Searching for mixtures of planetary ices

V. Naden Robinson,[1,3] Miriam Marquez[1], J. Christiansen[1], Y. Wang,[2]
Y. Ma,[2] and A. Hermann[1]

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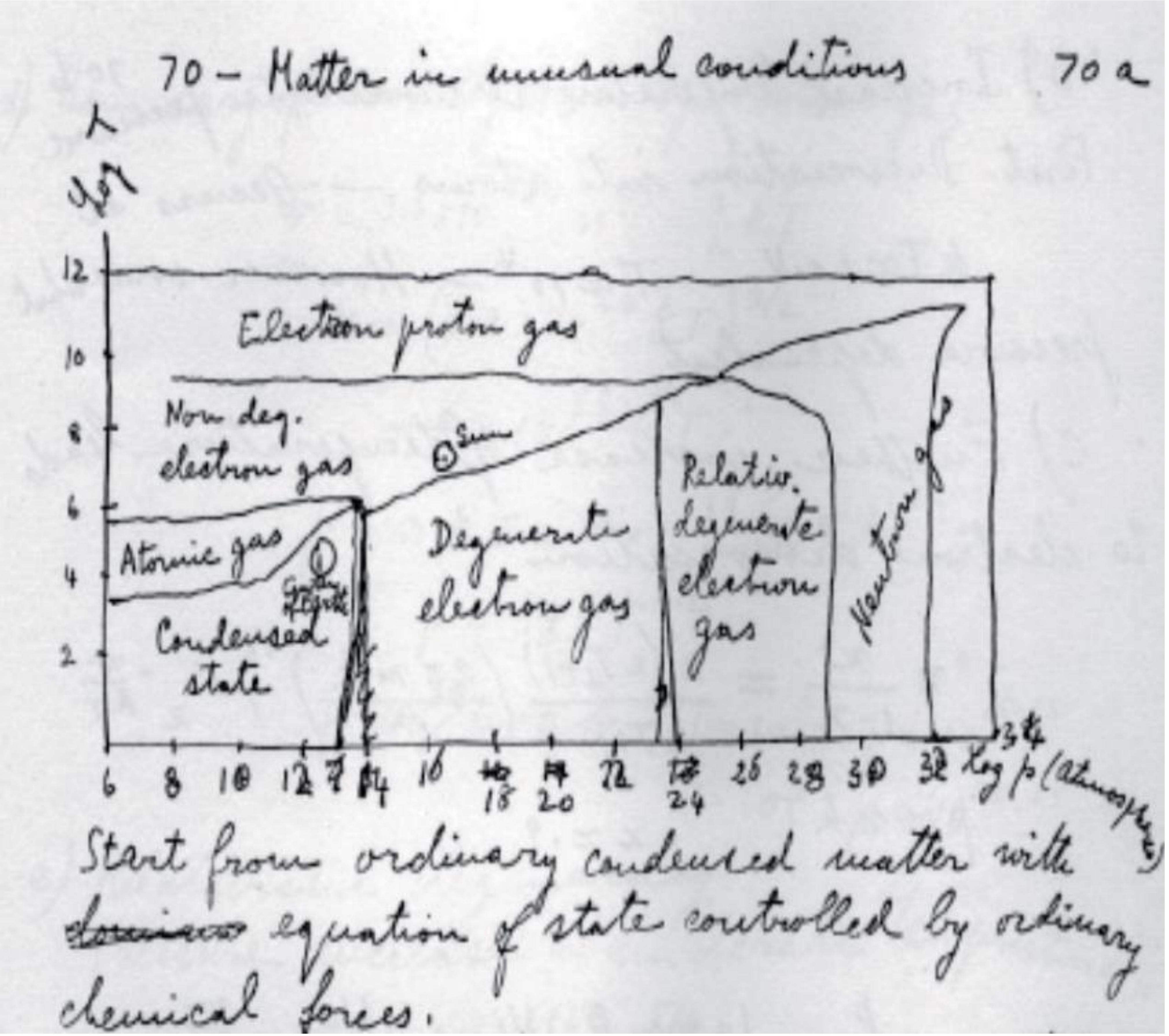
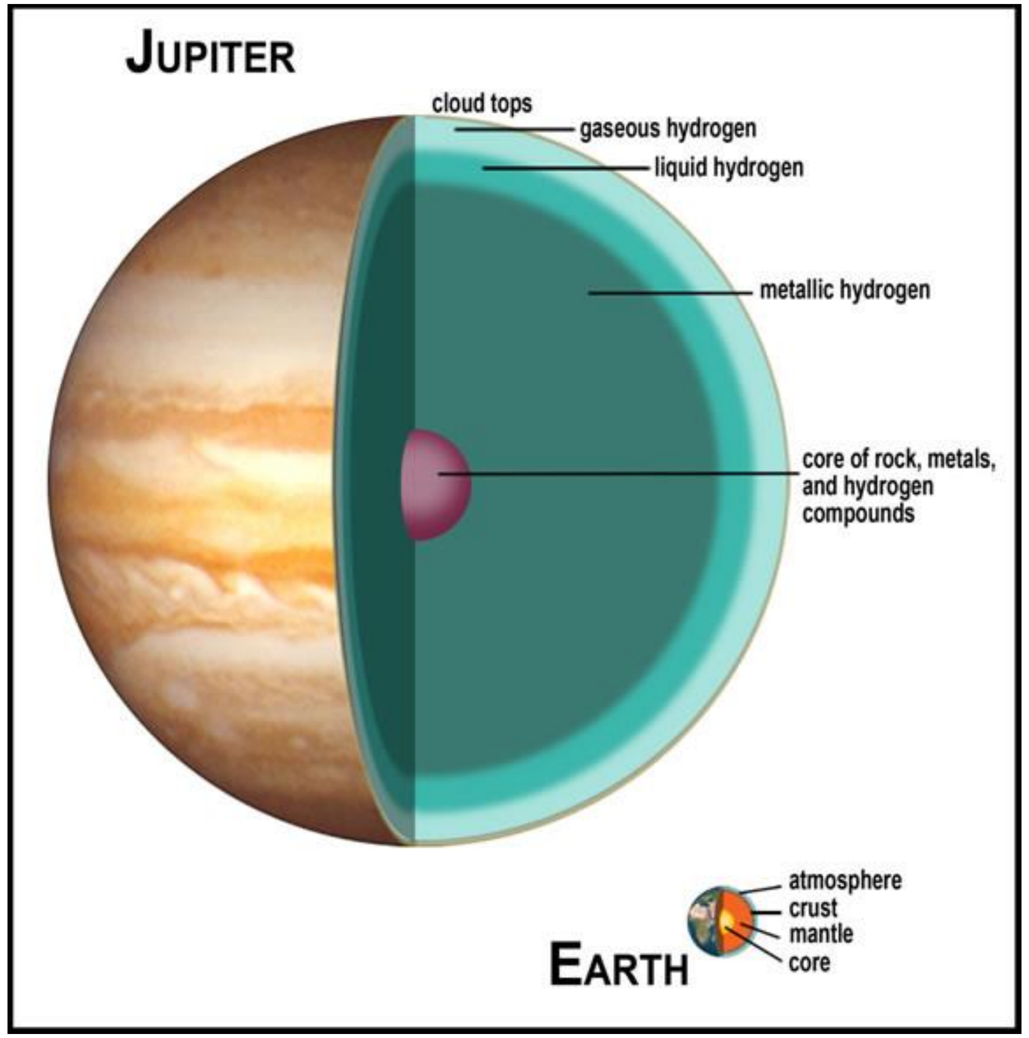
[2] State Key Laboratory for Superhard Materials, Jilin University
[3] International Centre for Theoretical Physics, Trieste

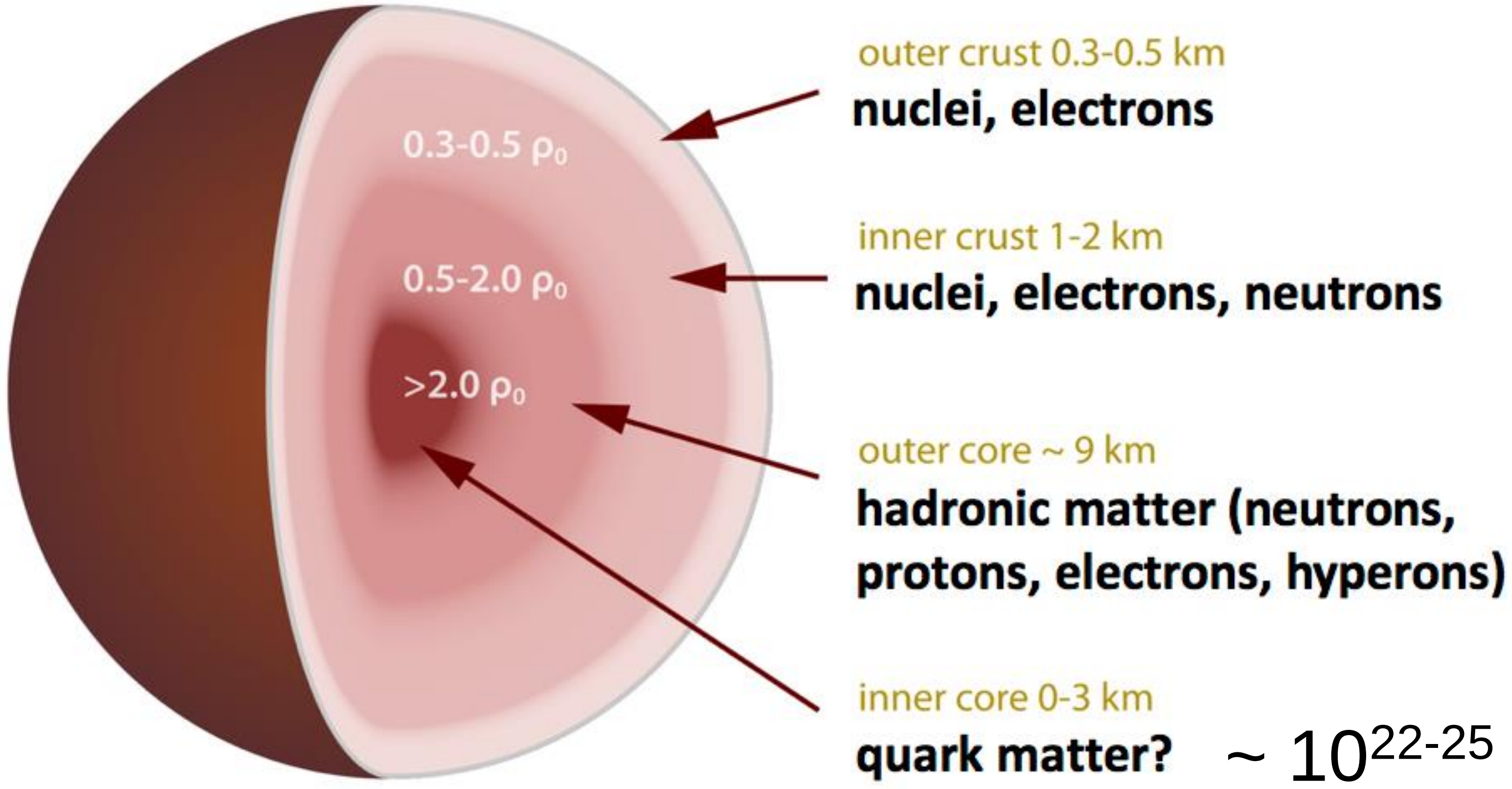
Workshop on Crystal Structure Prediction, ICTP – January 2019



E. Fermi:
Notes on thermodynamics and statistics, 1953

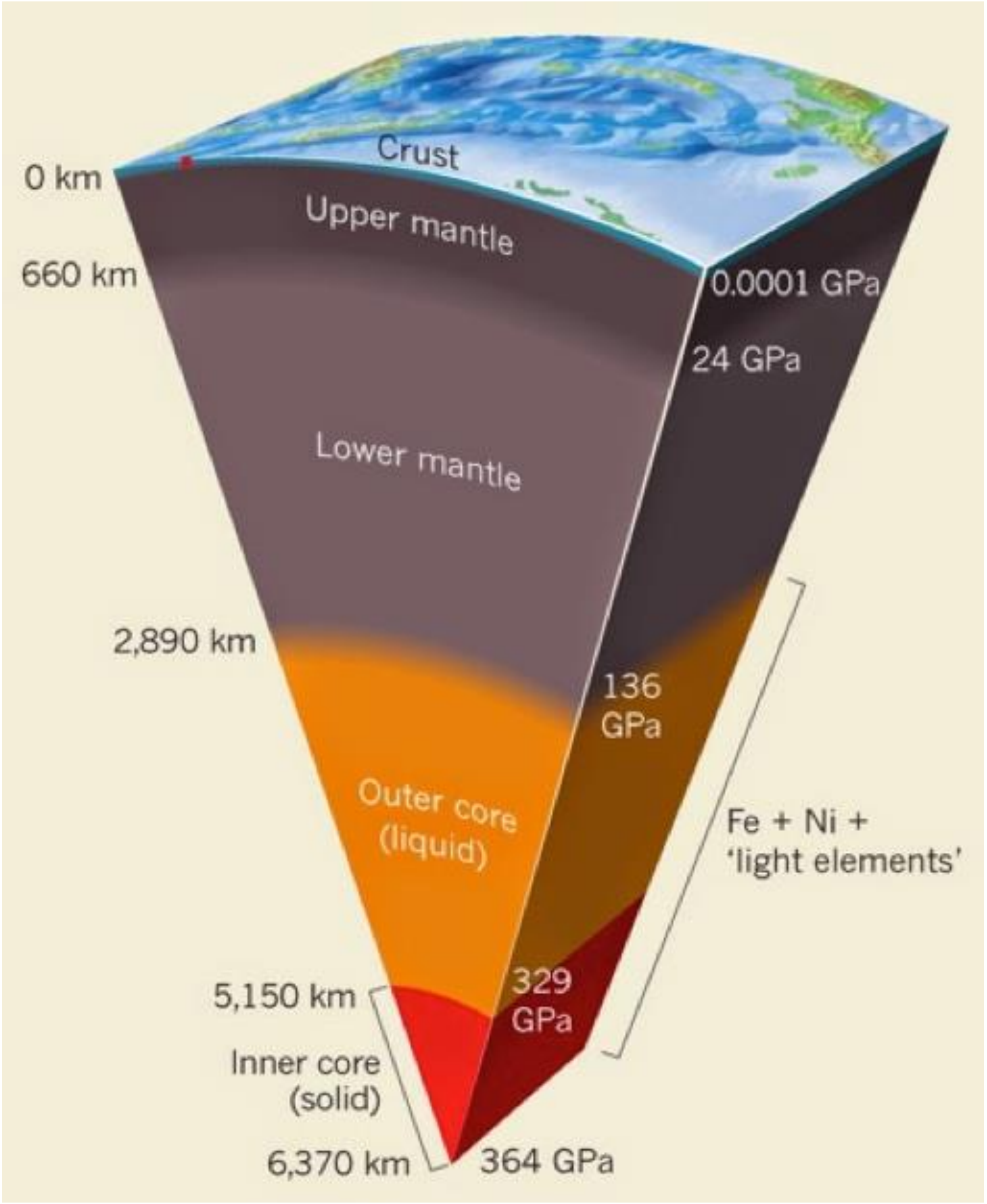


~ 20,000 GPa



~ $10^{22\text{-}25}$ GPa

Earth

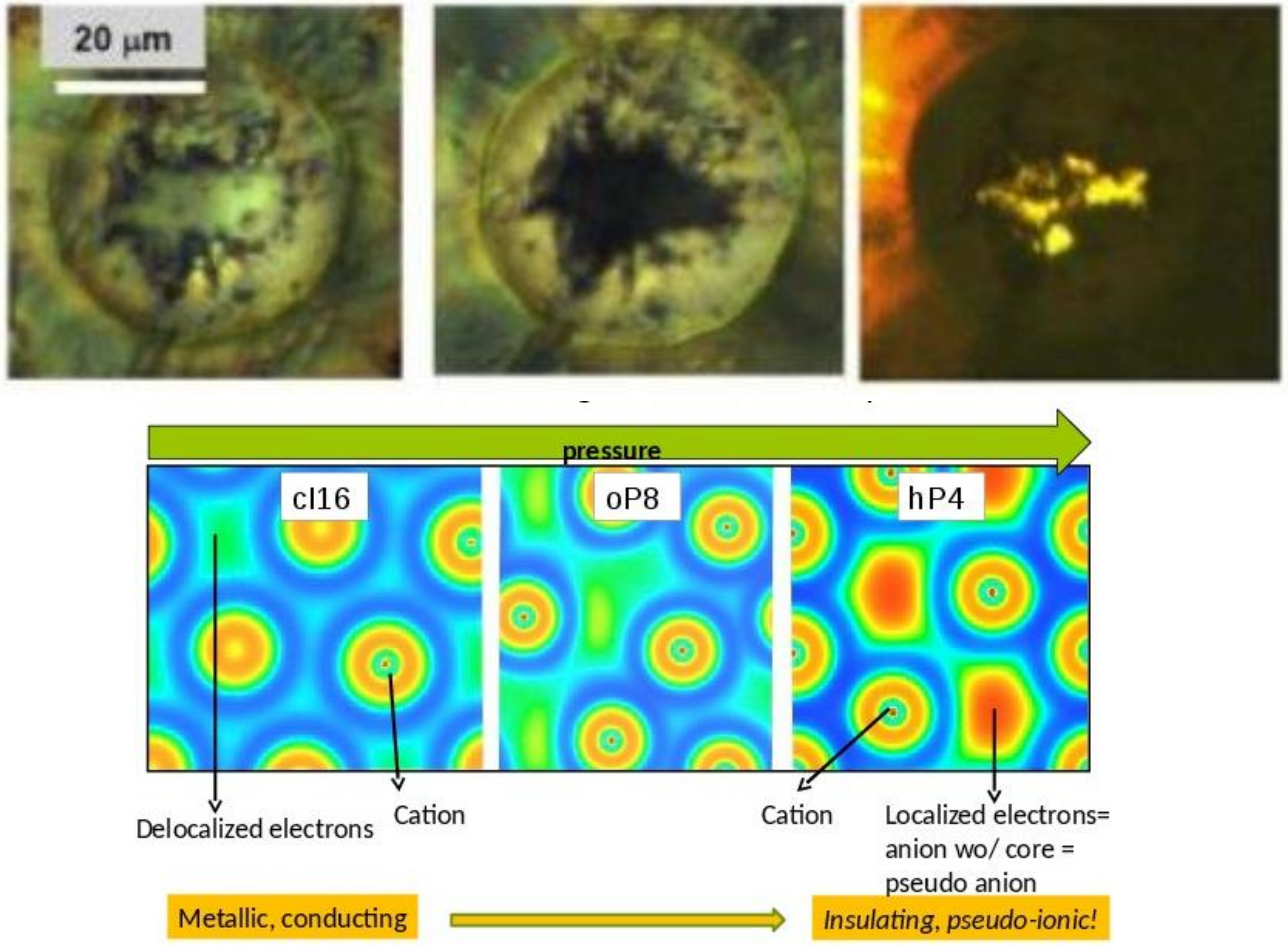


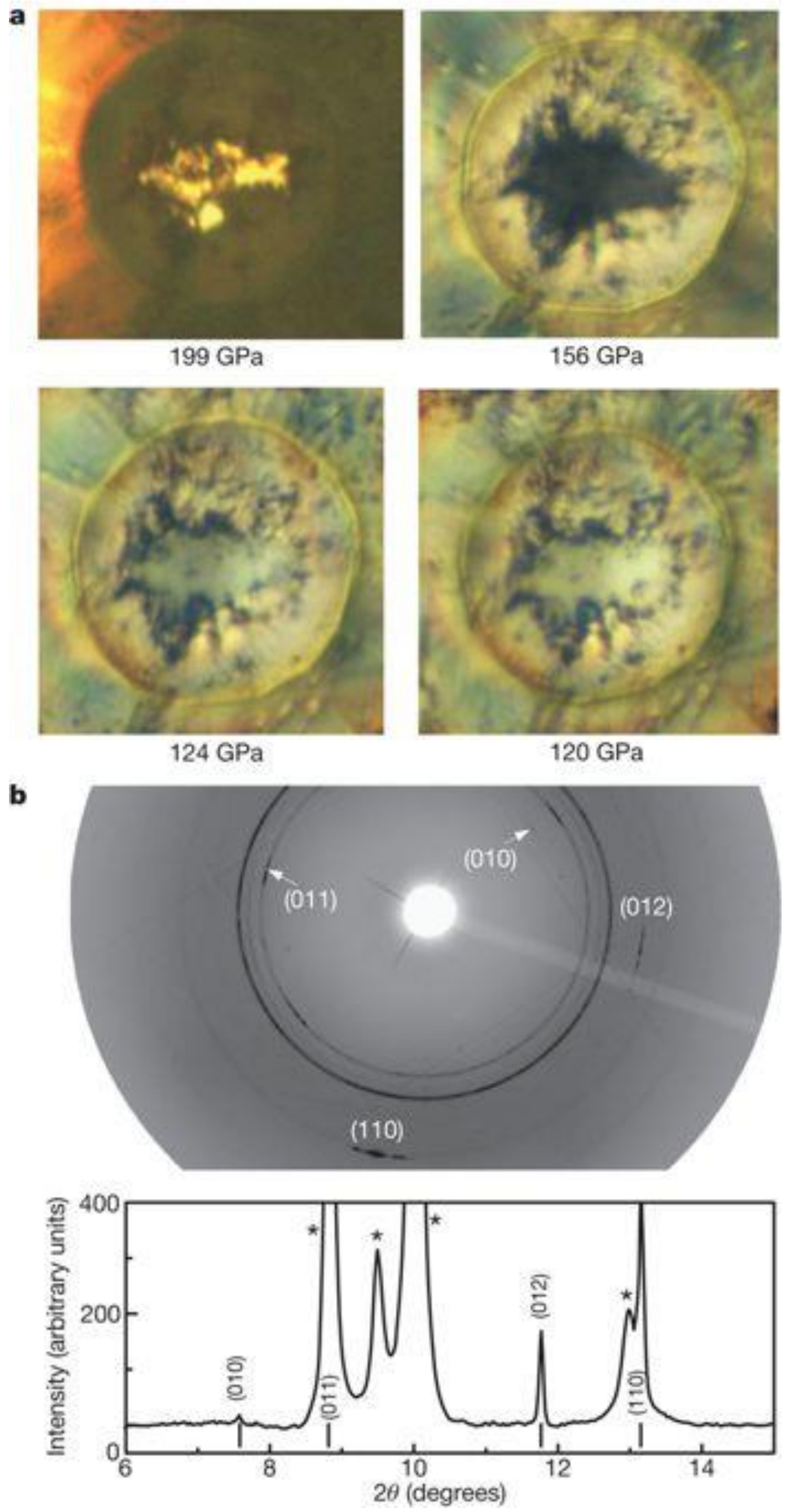
High Pressure

Transparent dense sodium

Yanming Ma, Mikhail Eremets, Artem R. Oganov, Yu Xie, Ivan Trojan, Sergey Medvedev, Andriy O. Lyakhov, Mario Valle & Vitali Prakapenka

Nature **458**, 182–185 (12 March 2009) | Download Citation



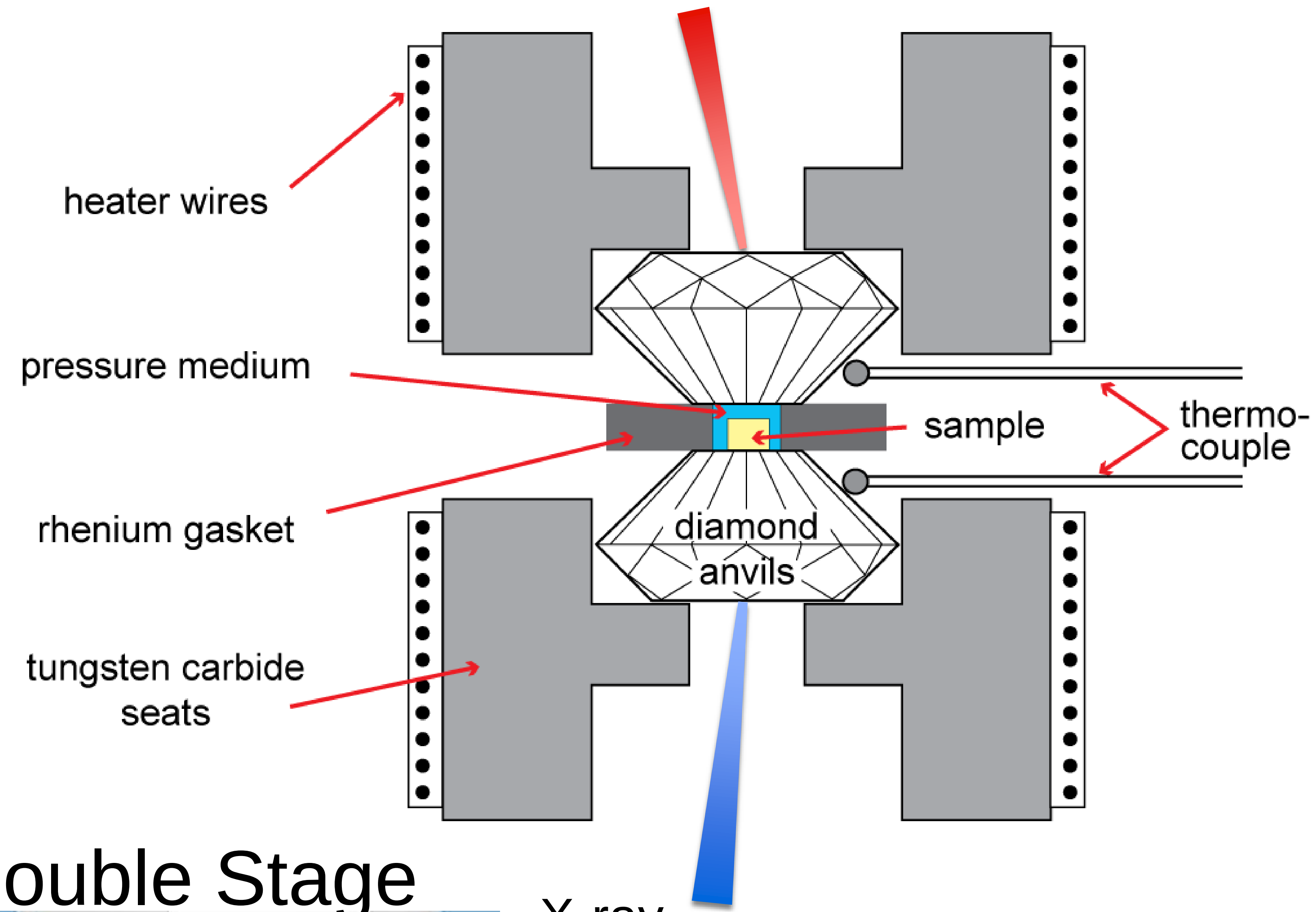


[Static]

