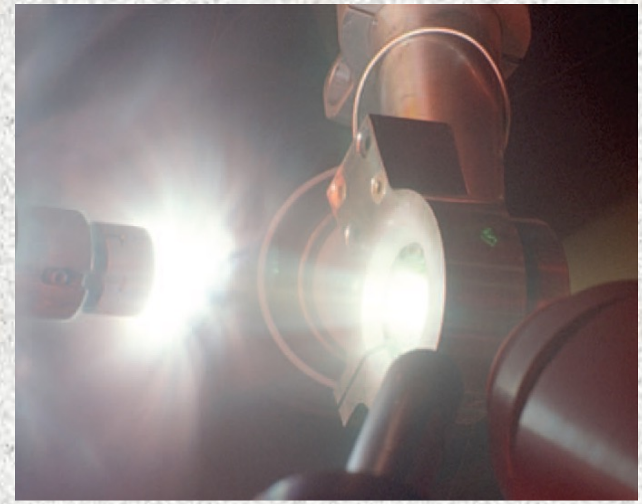




>100's GPa (~0.5 TPa)

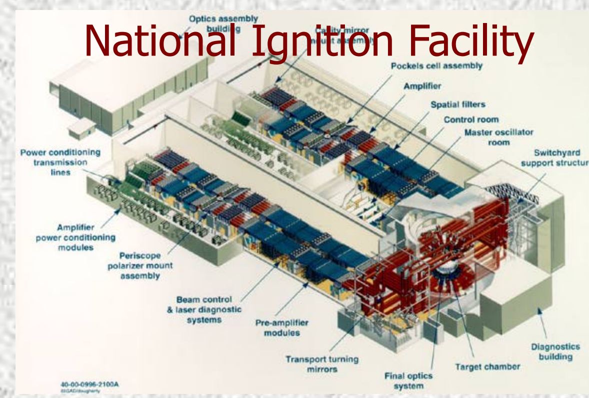
~ eV energies – valence electrons

Dynamic



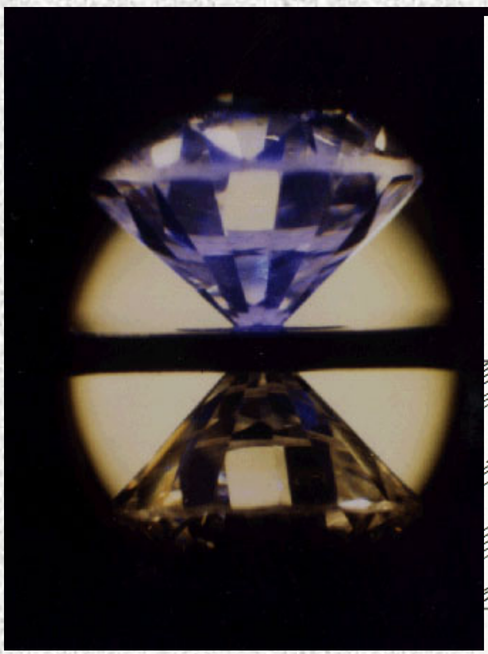
>100's Mbars (1 Gbar)

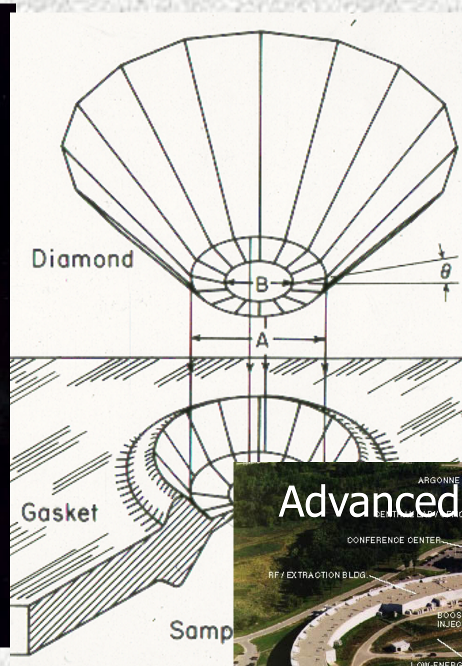
~ keV energies – core electrons

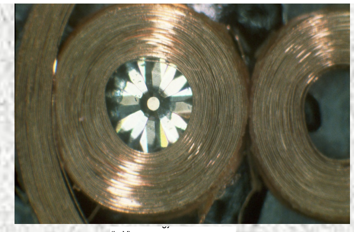


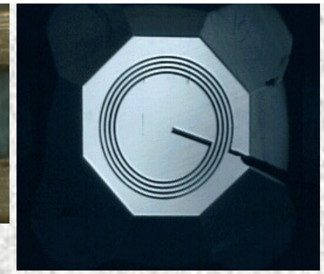
High-Pressure Technology:

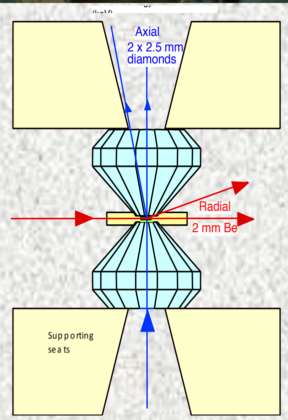
MYRIAD NEW TOOLS

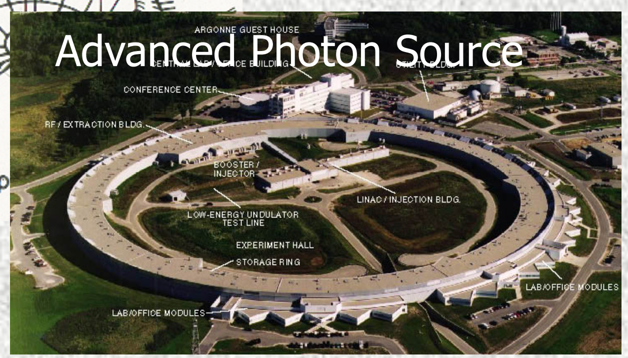


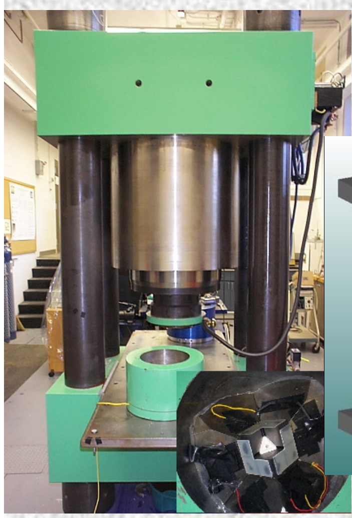


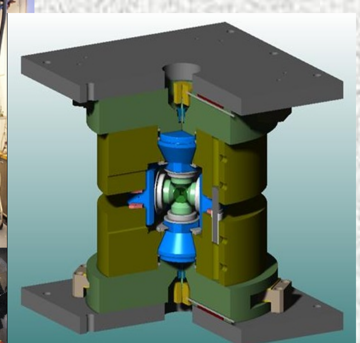


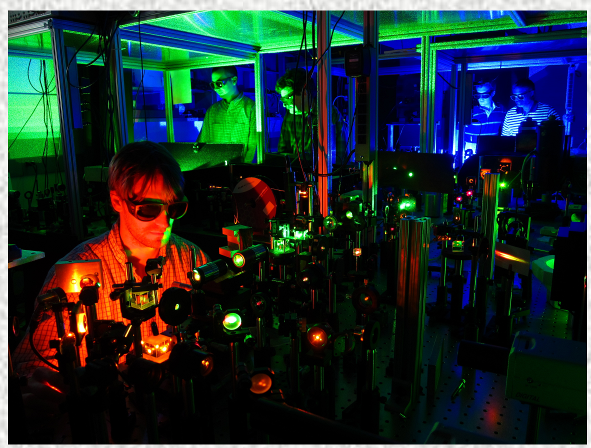


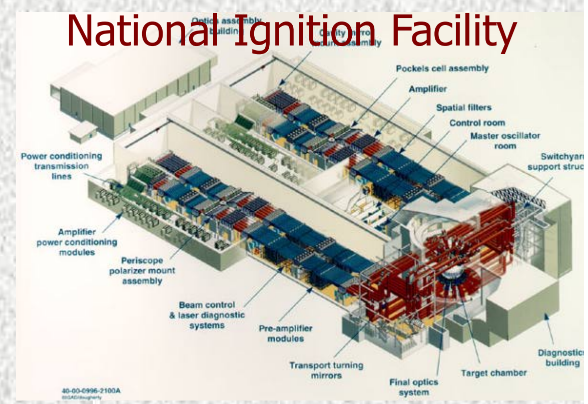












EXAMPLES

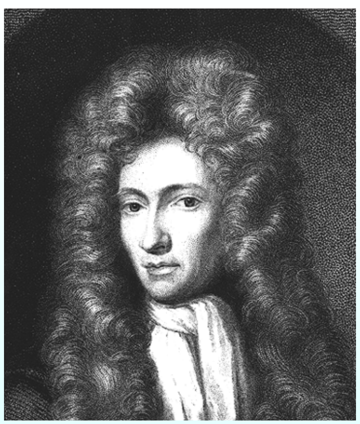
1. **‘Simple’ Molecules**
2. **Novel Compounds**
3. **Metals that are Not**
4. **Continuing with Carbon**
5. **Softest Matter**

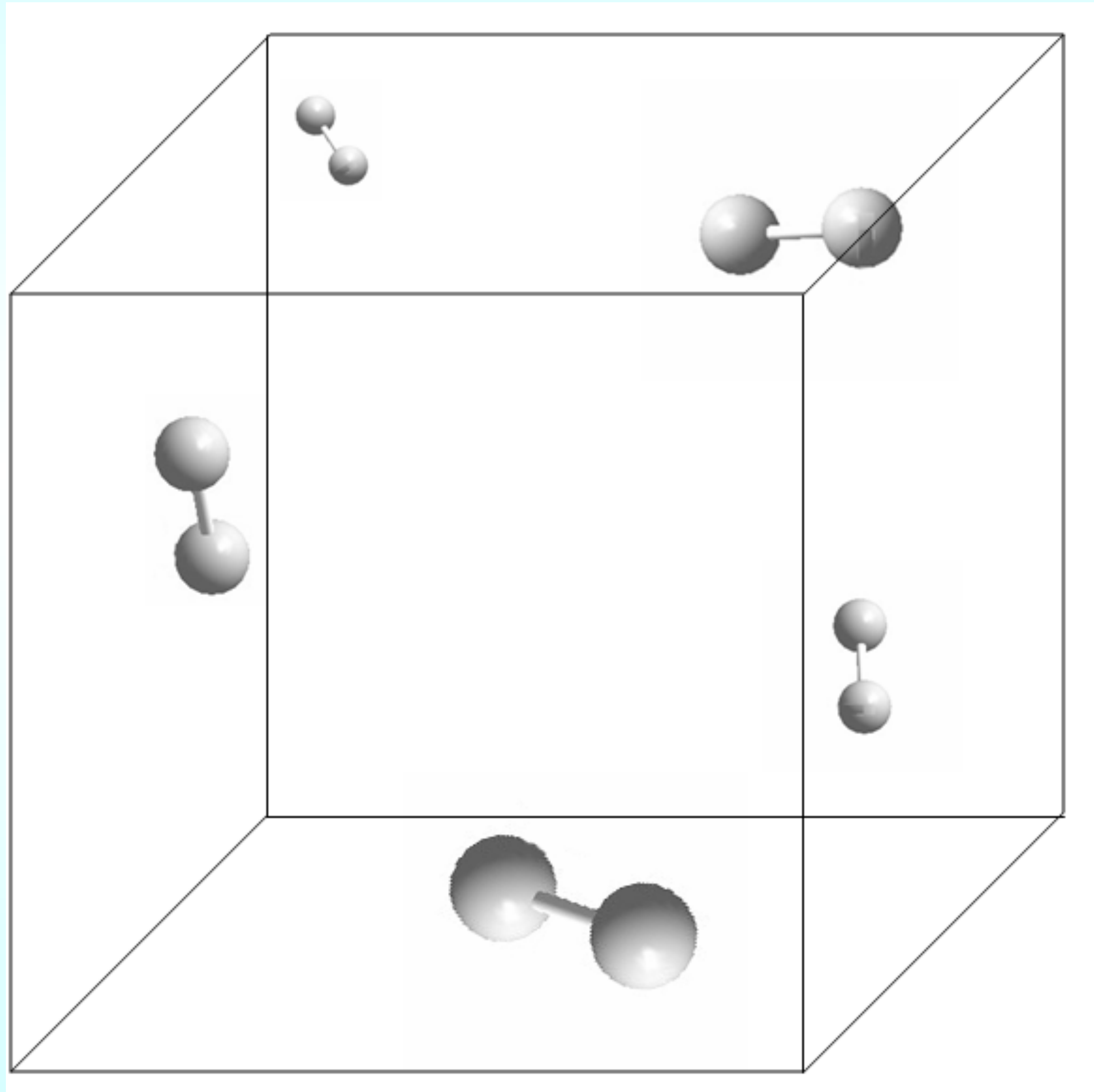
EXAMPLES

1. **‘Simple’ Molecules**
2. Novel Compounds
3. Metals that are Not
4. Continuing with Carbon
5. Softest Matter

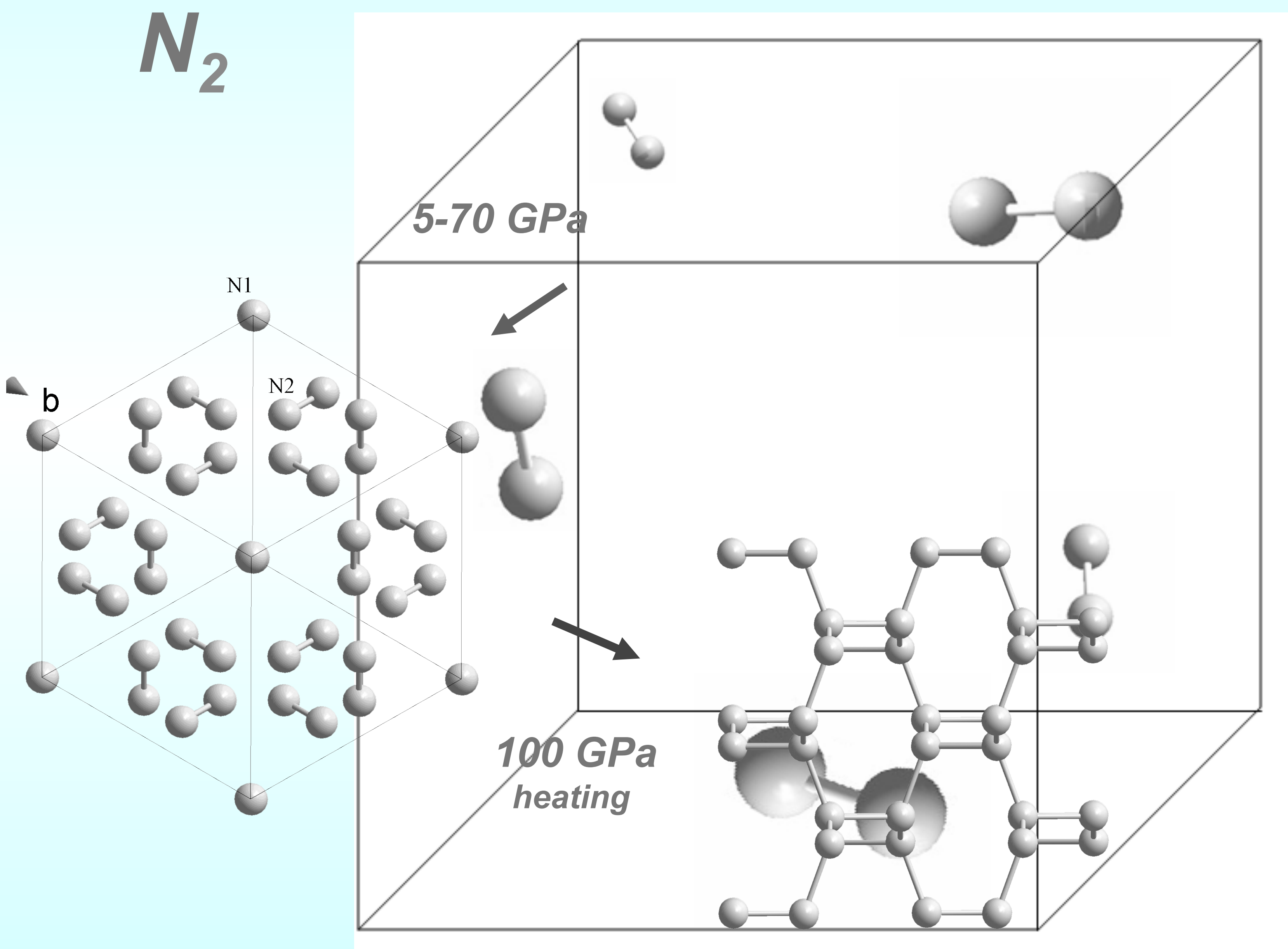
Compressing Nitrogen

N_2



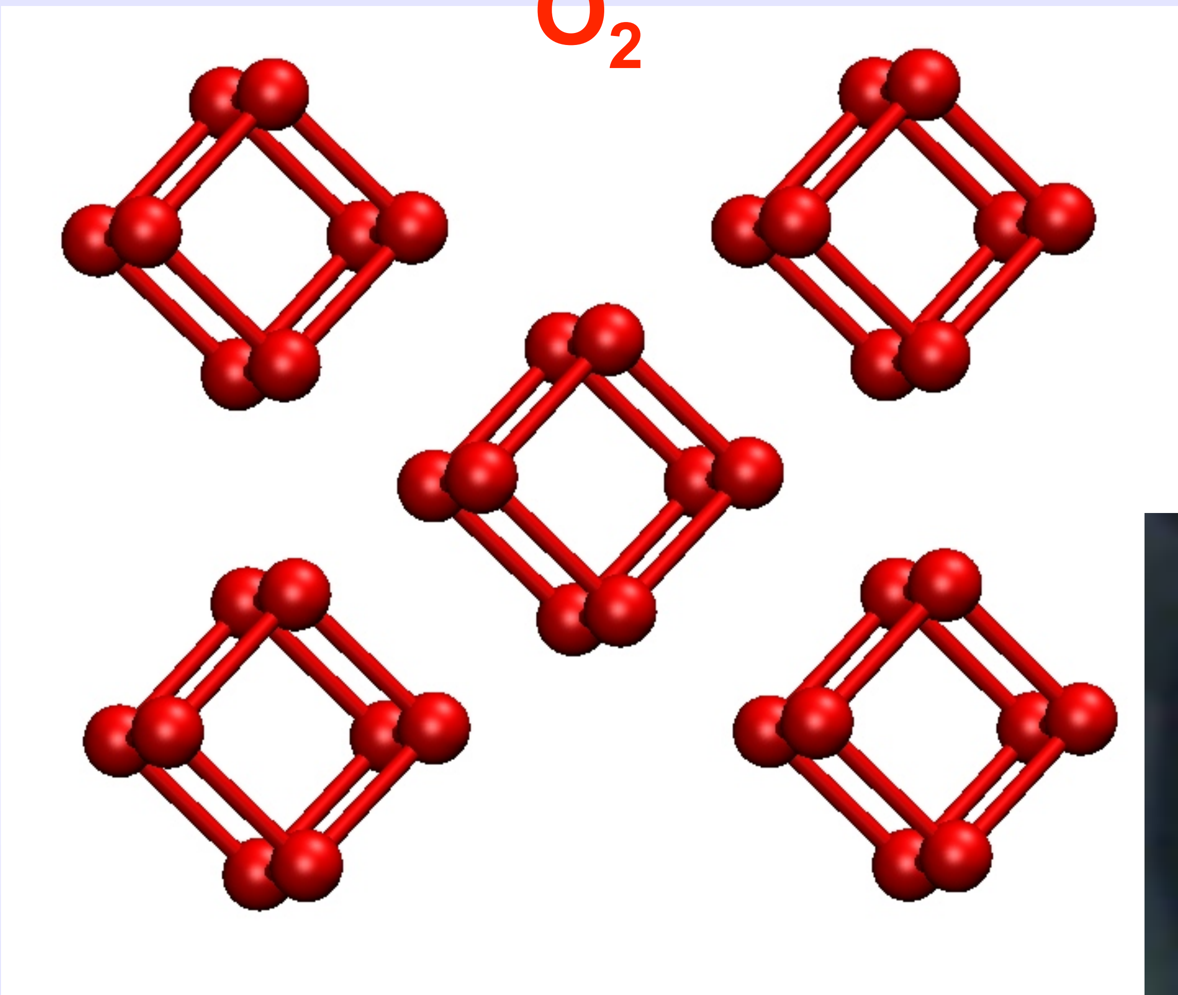


Compressing Nitrogen



Dense oxygen exhibits remarkable properties

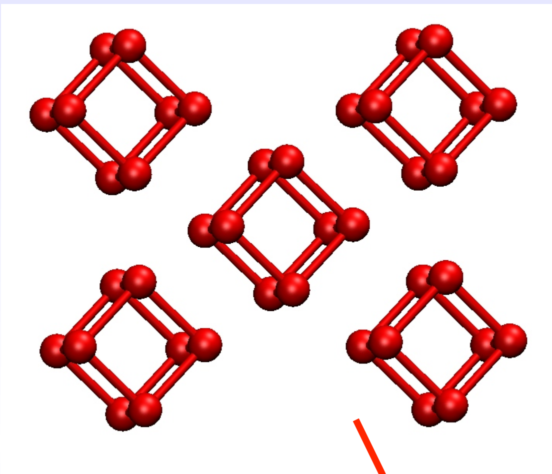
O_2

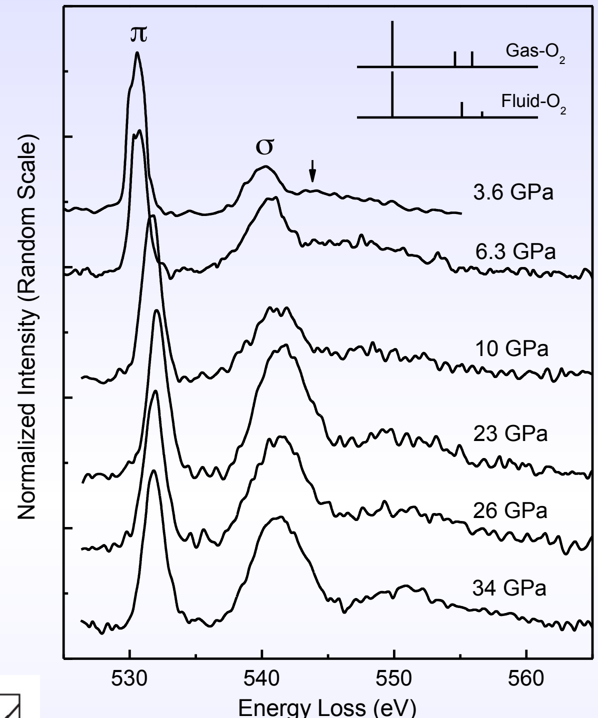


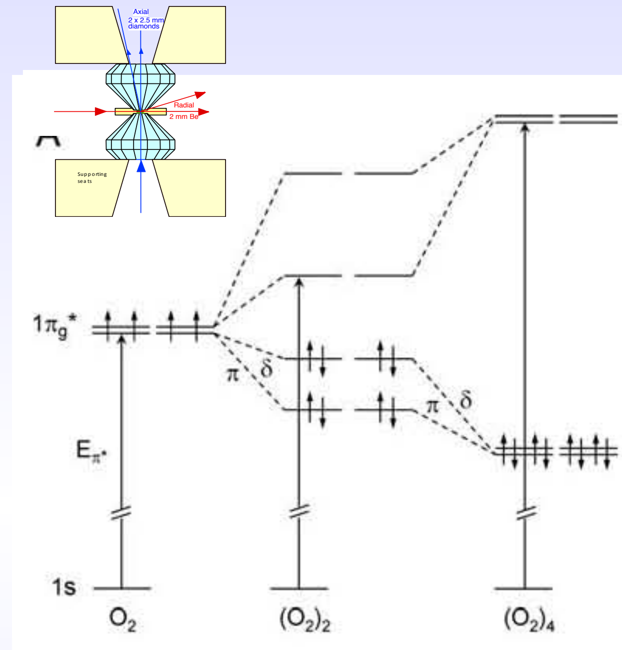
Magnetic Collapse to form O_8 Clusters (30 GPa)