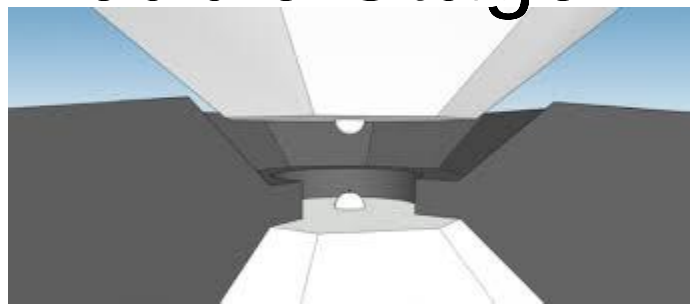
Experiments

[Dynamic]

Diamond Anvil Cell (DAC)



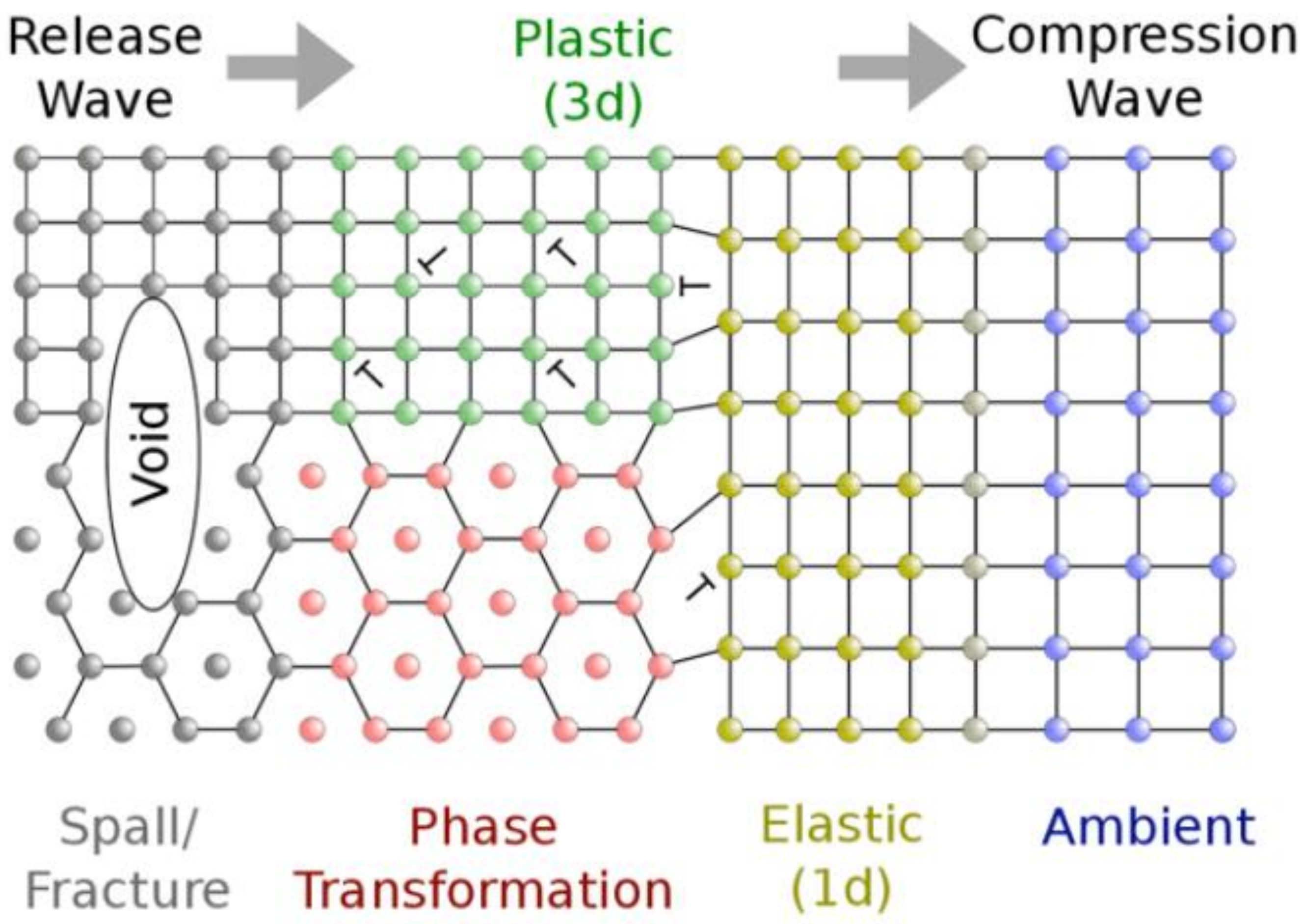
Double Stage



X-ray
Neutron
Raman-IR
Camera

NMR
Conductivity

Shock Compression



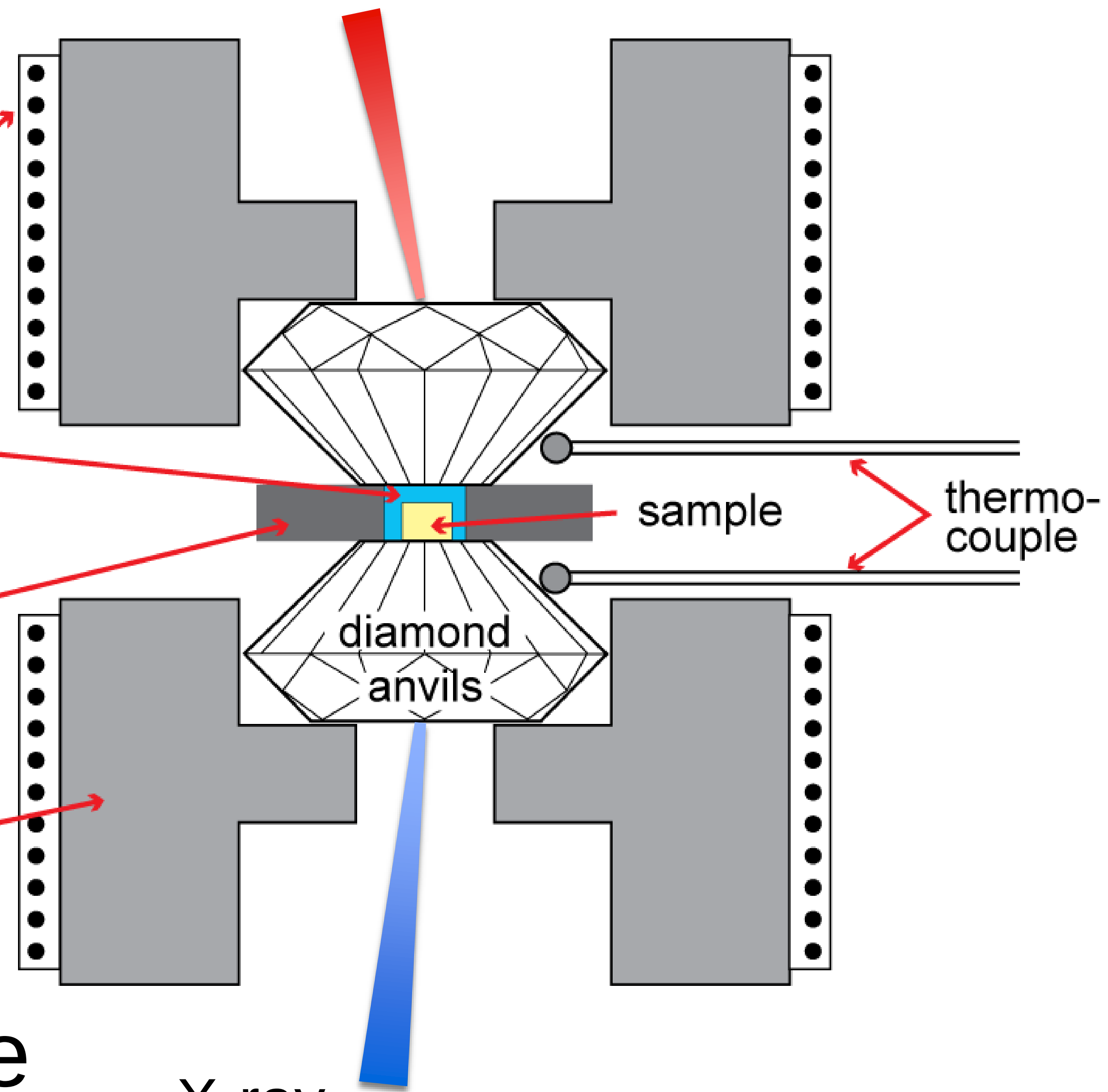
Generally non equilibrium

[Static]

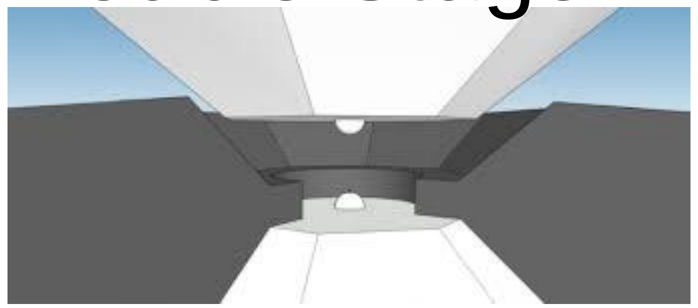
Experiments

[Dynamic]

Diamond Anvil Cell (DAC)

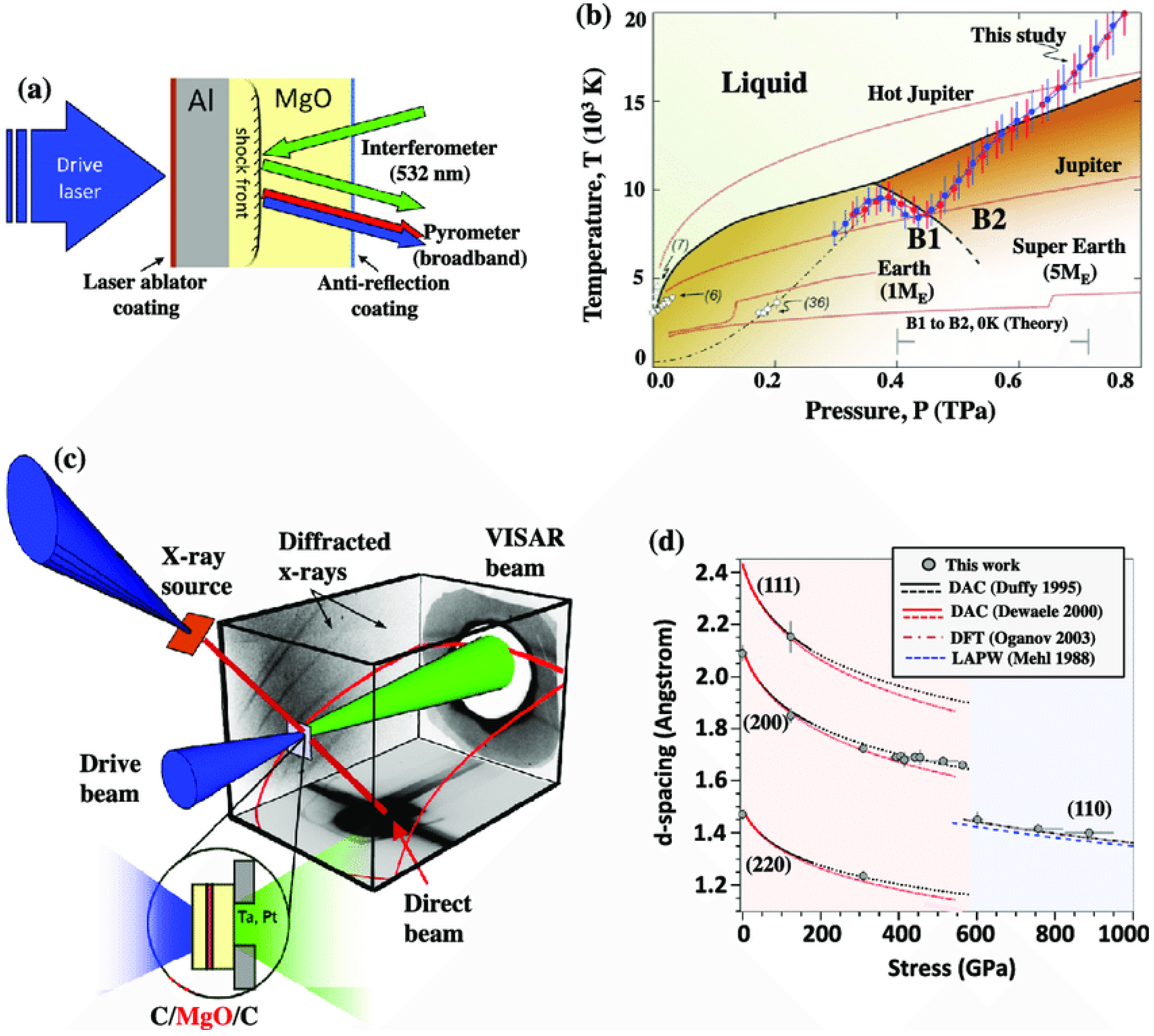


Double Stage



X-ray
Neutron
Raman-IR
Camera

NMR
Conductivity



DOI: 0.1063/1.4930134

High Pressure

- Strange Phenomenon

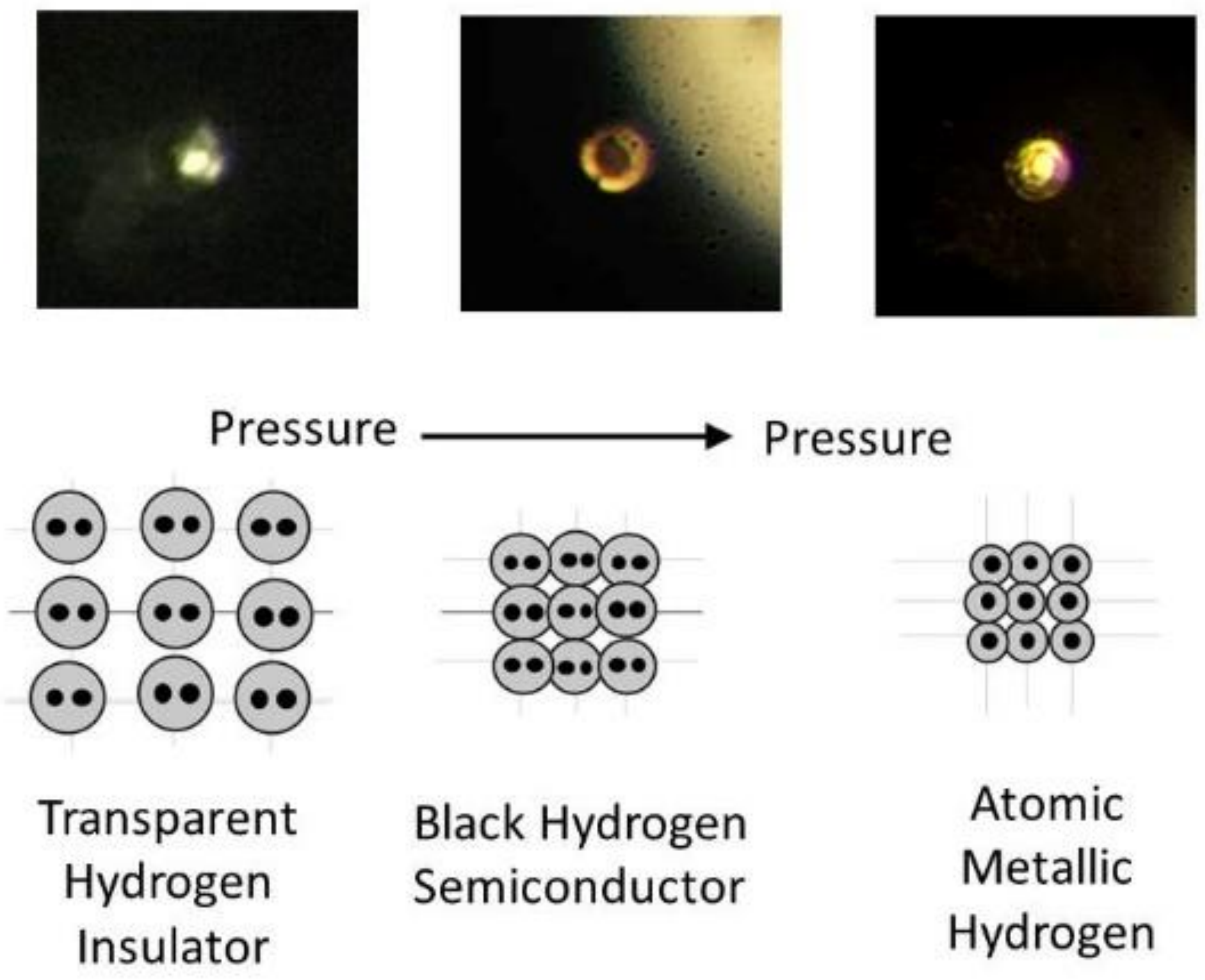
RESEARCH ARTICLE | HIGH-PRESSURE PHYSICS

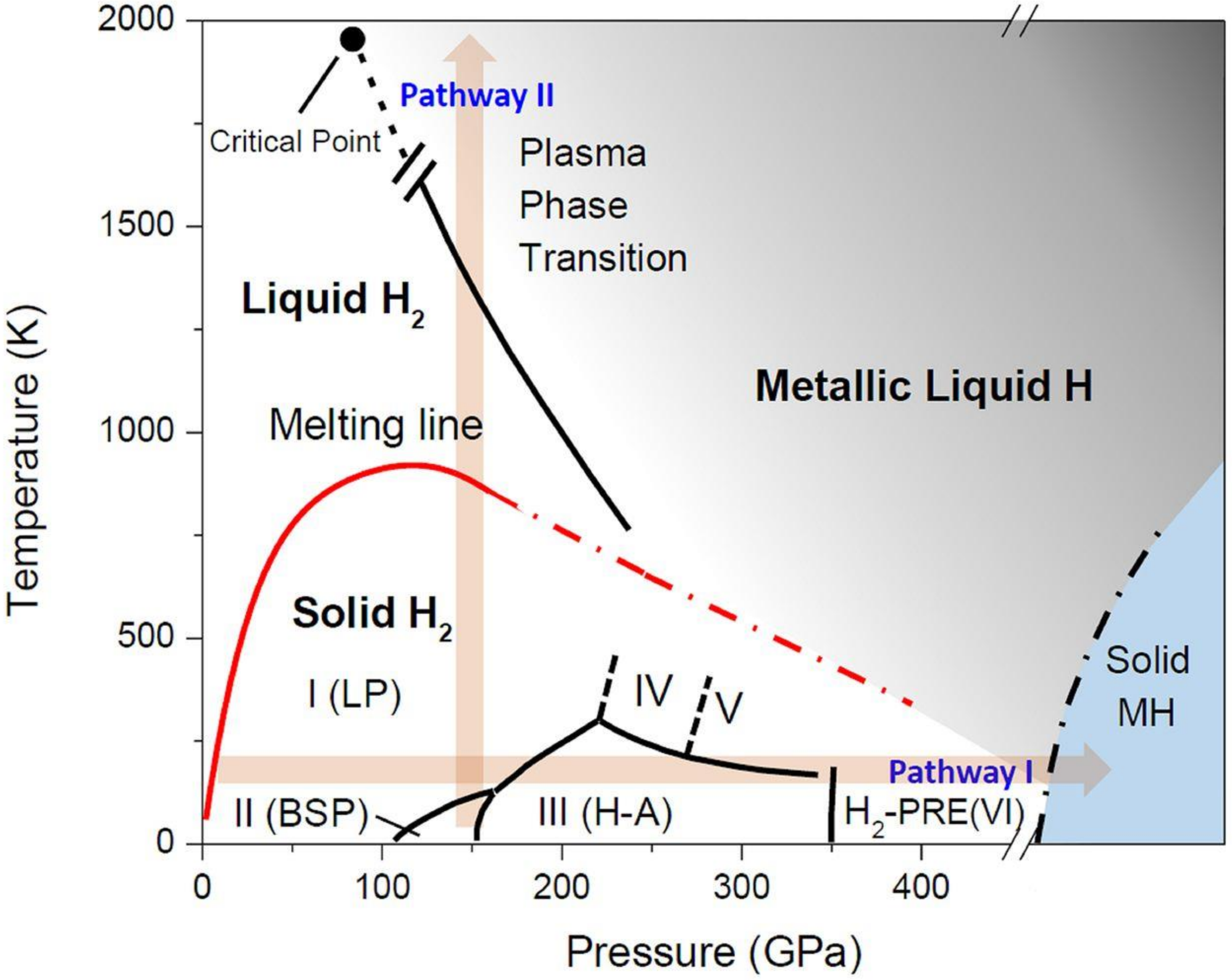
Observation of the Wigner-Huntington transition to metallic hydrogen

Ranga P. Dias, Isaac F. Silvera*

+ See all authors and affiliations

Science 26 Jan 2017:
eaal1579
DOI: 10.1126/science.aal1579



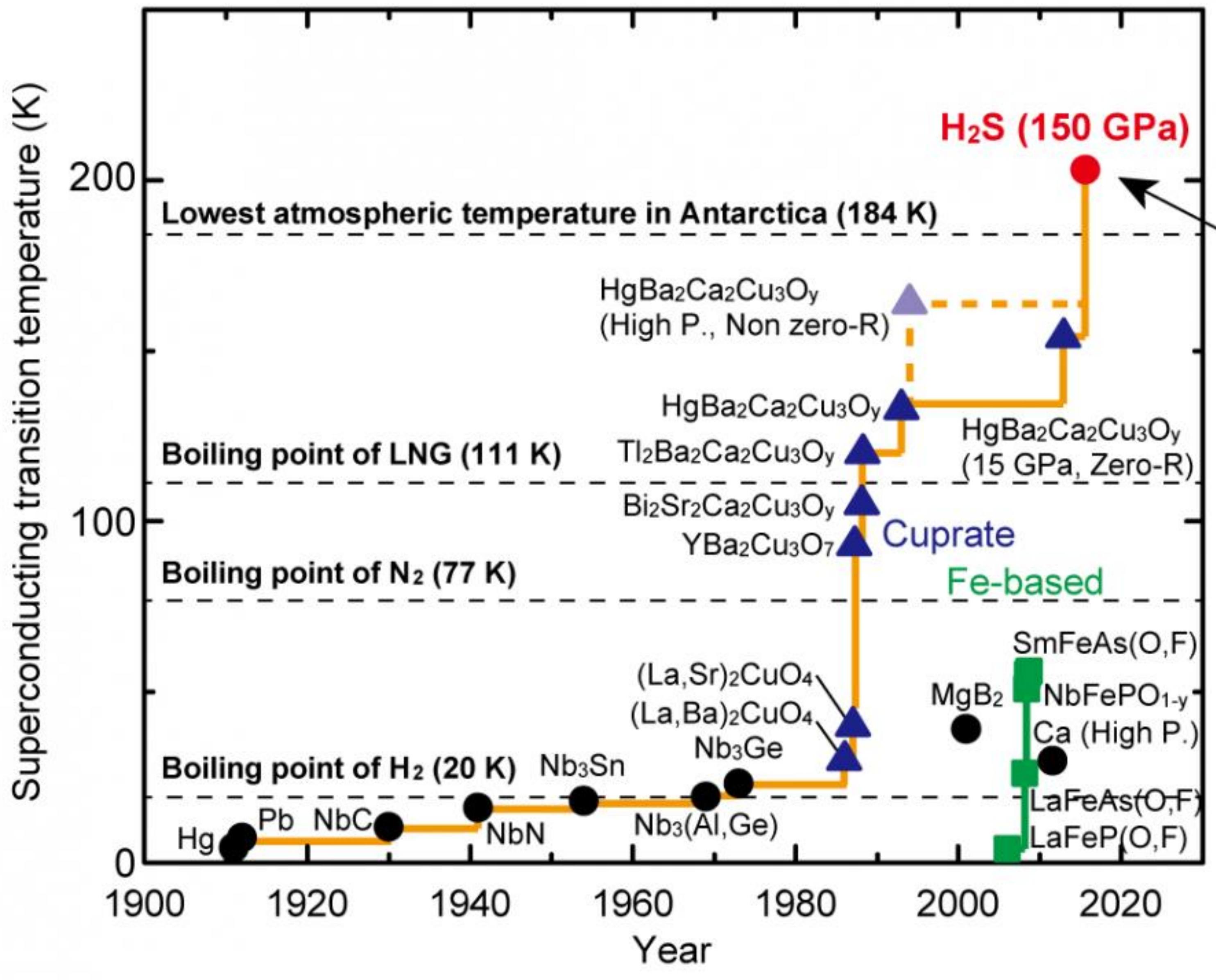


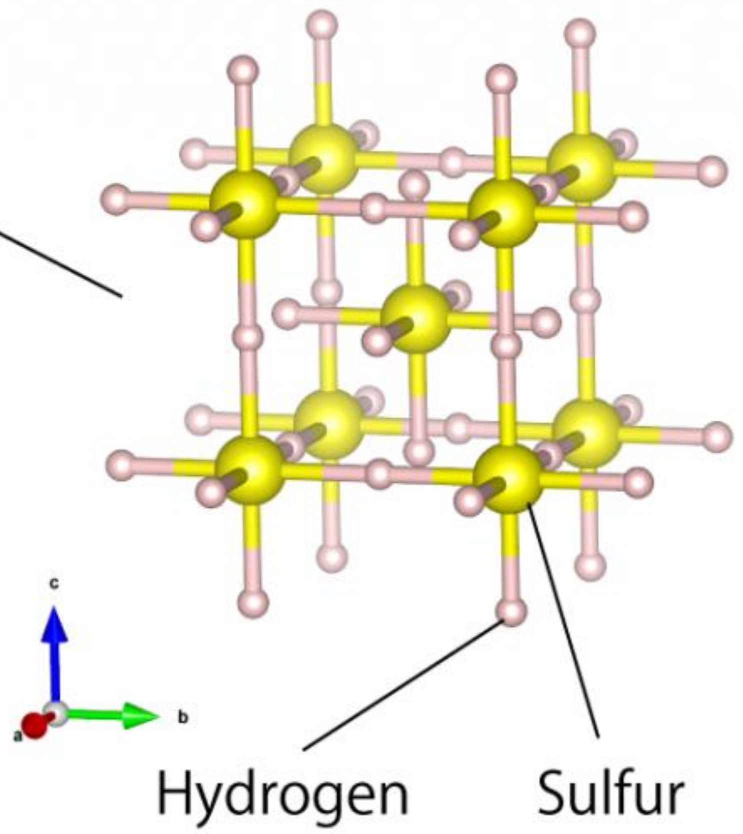
Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

High T_c

A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov & S. I. Shylin

Nature **525**, 73–76 (03 September 2015)





Exotic states of matter

NEWS HIGHLIGHTS

New scientific finding

The superionic form of water, both liquid and solid

15/02/2018 - Trieste

Water is liquid. Indeed, this is true at ambient conditions, as experienced in our daily life. But what would happen under extreme pressures and temperatures such as those inside planets rich in water like Uranus or Neptune? According to scientists, a new phase would appear, a form of water both liquid and solid: a “superionic” water. A team of researchers at ICTP and SISSA, among which Sandro Scandolo and Erio Tosatti, already theoretically predicted this almost 20 years ago in a study published in *Science* in 1999. Their paper was recently cited by a research team from Lawrence Livermore National Laboratory (LLNL), the University of California, Berkeley and the University of Rochester, which has provided the first experimental evidence for the existence of superionic water. A recent note about the study, featured in *Nature Physics*, was posted by the *New York Times* last week.

We have interviewed ICTP researcher Sandro Scandolo to find out more about the relevance and the impact of this new finding.

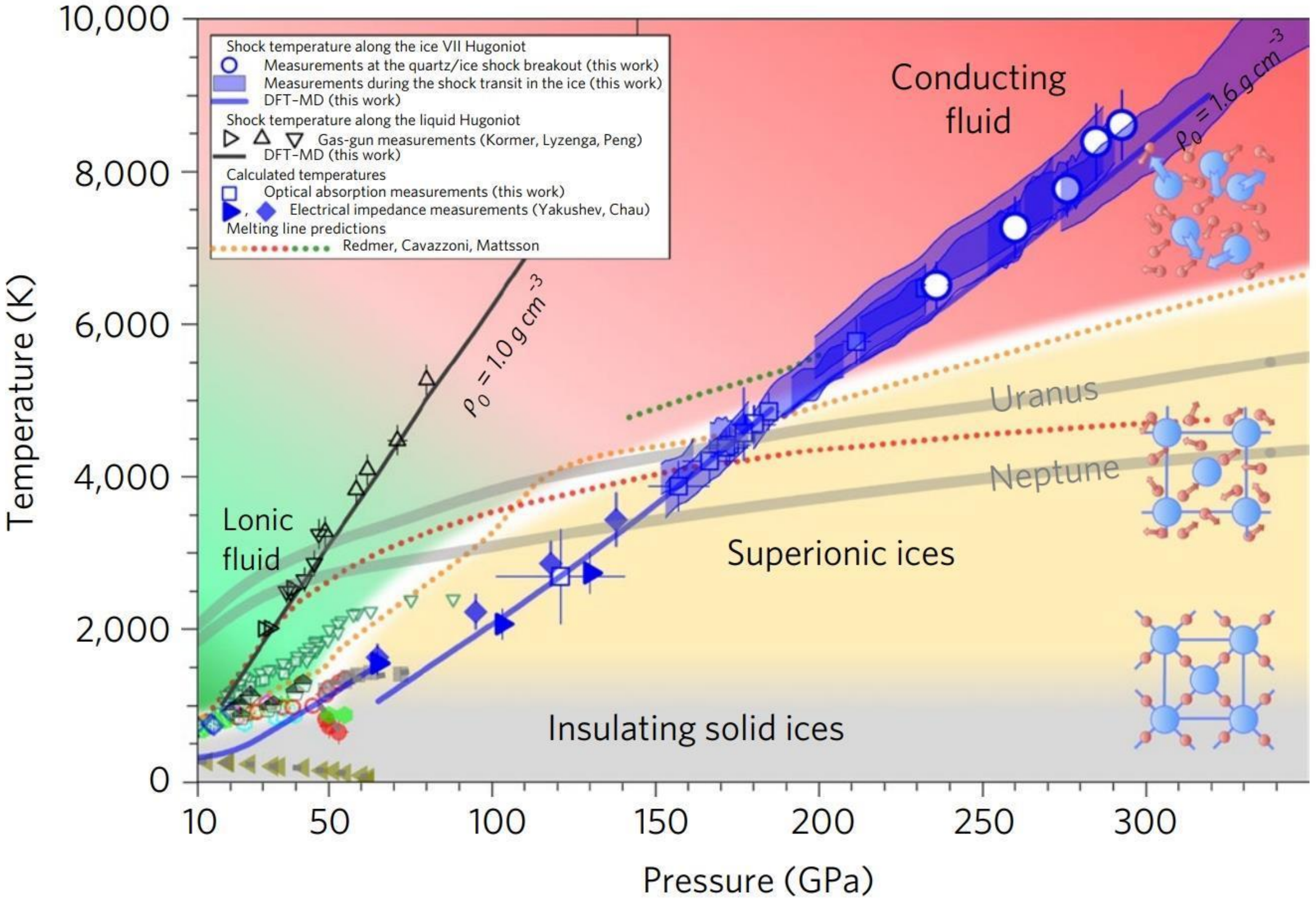
NEWS HIGHLIGHTS

Superionic Phase Validated?

31/03/2005

An article in *Nature* reports that recent experiments may have confirmed the existence of a superionic phase of water, a concept that previously existed solely as a theory. Superionic material represents a strange state that is halfway between solid and liquid. In the case of water, for example, the oxygens under ultra-high pressure remain solid, but the hydrogens flow like liquid. The findings seem to confirm, in simulation, the existence of deep ice layers in Uranus and Neptune, which formed under ultra-high pressures and temperatures. The superionic state had been predicted theoretically in the late 1990s by a group of scientists that includes former ICTP acting director Erio Tosatti and ICTP staff scientist Sandro Scandolo. The lead author in the *Science* article that first presented this theory was Carlo Cavazzoni, a former student at the International School for Advanced Studies (SISSA).

The Abdus Salam International Centre for Theoretical Physics



Experimental evidence for superionic water ice using shock compression

Marius Millot, Sebastien Hamel, J. Ryan Rygg, Peter M. Celliers, Gilbert W. Collins, Federica Coppari, Dayne E. Fratanduono, Raymond Jeanloz, Damian C. Swift & Jon H. Eggert

Nature Physics **14**, 297–302 (2018)

Exotic states of matter

SUPERIONIC TRANSITION IN ICE

I.A. Ryzhkin

Institute of Solid State Physics, Academy of Sciences of USSR, Chernogolovka, 142432, USSR

(*Received* 20 *May* 1985 *by V.M. Agranovich*)

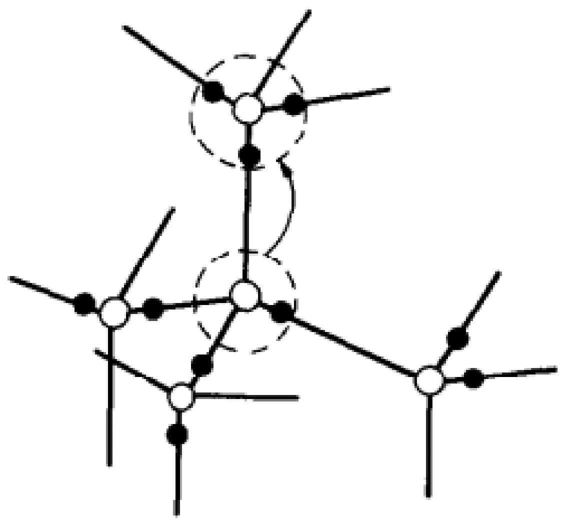
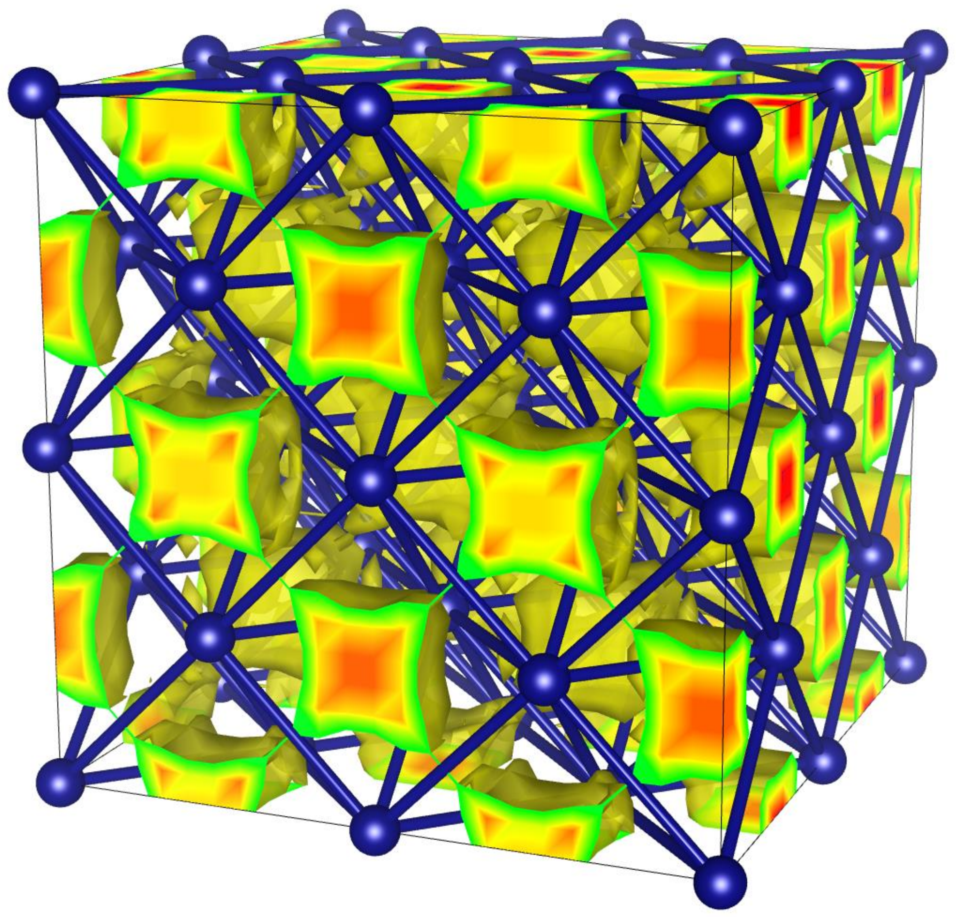


Fig. 2. Proton configuration with one pair of ionic defects.

Solid State Communications, Vol. 56, No. 1, pp. 57–60, 1985.
Printed in Great Britain.



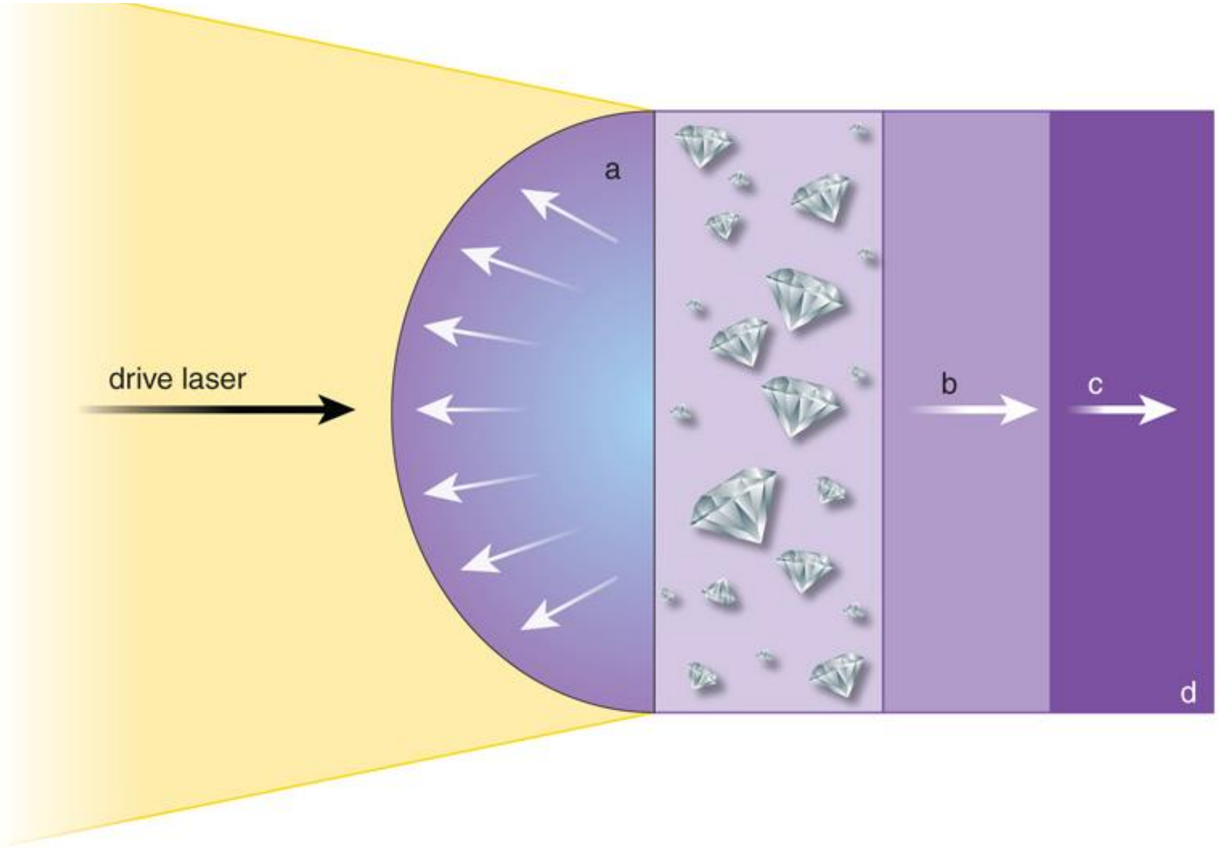
Superionic to superionic phase change in water: Consequences for the interiors of Uranus and Neptune

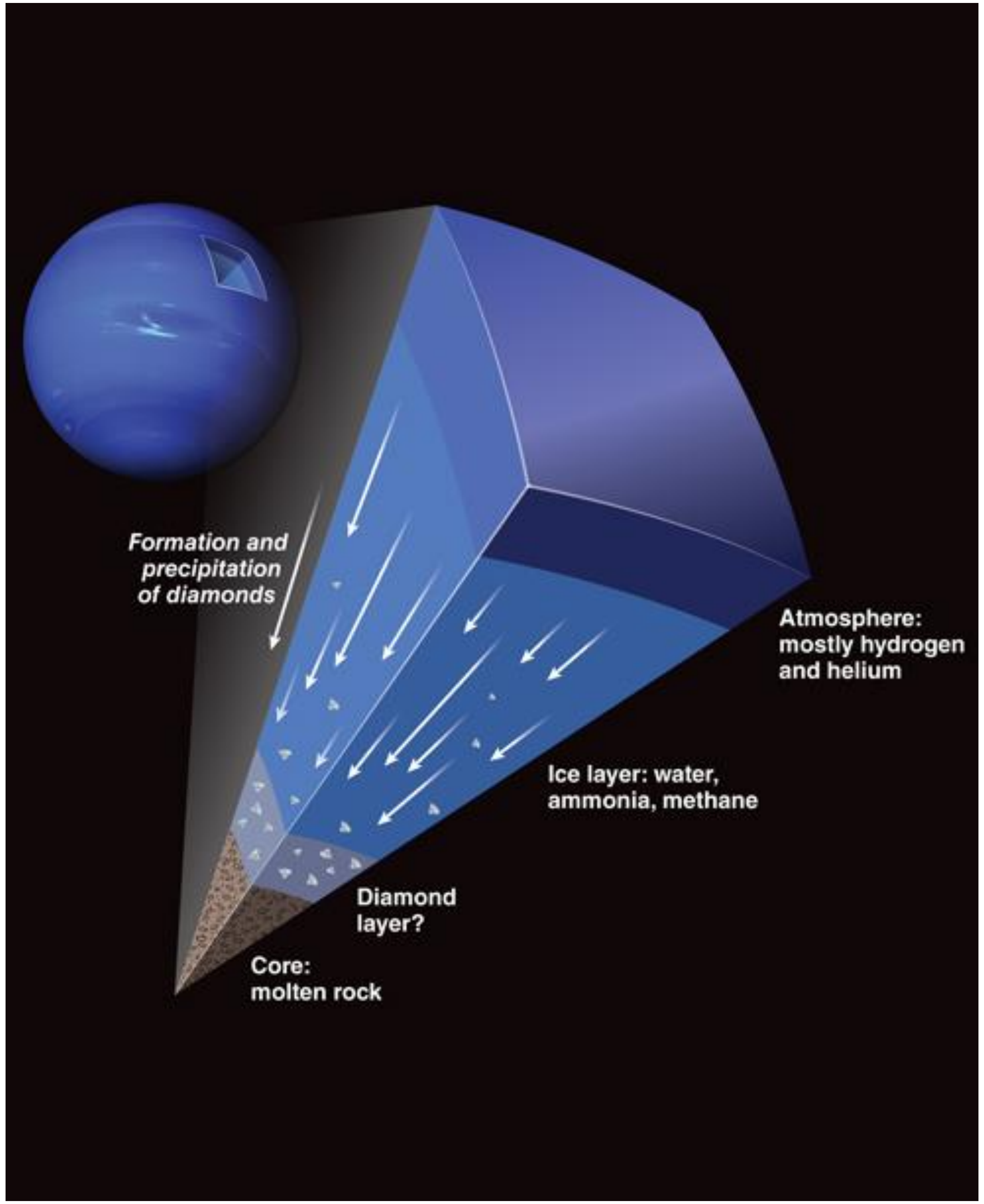
Hugh F. Wilson, Michael L. Wong, Burkhard Militzer **Phys.Rev.Lett. 110 (2013) no.15, 151102**

Formation of diamonds in laser-compressed hydrocarbons at planetary interior conditions

D. Kraus ✉, J. Vorberger, A. Pak, N. J. Hartley, L. B. Fletcher, S. Frydrych, E. Galtier, E. J. Gamboa, D. O. Gericke, S. H. Glenzer, E. Granados, M. J. MacDonald, A. J. MacKinnon, E. E. McBride, I. Nam, P. Neumayer, M. Roth, A. M. Saunders, A. K. Schuster, P. Sun, T. van Driel, T. Döppner & R. W. Falcone

Nature Astronomy **1**, 606–611 (2017)

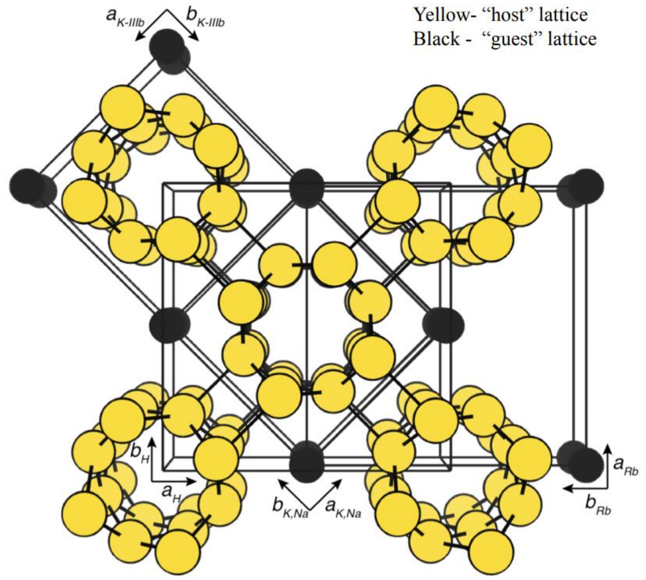


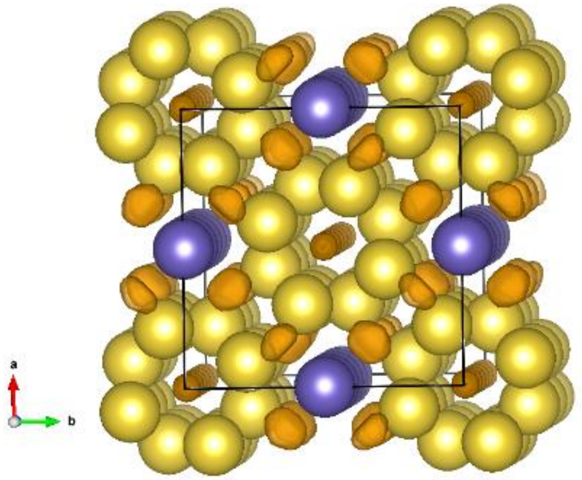


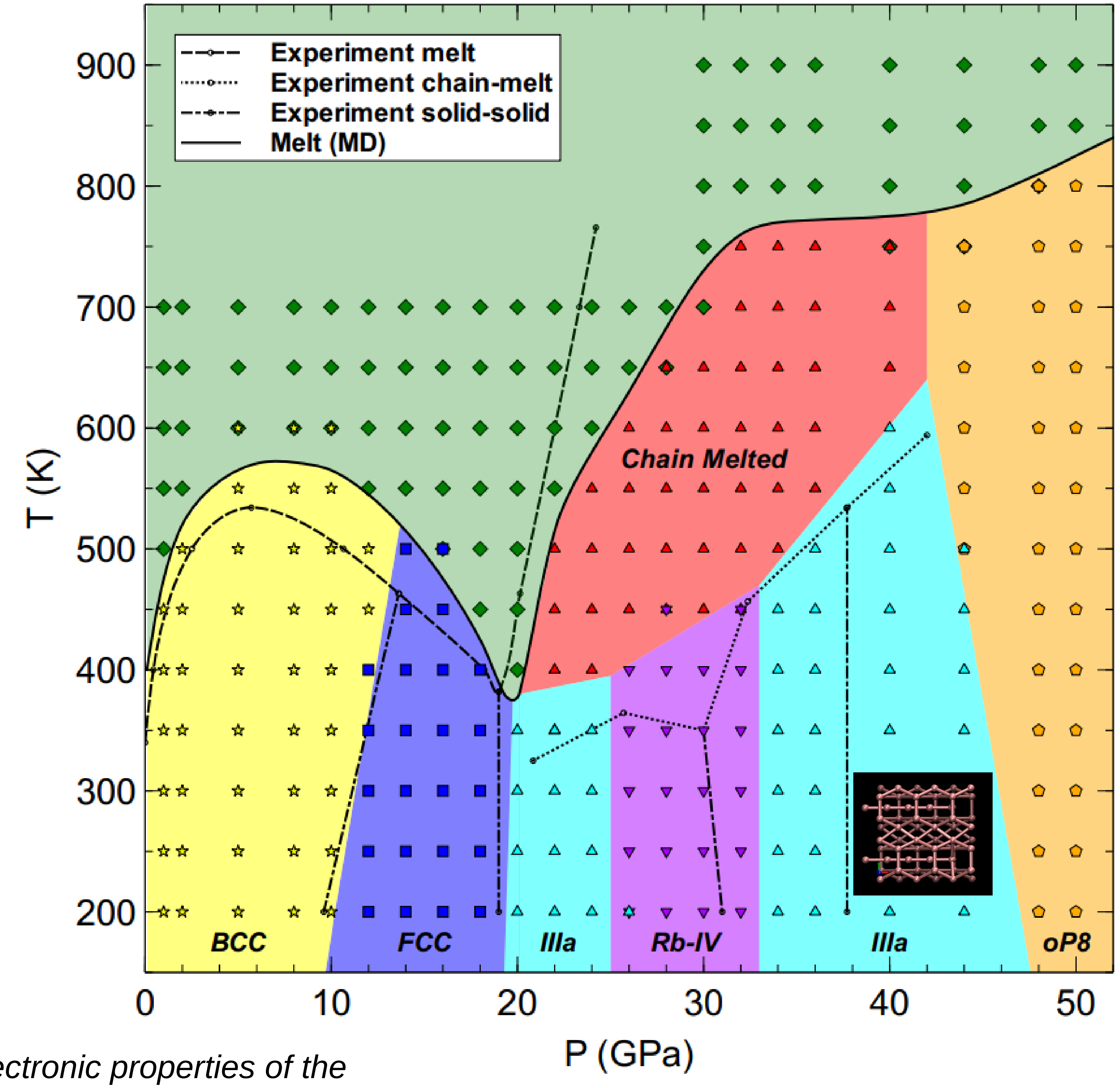
https://www.americanscientist.org/article/on-neptune-its-raining-diamonds