Dense oxygen exhibits remarkable properties

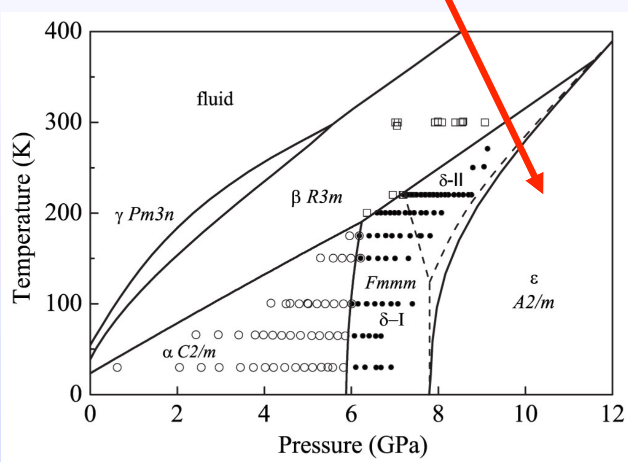
O K-edge X-ray Raman







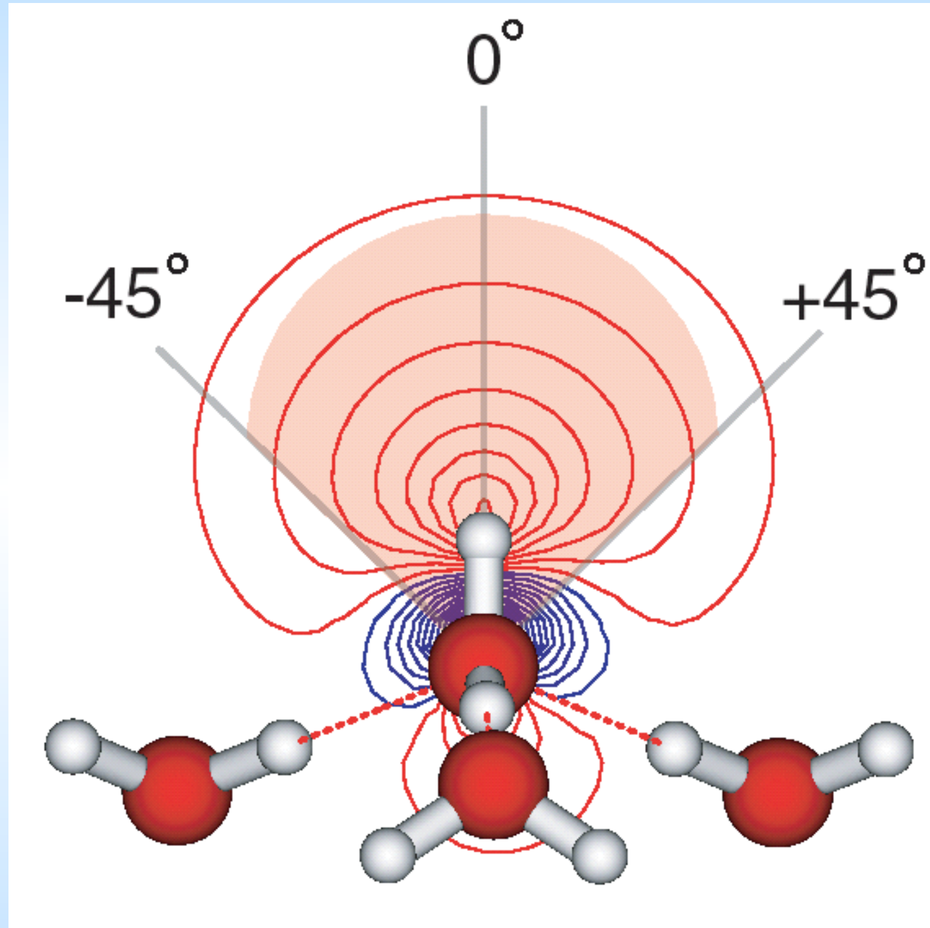
[Meng *et al.* *PNAS* (2008)]



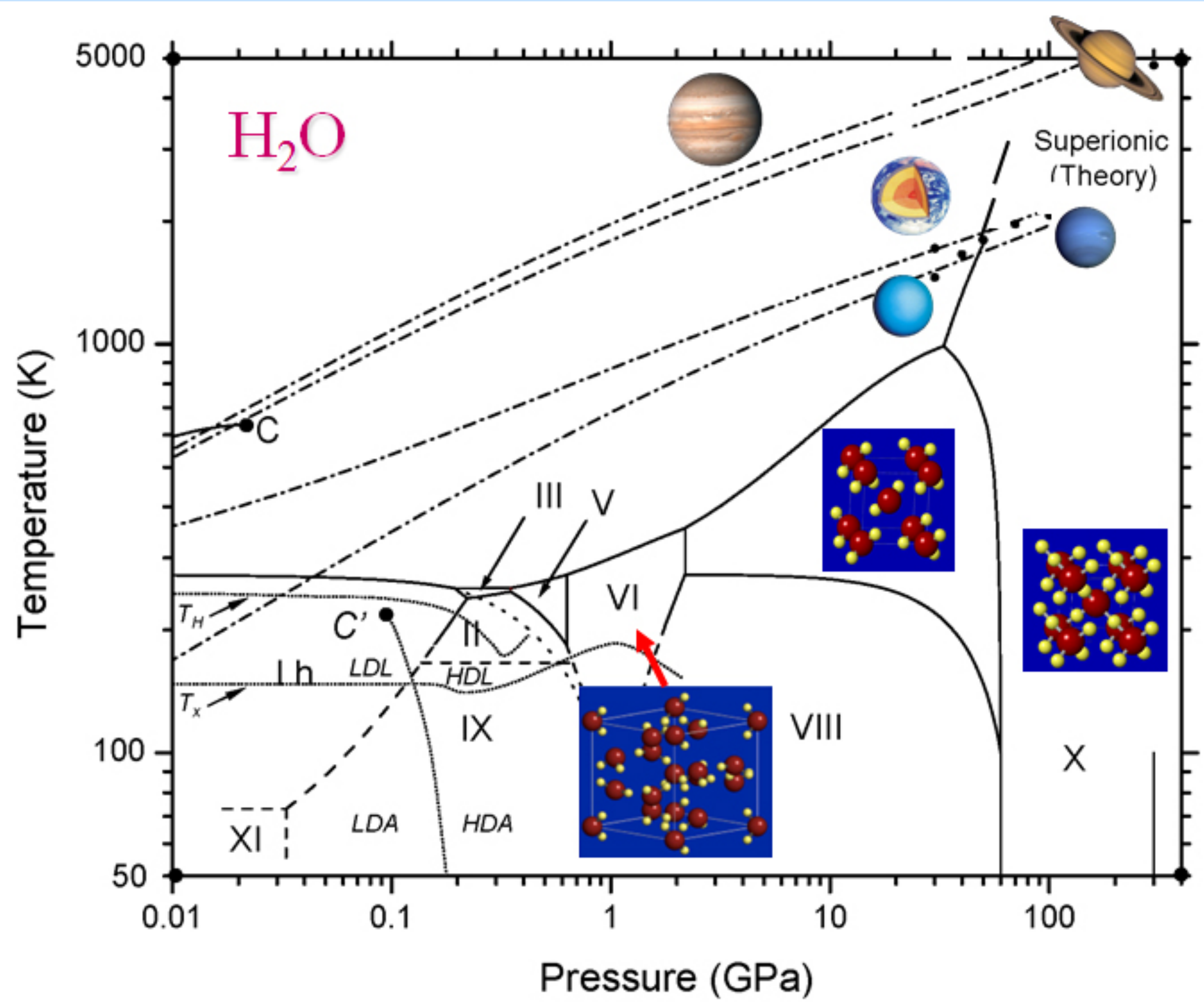
[Gorelli et al., *Phys. Rev. B* (2008)]

- **Increasing orbital overlap with pressure**
- **Intermolecular π^*-bonding in $(O_2)_4$ cluster**
- **Closed-shell interactions stabilize the cluster**
- **Superconducting phase at 90 GPa (T_c ~ 1 K)**

High-pressure behavior of water

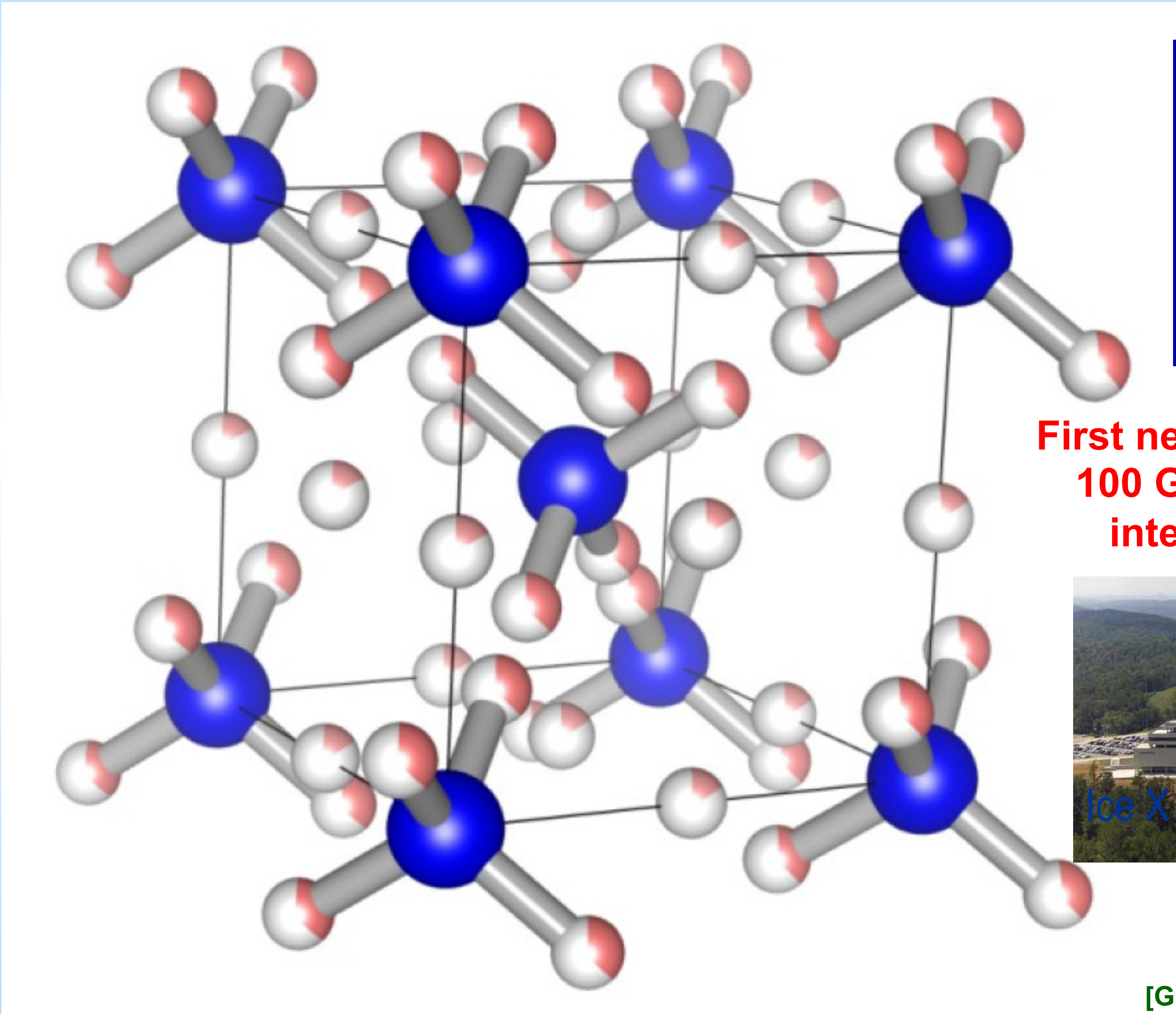


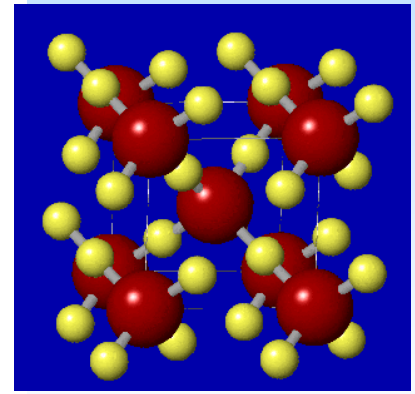
High-pressure behavior of water:
new questions and surprises



- ~20 stable and metastable phases
- Novel transitions
  - *non-molecular*
  - *amorphization*
  - *superionic*
  - *liquid/liquid trans*
- High *P-T* fluid
- New chemistry
- Breakdown of H_2O
- Supporting life at extreme *P-T*

High-pressure behavior of water:
new questions and surprises





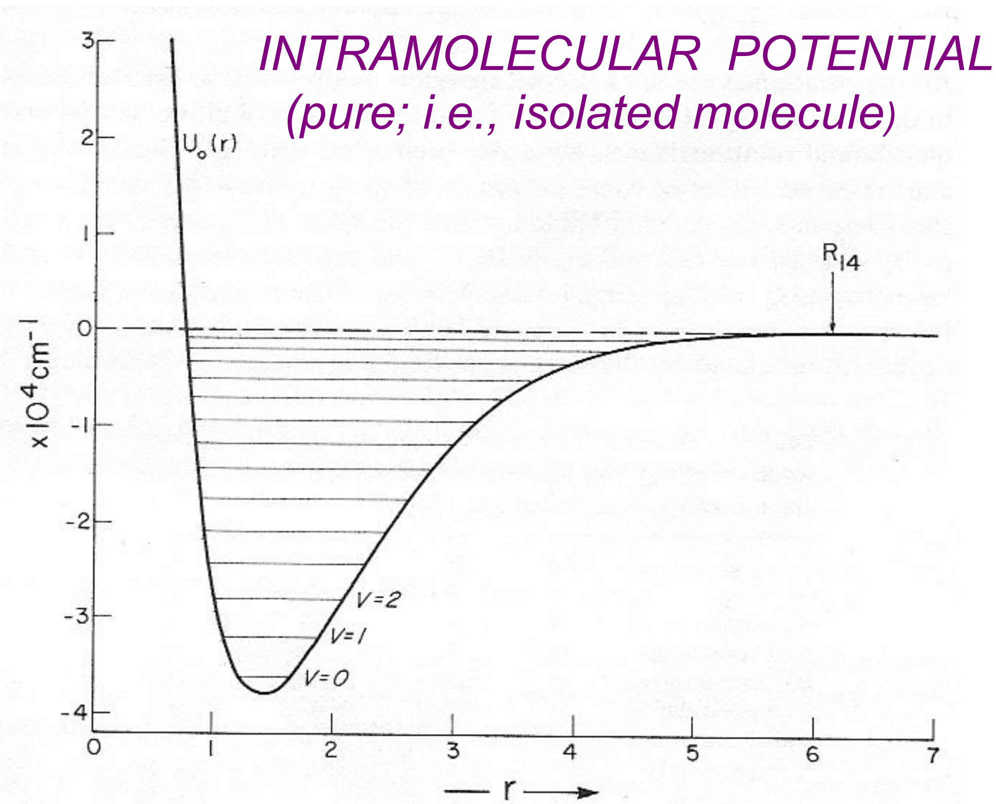
First neutron scattering at 100 GPa: evidence for interstitial protons

Spallation Neutron Source (ORNL)

[Guthrie et al. *PNAS* (2013)]

Hydrogen: *The 'Simplest' Molecule*

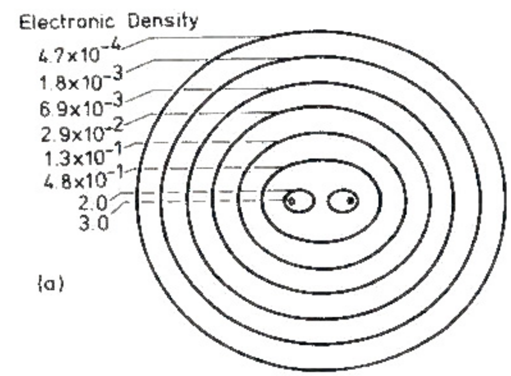
INTRAMOLECULAR POTENTIAL
(pure; i.e., isolated molecule)



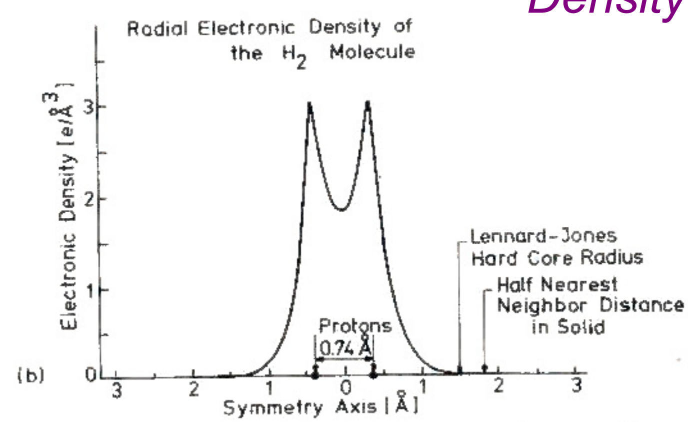
- **Strong covalent bond: 4.53 eV**
- **14 bound vibrational states**

[Kolos & Wolniewicz, *J. Chem. Phys.* (1964-1974)]

ISOLATED MOLECULE
Nearly spherical electron density

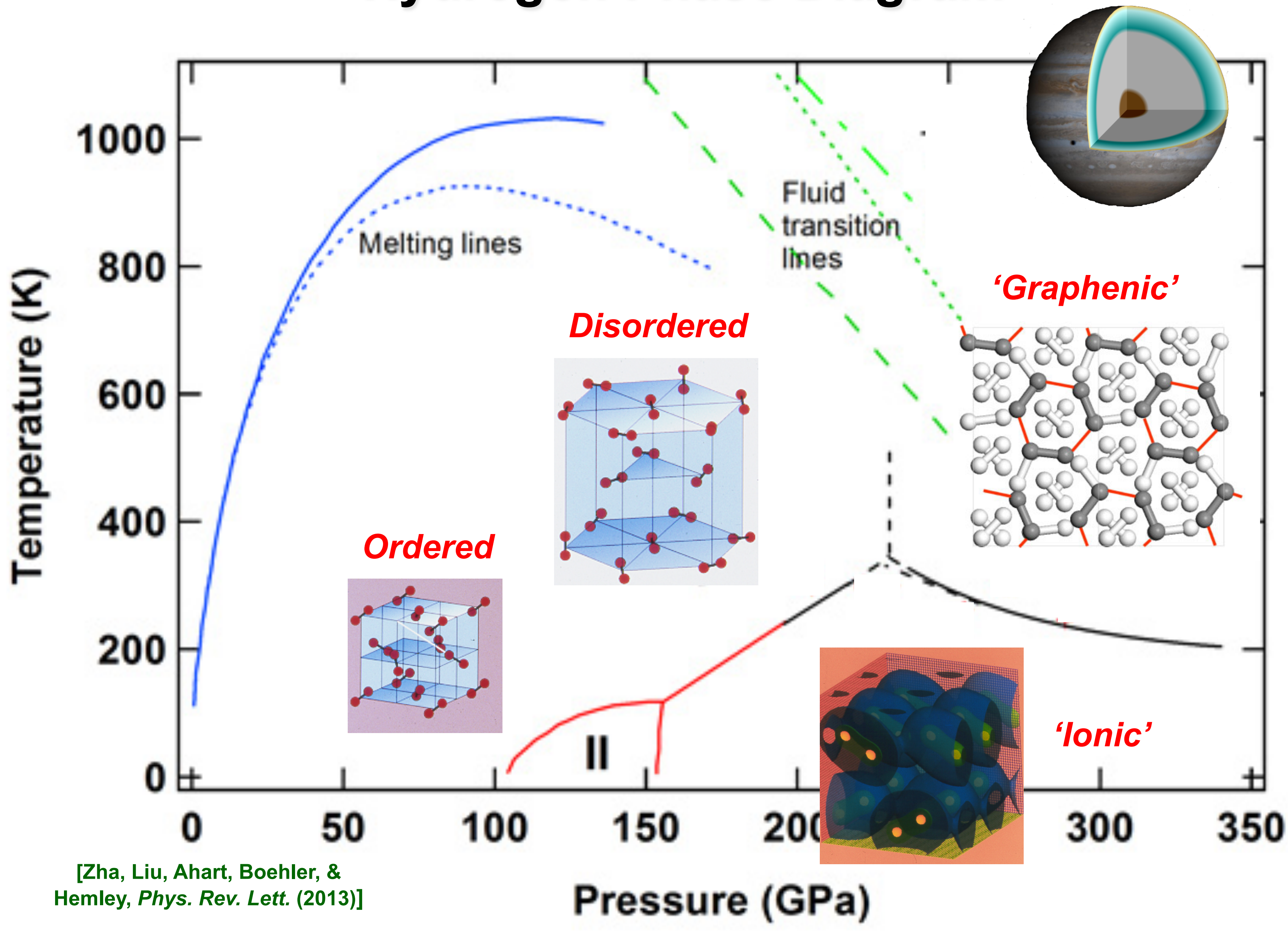


Charge Density



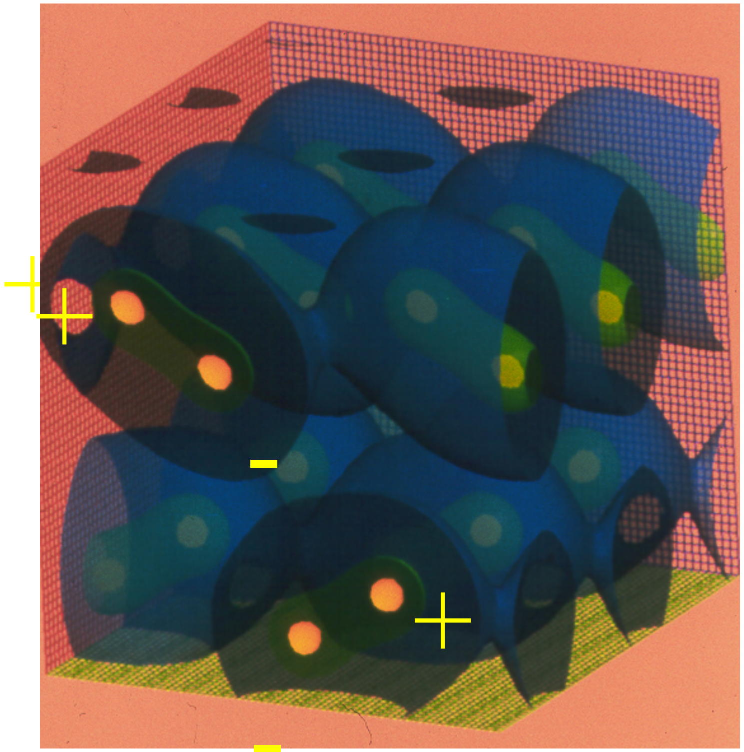
[Silvera, *Rev. Mod. Phys.* (1980)]