Partial Melts

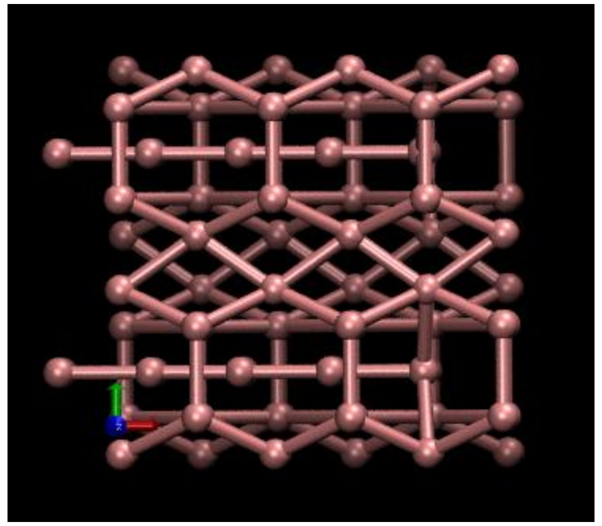
K



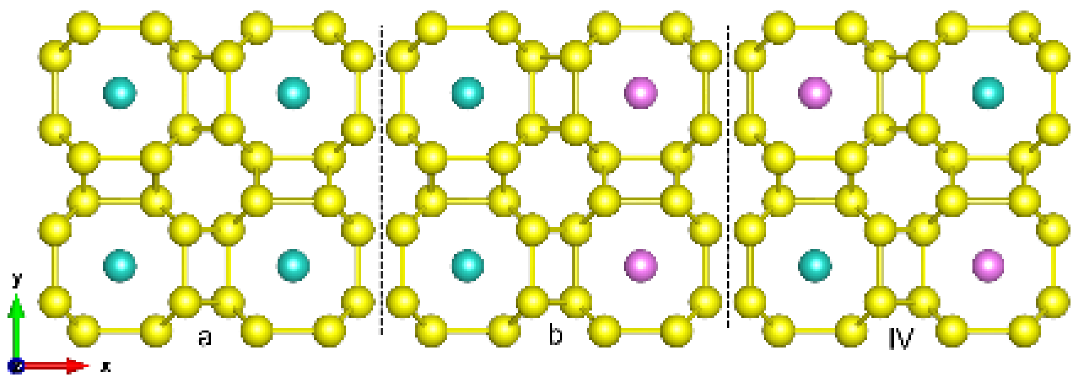




Machine Learned Force-field



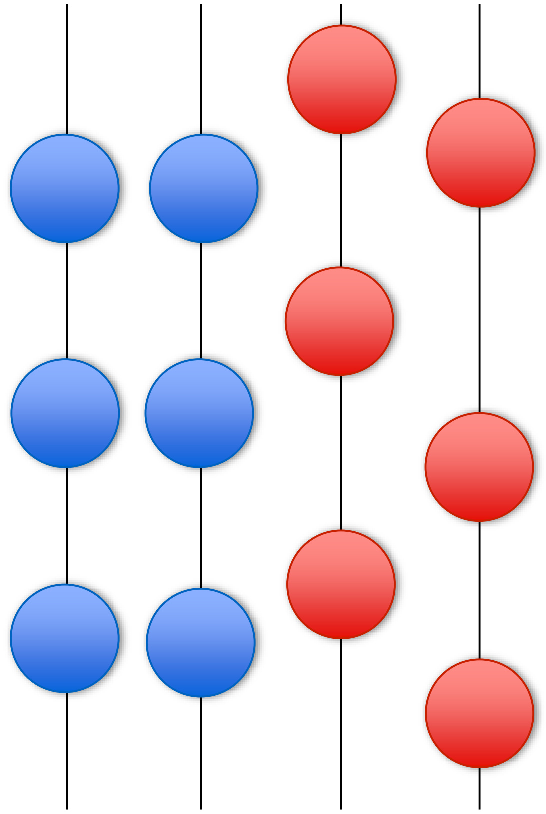
40 GPa
200 K

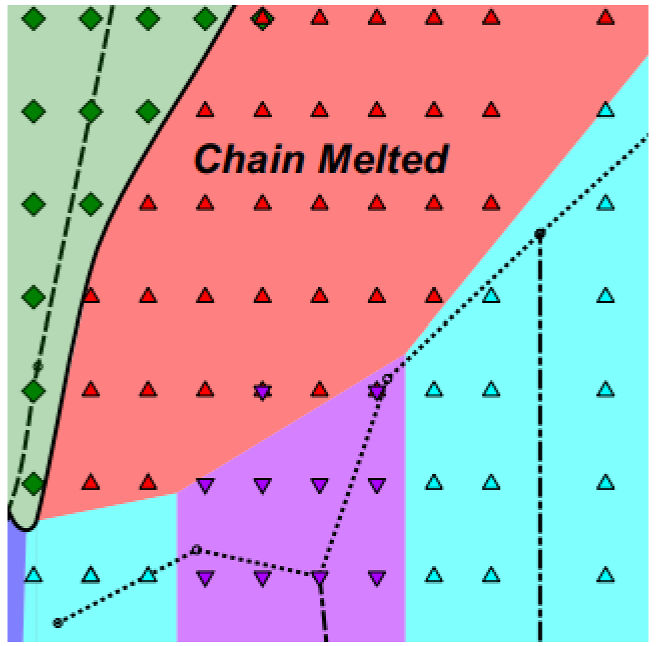


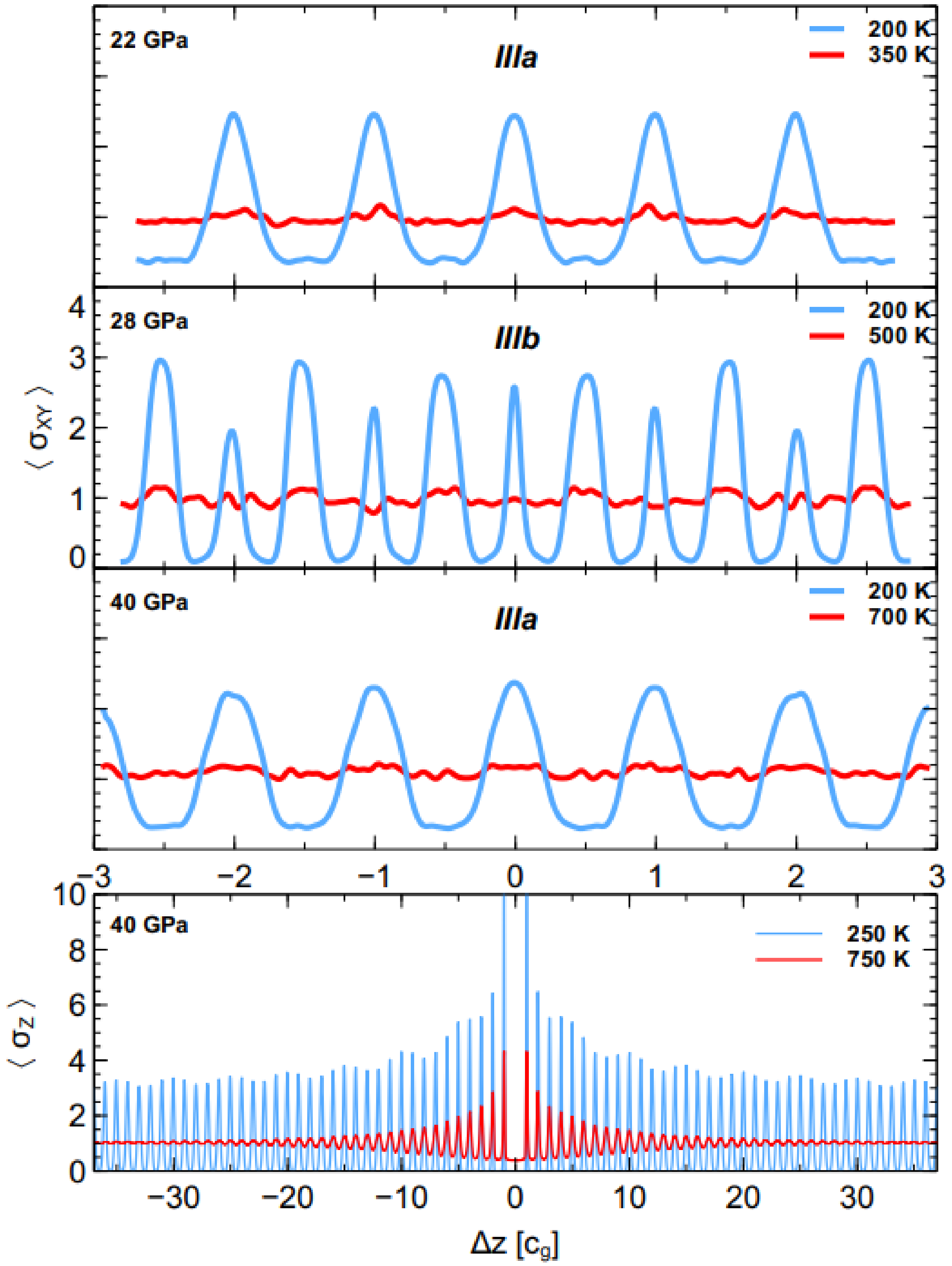
Submitted

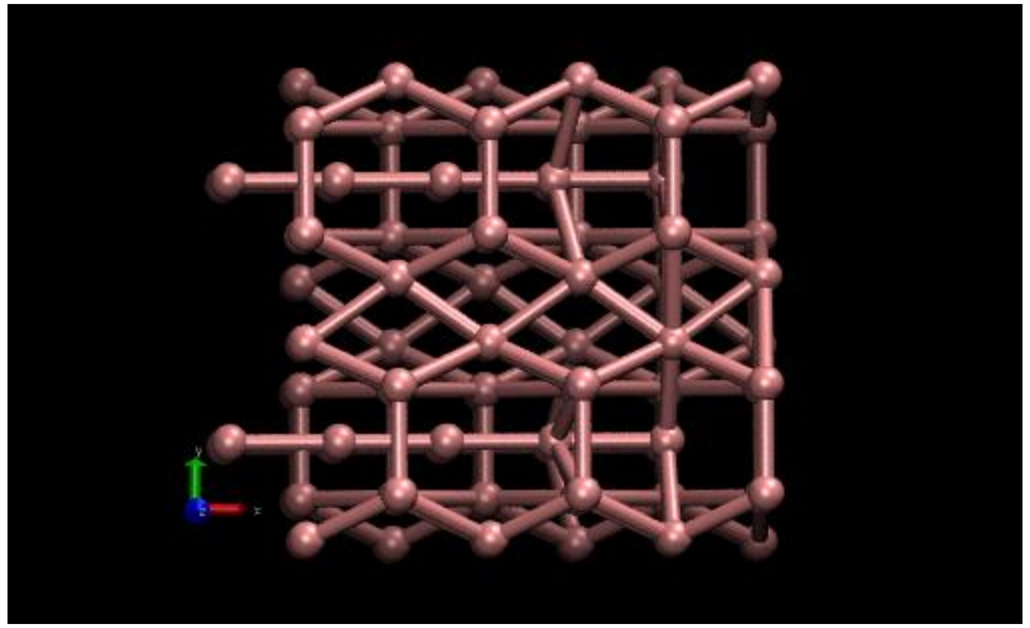
[1] Woolman, Gavin, et al. "Structural and electronic properties of the alkali metal incommensurate phases." Physical Review Materials 2.5 (2018): 053604.
[2] Emma E McBride, Keith A Munro, Graham W Stinton, Rachel J Husband, Richard Briggs, H-P Liermann, and Malcolm I McMahon.

Partial Melts







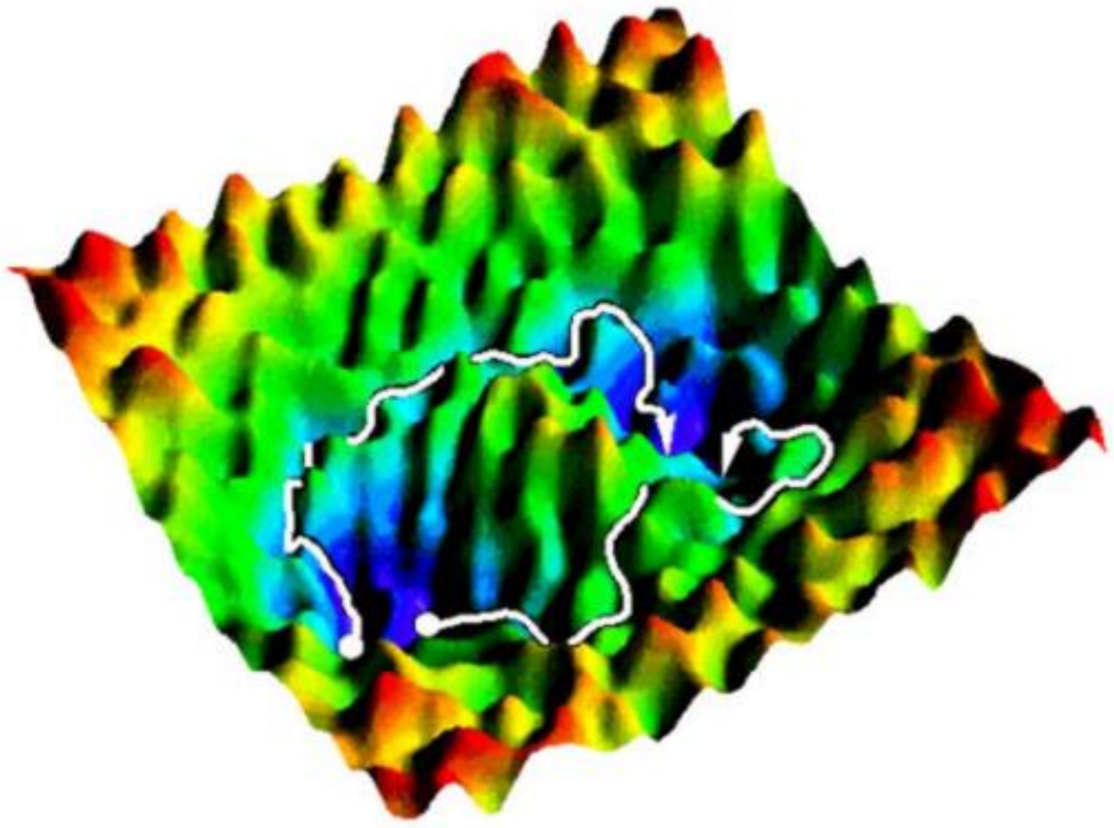


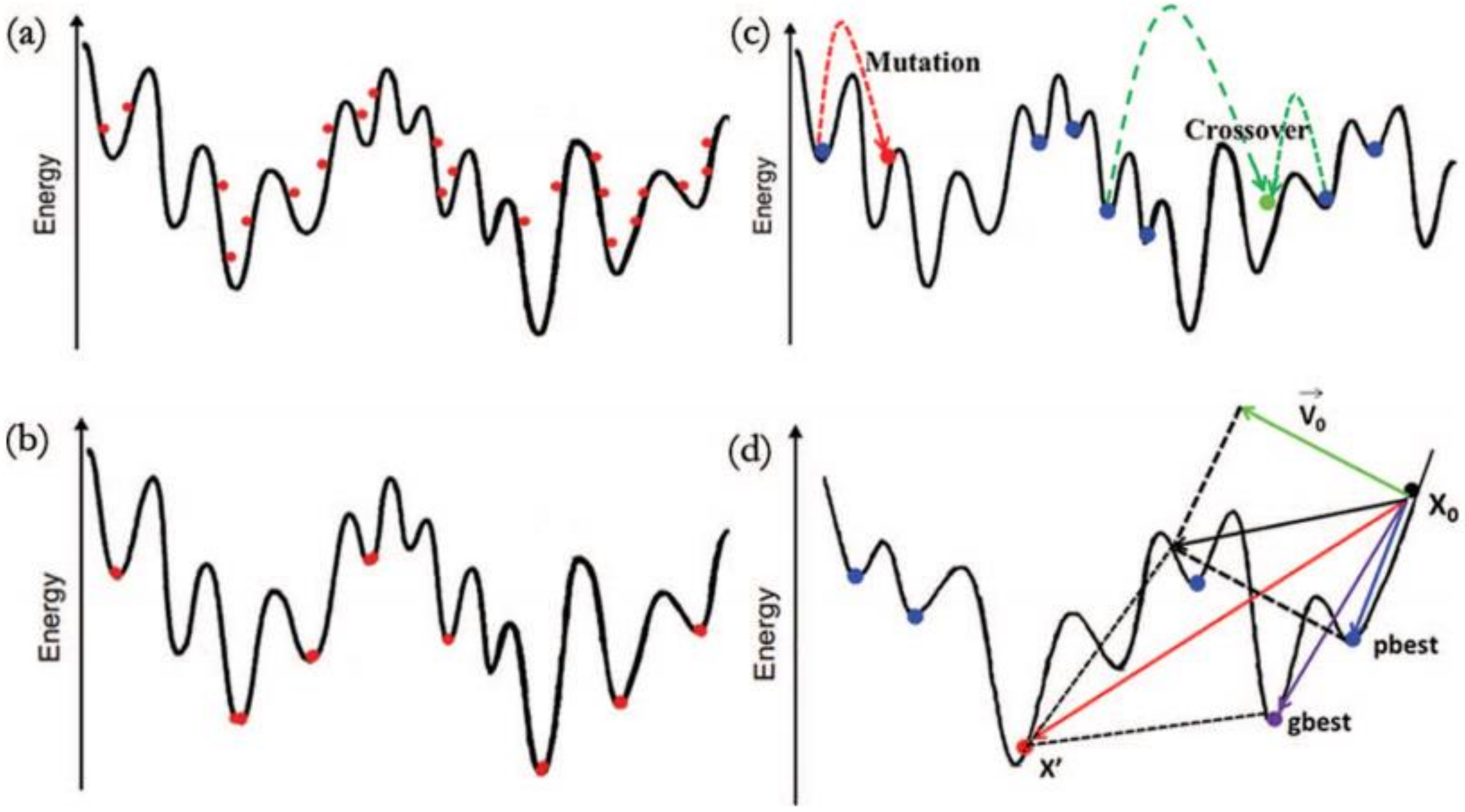
1000 K

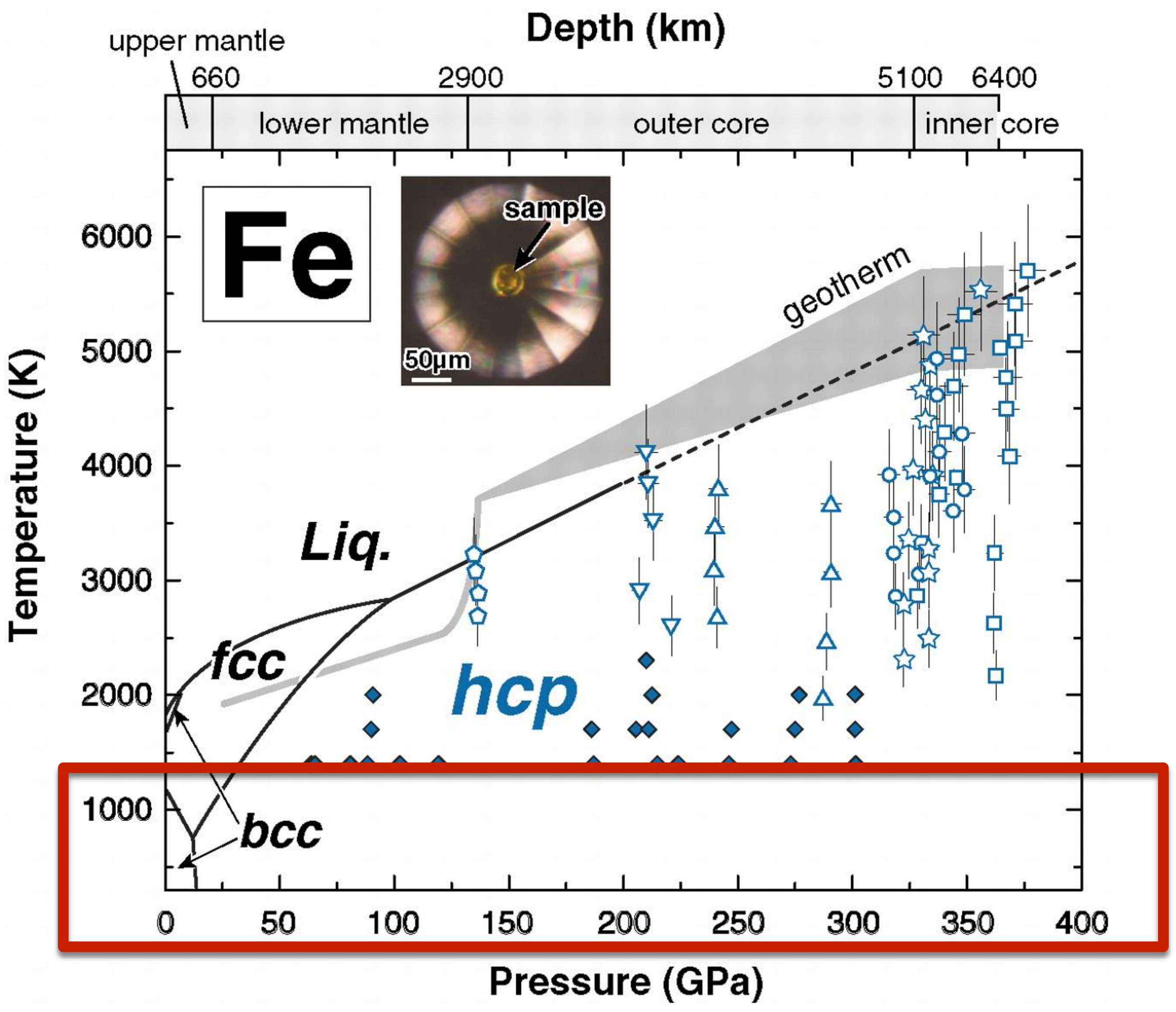
Submitted

Crystal Structure Prediction

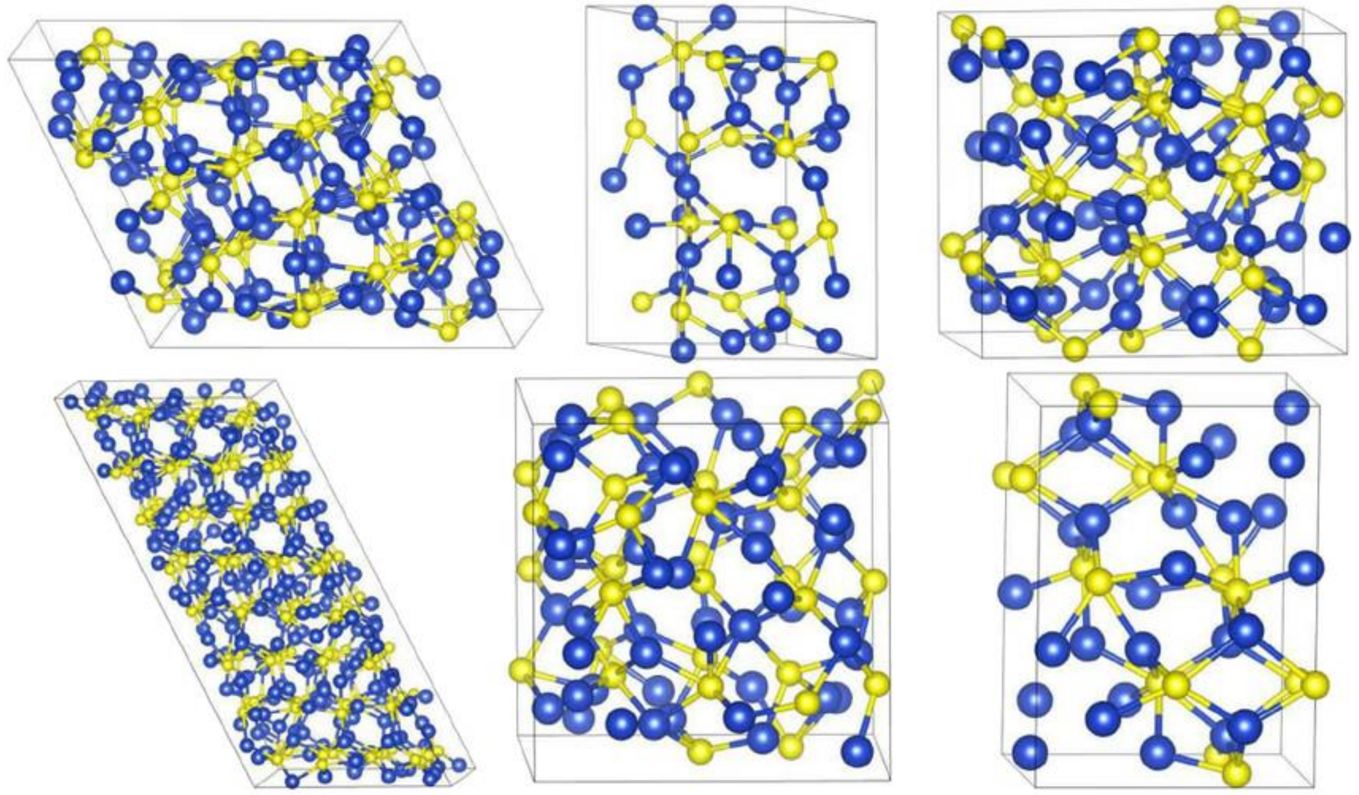
- Simplest form: Relax **many random** unit cells → lowest energy







many random unit cells

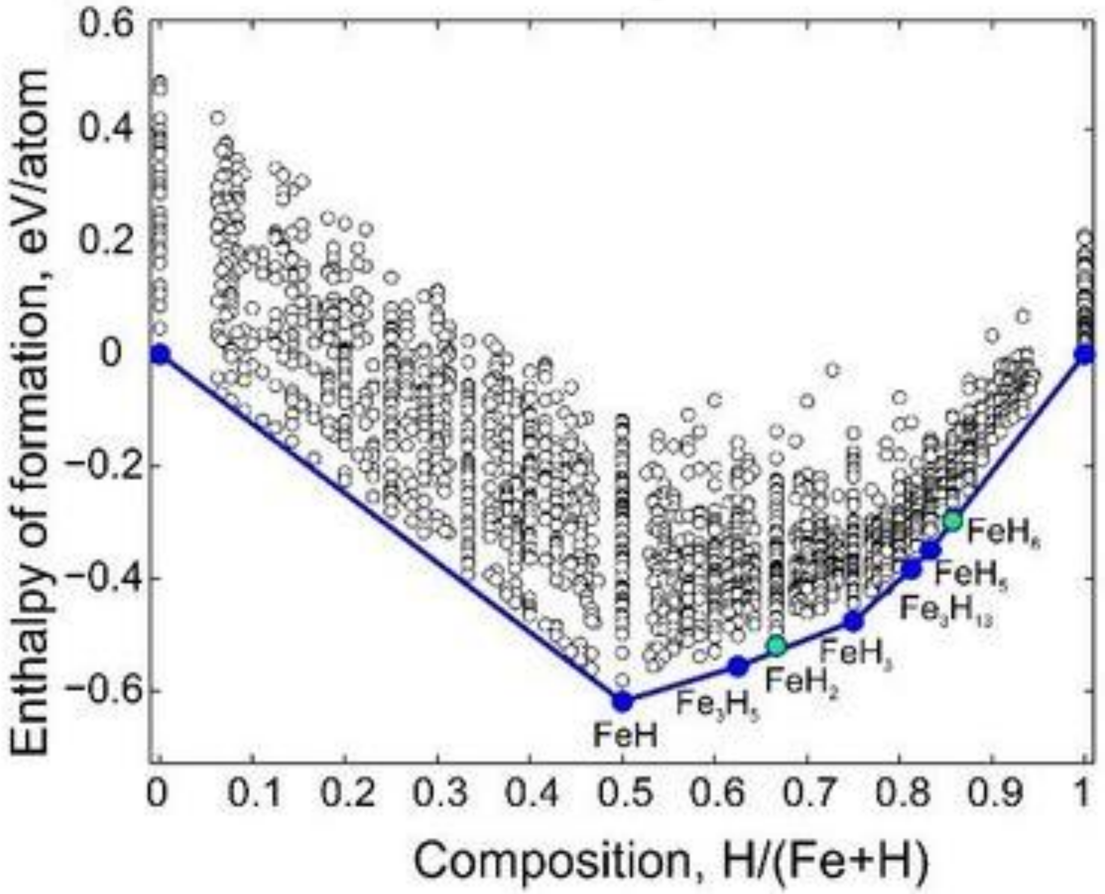


Machine Learning

Potentials

Ab initio (DFT)

QMC



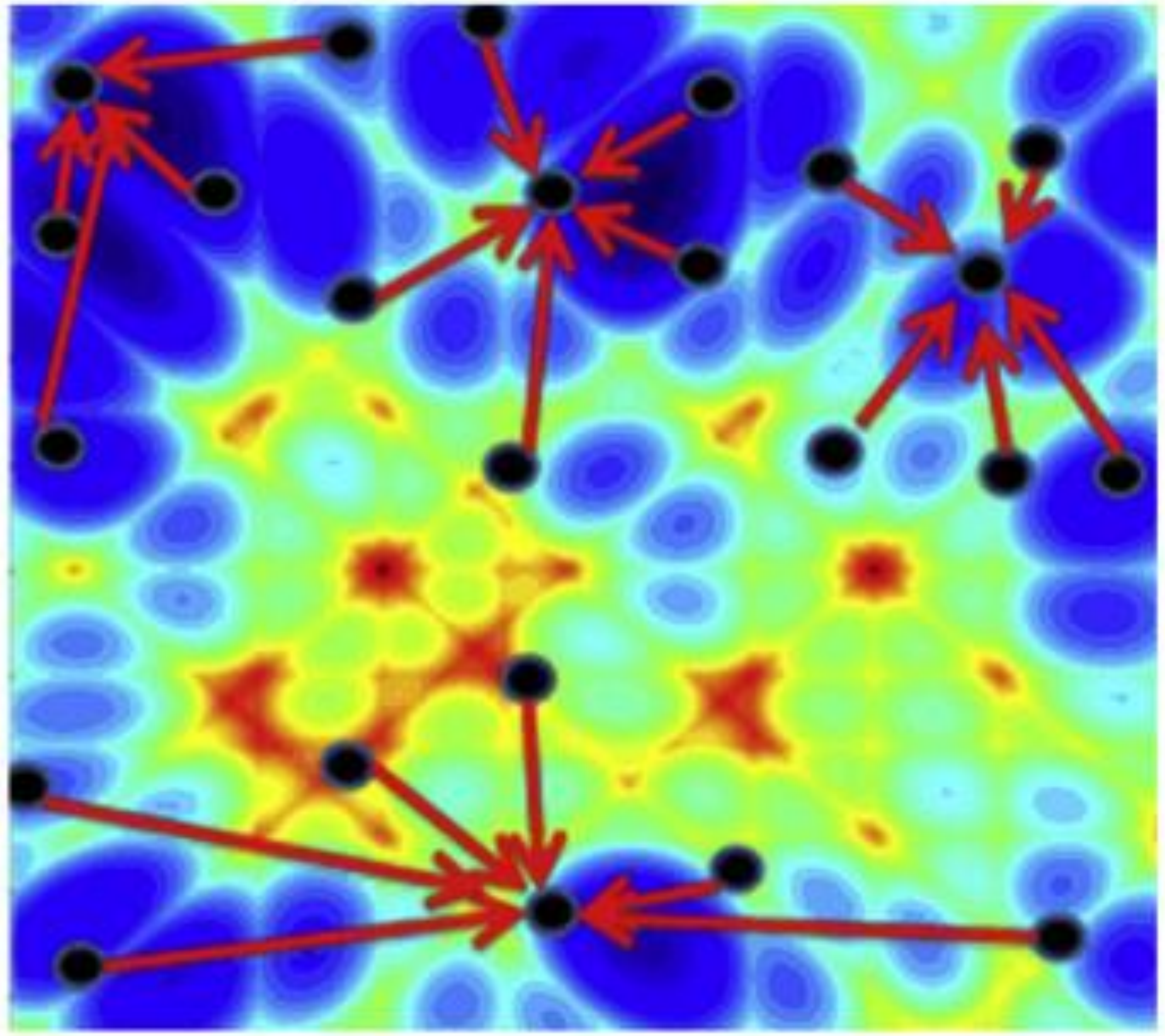
Energetic ranking

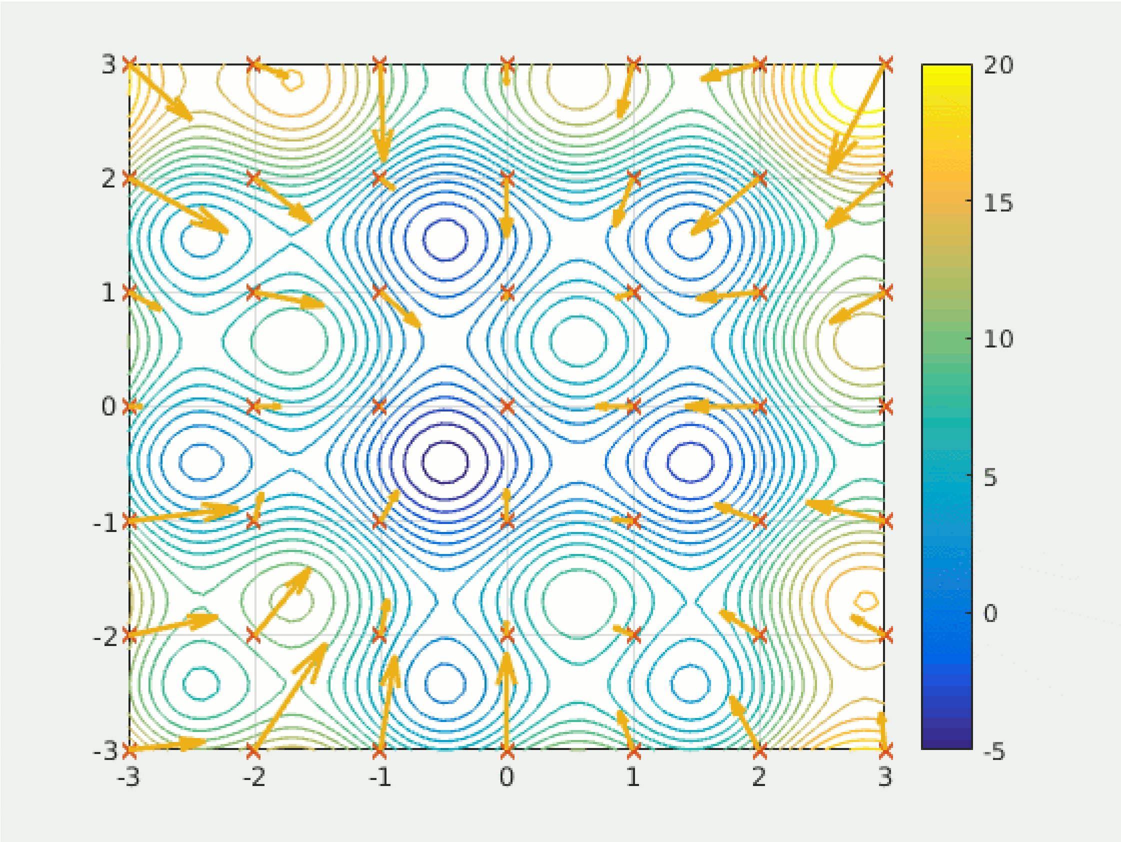
Crystal structure prediction

CALYPSO

- Particle-swarm optimization
  - Up to four formula units, 500,000 + structures
  - Pressures 5, 10, 20, 30, 50, 80, 100 … 1000 GPa

CASTEP





USPEX Computational Materials Discovery

XtalOpt Evolutionary Crystal Structure Prediction

TOPICAL REVIEW

Ab initio random structure searching

Chris J Pickard[1] and R J Needs[2]

Published 5 January 2011 • IOP Publishing Ltd

Journal of Physics: Condensed Matter, Volume 23, Number 5

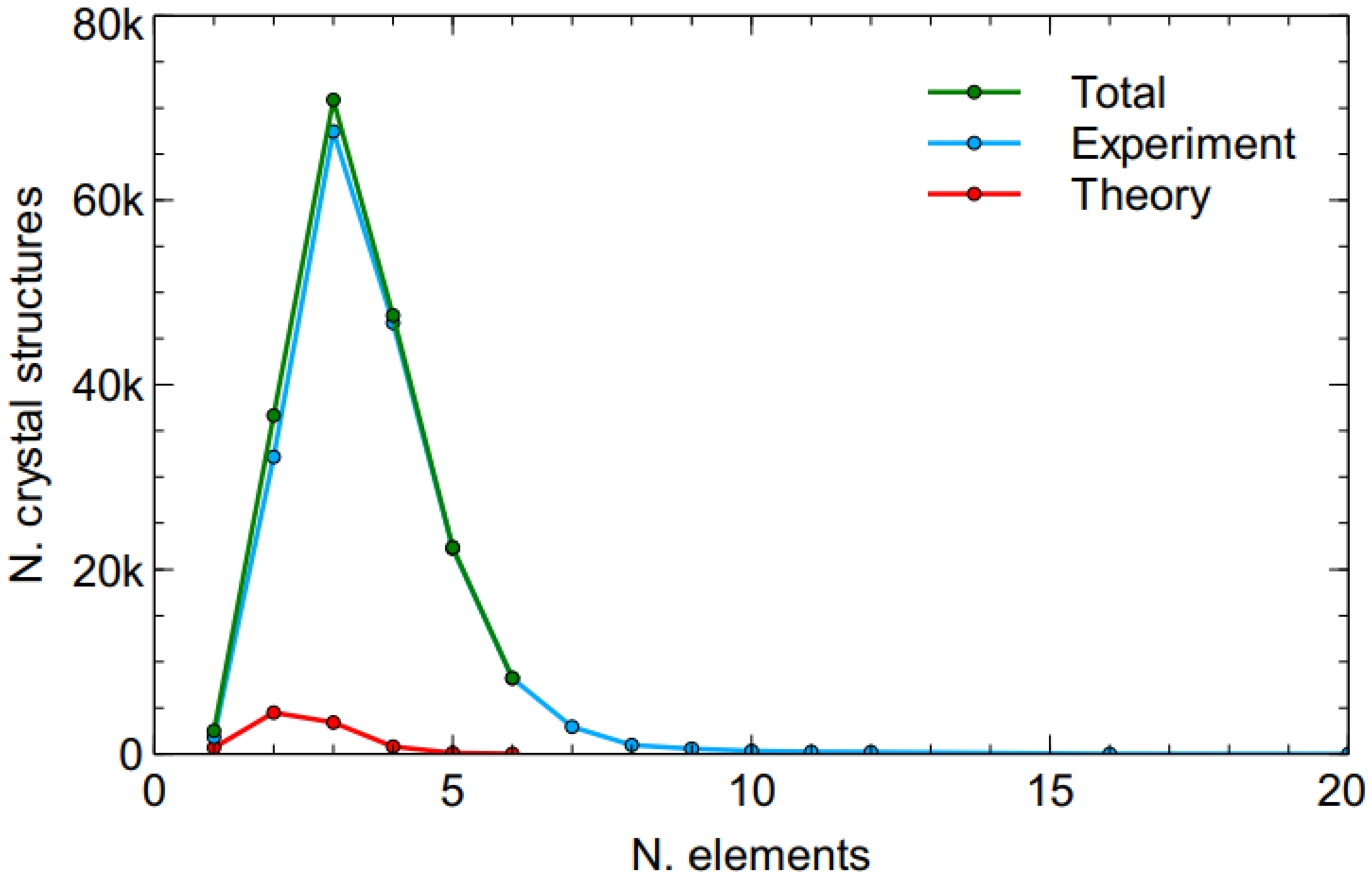


Figure 2.5 *ICSD statistics taken for the number of crystal structures consisting of a certain number of elements starting from unary, binary, ternary and so forth.*

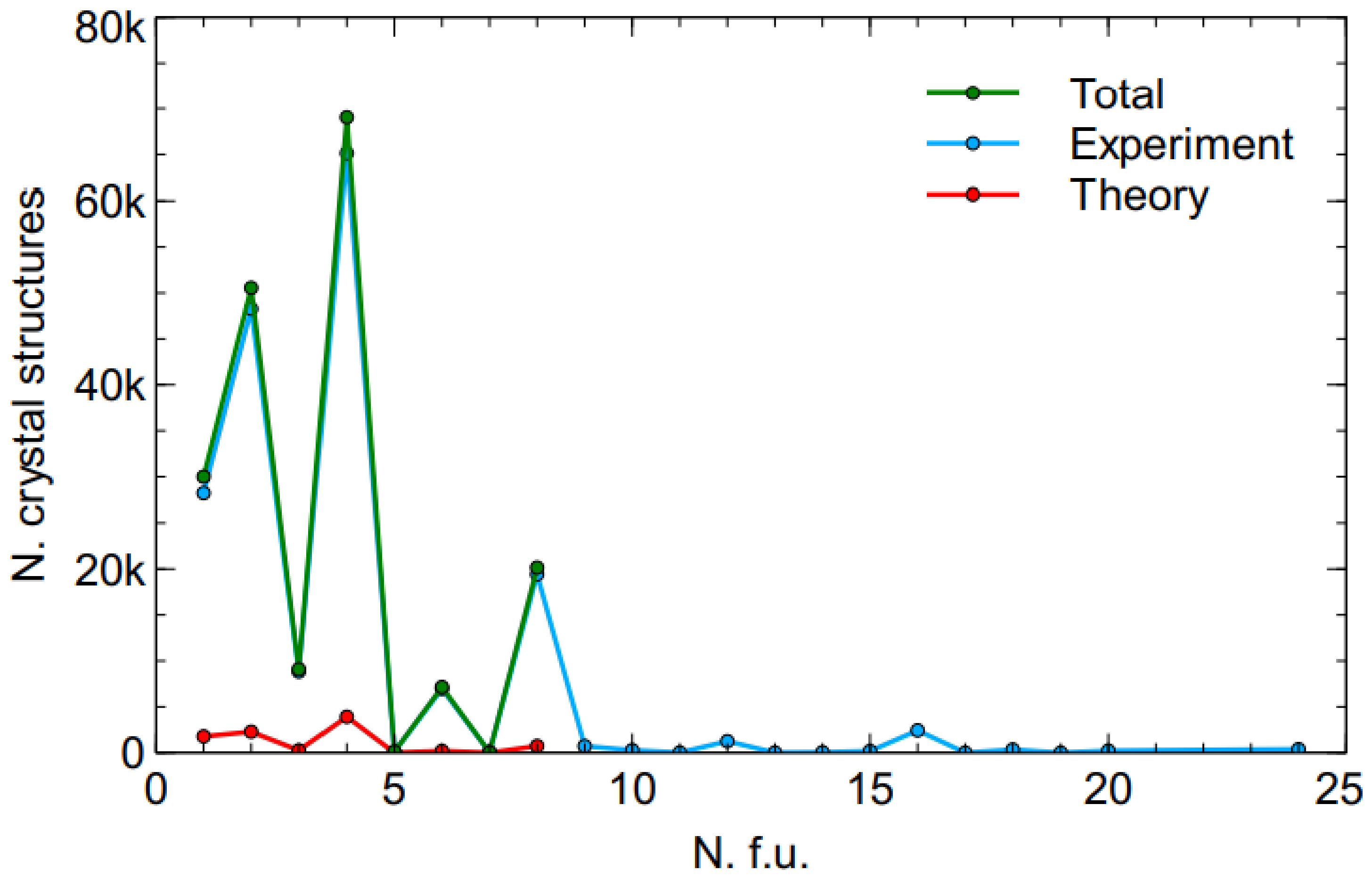


Figure 2.6 *ICSD statistics taken for the number of crystal structures with an integer number of formula units and any chemical composition.*

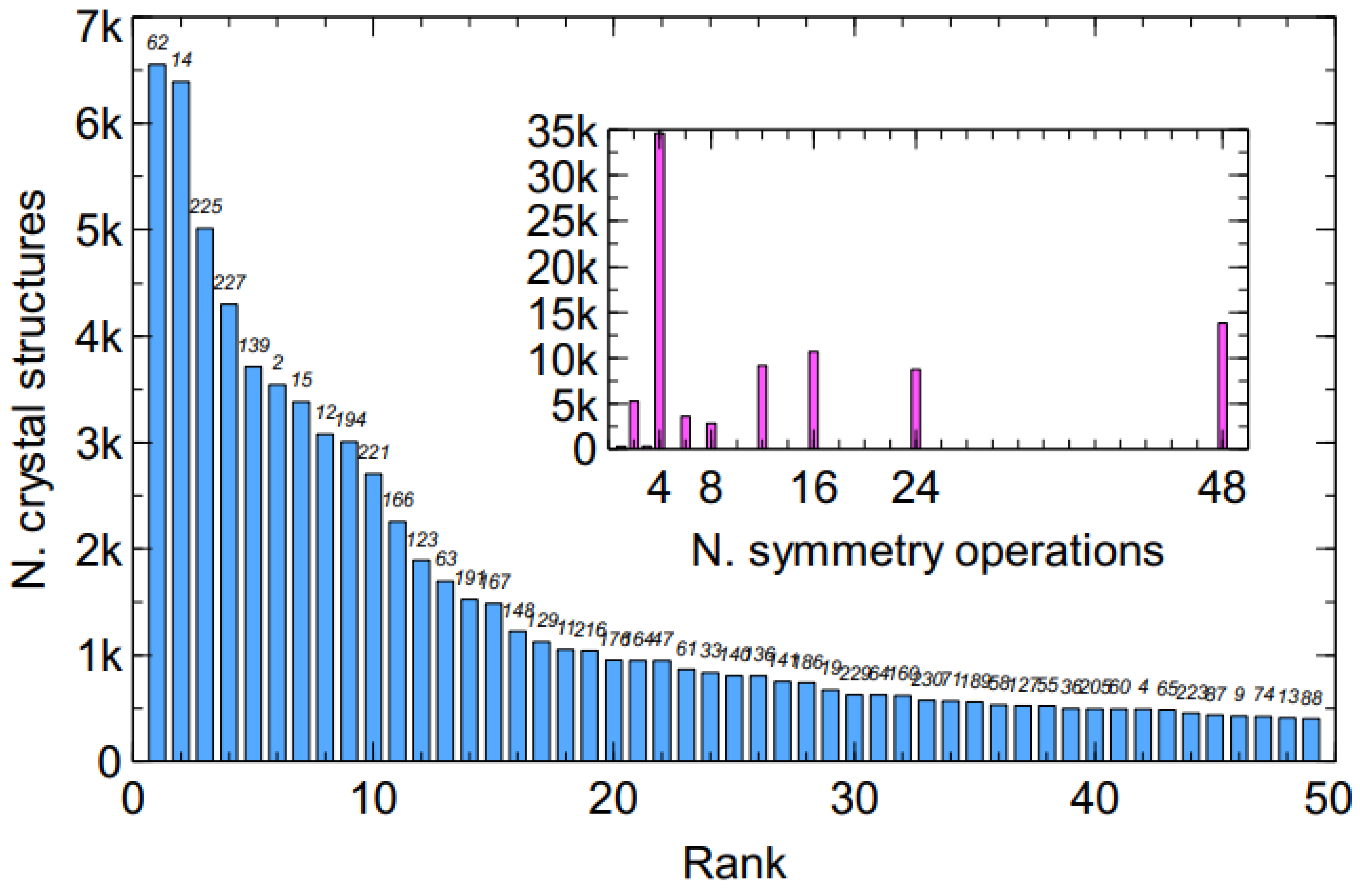


Figure 2.8 *ICSD statistics showing the number of crystal structures for the 50 most common space groups labeled with their space group number. Inset shows the number of structures with a certain integer number of symmetry operations.*