Hydrogen Phase Diagram

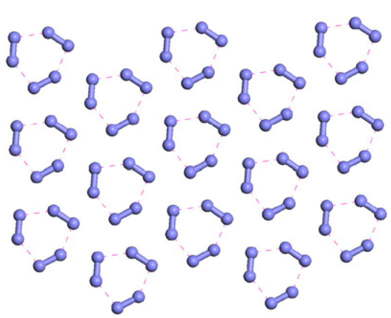


[Zha, Liu, Ahart, Boehler, & Hemley, *Phys. Rev. Lett.* (2013)]

Phase III: 'Ionic' phase of dense hydrogen



[Kaxiras *et al.*, *Phys. Rev. Lett.* (1992)]



[Pickard & Needs,
Nature Physics (2007)]
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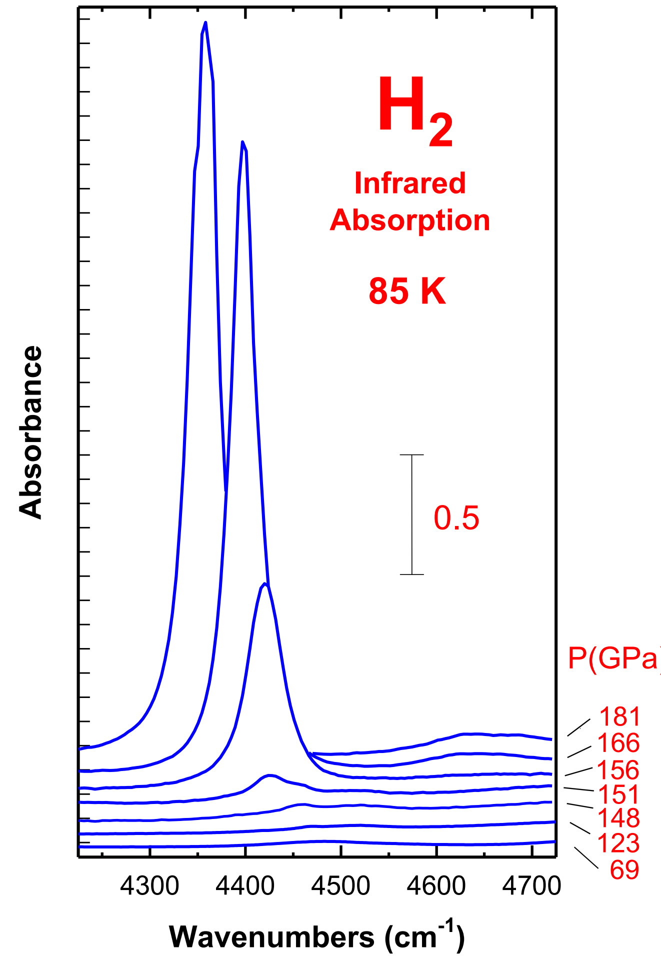
Infrared Vibron



[Hanfland *et al. Phys. Rev. Lett.* (1993);
Hemley et al., ibid. (1994) Chen *et al. ibid* (1995)]

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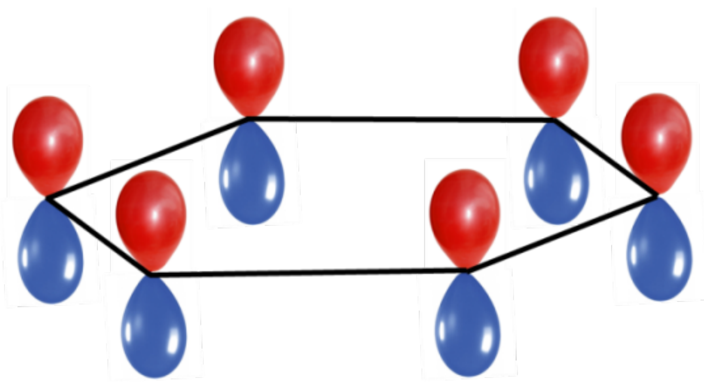
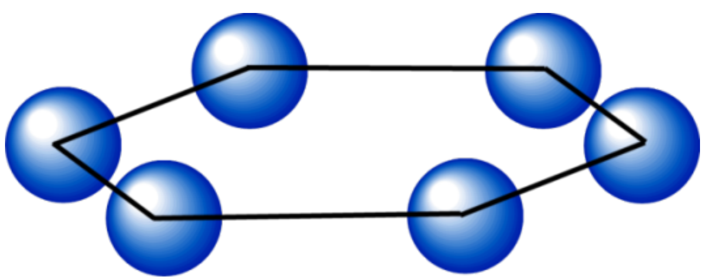
Phase IV is a graphene-based layer structure

C-graphene

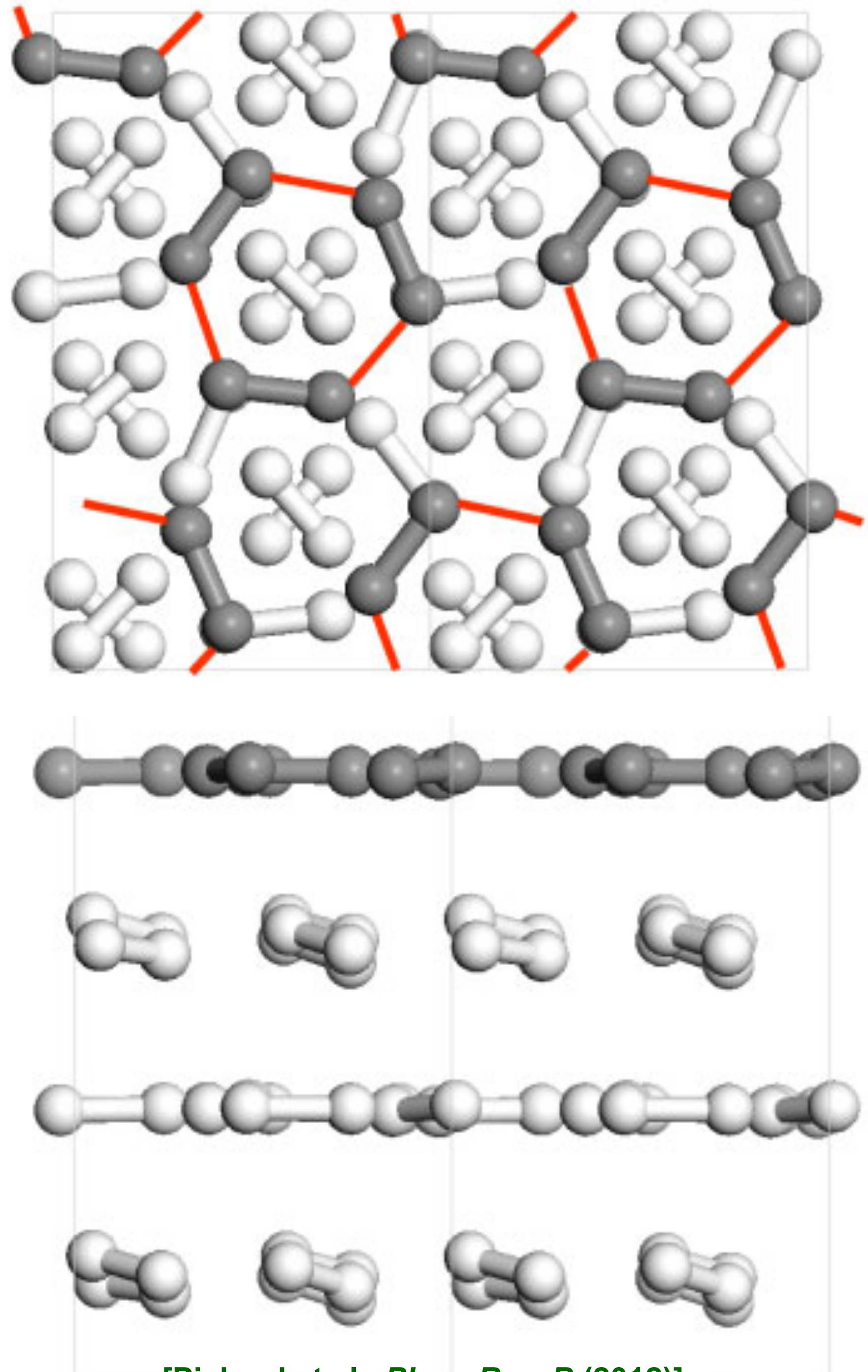


H-graphene



H_6 ‘aromatic cluster’

[Naumov & Hemley, *Acct. Chem. Res.* (2014);
see also, LeSar & Herschbach, *J. Phys. Chem.* (1981);
Dixon et al., *Faraday Disc.* (1977)]

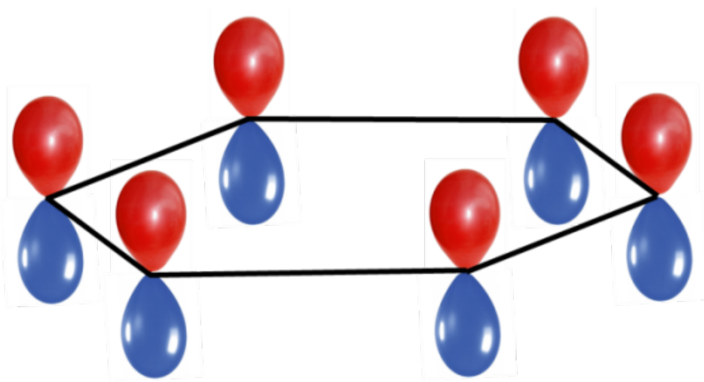


[Pickard et al., *Phys. Rev. B* (2012)]

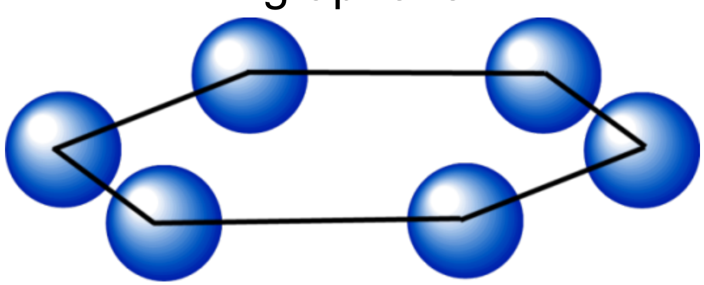
Graphene-based layer structures for dense hydrogen

[Cohen, Naumov & Hemley, *PNAS* (2013)]

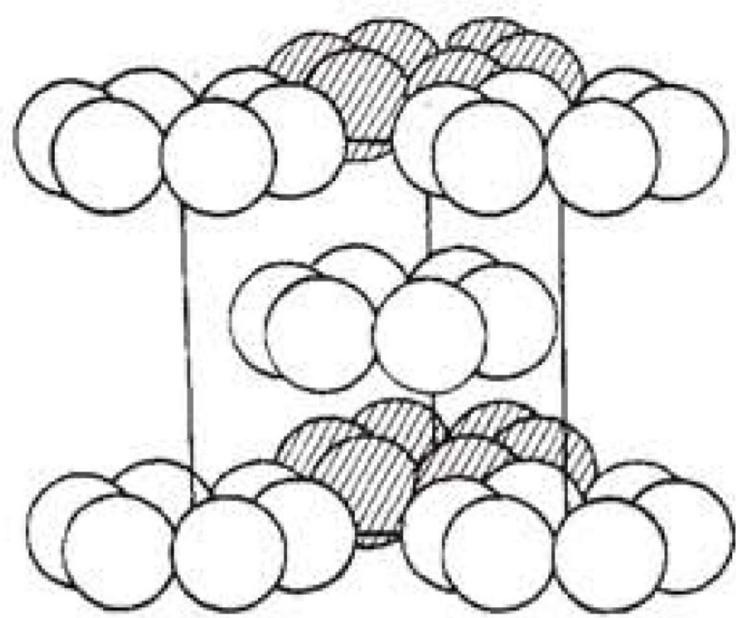
C-graphene



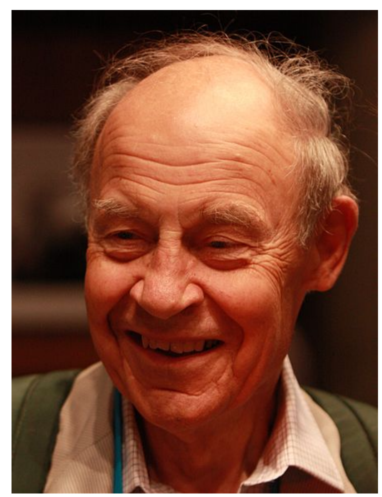
H-graphene



H_6 'aromatic cluster'

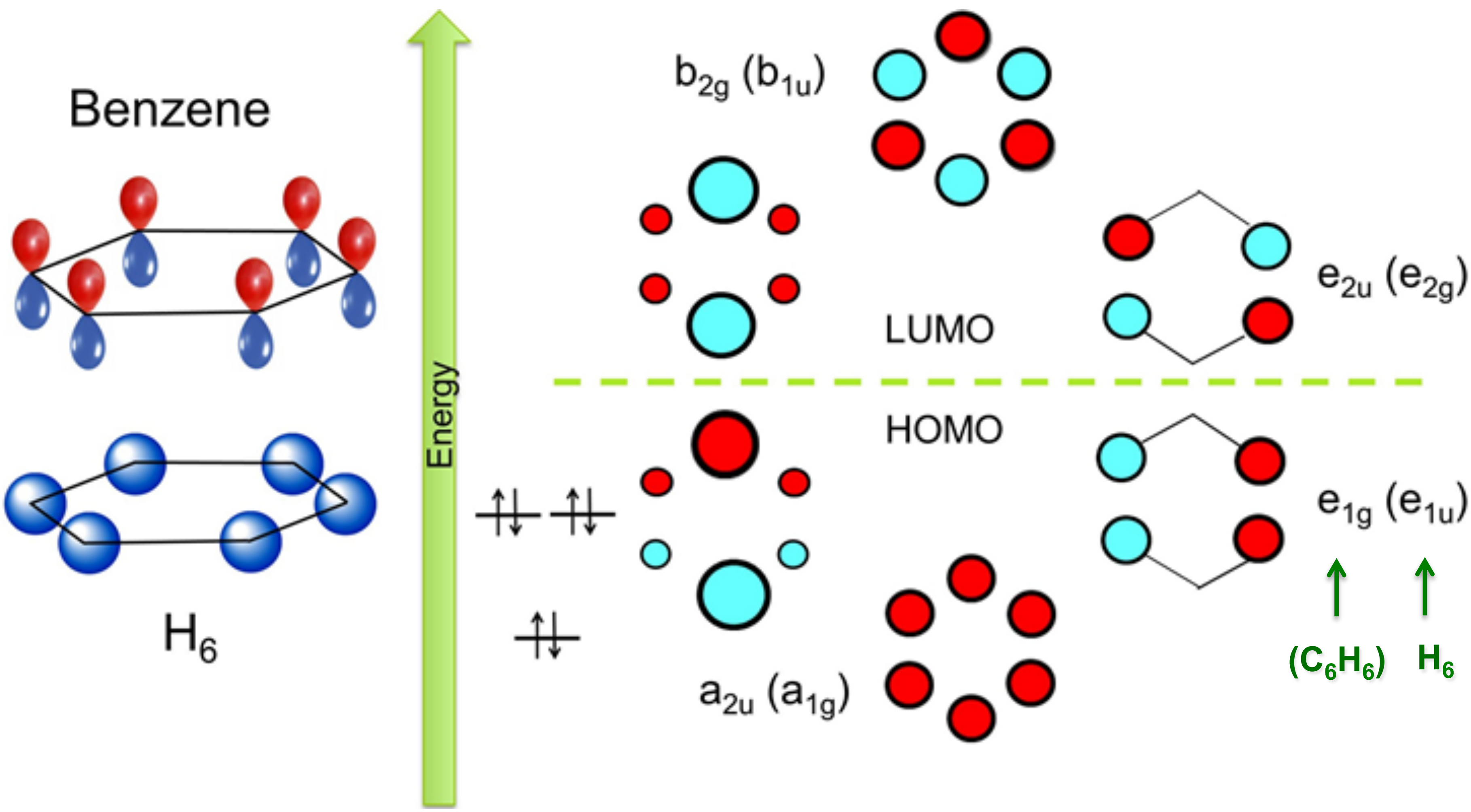


[LeSar & Herschbach, *J. Phys. Chem.* (1981);see also, Dixon et al., *Faraday Disc.* (1977)]



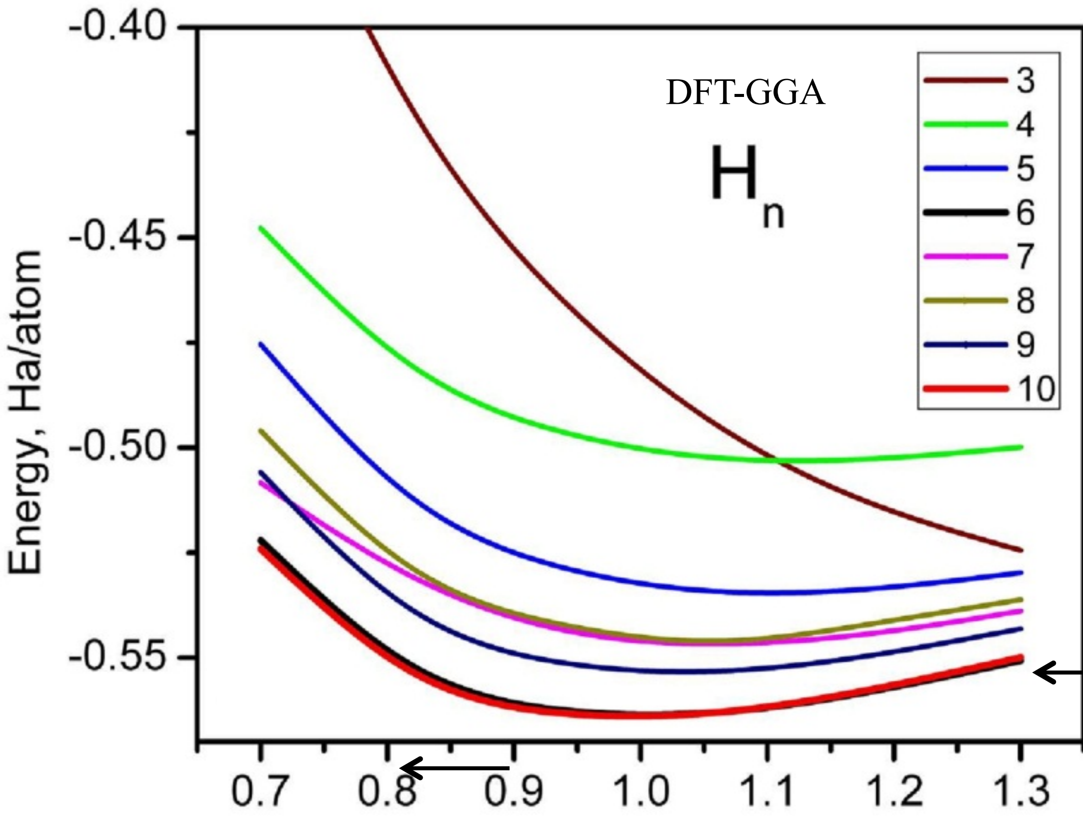
Dudley R. Herschbach

Analogy between 1*s* electrons in hydrogen and π electrons in carbon



[Naumov & Hemley, *Accts. Chem. Res.* (2014)]

Total energies per atom for H_n rings ($n = 3 - 10$)



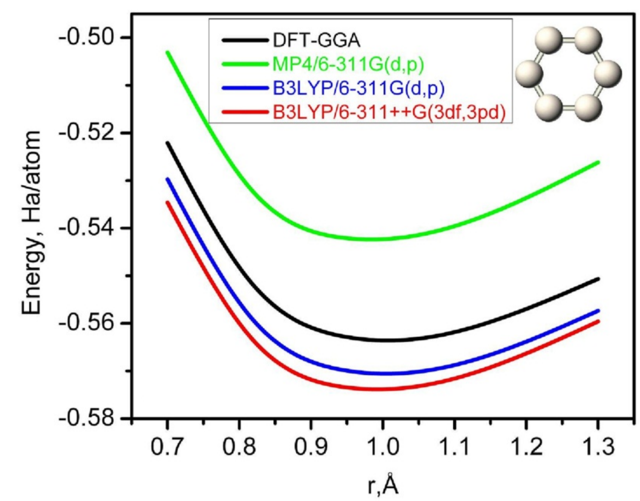
Hückel's rule:

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

$n = 6, 10$

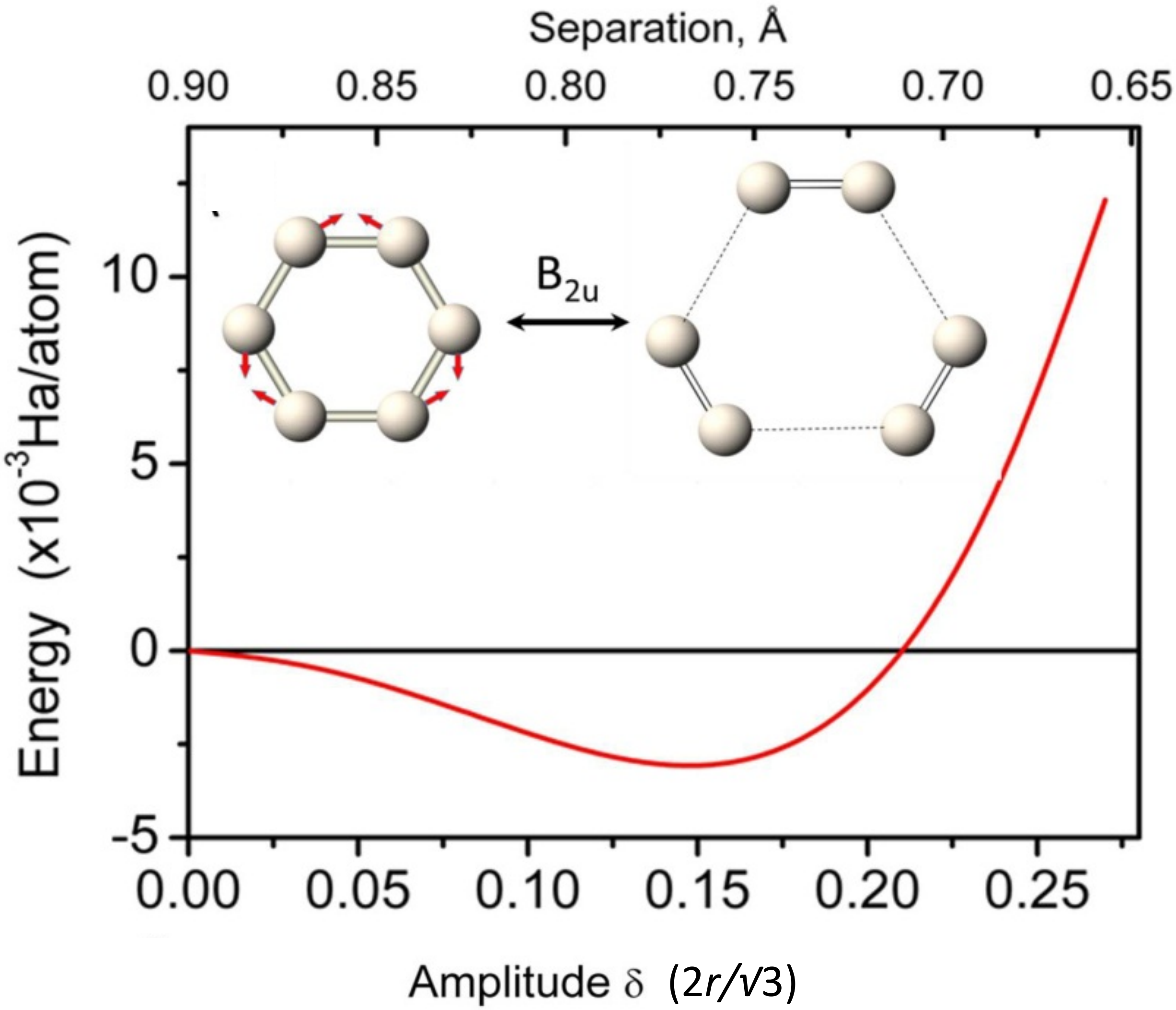
Correlation corrections:

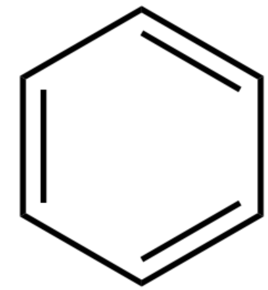
Lower the total energy but have little effect on energy differences



[Naumov & Hemley, *Accts. Chem. Res.* (2014)]

H_6 ring energetics with respect to the B_{2u} mode





- D_{6h} to D_{3h}
- The closed shell electronic structure becomes more stable
- Both are aromatic

B3LYP/6-331G(3df,3pd)

[Naumov & Hemley, *Accts. Chem. Res.* (2014)]

EXAMPLES

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2. **Novel Compounds**
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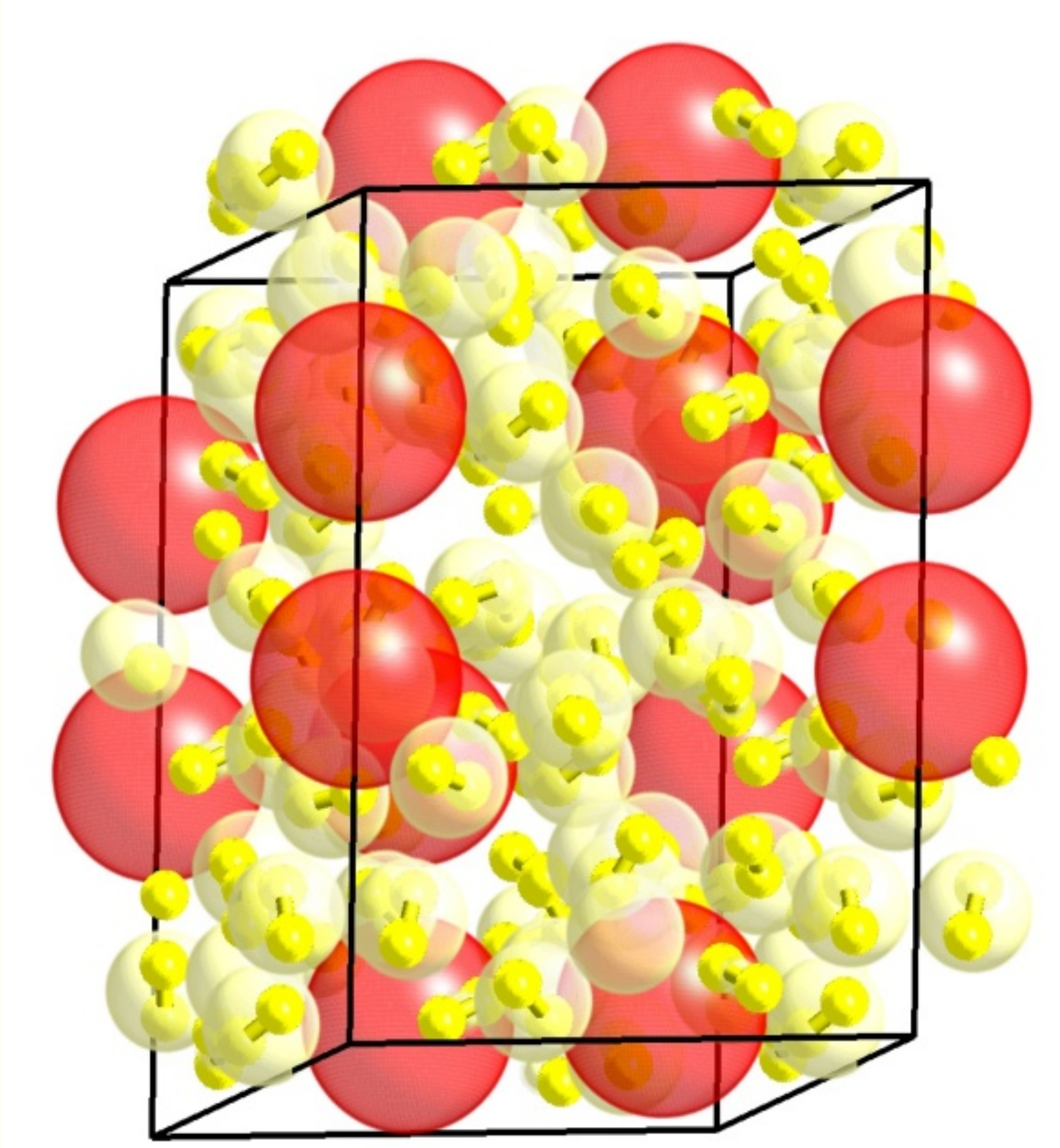
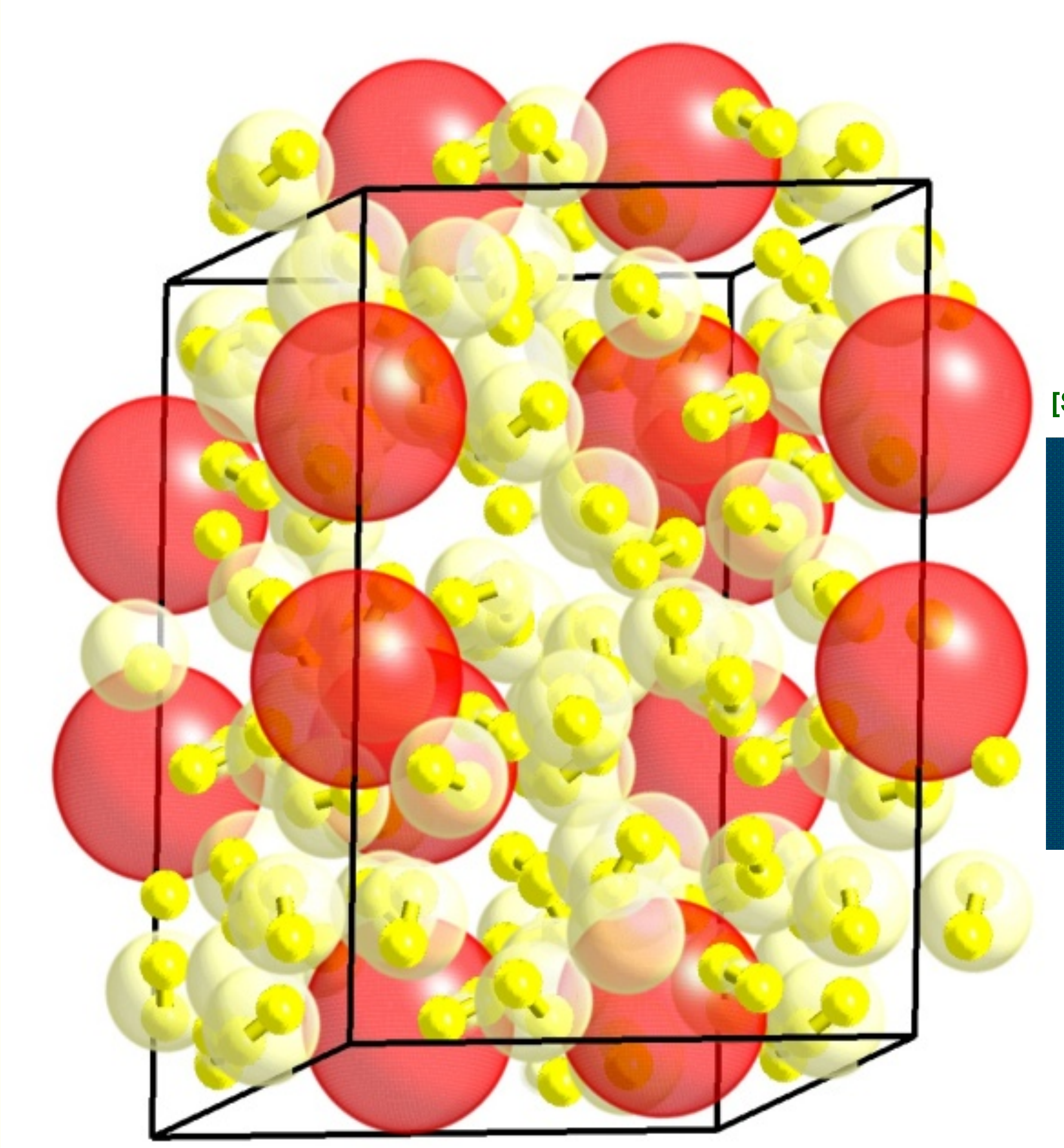
5. Softest Matter



Novel Molecular Compounds

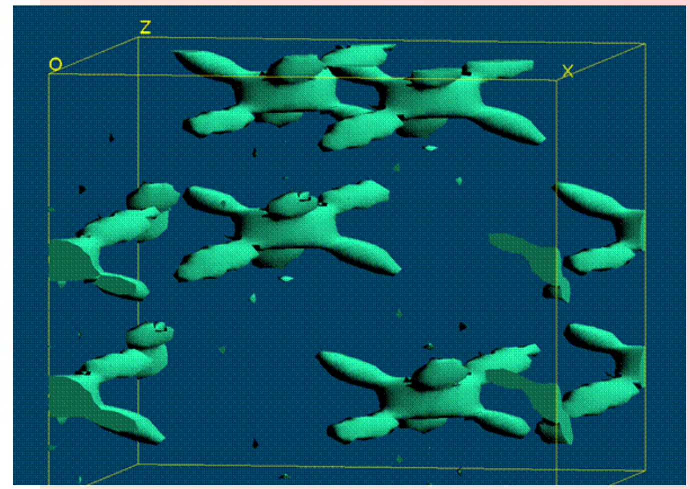
$Xe(H_2)_8$



Novel Molecular Compounds

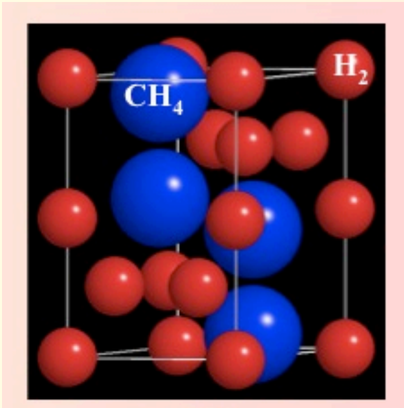
$Xe(H_2)_8$

[Somayazulu et al., *Nature Chem.* (2009)]



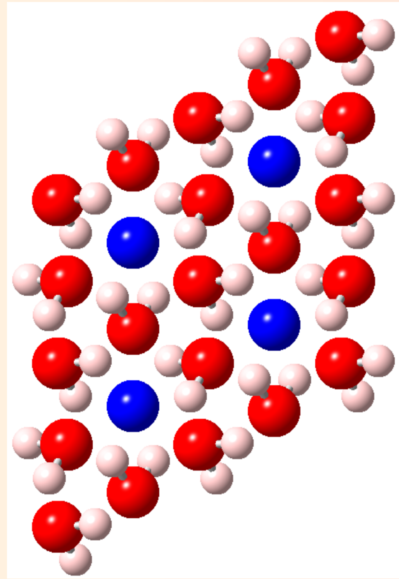
Xe electron density

Novel Molecular Compounds



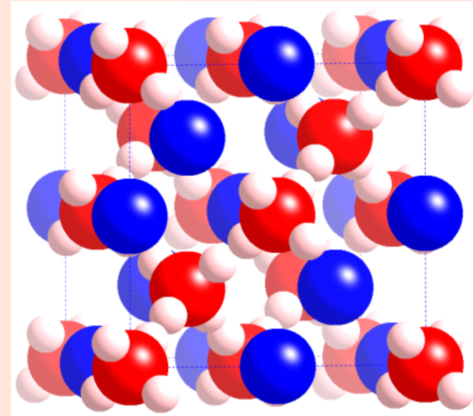
$CH_4(H_2)_4$
33.4 wt% H_2

[Somayazulu *et al., Science* (1996);
W. Mao *et al. Chem. Phys. Lett.* (2005)]



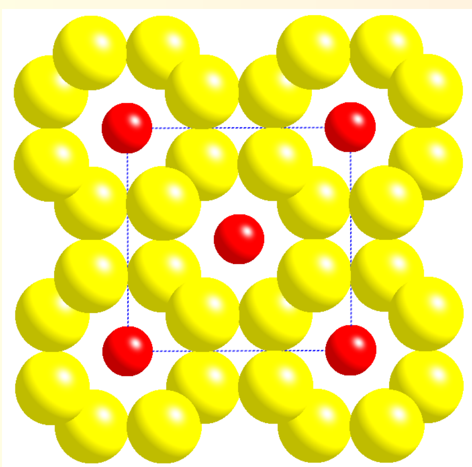
$(H_2O)_2H_2$
α-quartz-type

[Strobel et al.,
J. Phys. Chem.
(2011)]



H_2O-H_2
11.3 wt% H_2

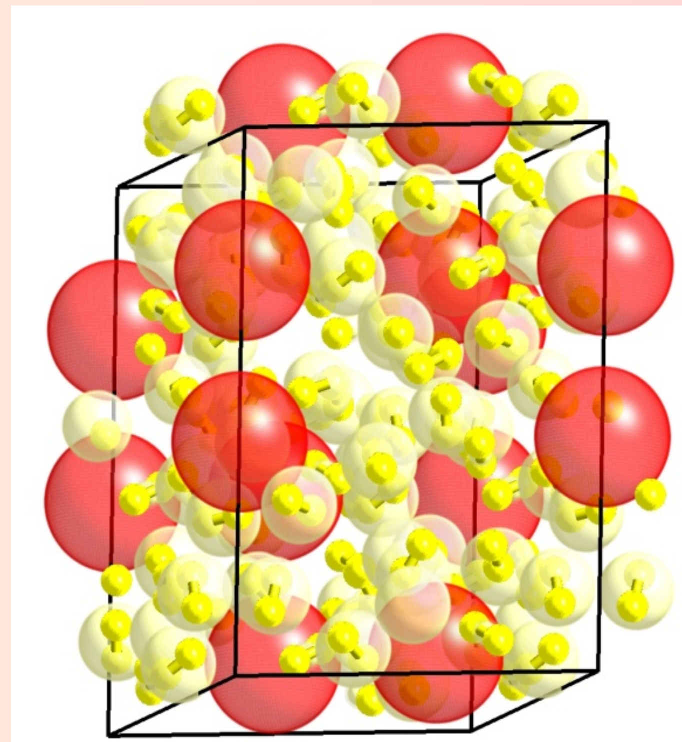
[Vos et al.,
Phys. Rev. Lett. (1993)]



$(H_2S)_2H_2$
Al_2Cu type

[Strobel et al., *Phys. Rev. Lett.* (2010)]

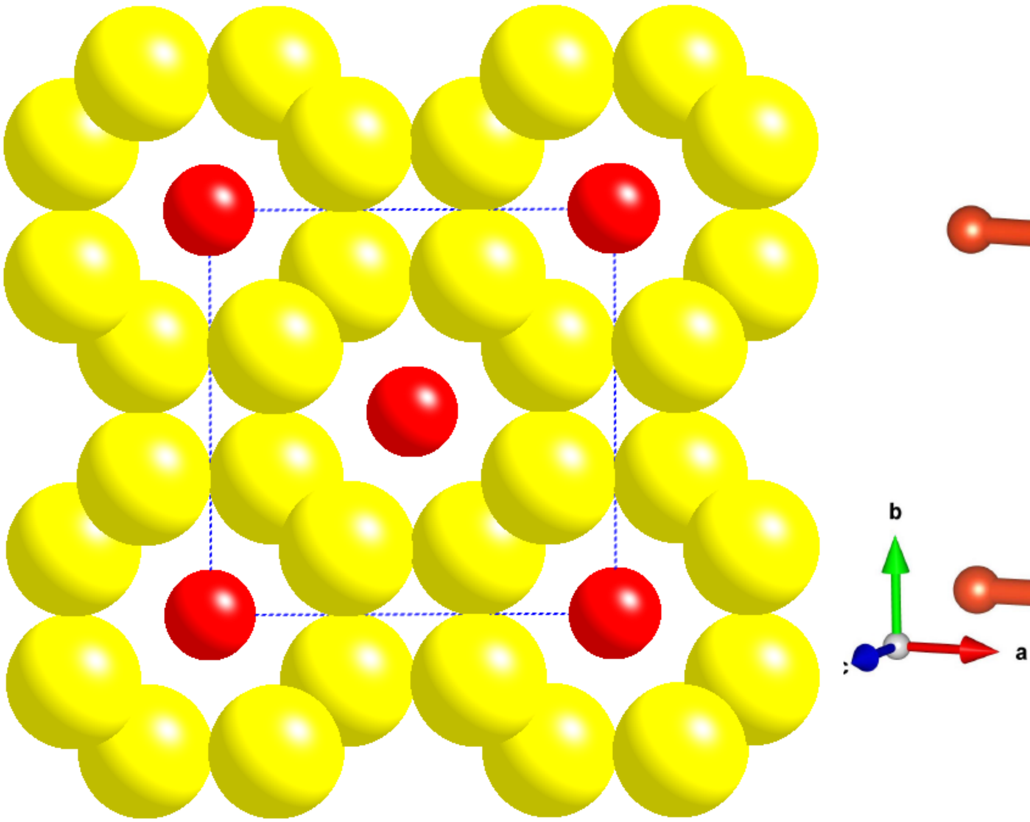
- ***PRECURSOR TO HIGH T_c H_3S***
  T_c = 203 K
  [Drozdov et al., *Nature.* (2015)]



$Xe(H_2)_8$
[Somayazulu et al., *Nature Chem.* (2009)]

New high T_c superconductors

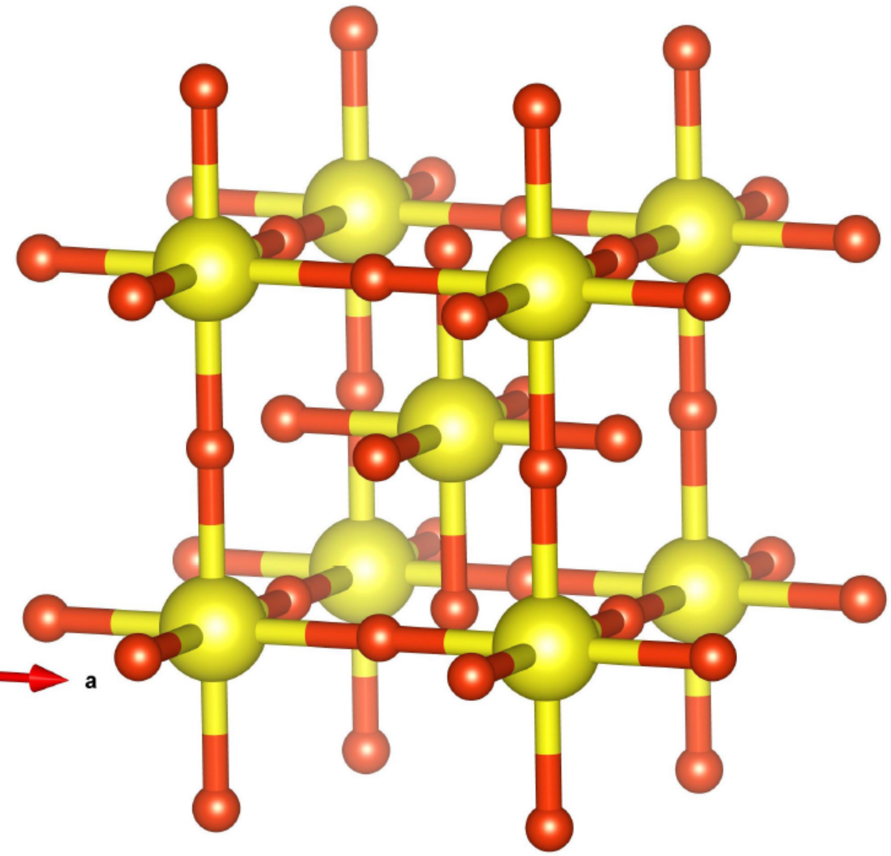
$(H_2S)_2H_2$



Al_2Cu type

[Strobel et al., *Phys. Rev. Lett.* (2010)]

H_3S



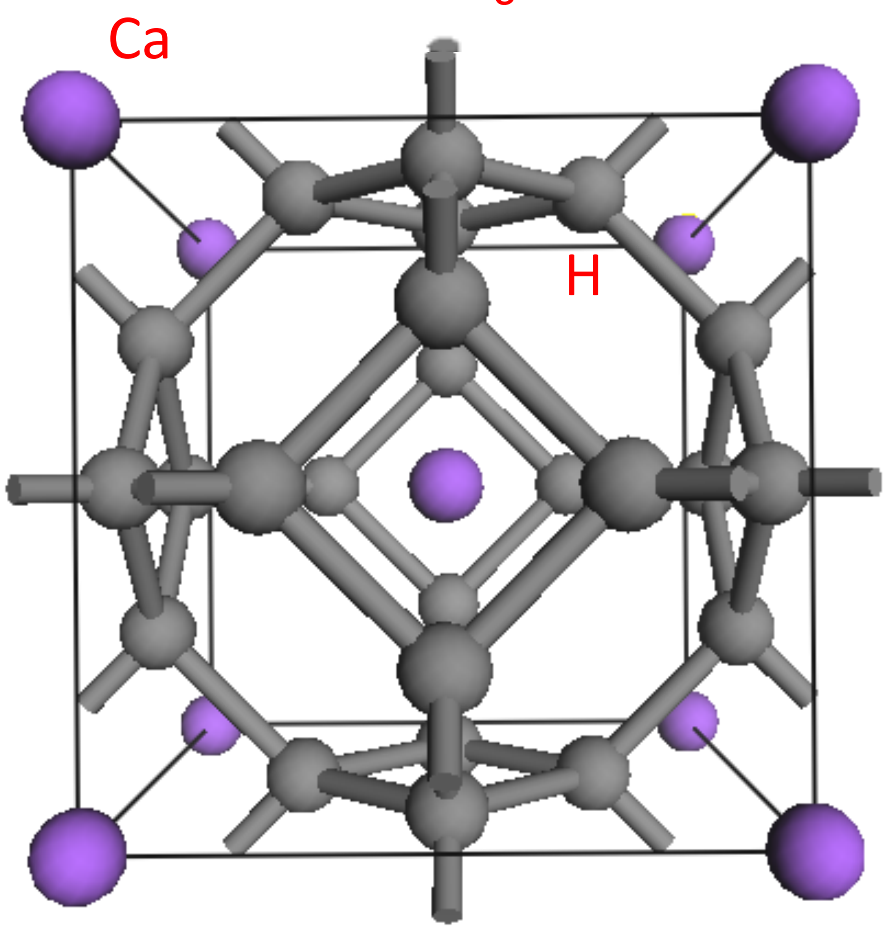
T_c = 203 K

[Drozdov et al., *Nature* (2015)]