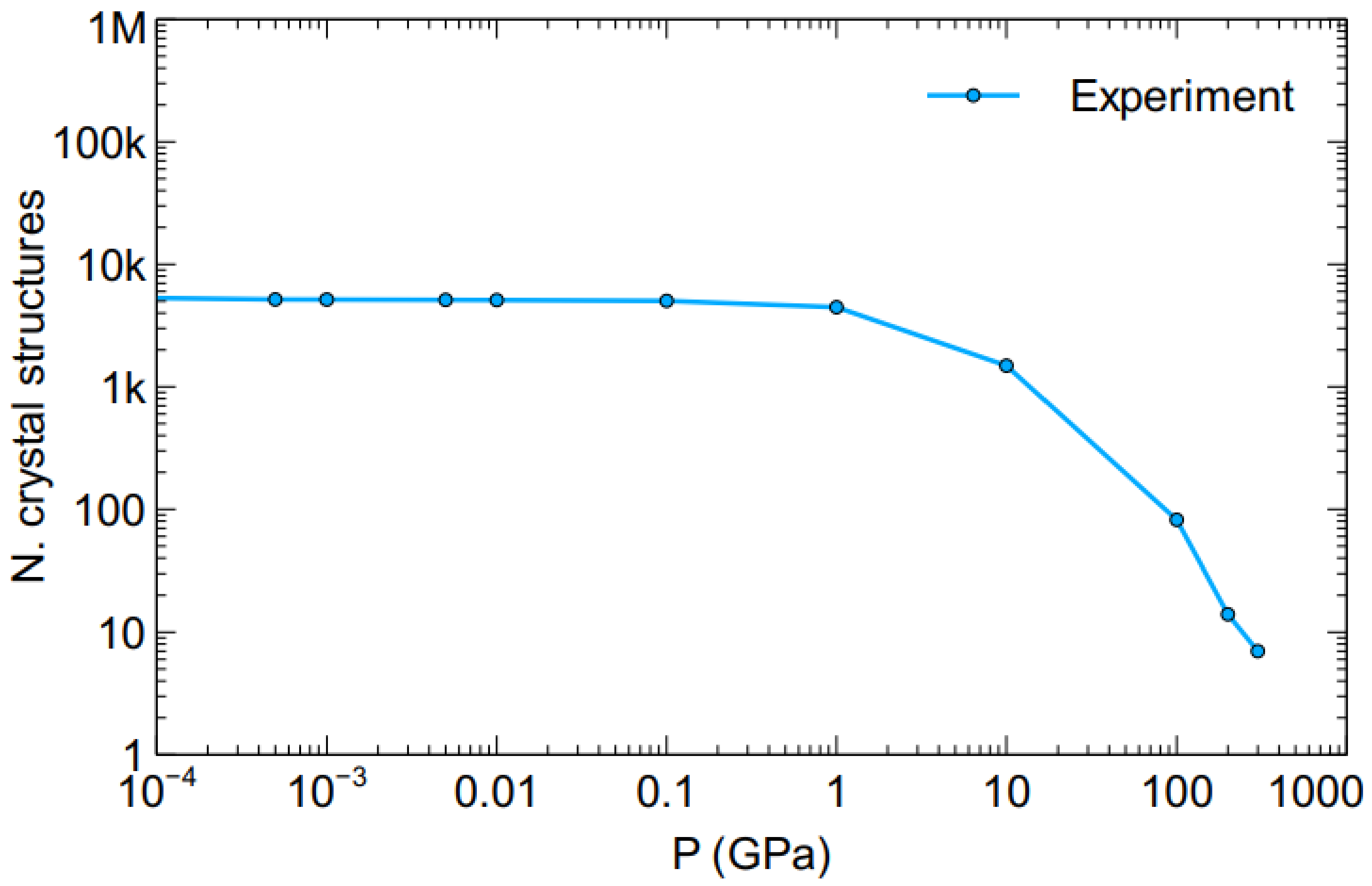
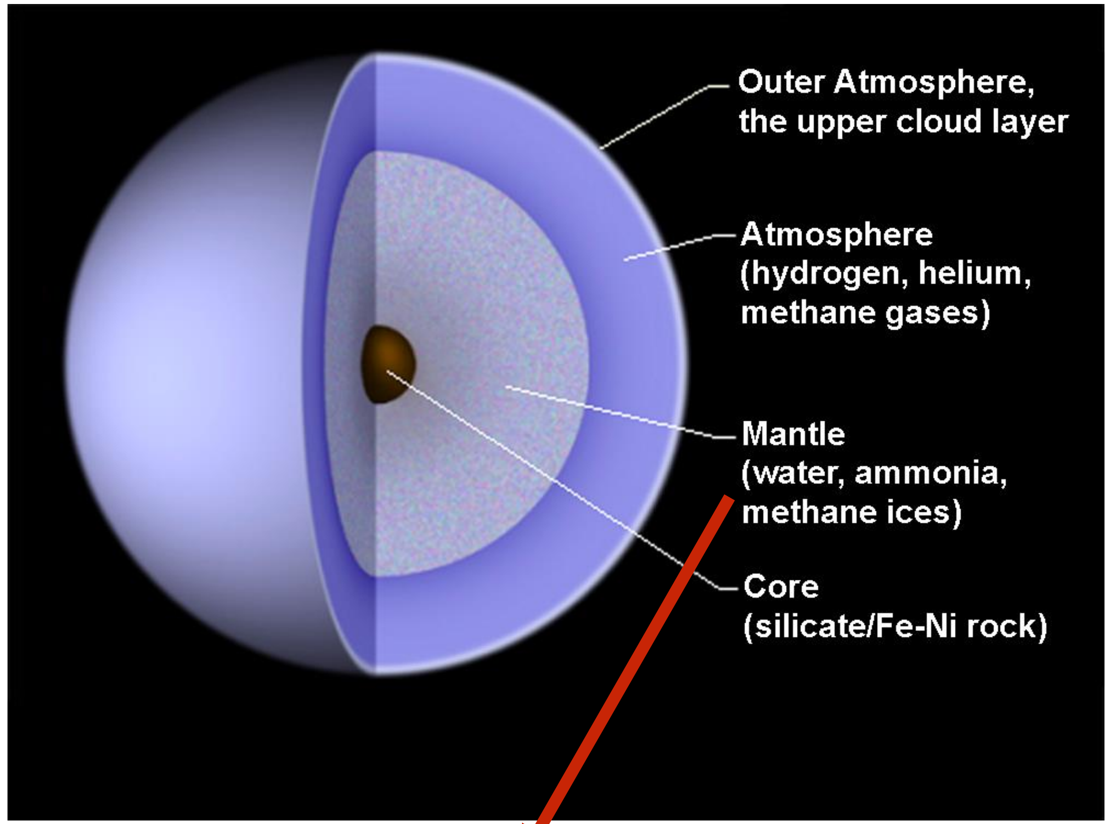


Figure 2.7 *ICSD statistics taken for the number of crystal structures stored up to a given pressure. Note that the value for zero pressure is 182,757 crystal structures and pressures are not always given in the metadata.*

Planetary ice mixtures

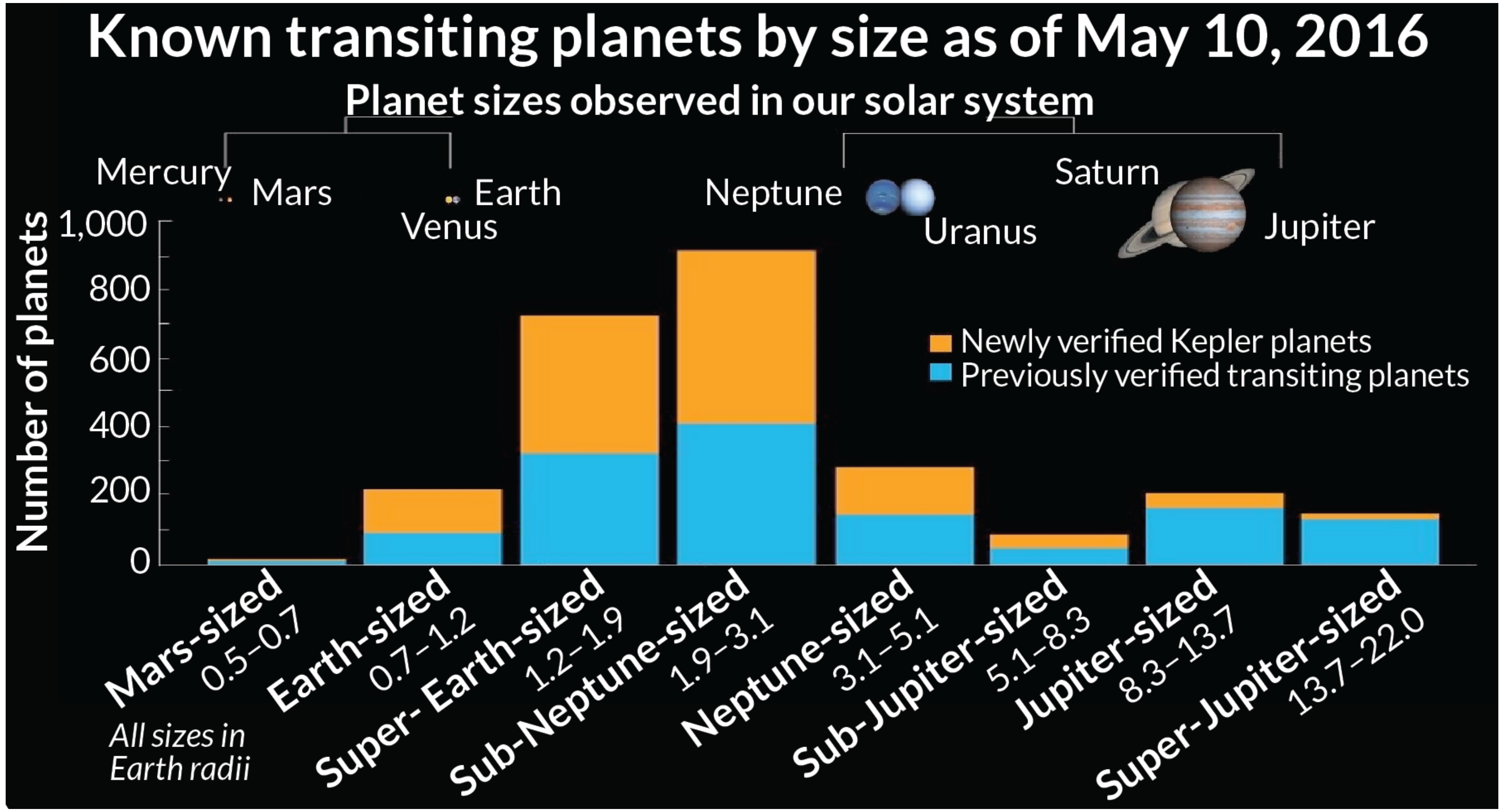
Our picture of icy planets

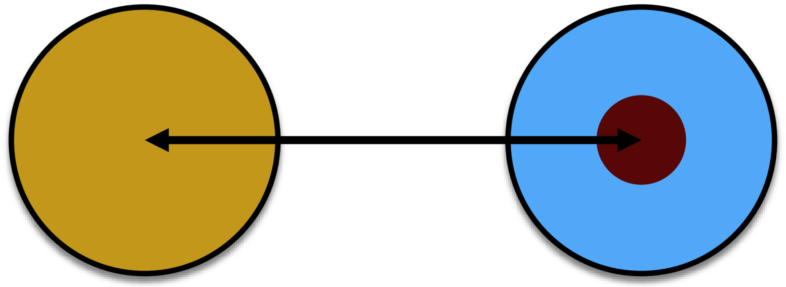


Planetary ices

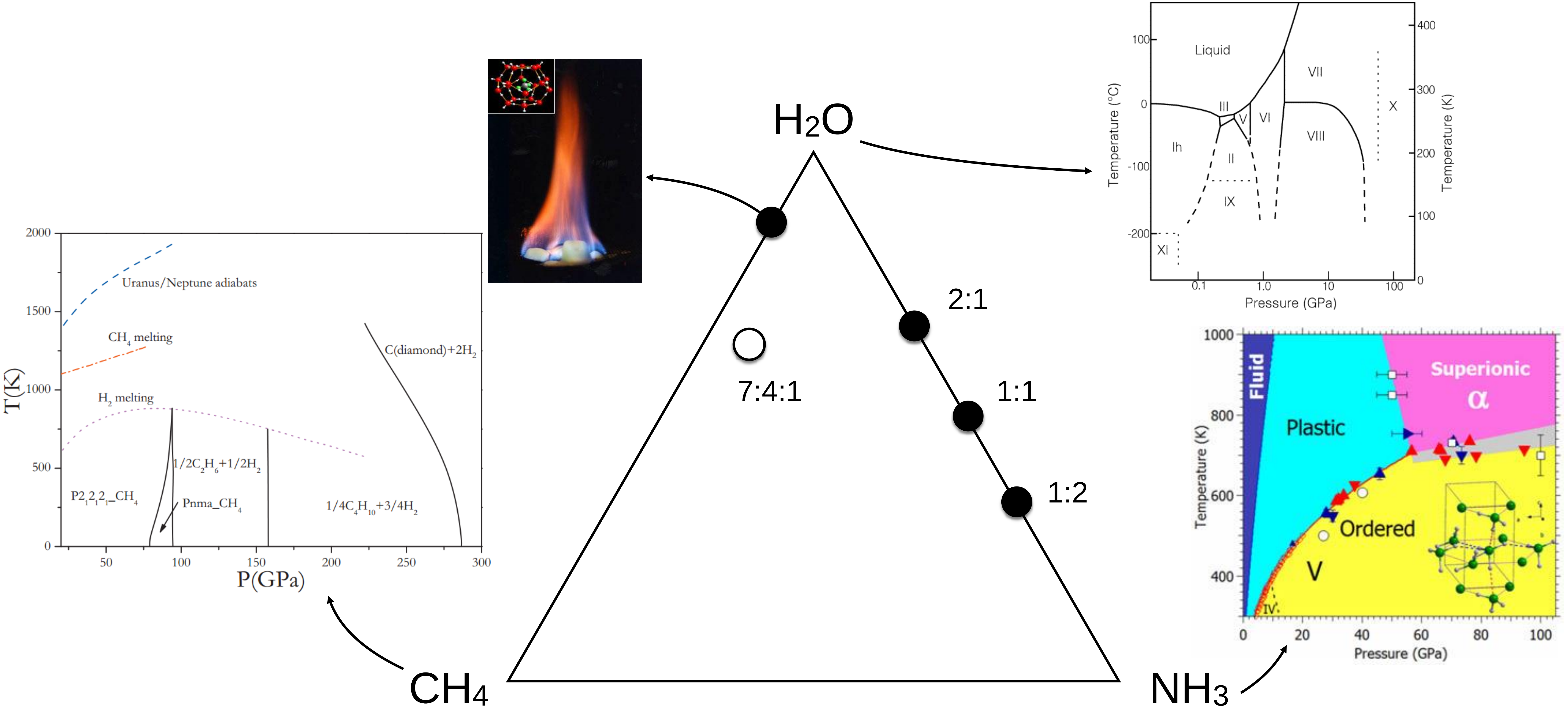
- Mixtures of H_2O, NH_3, CH_4
- Mixing vs de-mixing?
- Stoichiometric compounds?
- Ground state vs high temperature?

Exoplanets:
super-Earths & mini-Neptunes





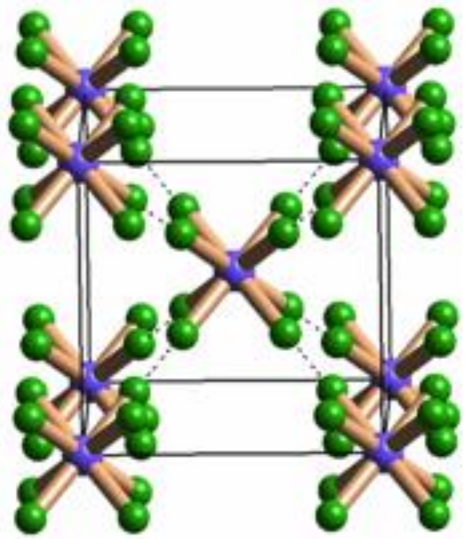
Planetary ice mixtures



Ammonia hydrates

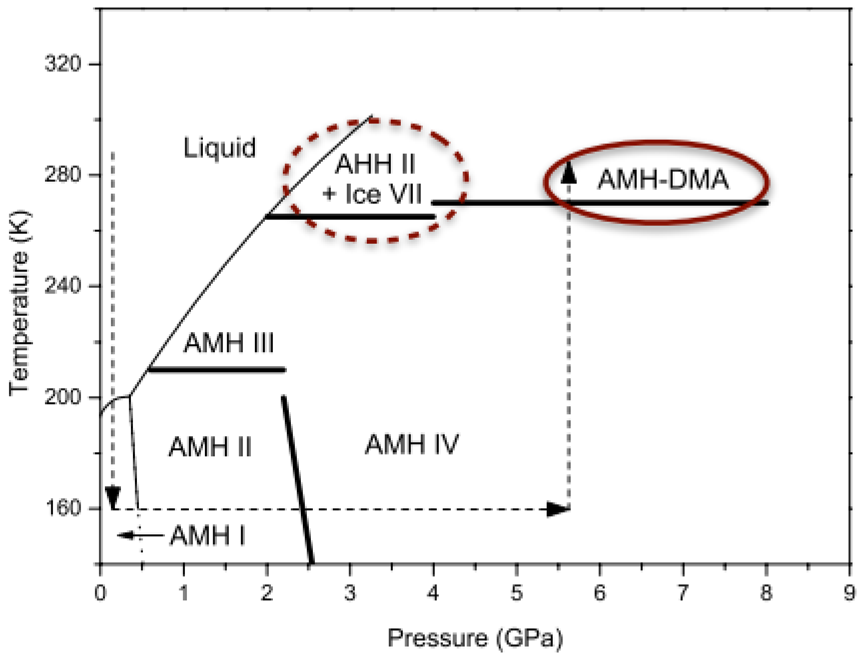
Three known phases:

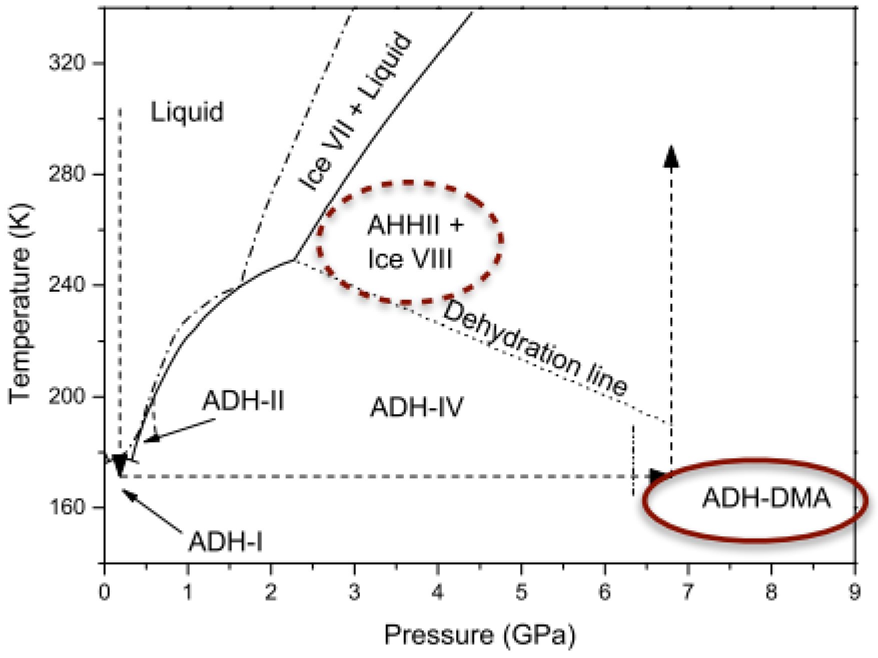
- **AMH**: ammonia **monohydrate**, $(H_2O)(NH_3)$
- **ADH**: ammonia **dihydrate**, $(H_2O)_2(NH_3)$
- **AHH**: ammonia **hemihydrate**, $(H_2O)(NH_3)_2$

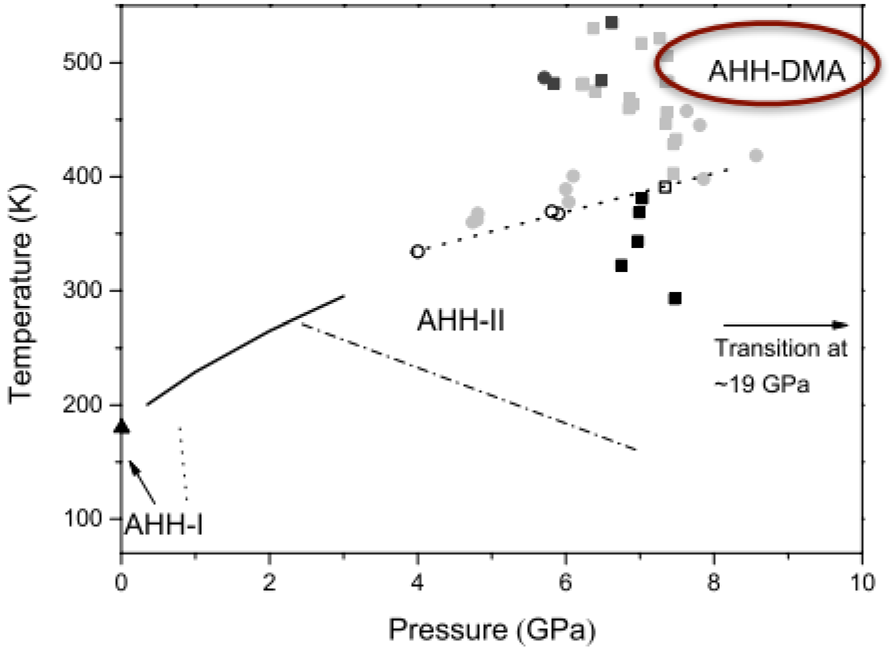


Experimental phase diagrams:

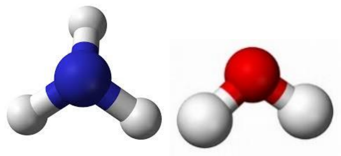
C.W. Wilson et al., *J. Chem. Phys.* 2015.
J.S. Loveday, R.J. Nelmes, *Phys. Rev. Lett.* 1999.