[Quan and Pickett, arXiv (2015)]

New high T_c superconductors

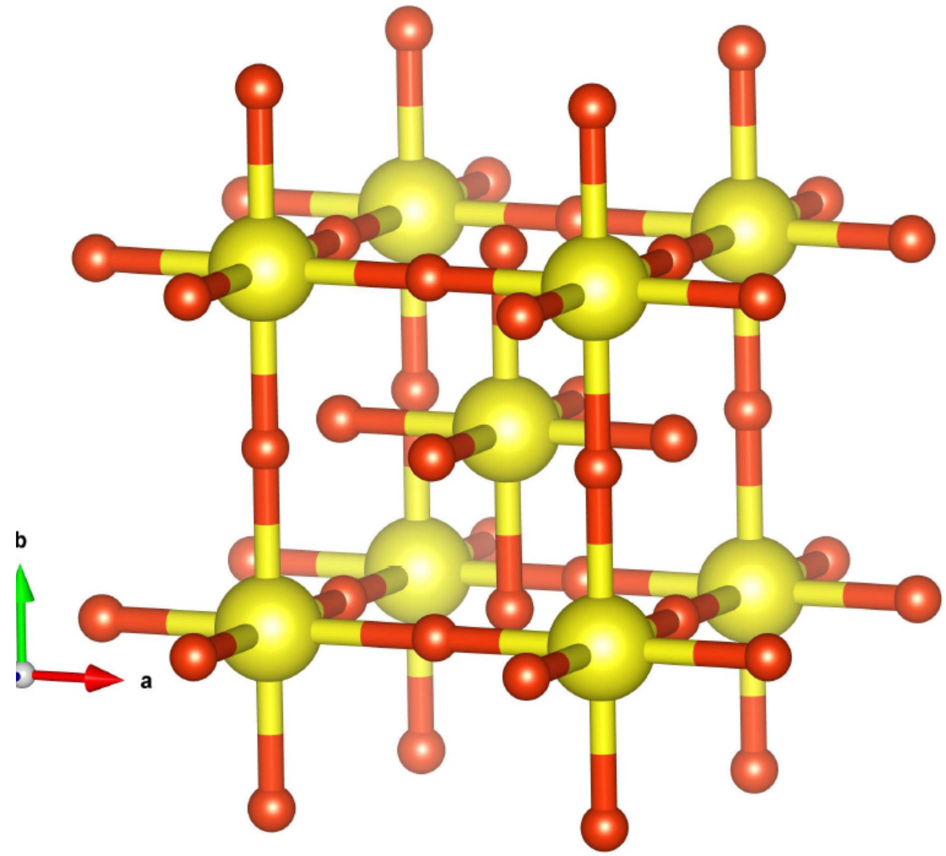
CaH_6



T_c = 220-235 K *(predicted)*

[Wang et al., *PNAS* (2013)]

H_3S

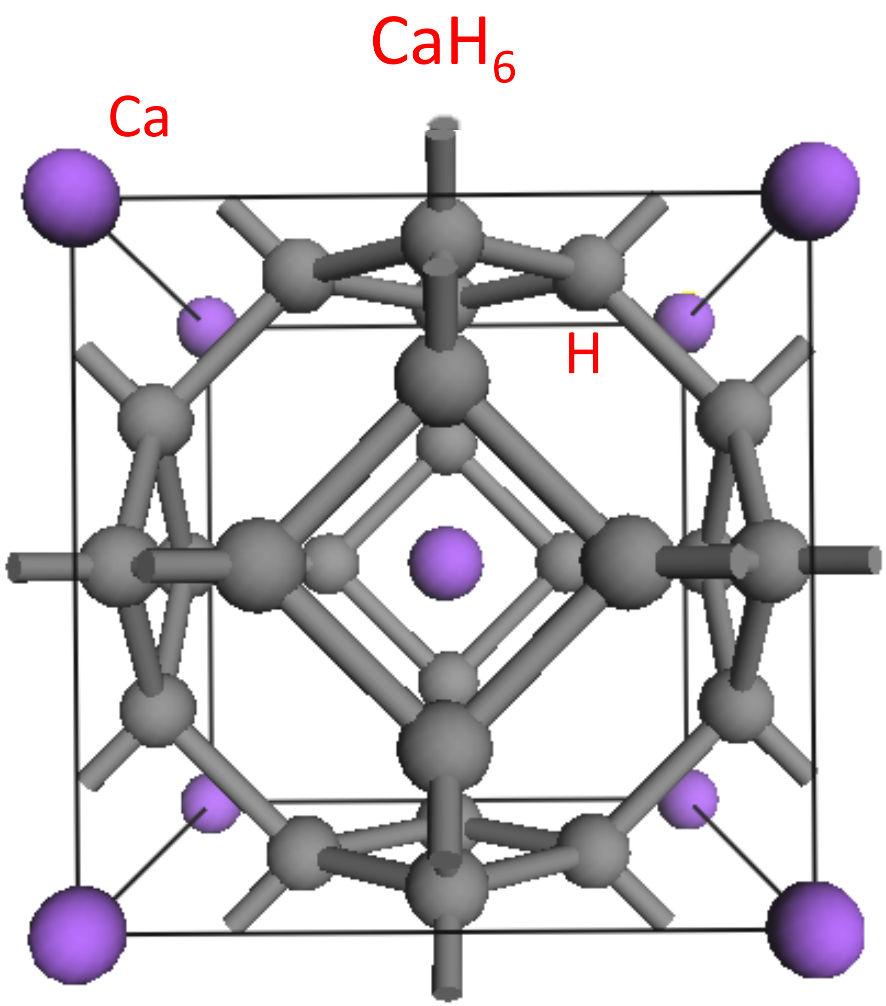


T_c = 203 K

[Drozdov et al., *Nature* (2015)]

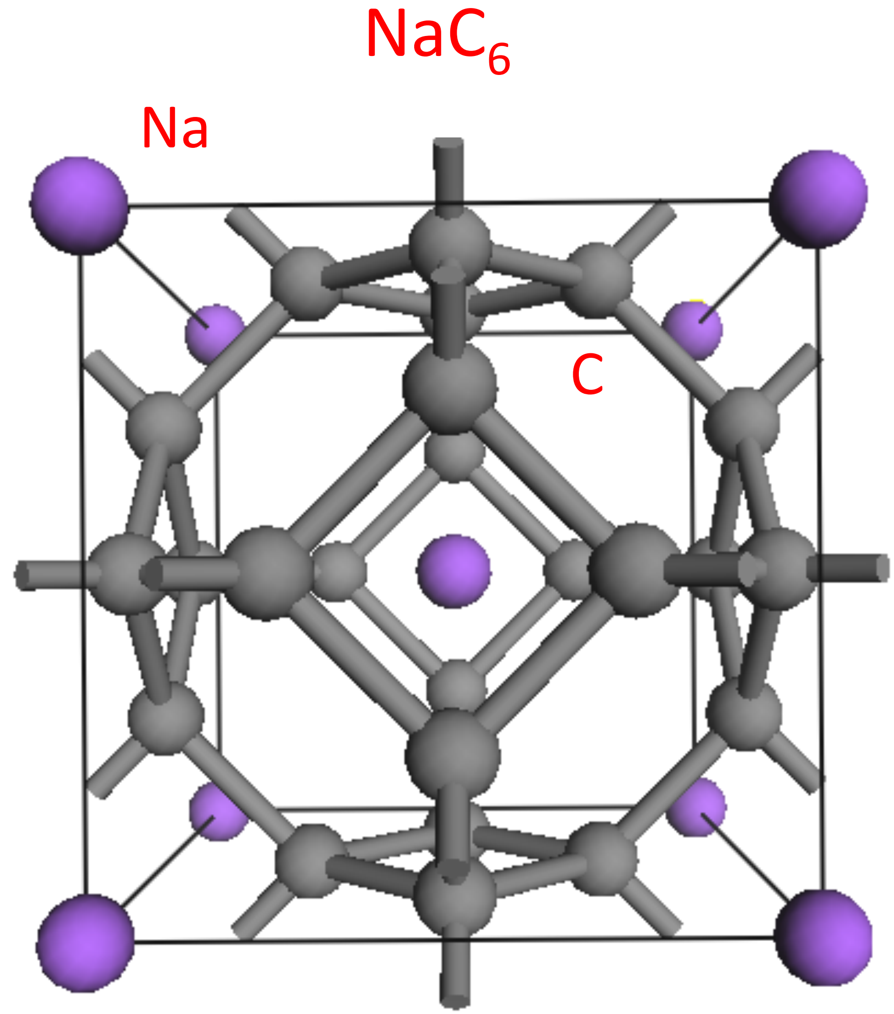
[Quan and Pickett, arXiv (2015)]

New high T_c superconductors



T_c = 220-235 K *(predicted)*

[Wang et al., *PNAS* (2013)]



T_c = 116 K *(predicted)*

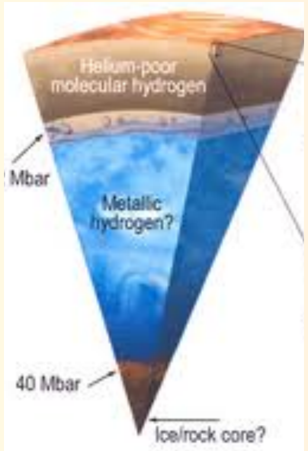
[Lu et al., *Phys. Rev. B* (2016)]

- ***Predicted stable at 1 bar***

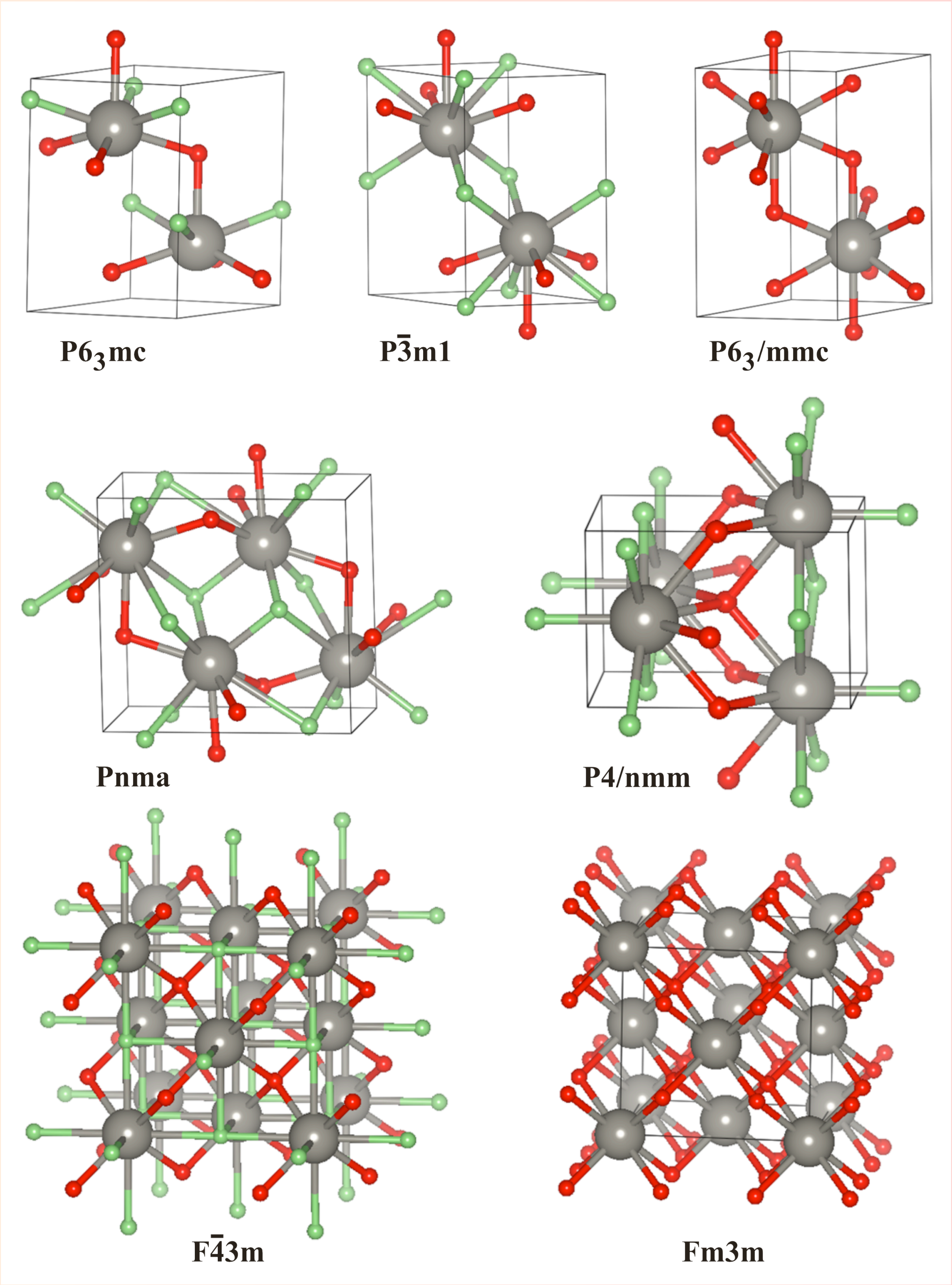
Hydriding of 'Inert' Metals:
Re, Ir, Pt, W

Structures of WH_n

Planetary Implications



- ***Extreme reactivity will 'erode' metallic Jovian cores***

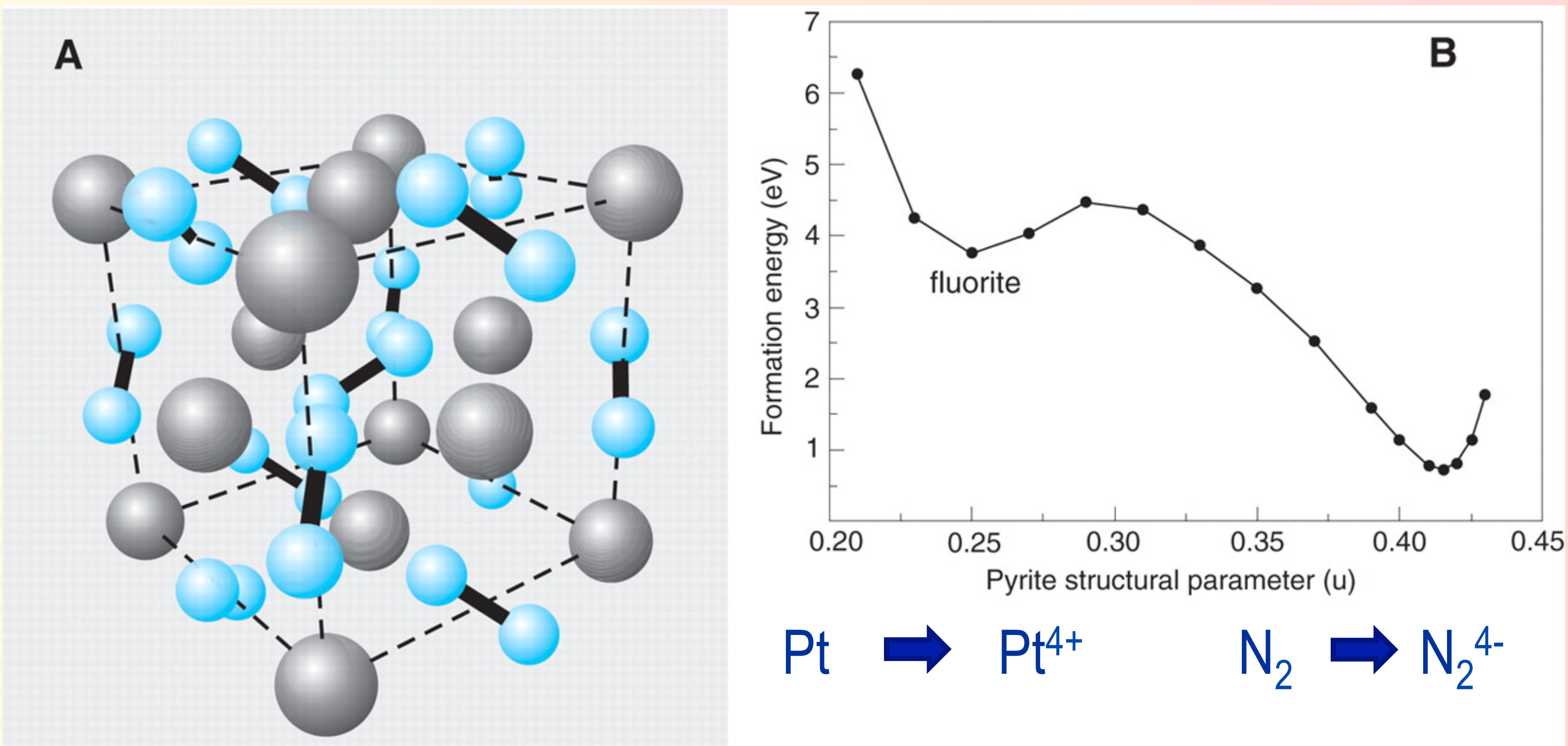


[Zaleski-Eigierd et al., *Phys. Rev. B* (2012)]

LETTERS

Synthesis and characterization of a binary noble metal nitride

EUGENE GREGORYANZ[1,2*†], CHRYSTELE SANLOUP[3], M. SOMAYAZULU[4], JAMES BADRO[1], GUILLAUME FIQUET[1], HO-KWANG MAO[2] AND RUSSELL J. HEMLEY[2]



$Pt \rightarrow Pt^{4+}$ $N_2 \rightarrow N_2^{4-}$

EXAMPLES

1. ‘Simple’ Molecules
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4. Continuing with Carbon
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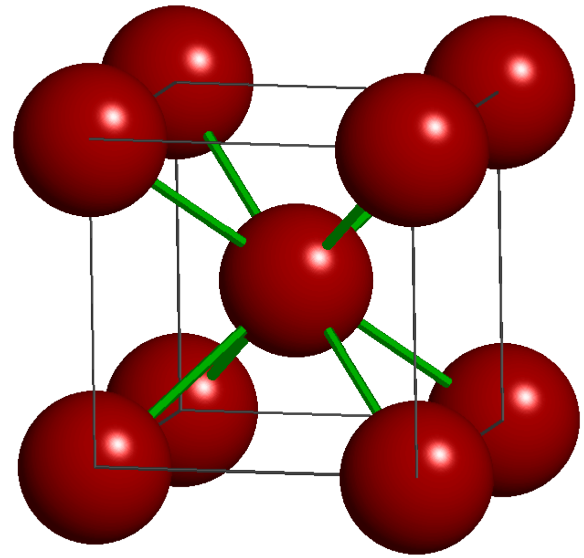
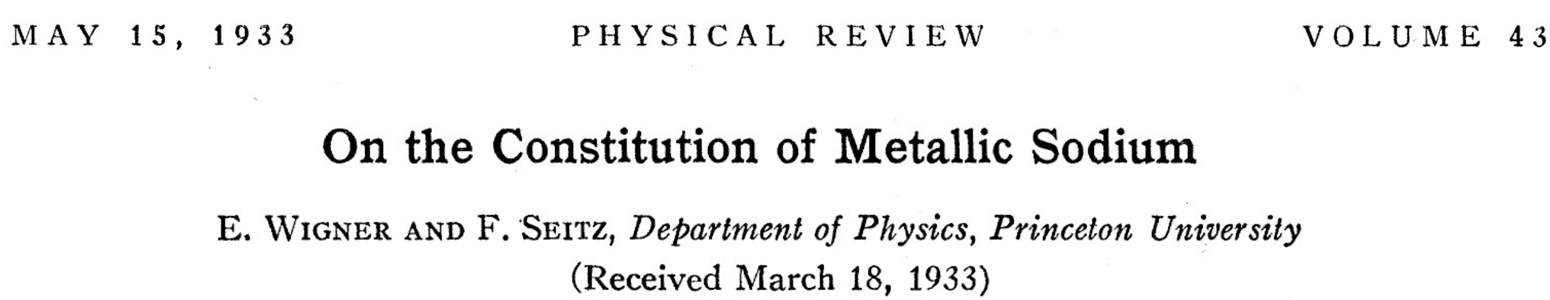
The Simple Metals?



Body Centered Cubic (BCC)


MAY 15, 1933 PHYSICAL REVIEW VOLUME 43

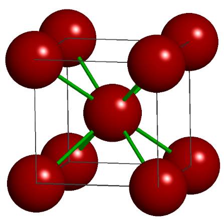
On the Constitution of Metallic Sodium

E. WIGNER AND F. SEITZ, *Department of Physics, Princeton University*

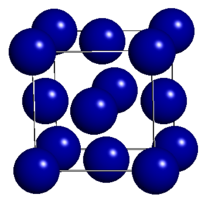
(Received March 18, 1933)

The Simple Metals?

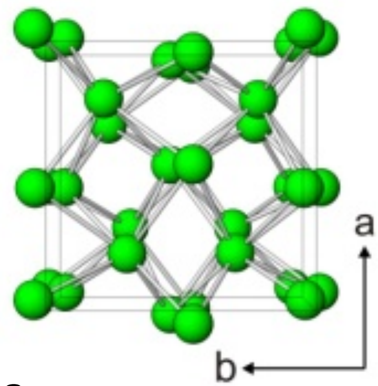
BCC



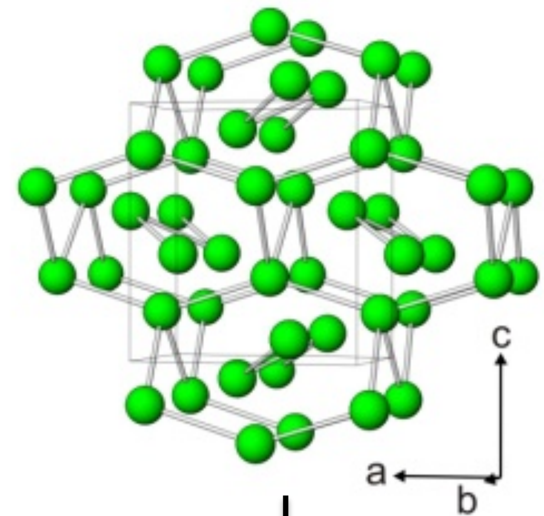
FCC



cI16



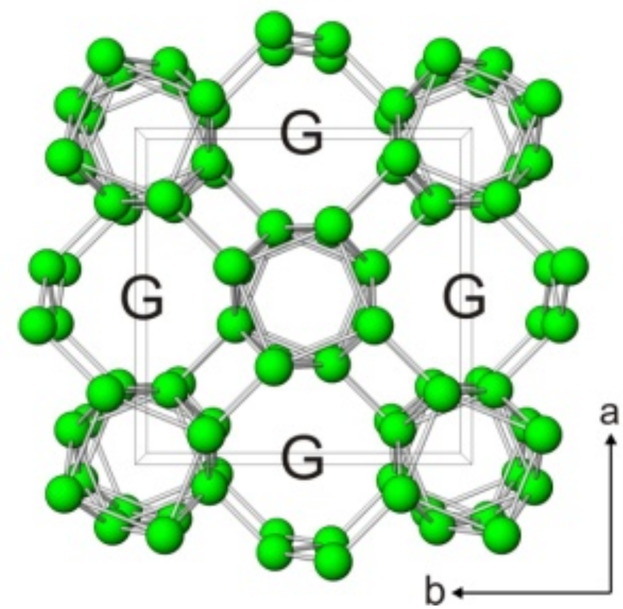
oP8

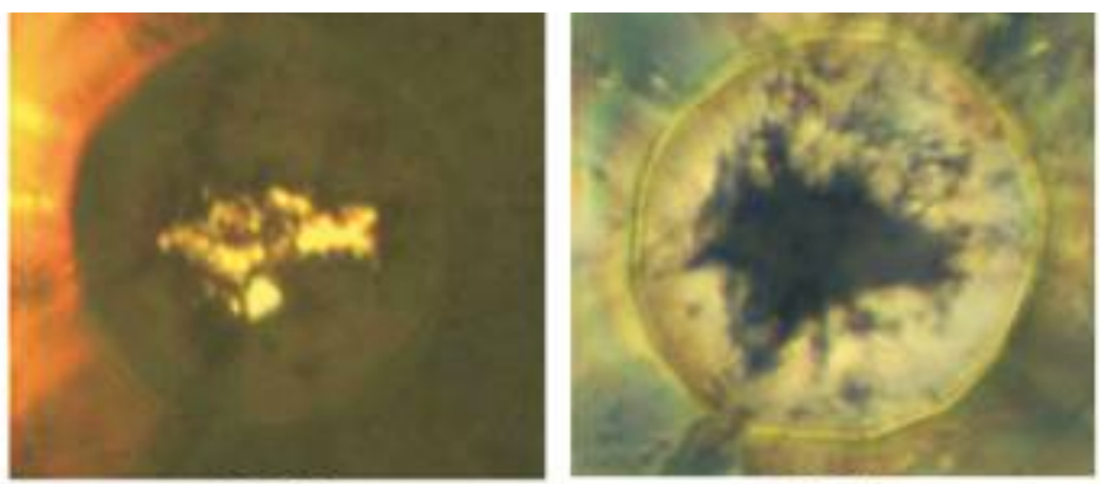


[Wigner & Seitz, *Phys. Rev.* (1933)]

>100 GPa

tI19





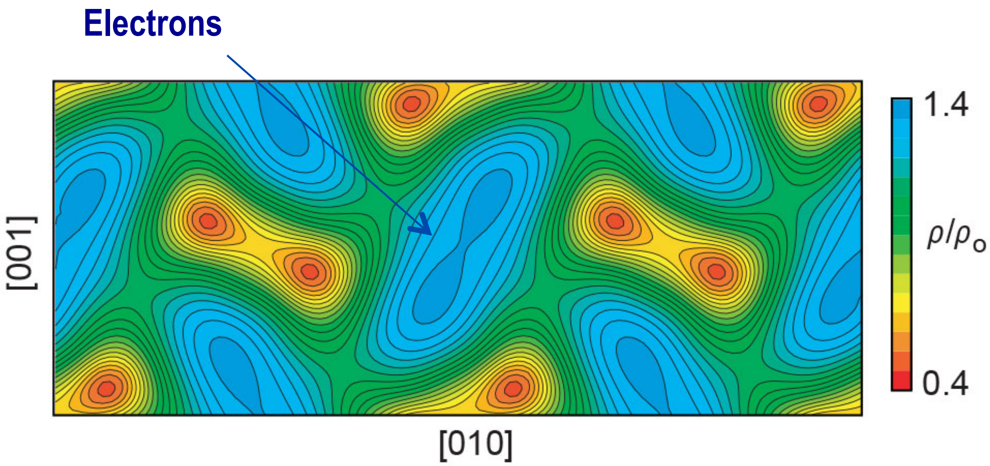
199 GPa 156 GPa

[Gregoryanz et al., *Phys. Res. Lett.* (2005); Science (2008); Ma et al., *Nature* 2009); Lazicki et al., *PNAS* (2009)]

- **>11 Phases in Na**
- **Na melts <300 K**
- **Transparent >200 GPa!**

From Metals to Insulators and Back

Interstitial Electron Localization

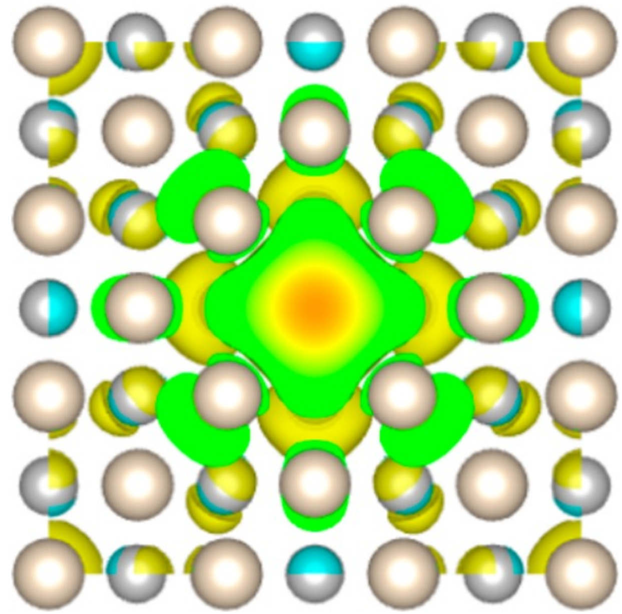


Lithium ***Cmca-4***

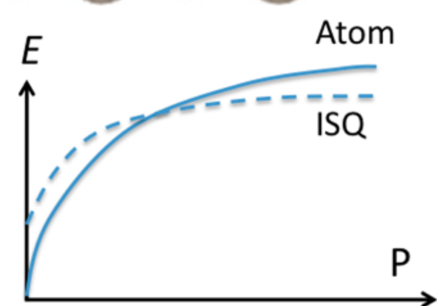
- Repulsion effects: Coulomb repulsion + Pauli exclusion + orthogonality
- The valence electrons avoid the regions in the vicinity of the atoms
- Predicted loss of metallic character

[Neaton & Ashcroft, *Nature* (2000)]

Electride: '*Interstitial Quasiatom*'



- Under pressure, 1*s* levels drop below other atomic *s* levels

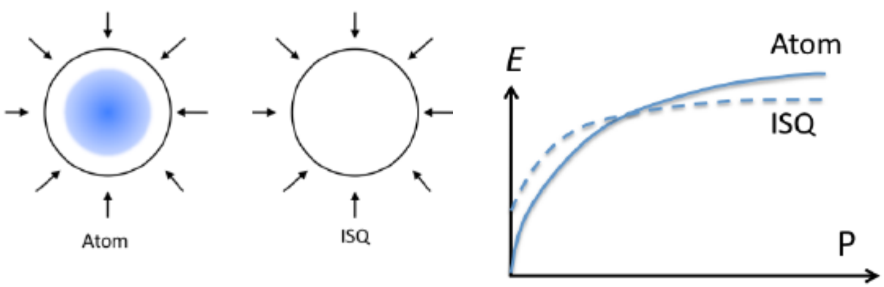


[Miao & Hoffmann, *Accts. Chem. Res.* (2014)]

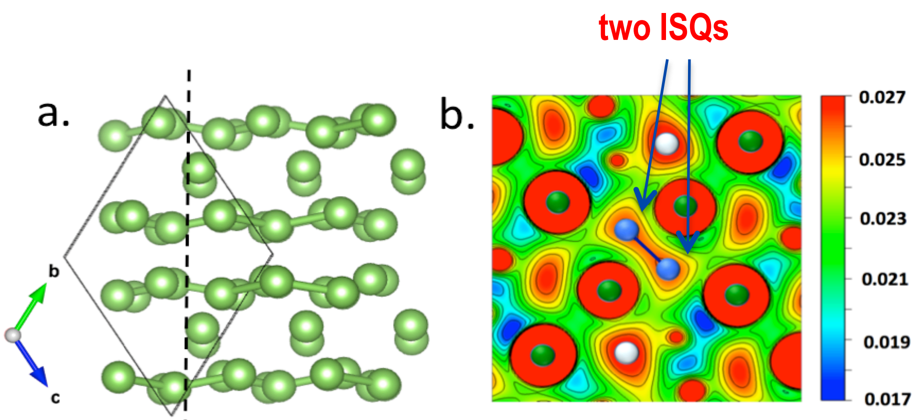
From Metals to Insulators and Back

Formation of Quasimolecules in Insulating States

Interstitial quasiatoms and quasimolecules form when the valence *p* electrons move down relative to s electrons: Li, Na, Mg, Al…



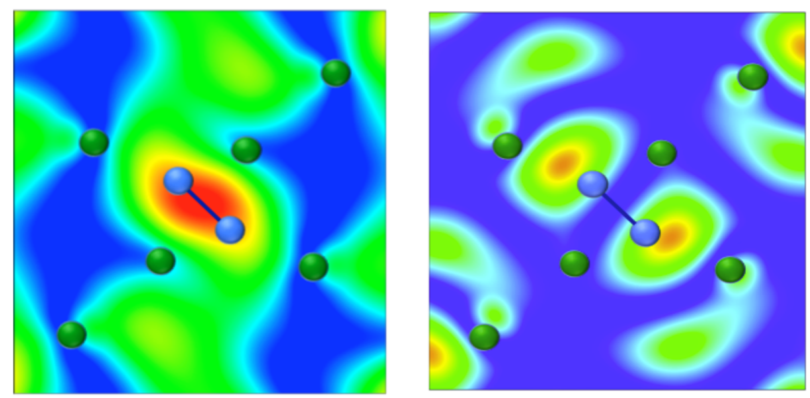
Two nearest ISQ's in *Aba*2-Li form a "molecule"within the structure



Like two H atoms, two ISQs can form both bonding and antibonding orbitals

Charge density for bonding orbital

Charge density for antibonding orbital



The "molecular" orbitals can be understood as maximally localized Wannier functions

isosurface=±2.5

[Miao, Naumov, Hoffmann, & Hemley, *submitted*]

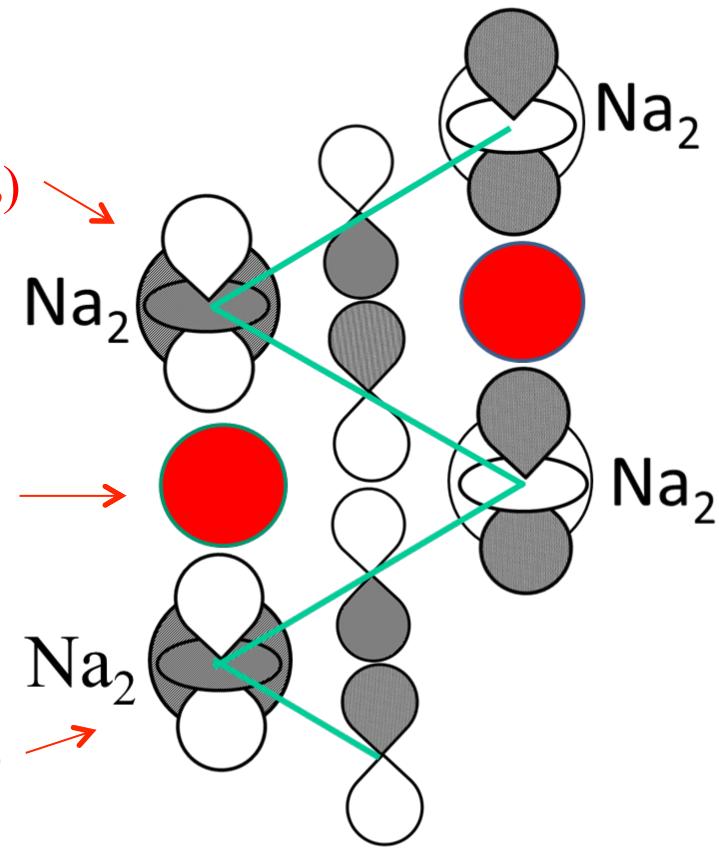
From Metals to Insulators and Back

Overall Crystal Symmetry Constraints

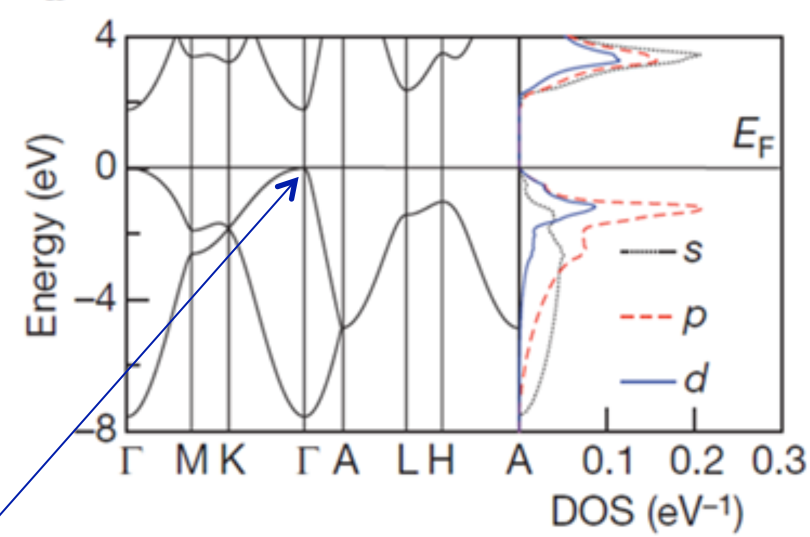
Example: dhcp (hP4), *$P6_3/mmc$* Na

$$\underset{\text{enthalpy}}{\underset{\uparrow}{H}} = -E_{kin} + 4P\Omega + \int \rho(\mathbf{r})(4\varepsilon_{xc} - 3\mu_{xc})d\mathbf{r} + \sum_{i,\mu} \int \psi_i^*(\mathbf{r}) \sum_l \left[\frac{d(r' V^{ps}{}_{\mu,l}(\mathbf{r}'))}{dr'} \hat{P}_l \right]_{\mathbf{r}'=\mathbf{r}-\mathbf{R}_\mu} \psi_i(\mathbf{r}) d\mathbf{r}.$$

repulsion of 3s electron (l=0)



To minimize the enthalpy the s-electrons avoid the core regions and hybridize mainly with *p* electrons



For example, at the top of valence band at Γ

[Naumov & Hemley, *Phys. Rev. Lett.* (2015)]

EXAMPLES

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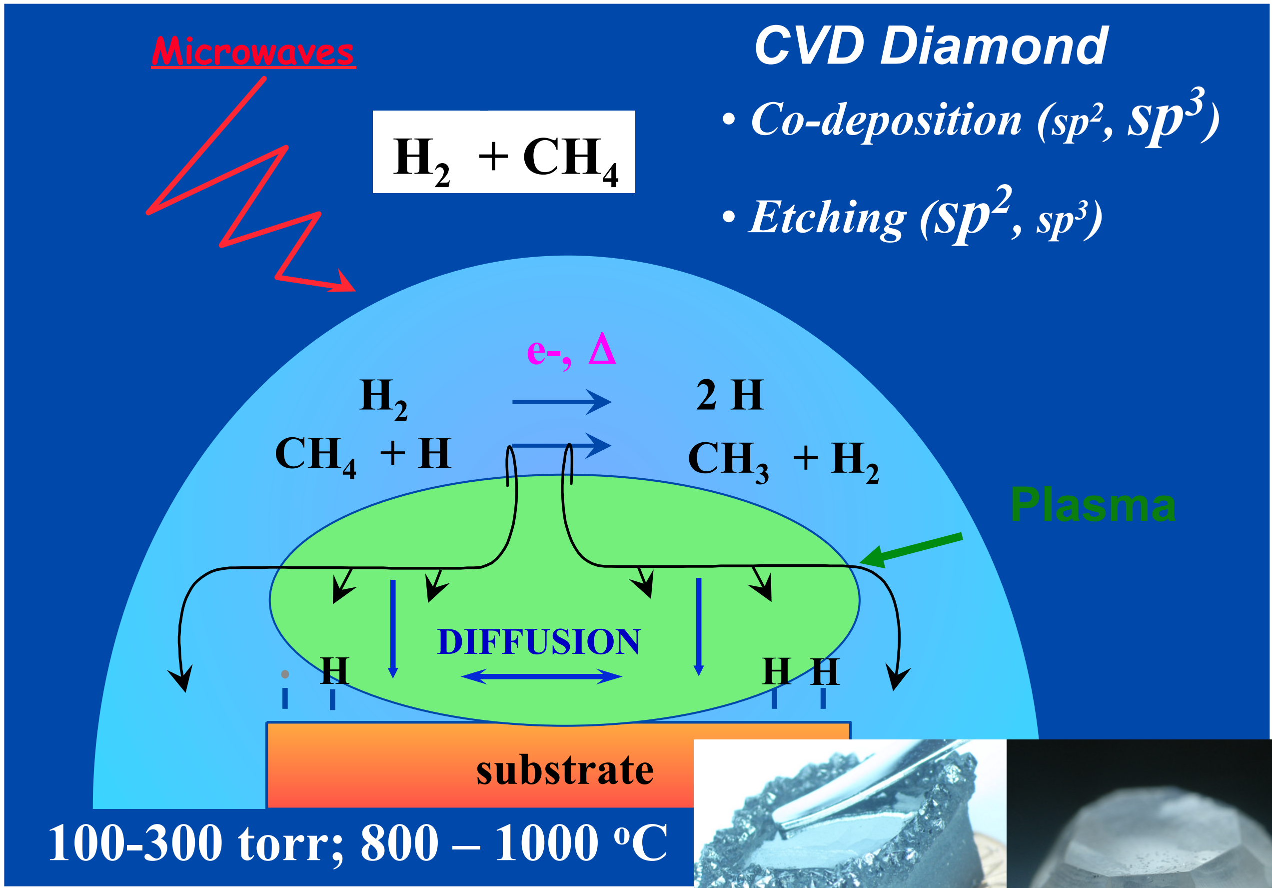
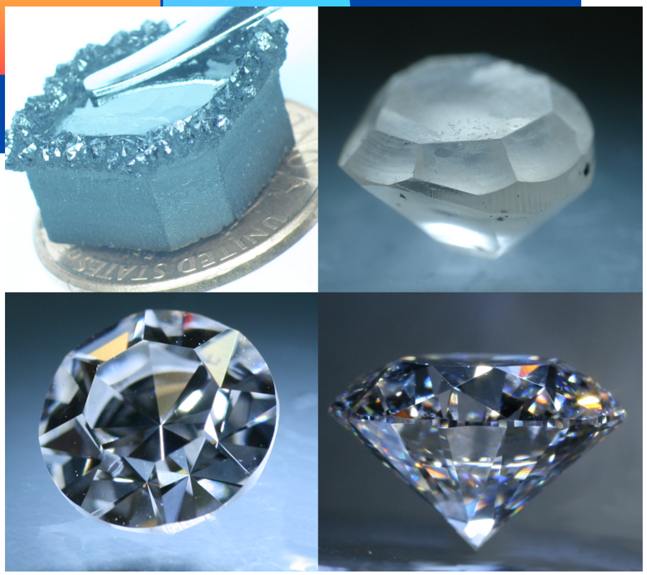
5. Softest Matter

Alternative Routes to Synthesis of Novel Phases

Diamond Synthesis
General Electric, Co.
(1954)



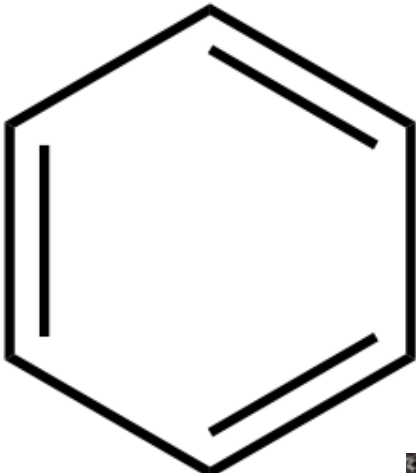


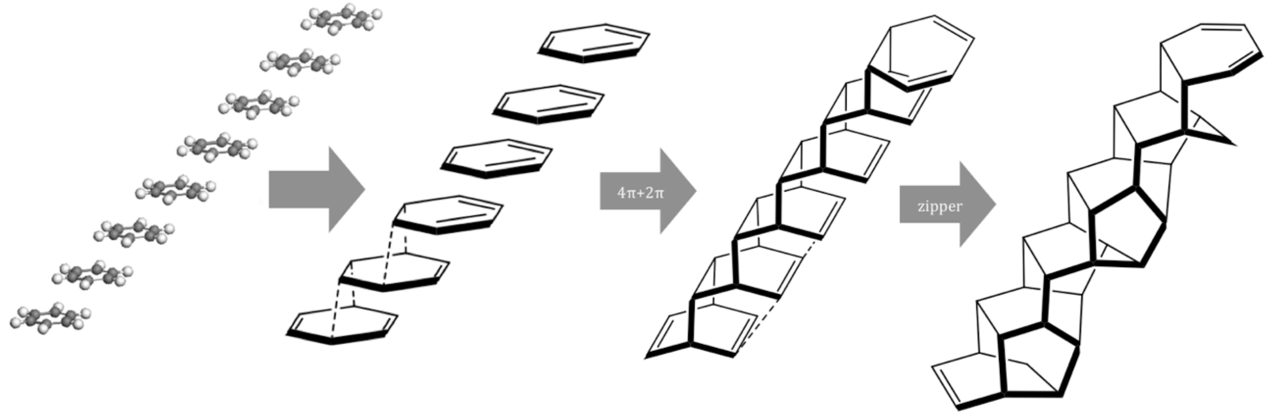
- **Limited in size and quality from Nature and conventional synthesis**
- **Optimized properties: strength, toughness, doping**

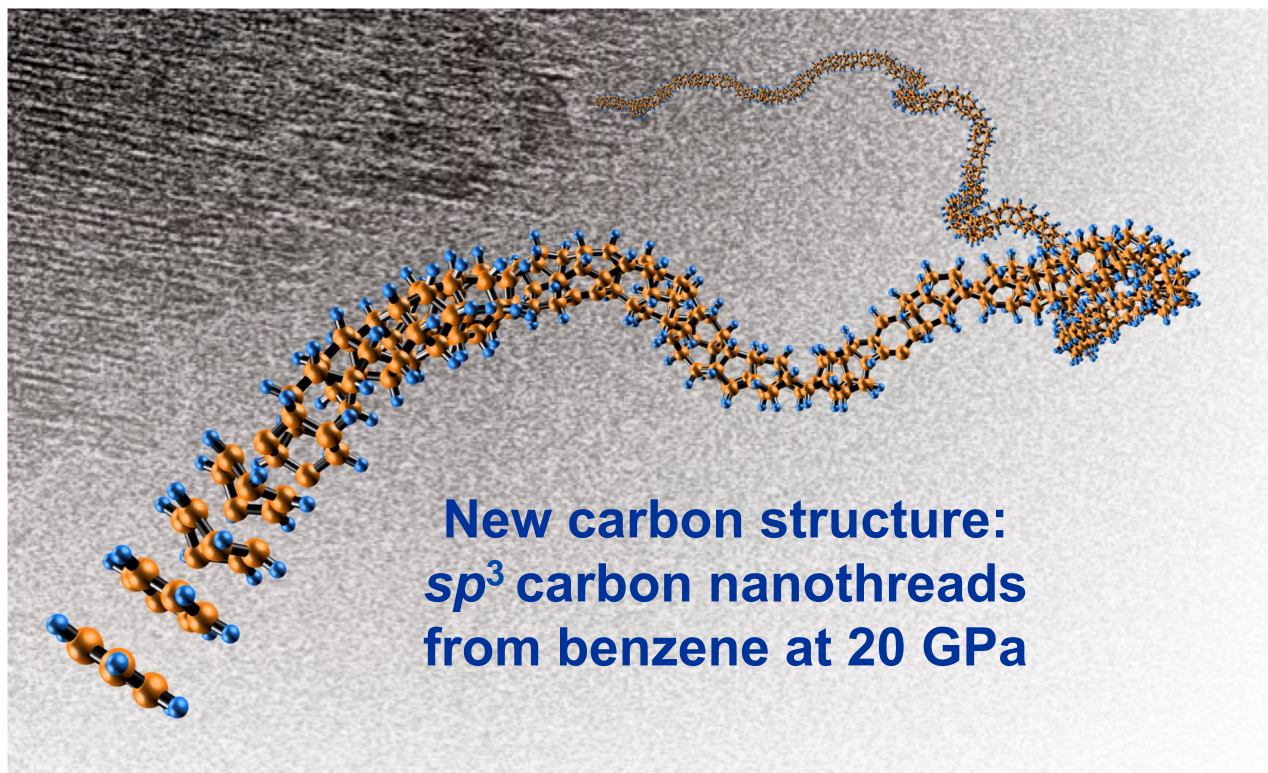
[Liang *et al.*, *Superhard Materials* (2013)]