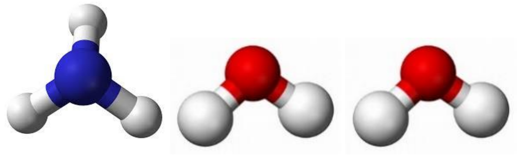




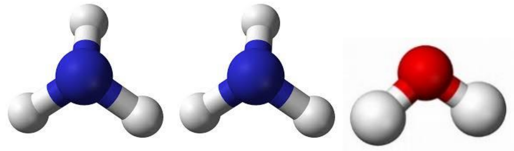
AMH



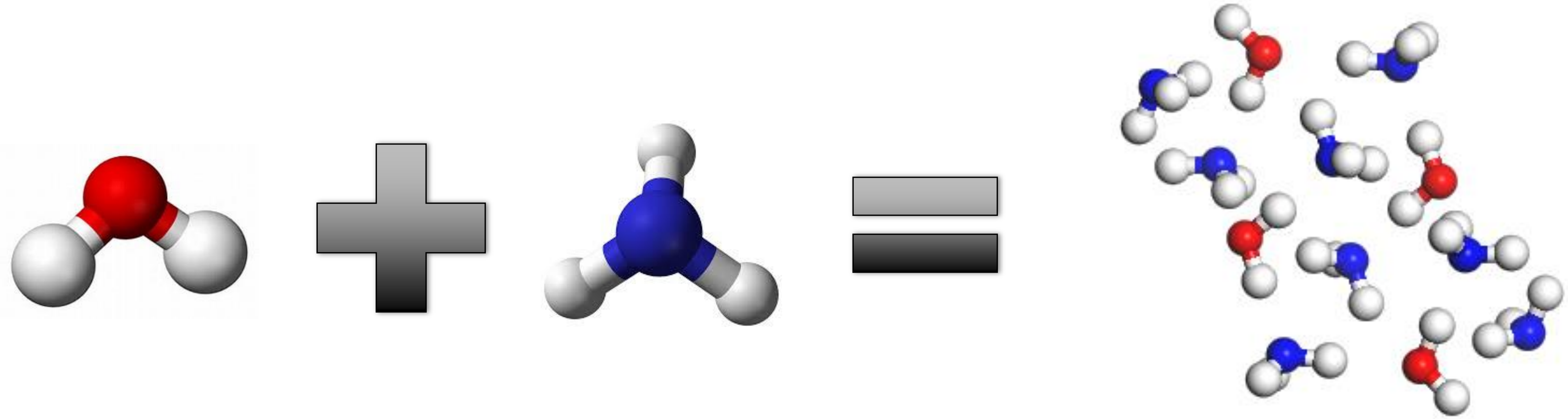
ADH



AHH

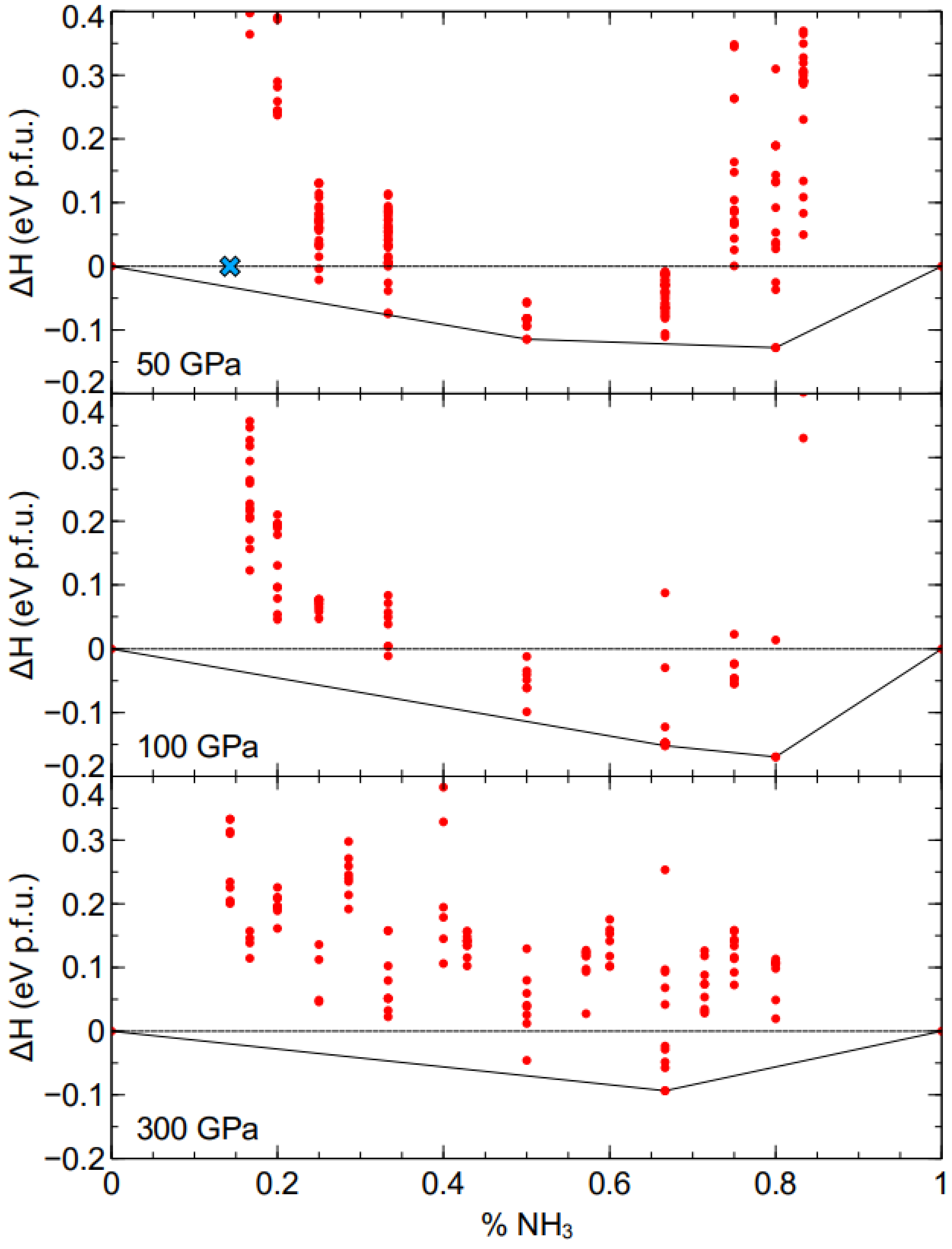


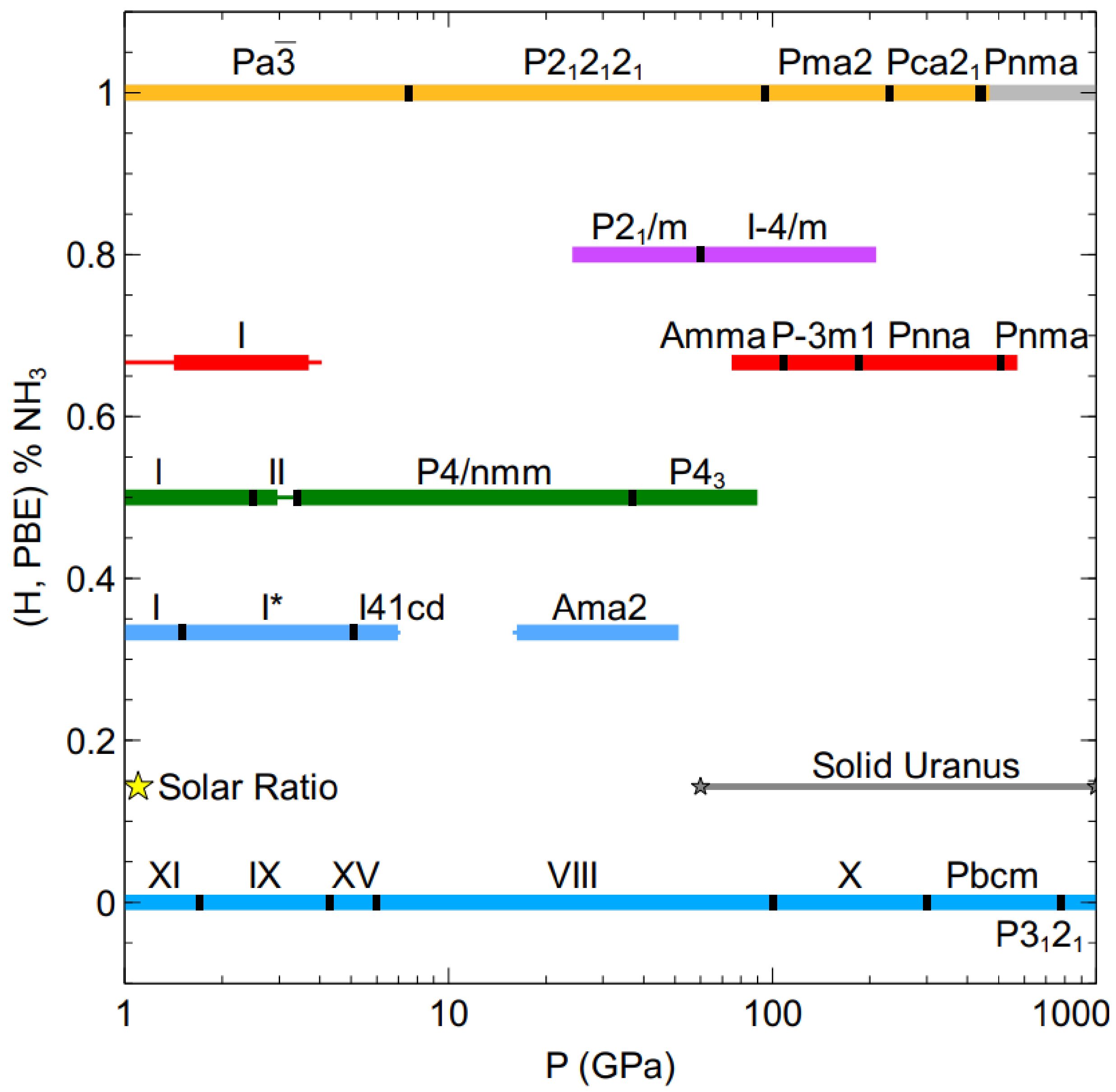
Ammonia water



High pressure?

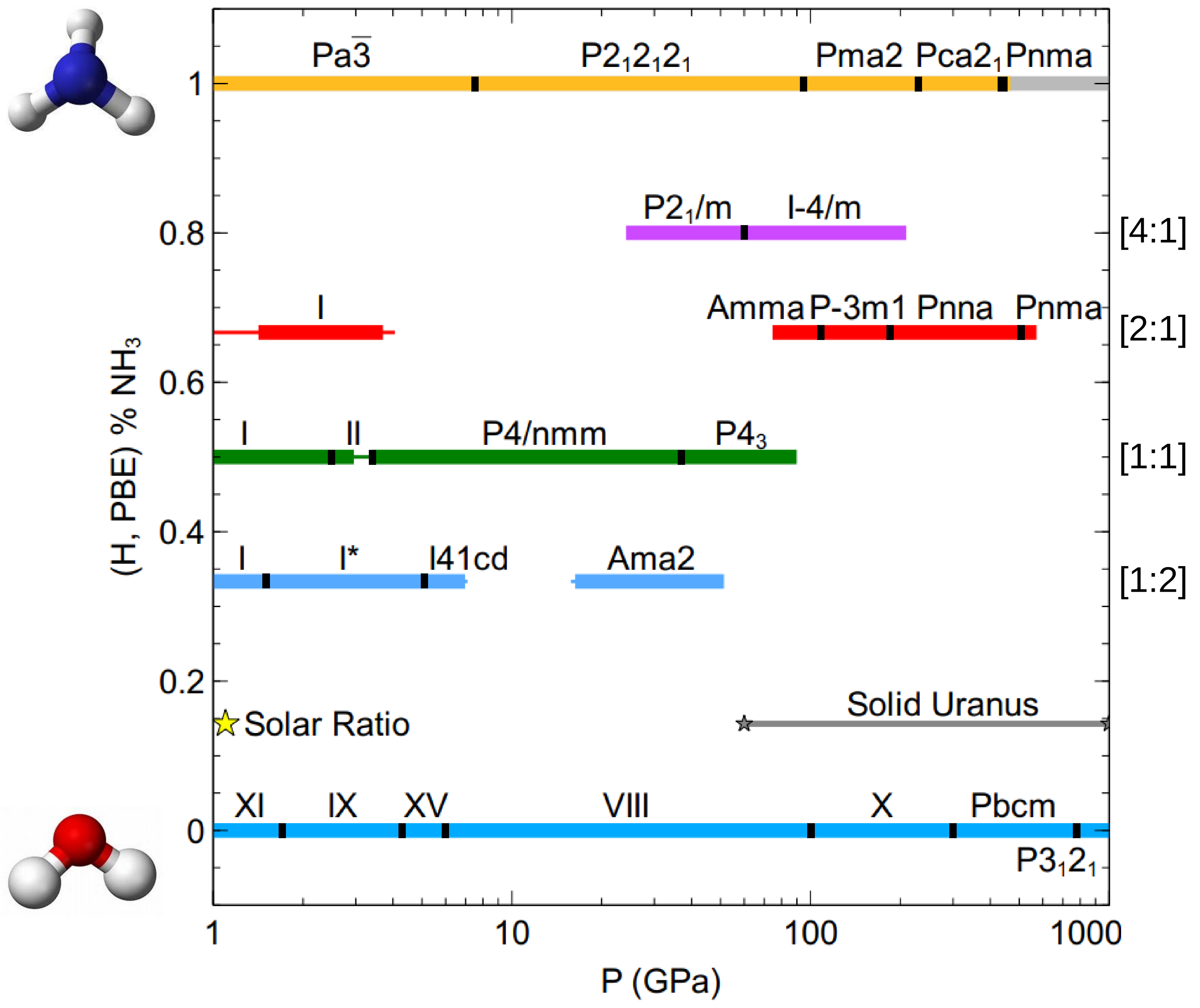
Binary Searches





$$\Delta H((H_2O)_m + (NH_3)_n) = \frac{1}{m+n}[((H_2O)_m + (NH_3)_n) - m \cdot (H_2O) - n \cdot (NH_3)]$$

$[NH_3:H_2O]$ phase diagram



- AMH, ADH: decompose below 1 Mbar
- AHH, AQH: stable up to 5 Mbar
- Stabilization by water ionization
- High pressure favors mixtures with **$NH_3:H_2O \geq 2$**