2.4 carat CVD
[Meng et al., NDNC (2009)]
0.3 carat
natural

New Carbon Materials







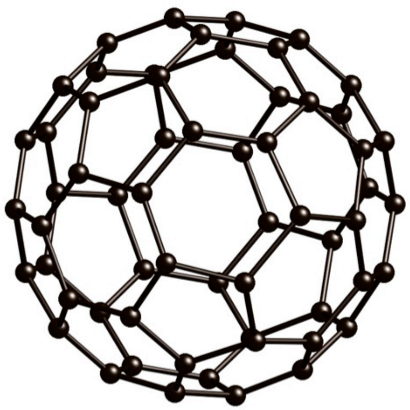
[Fitzgibbons et al., *Nature Mater*. (2014)]

Carbon Nanomaterials
Dimensionality and Hybridization

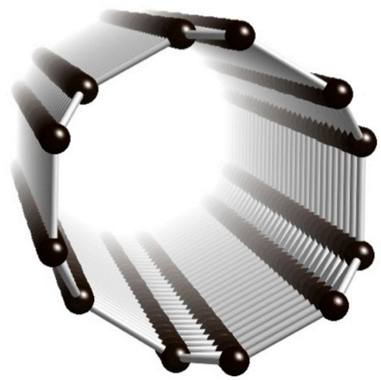
Energy Frontier Research Center

0-d | 1-d | 2-d

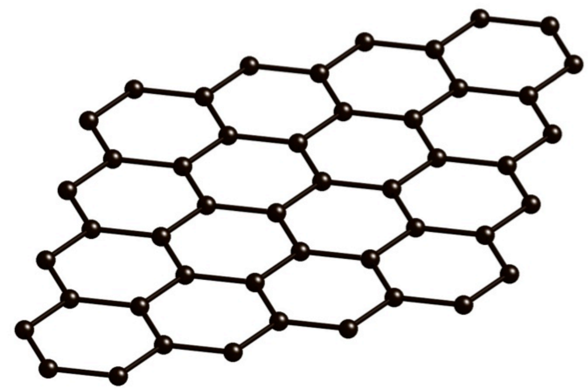
sp^2



C_{60}

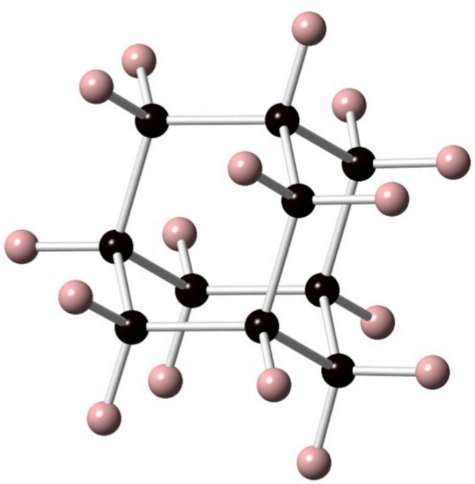


nanotubes

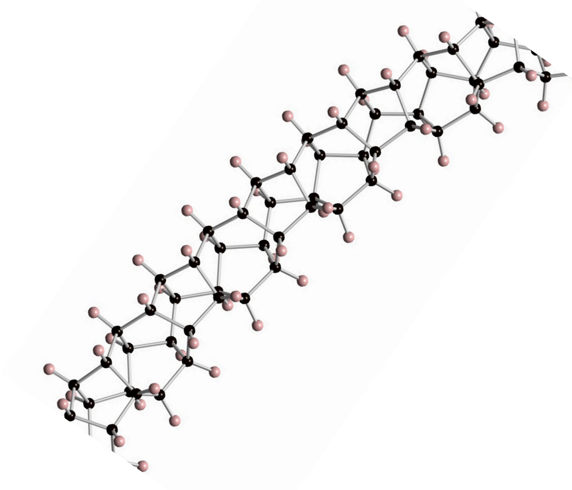


graphene

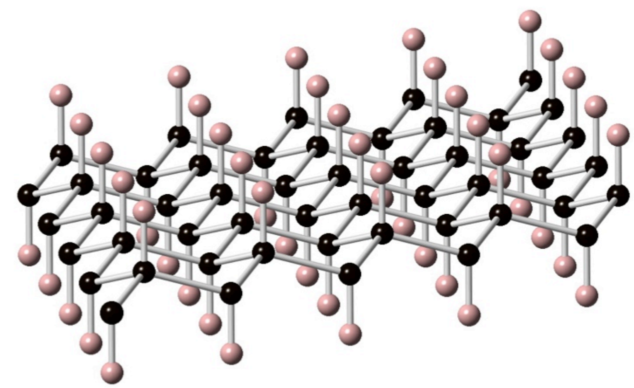
sp^3



diamondoids

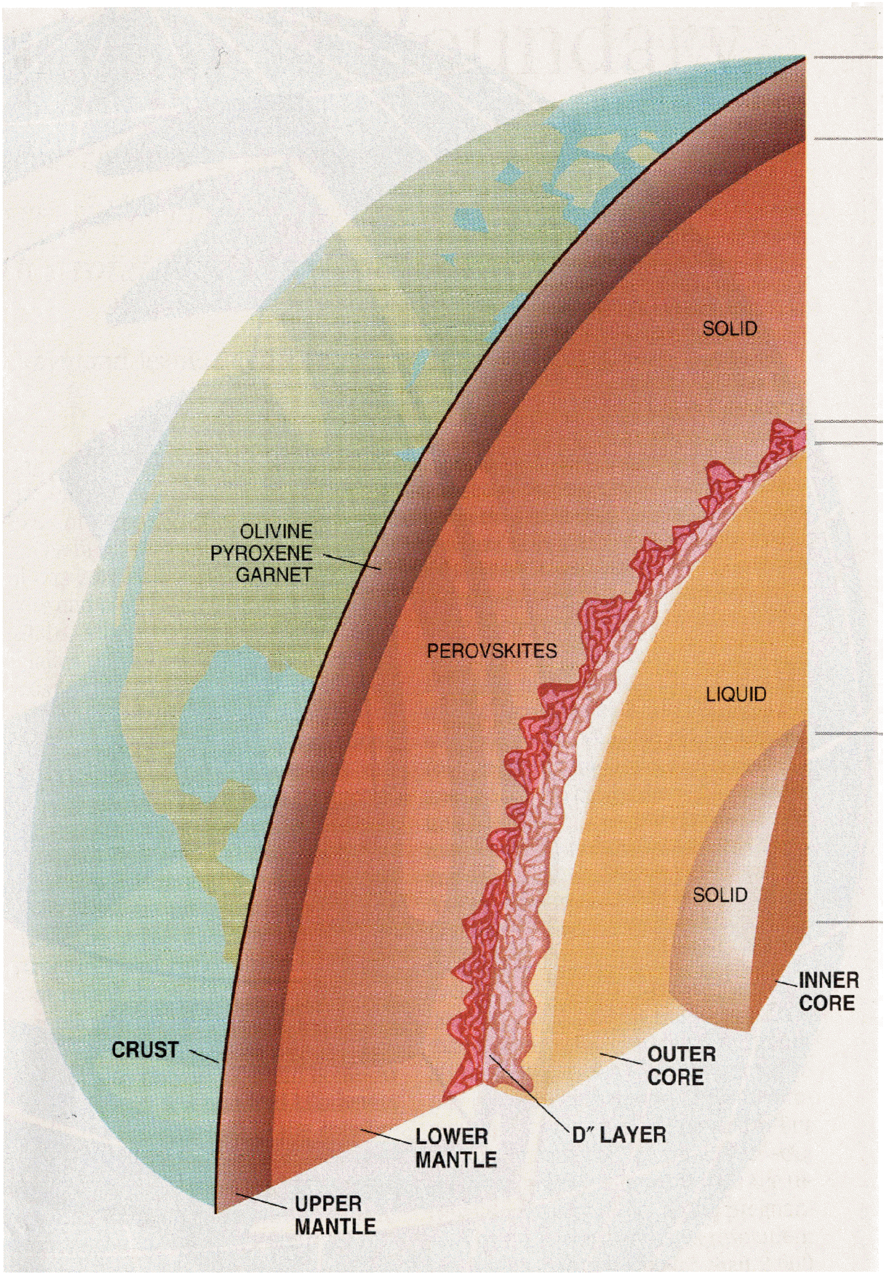


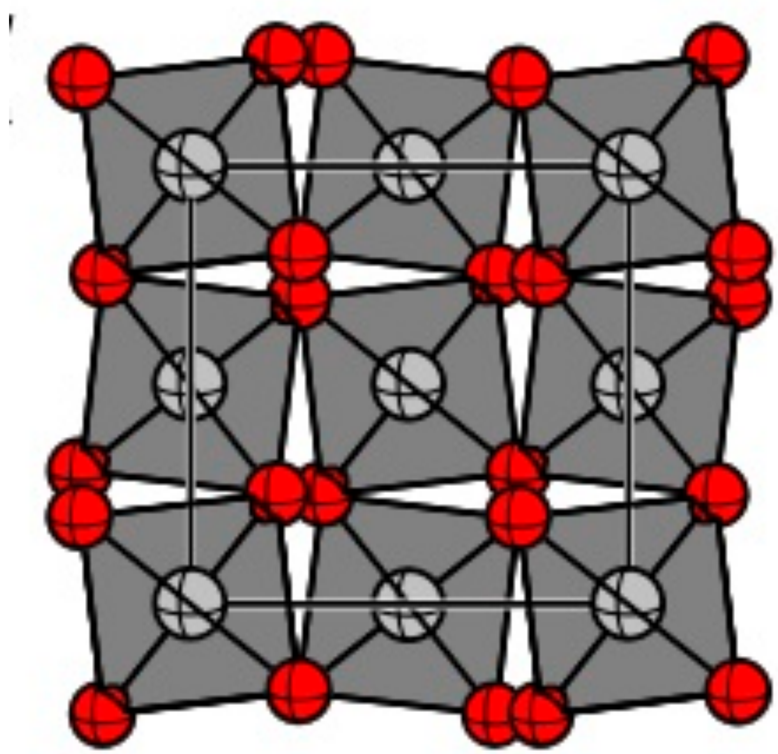
nanothreads



graphane

Discovery of New 'Minerals'

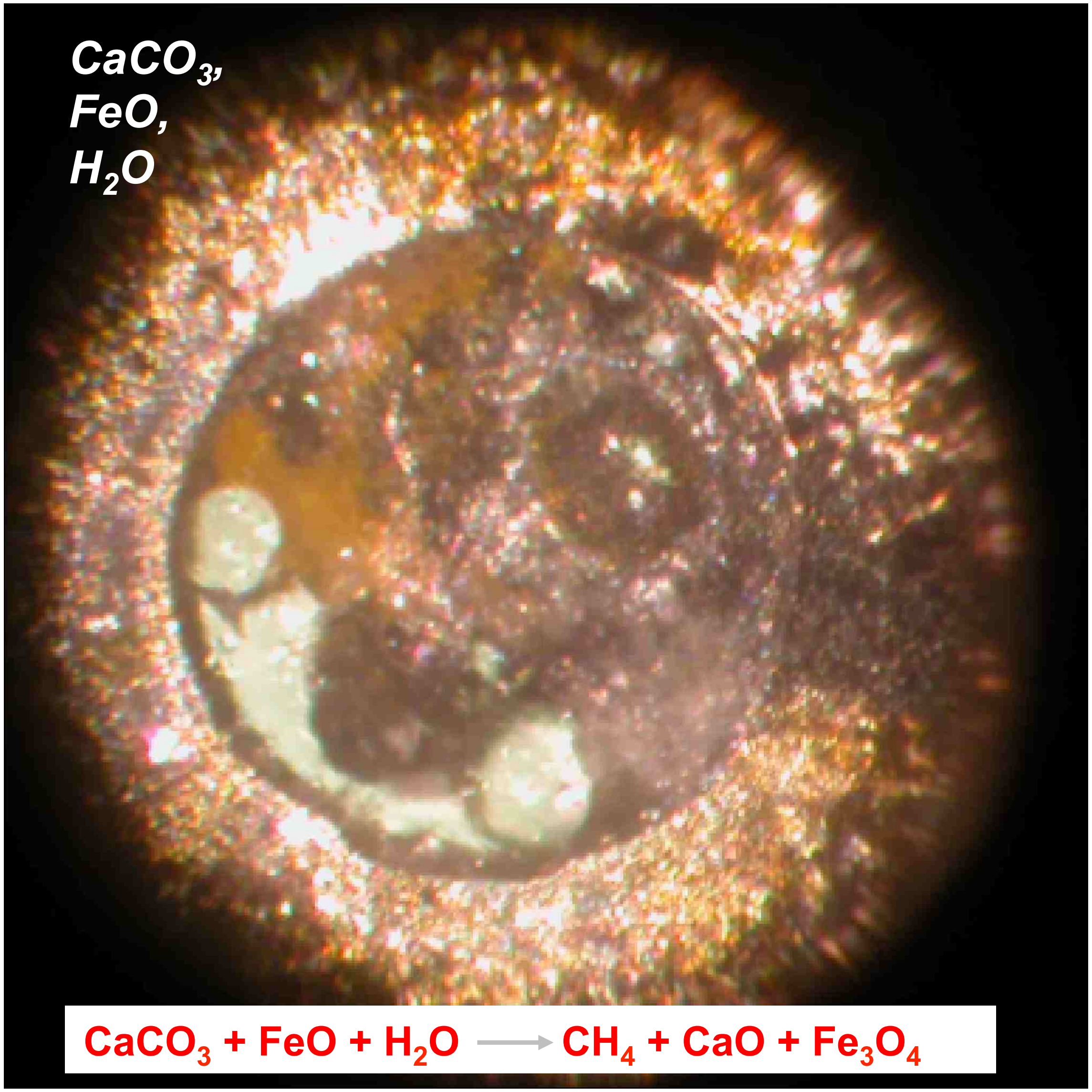


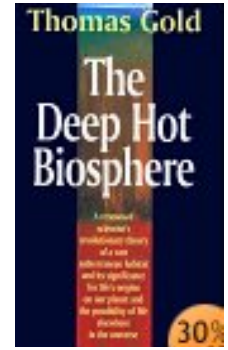


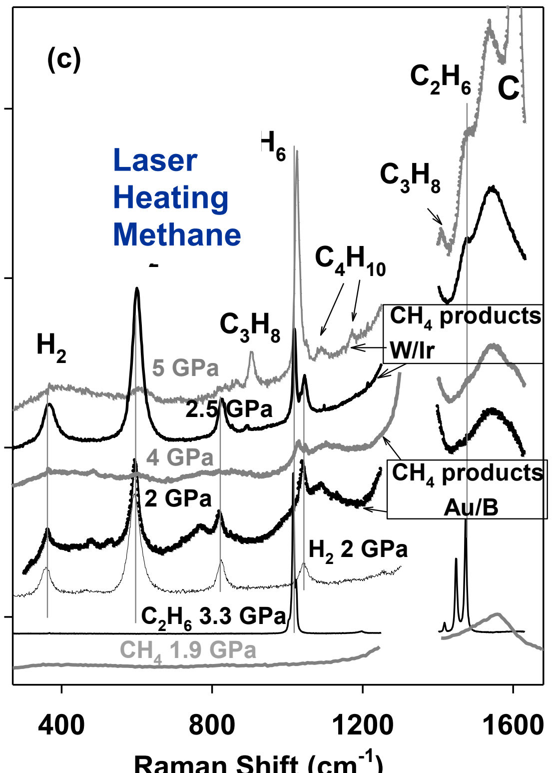
CO_2

[Santoro et al. *PNAS* (2012)];
Datchi et al., *Phys. Rev. Lett.* (2012)

Abiogenic formation of hydrocarbons at high P-T



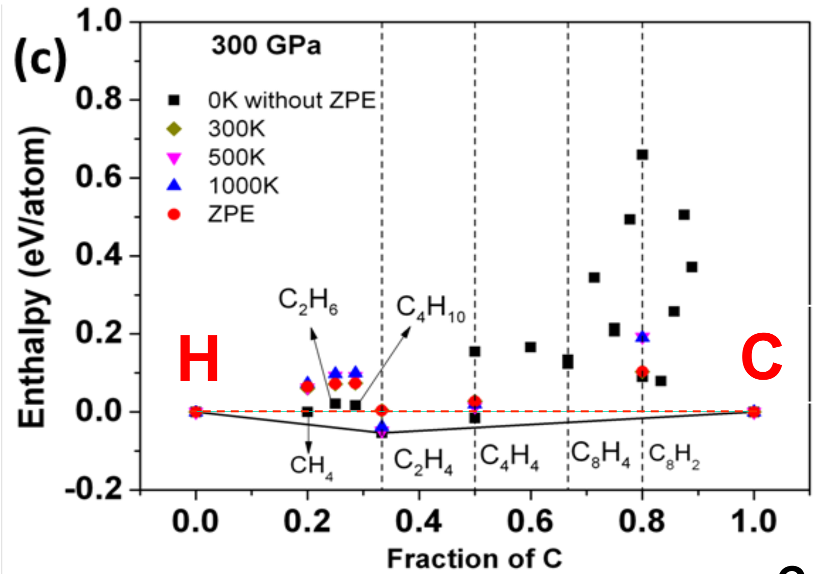




[Scott *et al. PNAS* (2004)]

[Kolesnikov *et al., Nature Geoscience* (2009)]

New Predicted Dense C-H Phases >100 GPa

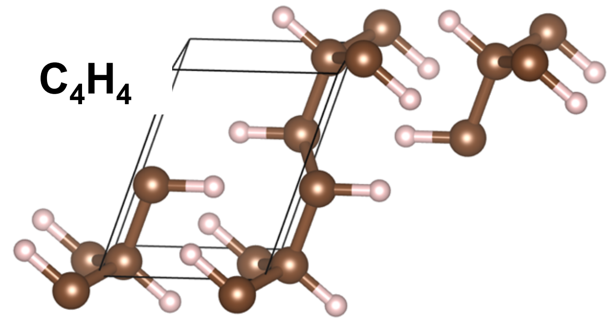


DFT-GGA
~500 structures
(CALYPSO)
Static – 1000 K

[Liu *et al., in preparation*]

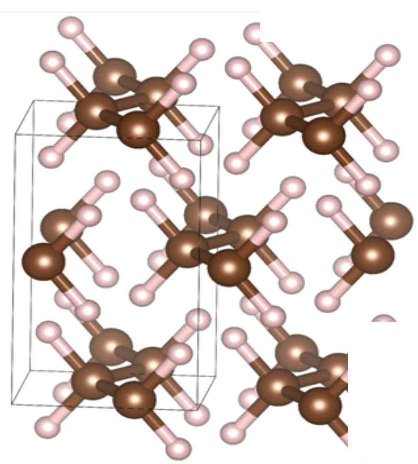
- *Hydrogen-rich planetary interiors*
- *Hydrogen containment in high P-T experiments*

C_4H_4



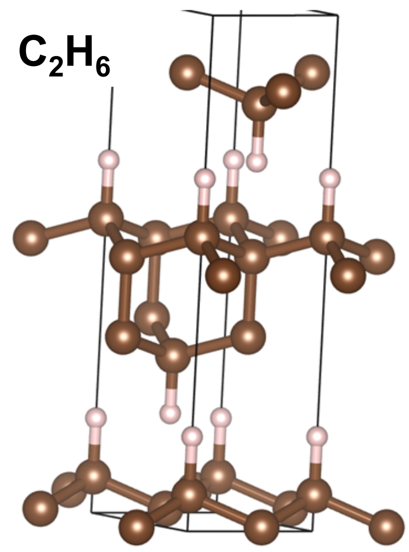
metastable

C_2H_4



stable at 100 GPa

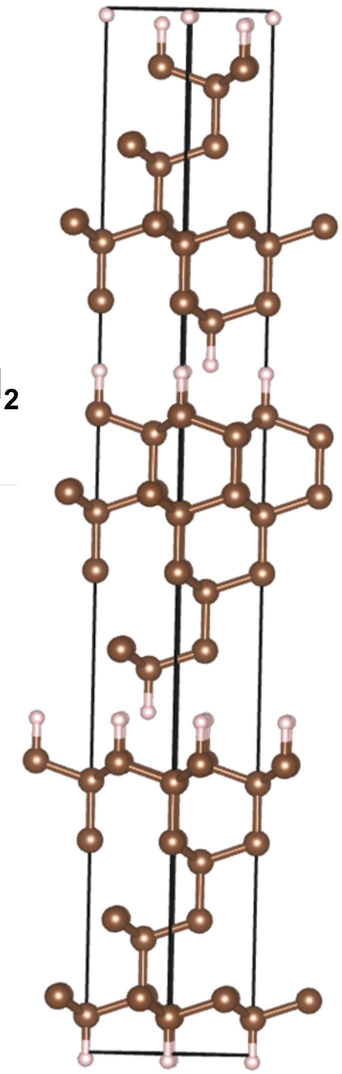
C_2H_6



stable at 100 GPa

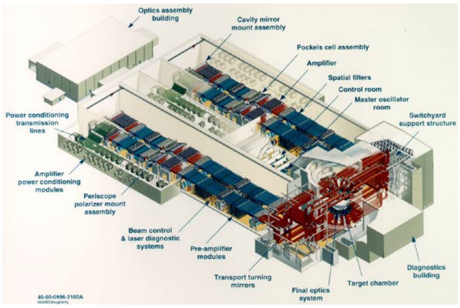
[Oganov et al., *J. Chem. Phys.* (2013)]

C_8H_2

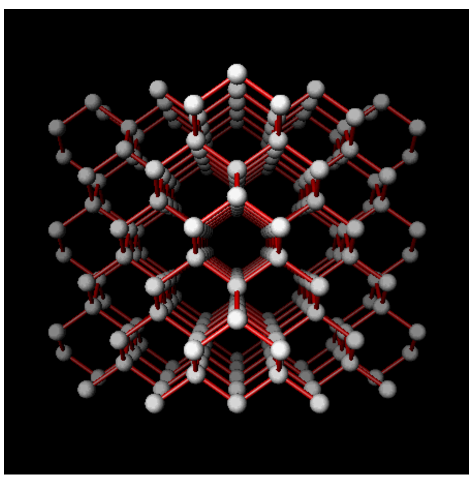


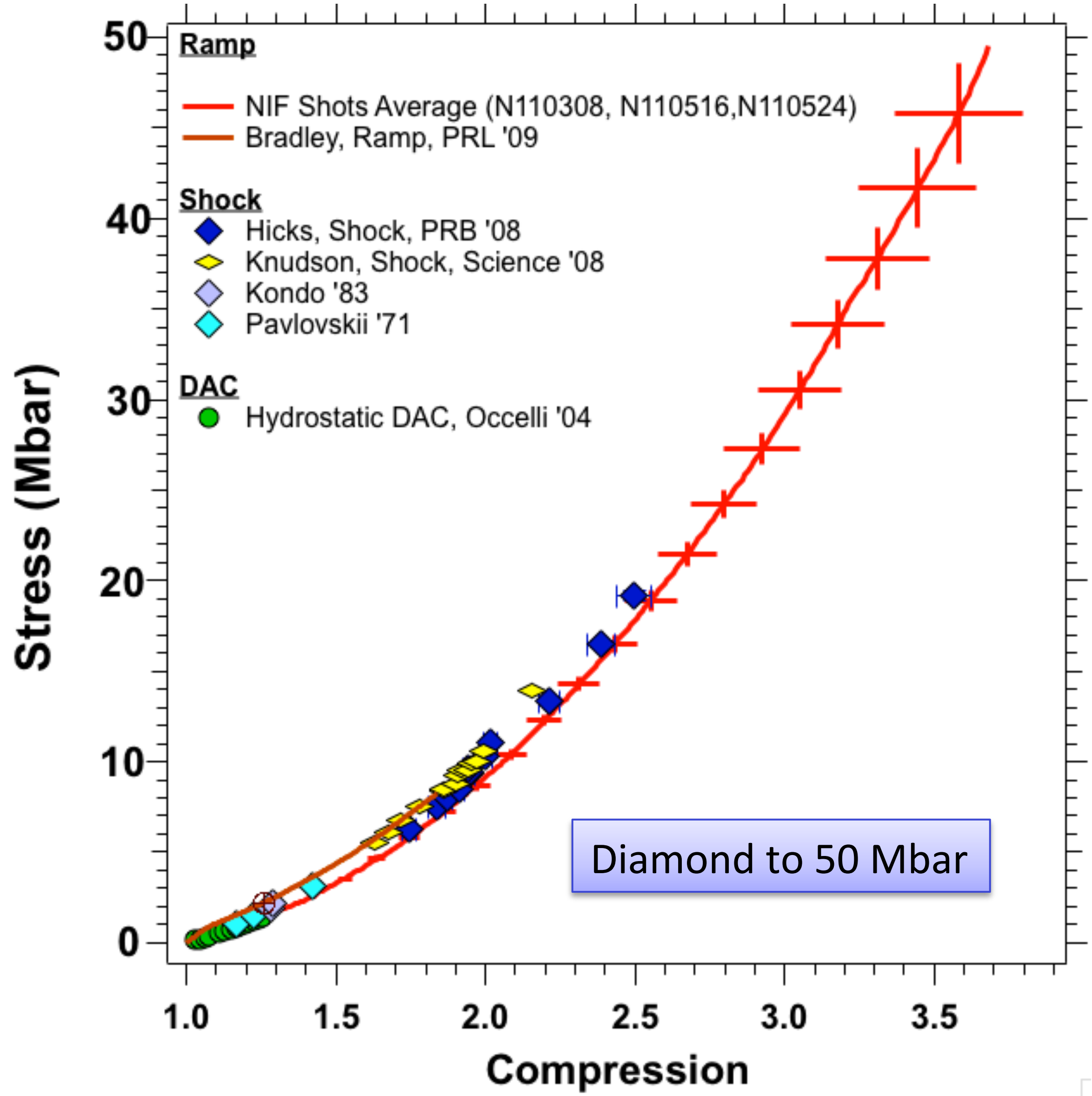
metastable

Compression of diamond to 50 Mbar



LASER DRIVEN RAMP “ADIABATIC” COMPRESSION

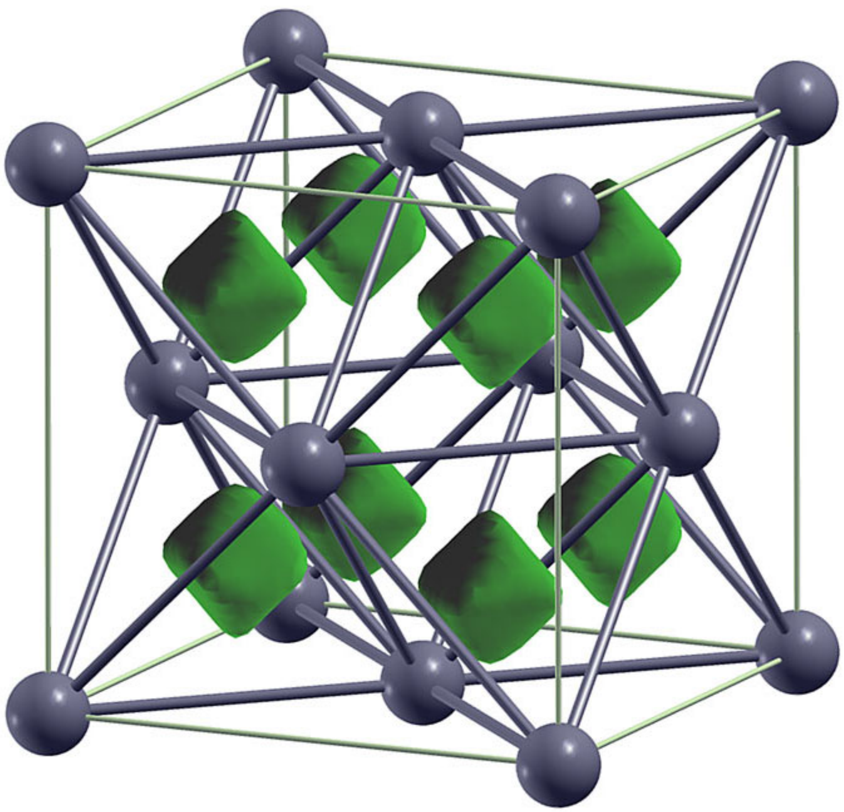




[Smith, Eggert, Braun, Jeanloz, Duffy]

Structure and Bonding at Ultrahigh Pressures

Carbon 'Electride' Predicted at 25 TPa (250 Mbar)



[Martinez-Canales et al., *Phys. Rev. Lett*. (2012)]

Insulating Ni Predicted at 34 TPa (340 Mbar)

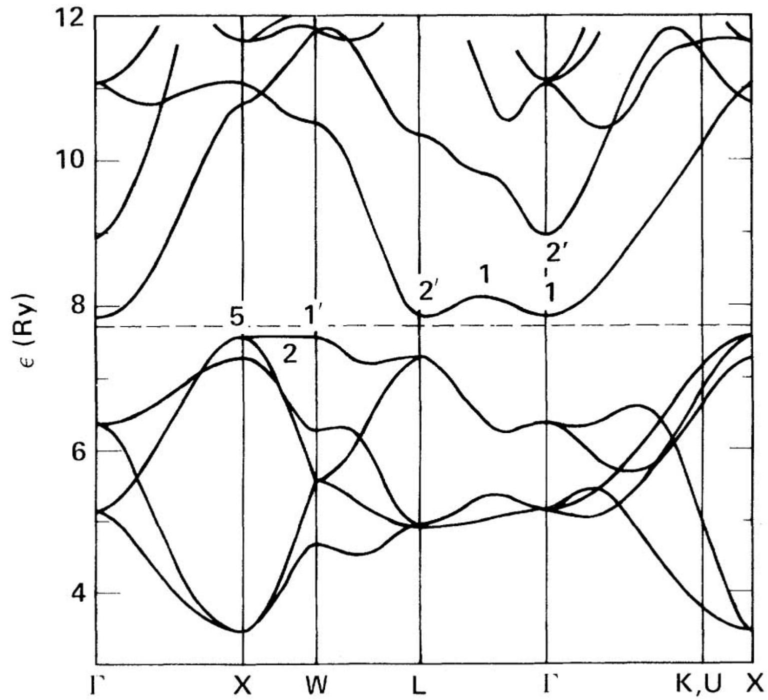


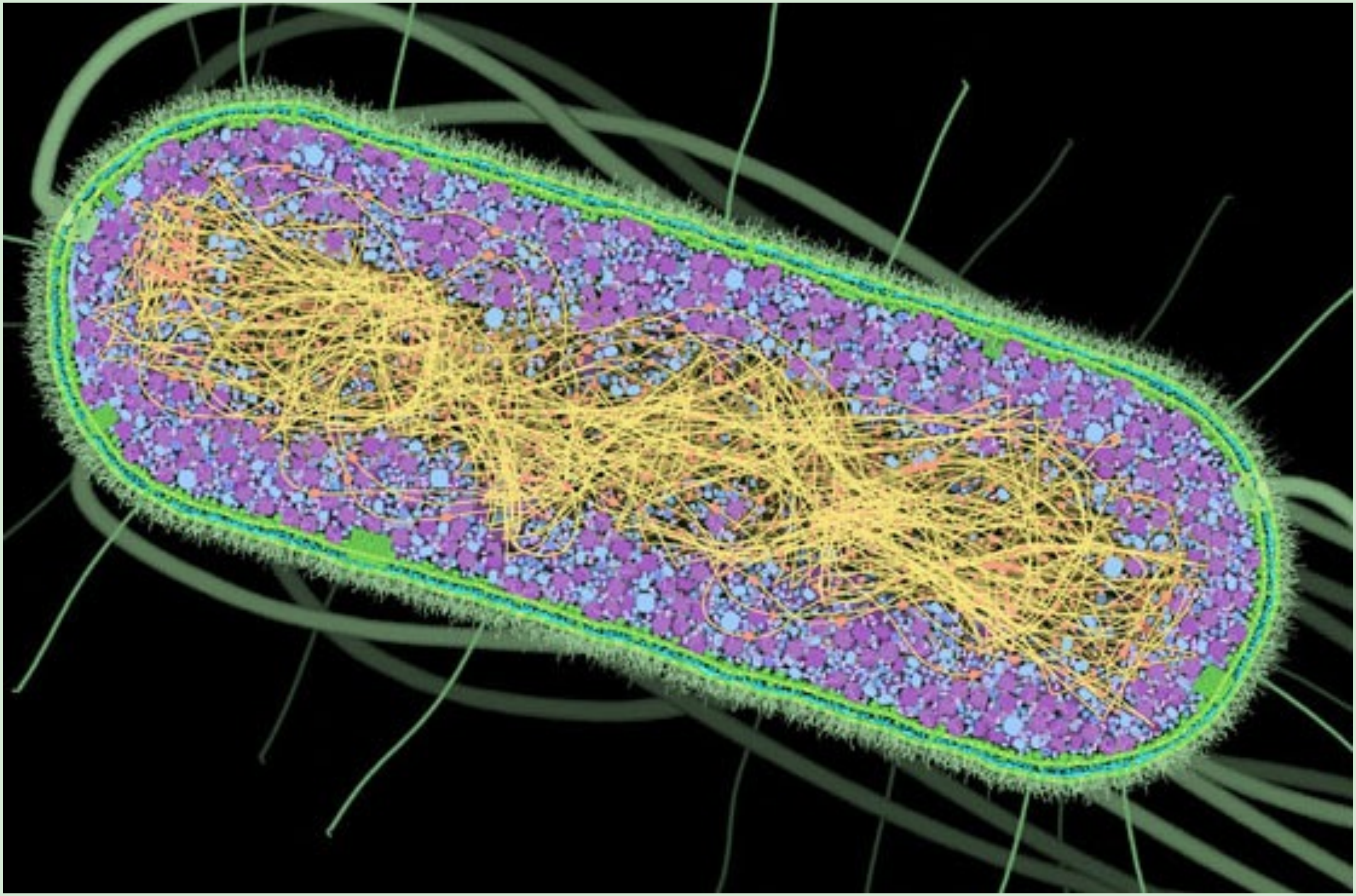
FIG. 2. Nonrelativistic APW band structure of fcc Ni at $V_0/V = 7.5$. The dashed line is the Fermi level.

[McMahan & Albers, *Phys. Rev. Lett*. (1982)]

EXAMPLES

1. ‘Simple’ Molecules
2. Novel Compounds
3. Metals that are Not
4. Continuing with Carbon
5. **Softest Matter**

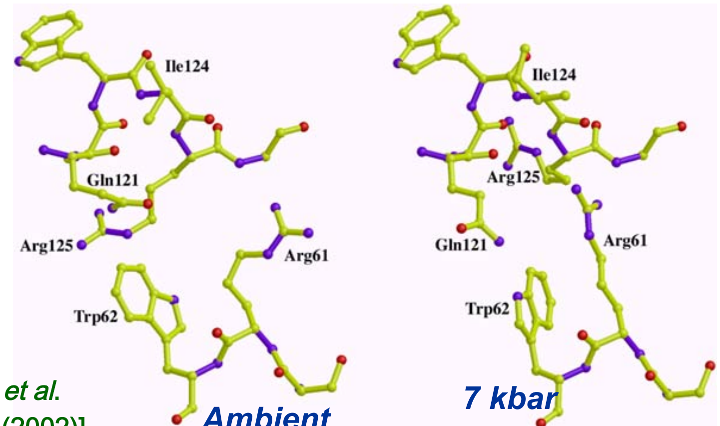
EXTREME SOFT MATTER AND BIOPHYSICS



EXTREME SOFT MATTER AND BIOPHYSICS

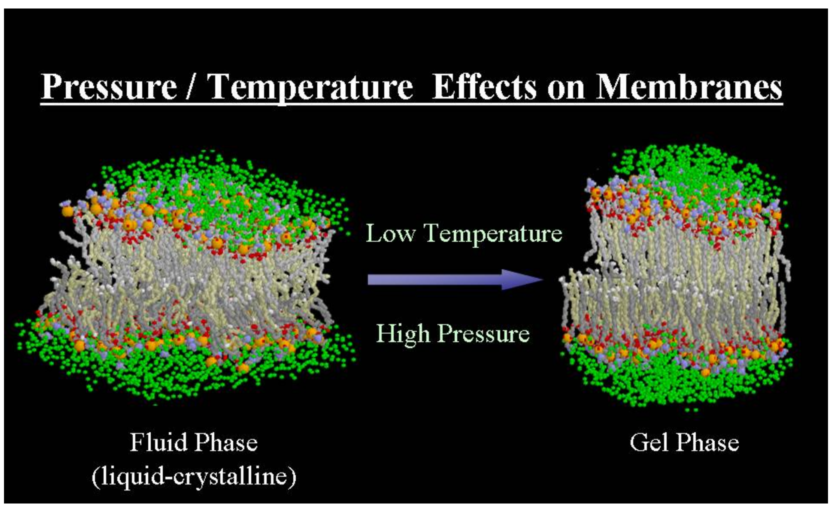
Structure-function in biological systems

Lysozyme



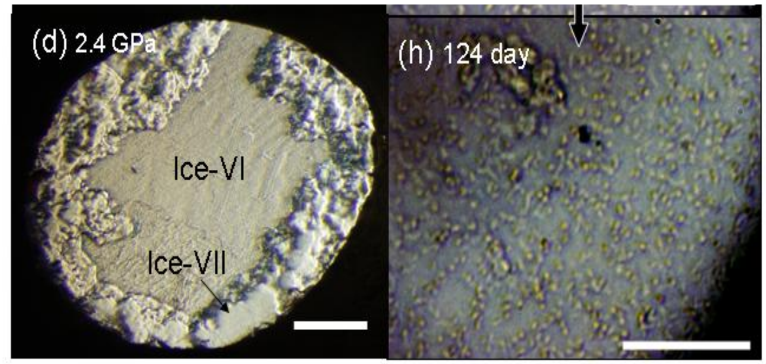
[Fourme *et al.* . *Mol. Bio.* (2002)]

Ambient ***7 kbar***



Microbial viability to >25 kbar

Direct observations



[Sharma *et al.*, *Science* (2002);

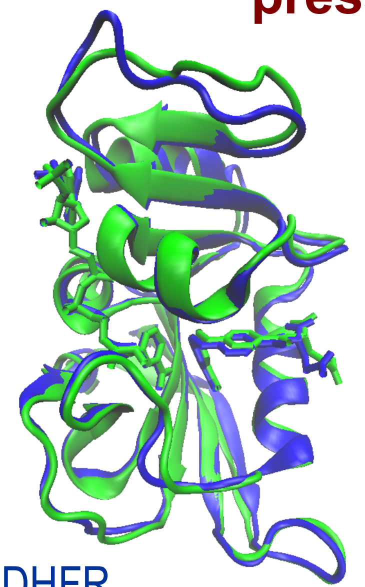
Pressure-induced directed evolution

[Vanlint *et al.*, *mBio* (2011)]

- ***What are the limits of survivability?***

EXTREME SOFT MATTER AND BIOPHYSICS

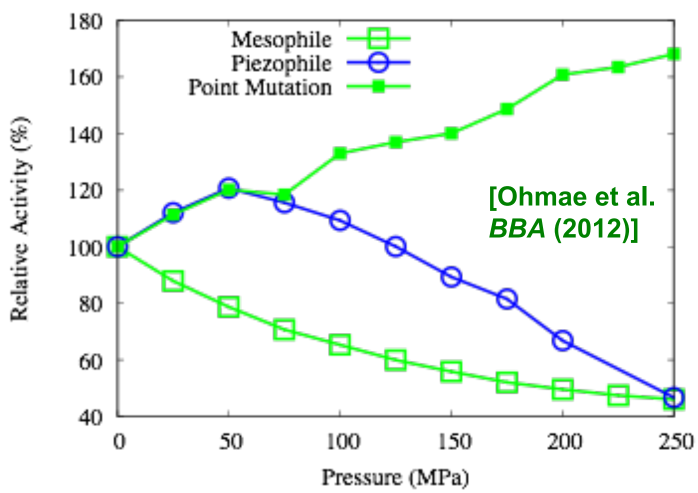
Protein dynamics under pressure



DHFR

How can simulations inform structure-function relations at high pressures?

[Rodgers et al. In preparation]

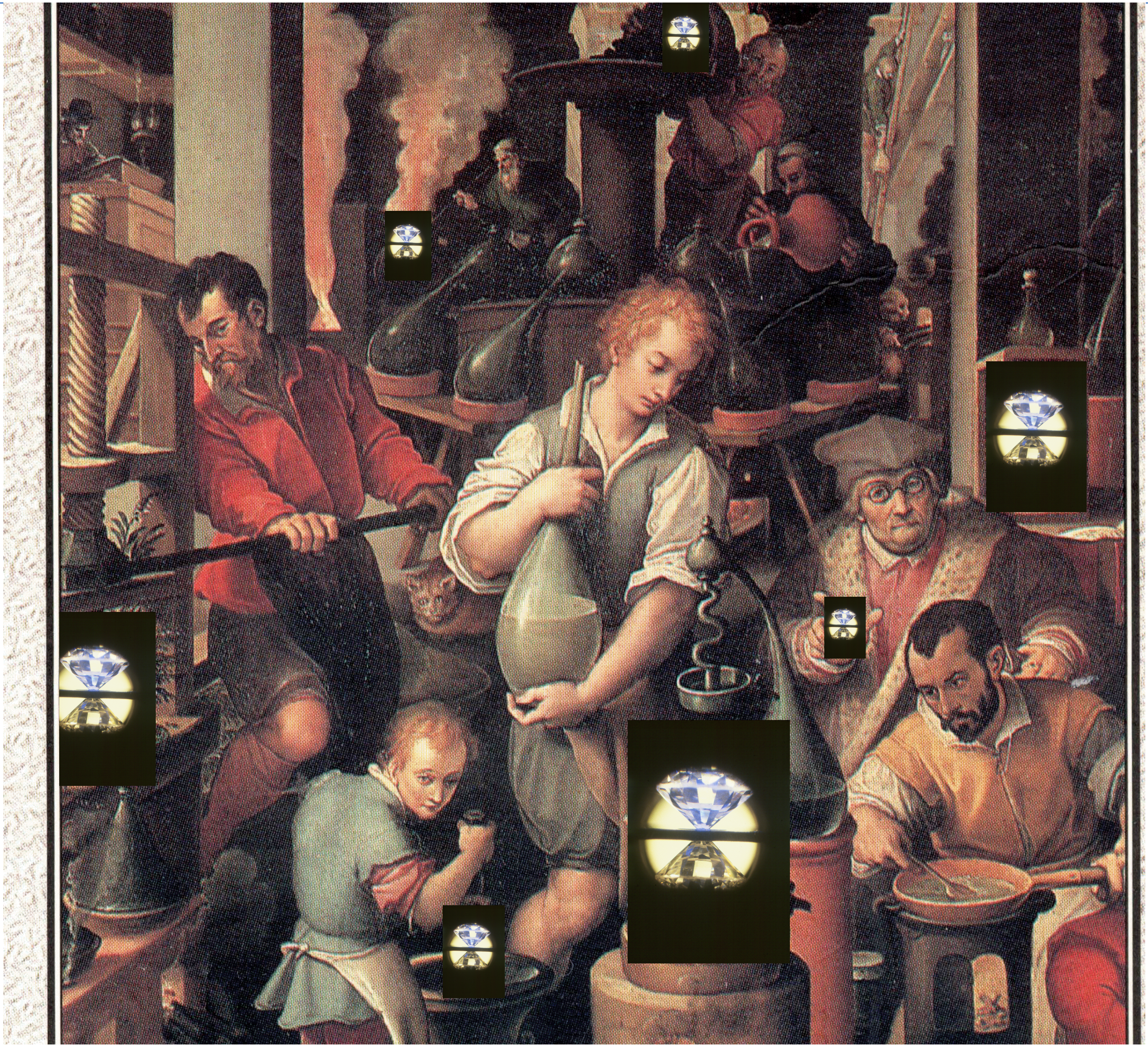


[Ohmae et al. *BBA* (2012)]

- ***What are the P-T limits of growth and metabolism?***
  - ***Does "corresponding states" of flexibility hold for growth at high P-T conditions ?***
  - ***How to quantitate flexibility?***

CONCLUSIONS AND OUTLOOK

1. **High pressure studies are revealing a variety of new chemical phenomena over a range of conditions**
2. **New models are needed to understand and predict this behavior**
3. **The findings provide new insights on bonding under ‘normal’ conditions**
4. **There is the prospect for the creation of new useful materials**
5. **There are potentially important implications for soft matter and biology**



ACKNOWLEDGEMENTS

Collaborators

CARNEGIE INSTITUTION

Ivan Naumov
M. Somayazulu
Viktor Struzhkin
Timothy Strobel
Zhenxian Liu
Reini Boehler
Yingwei Fei
Guoyin Shen
Ronald E. Cohen
Ho-kwang Mao
Muhetaer Aihaiti
Alexander Goncharov
Changsheng Zha
Yufei Meng
Stephen Gramsch

OTHER INSTITUTIONS

K. Landstron (Lehigh)
John Badding (Penn State)
E. Gregoryanz (Edinburgh)
Yusheng Zhao (LANL)
Anurag Sharma (Boston)
Neil Ashcroft (Cornell)
Roald Hoffman (Cornell)
Raymond Jeanloz (UCB)
Paul Loubeyre (CEA)
G. W. Collins (LLNL)
Toshiko ichiye (Georgetown)

Financial Support

DOE/NNSA, DOE/OS/BES, NSF, A. P. Sloan Foundation, Carnegie Institution

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