* PBE ground state results

V. Naden Robinson *et al.*, J. Chem. Phys. 149, 234501 (2018).

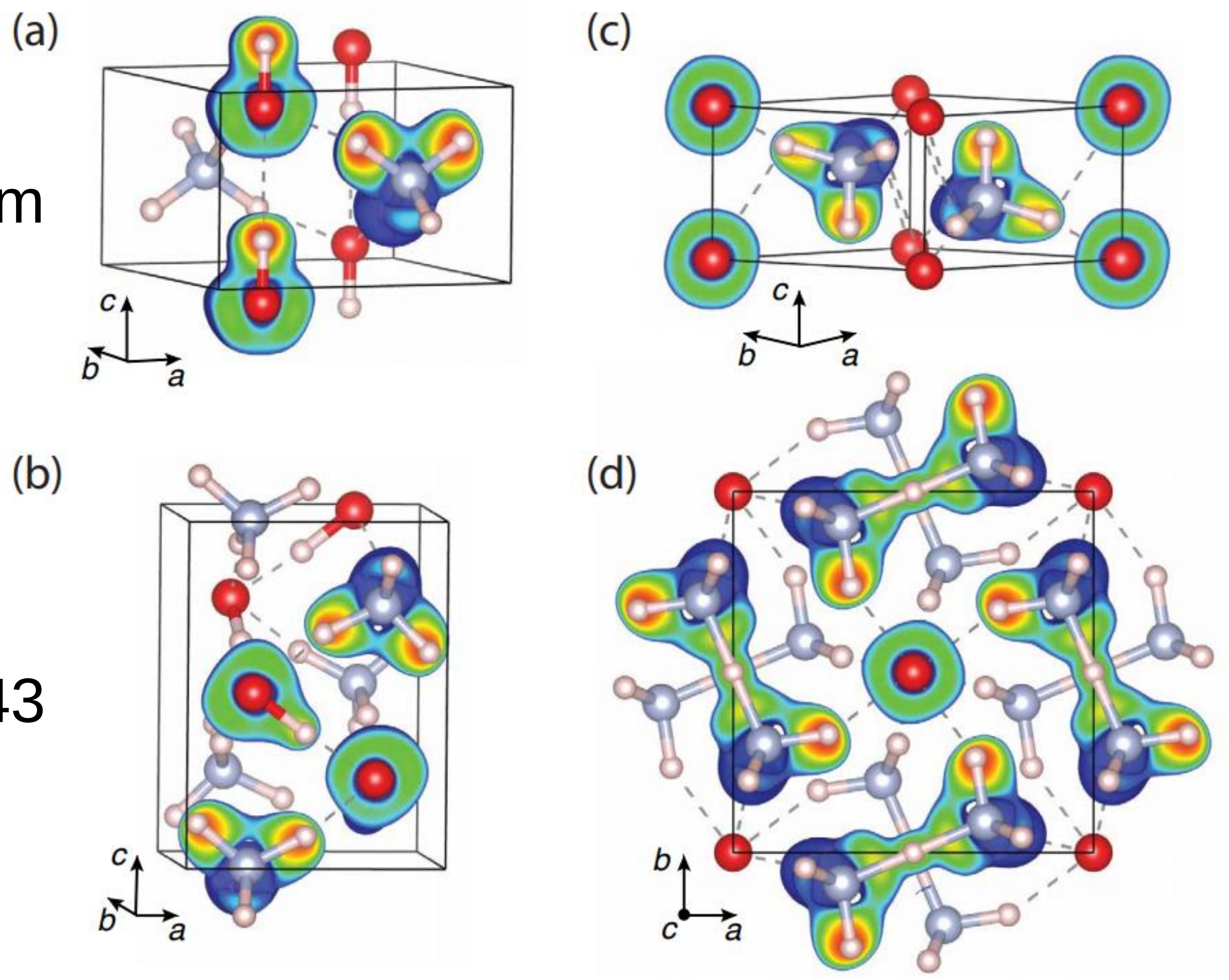
Ionization of Water

AMH [1:1] P4/nmm

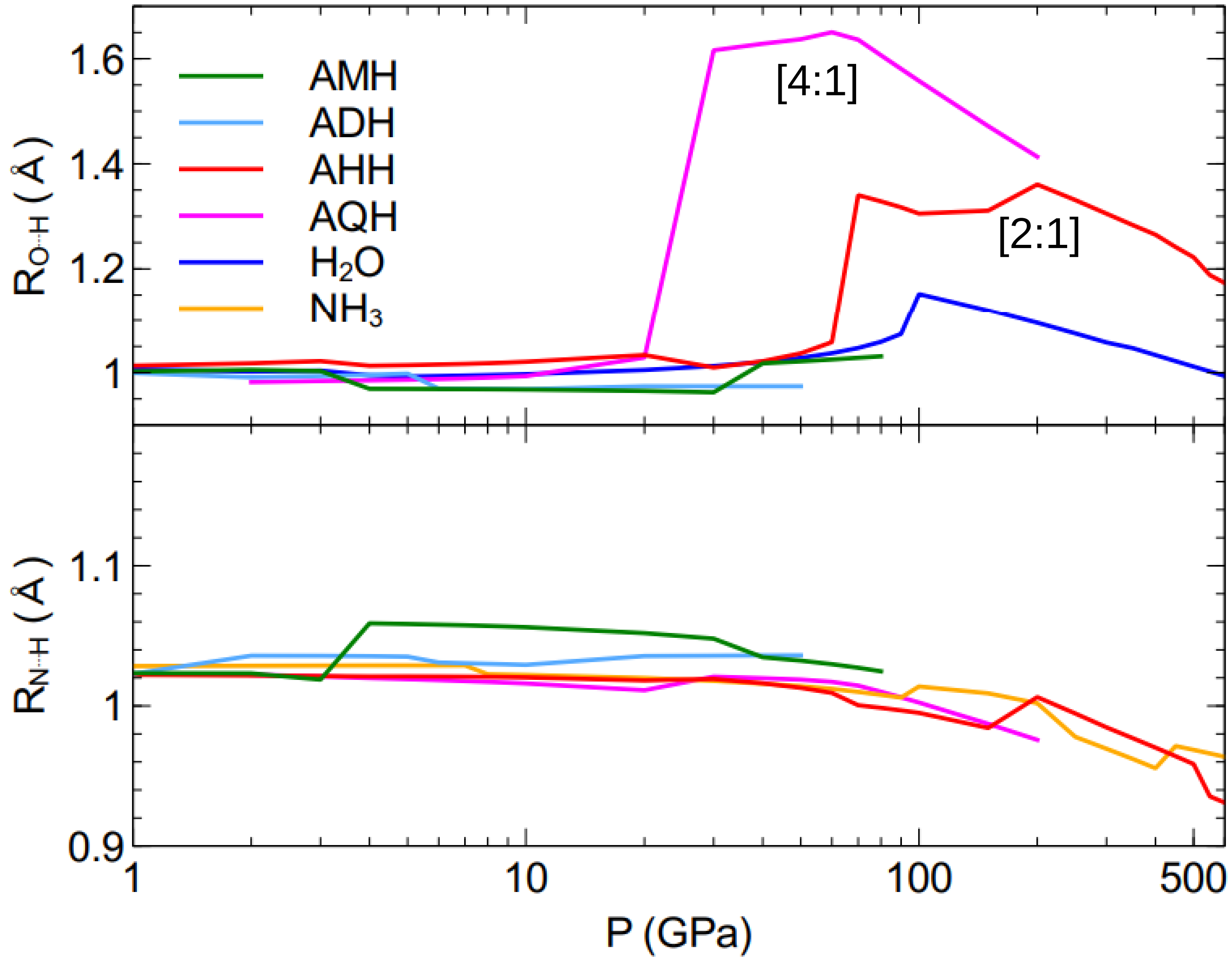
AHH [2:1] I4/m

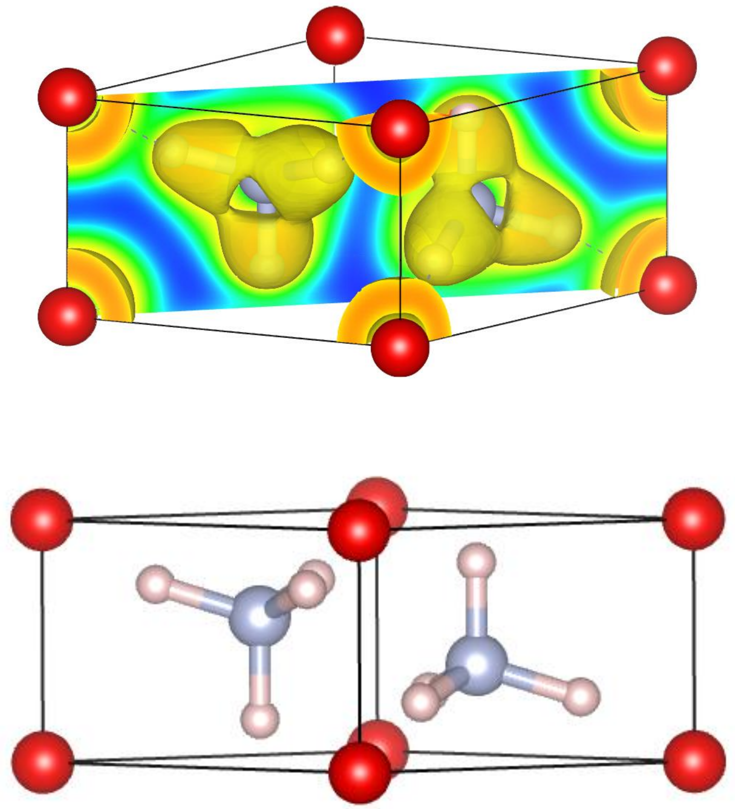
AMH [1:1] P43

AQH [4:1] I4/m



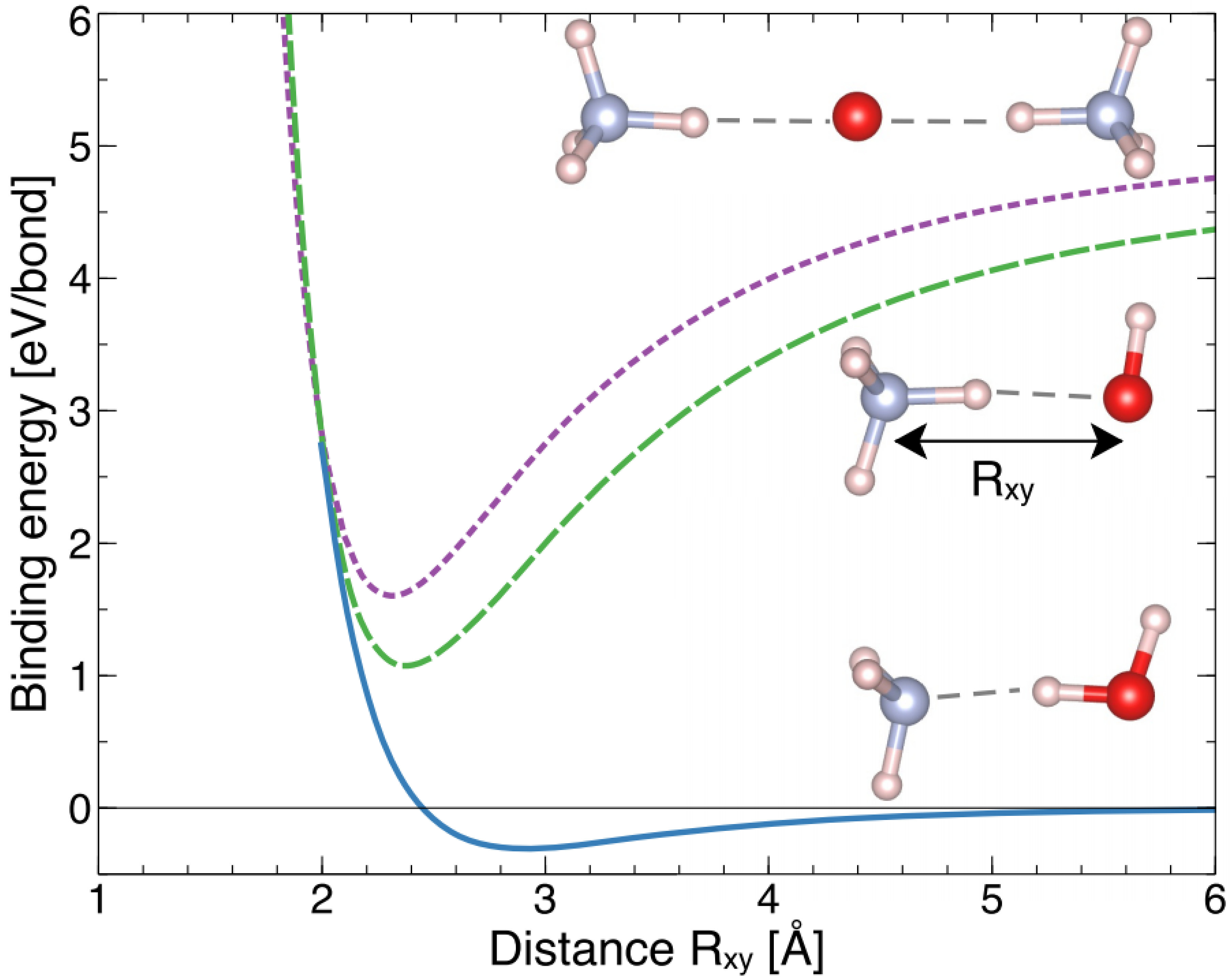
Proton Transfer



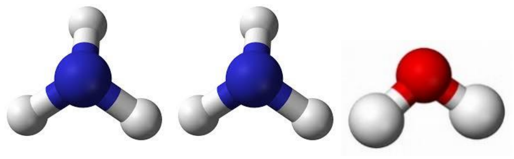


V. Naden Robinson *et al.*, J. Chem. Phys. 149, 234501 (2018).

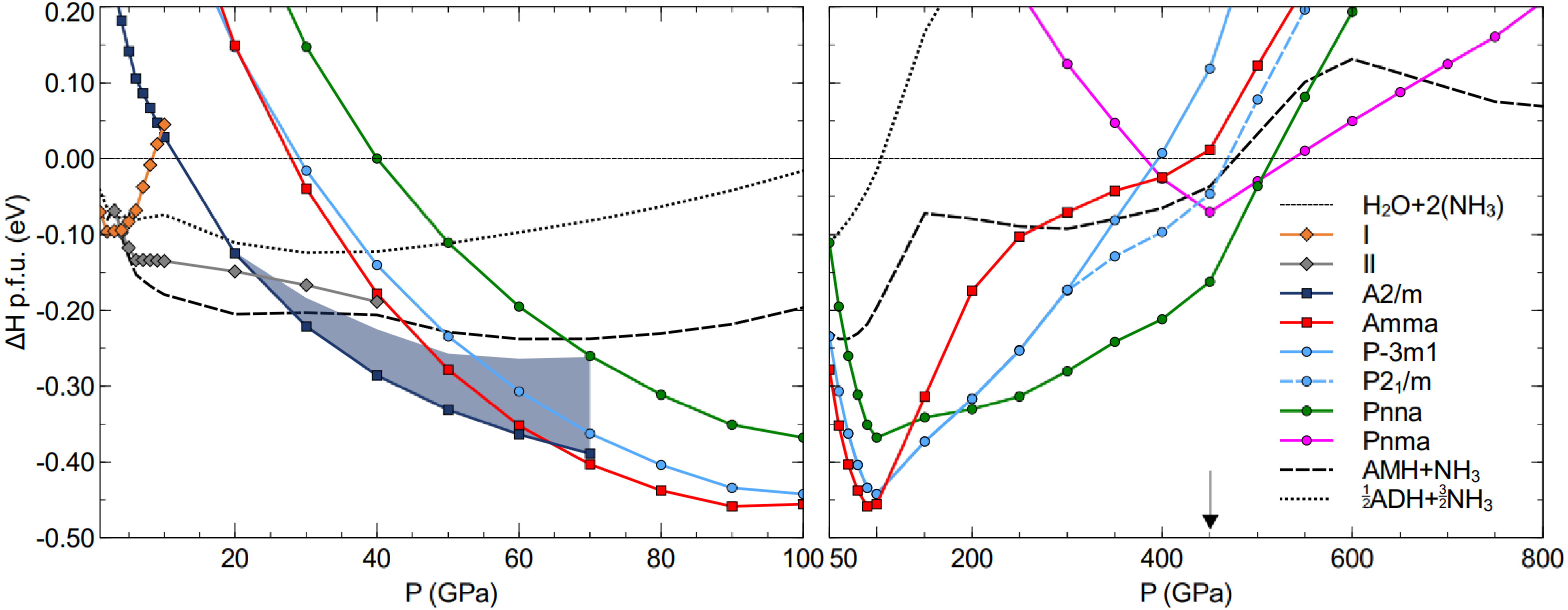
Ionization Energy Cost

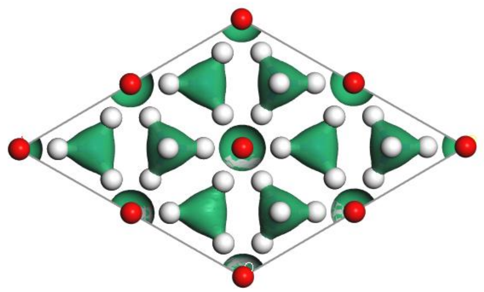


AHH [2:1] Higher-pressure phases



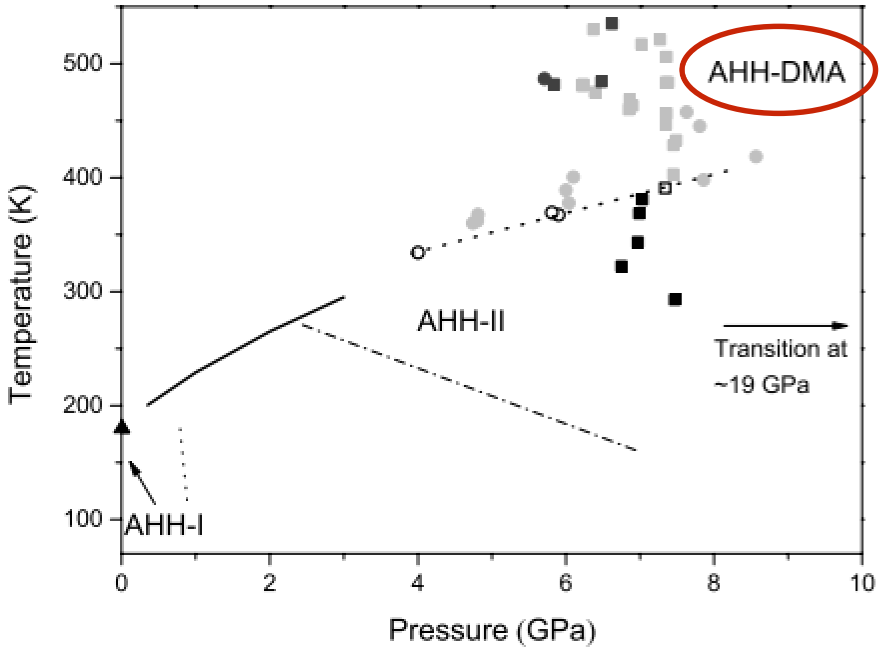
Stability to 550 GPa

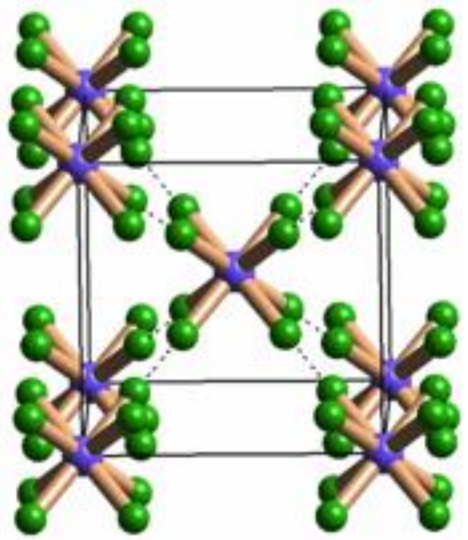


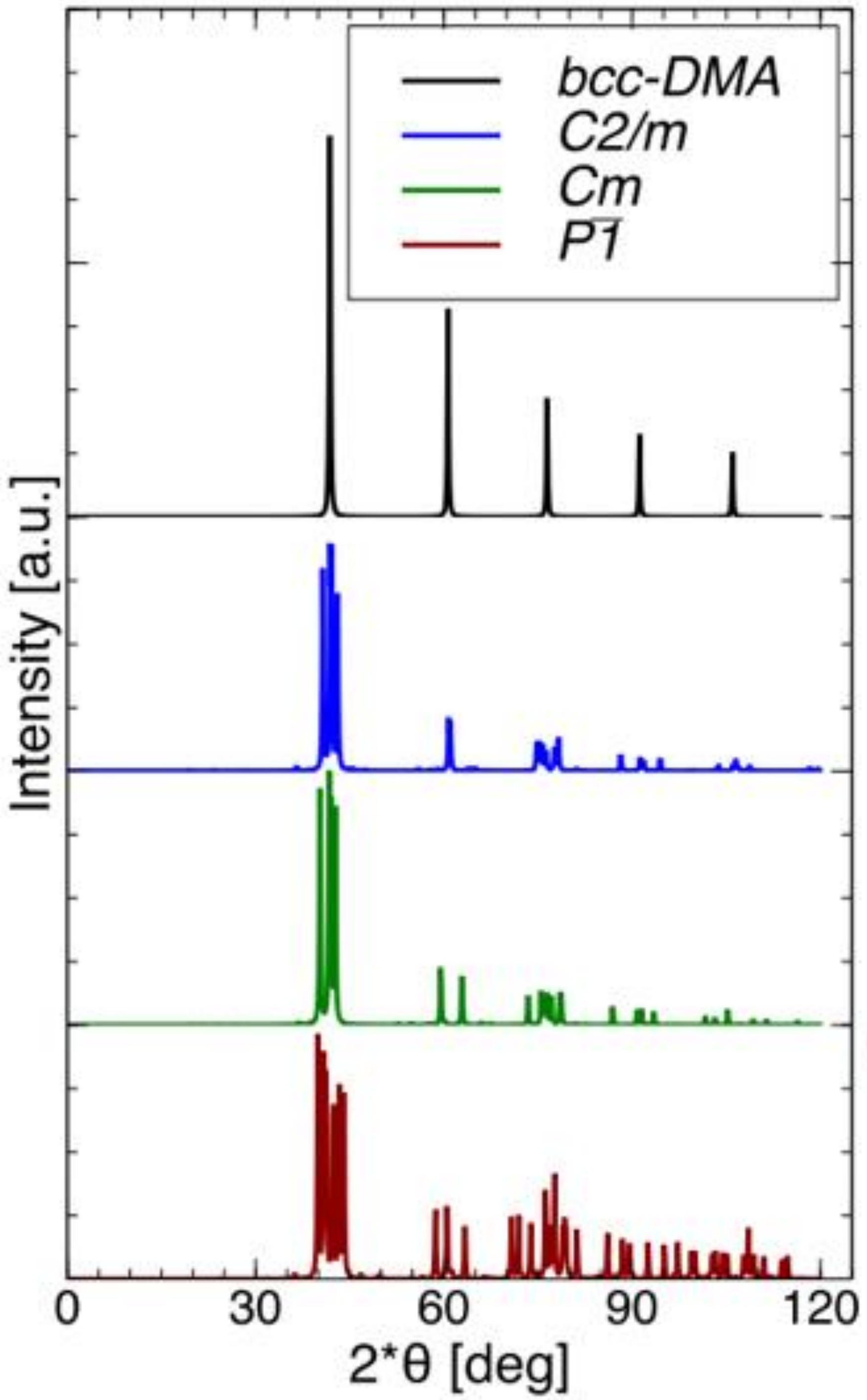


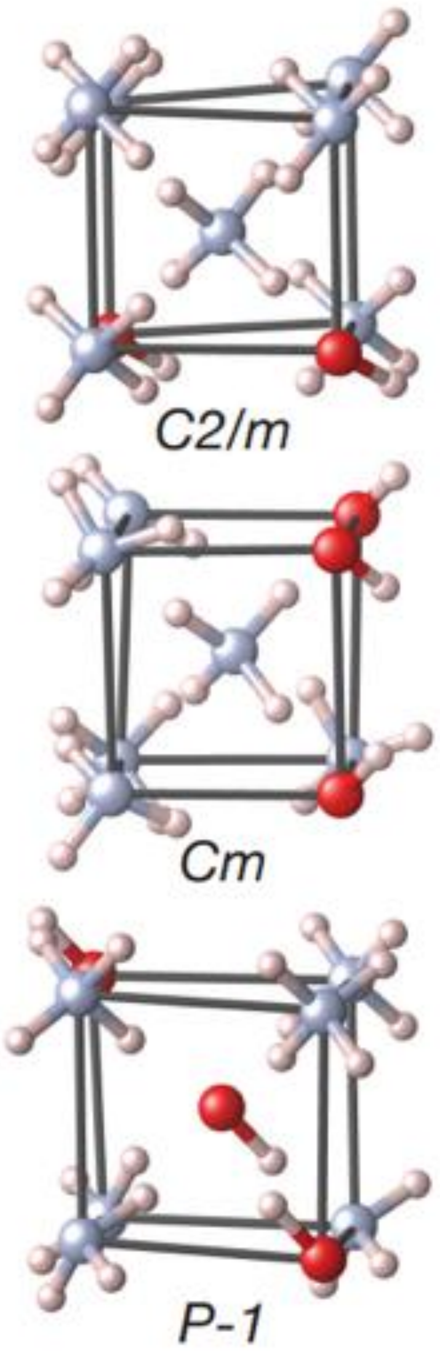
V. Naden Robinson *et al.*, *Proc. Natl. Acad. Sci.*, 2017.

DMA approximants

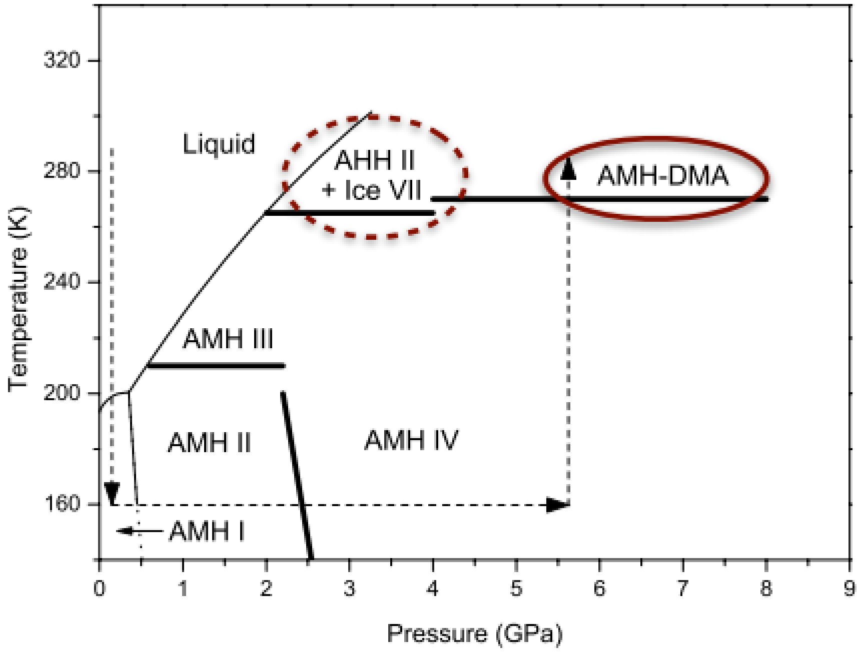


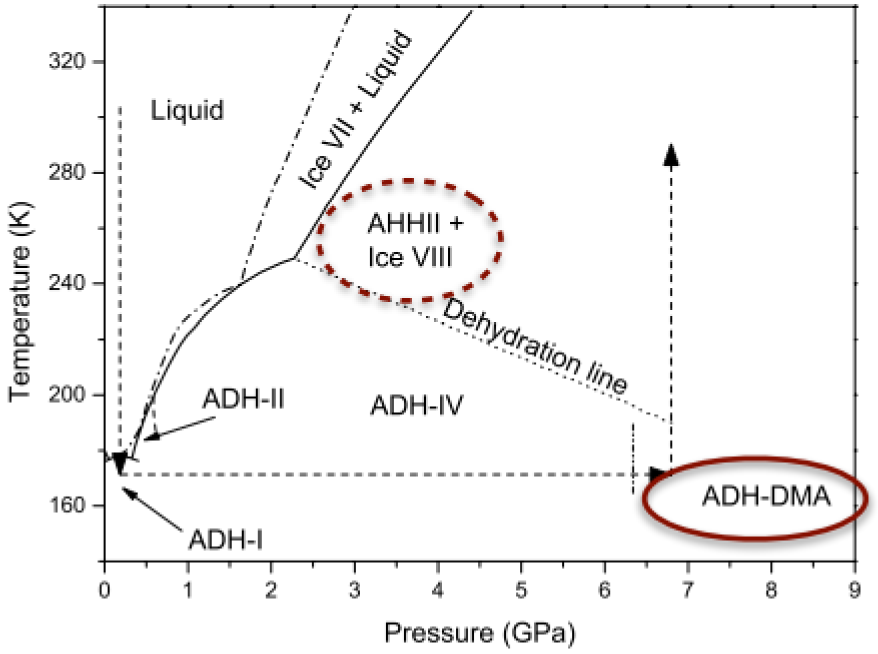


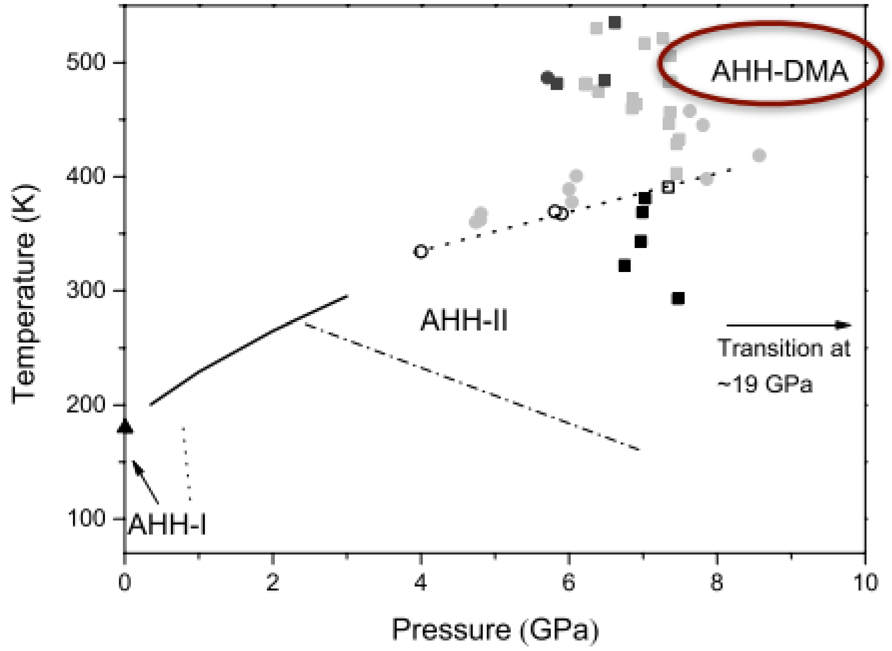


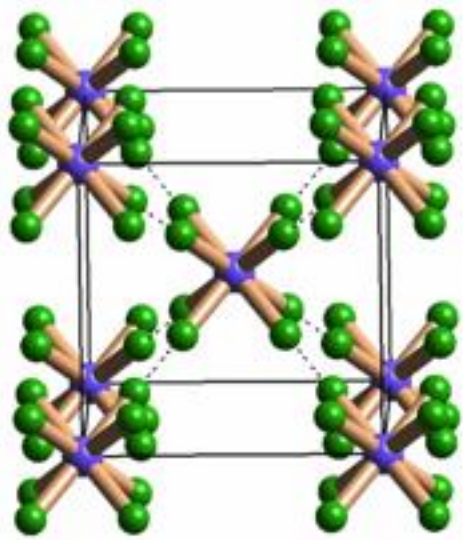


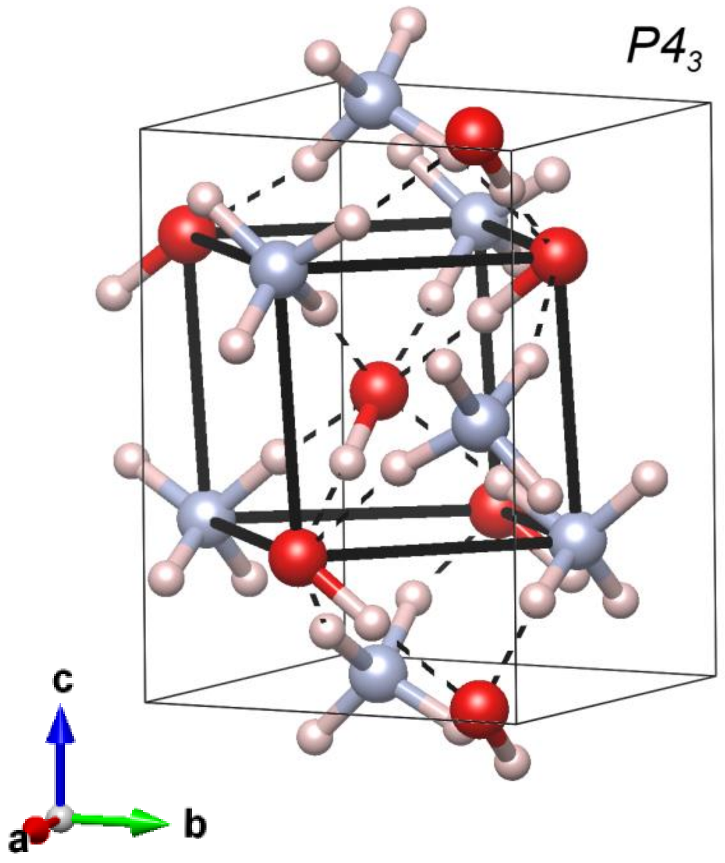
In all hydrates

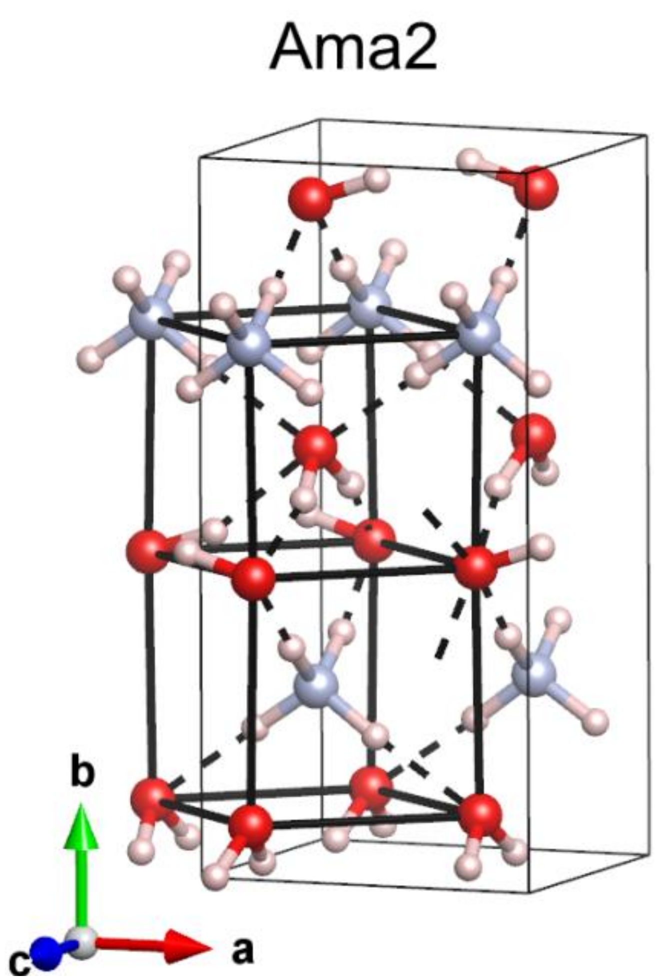


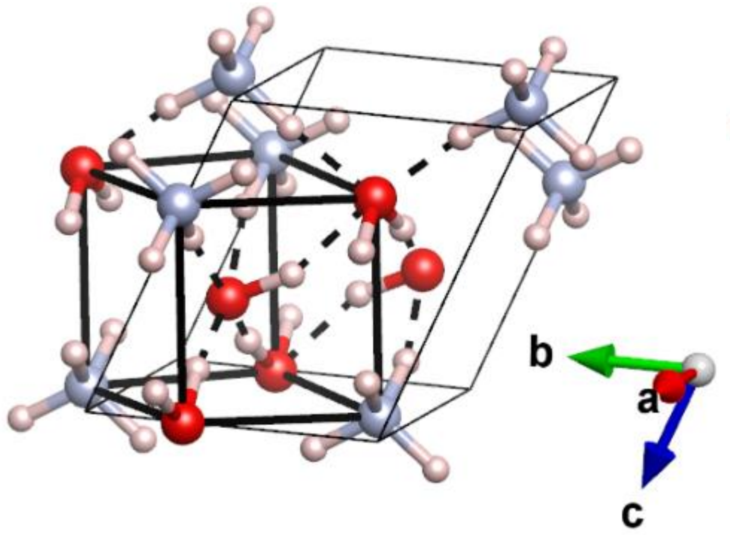


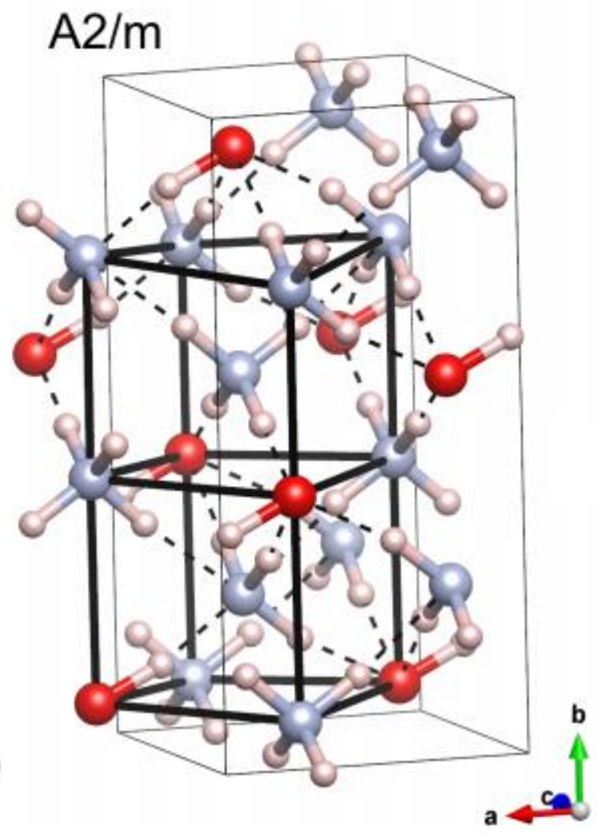








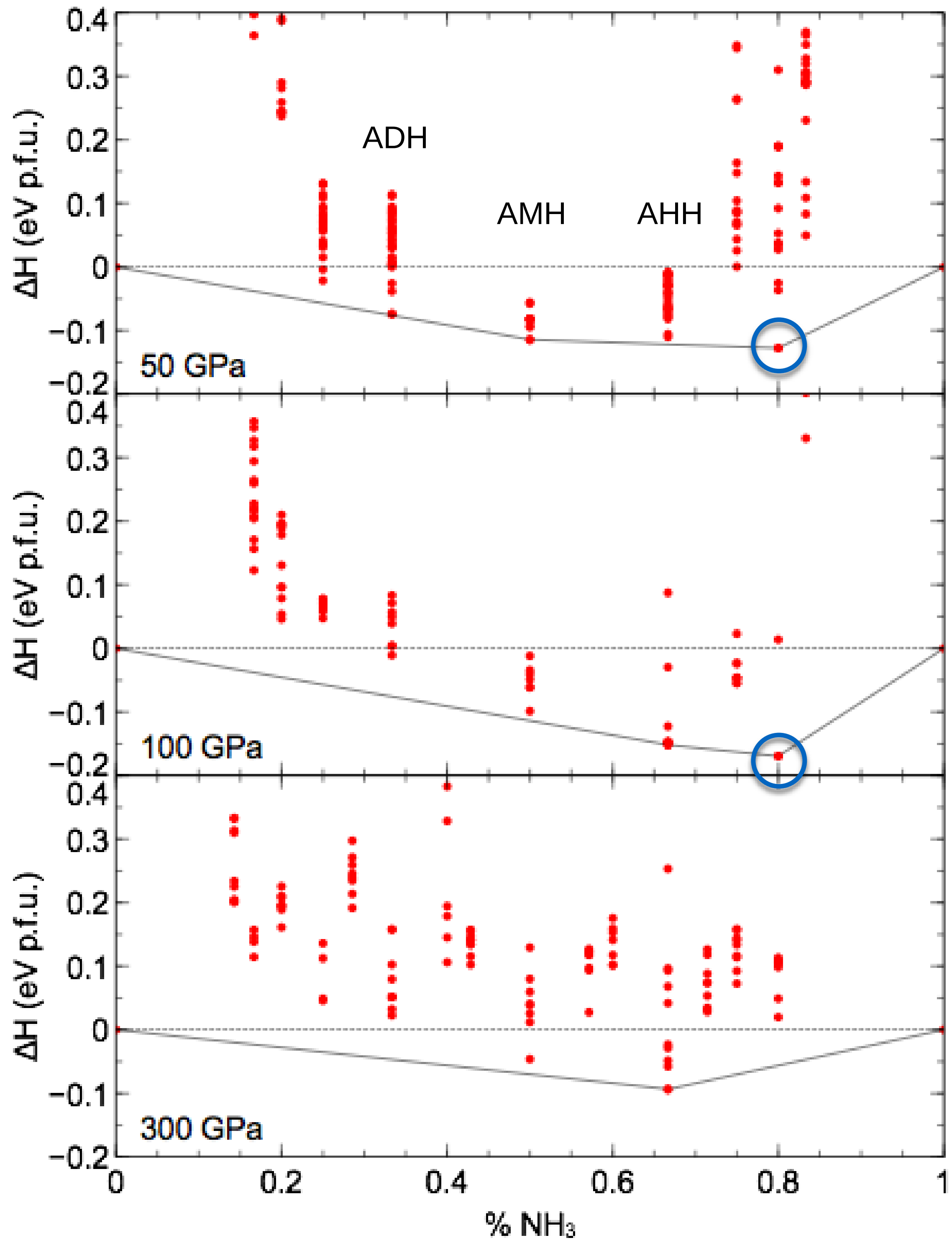




V. Naden Robinson *et al., J. Chem. Phys. 149, 234501 (2018).*

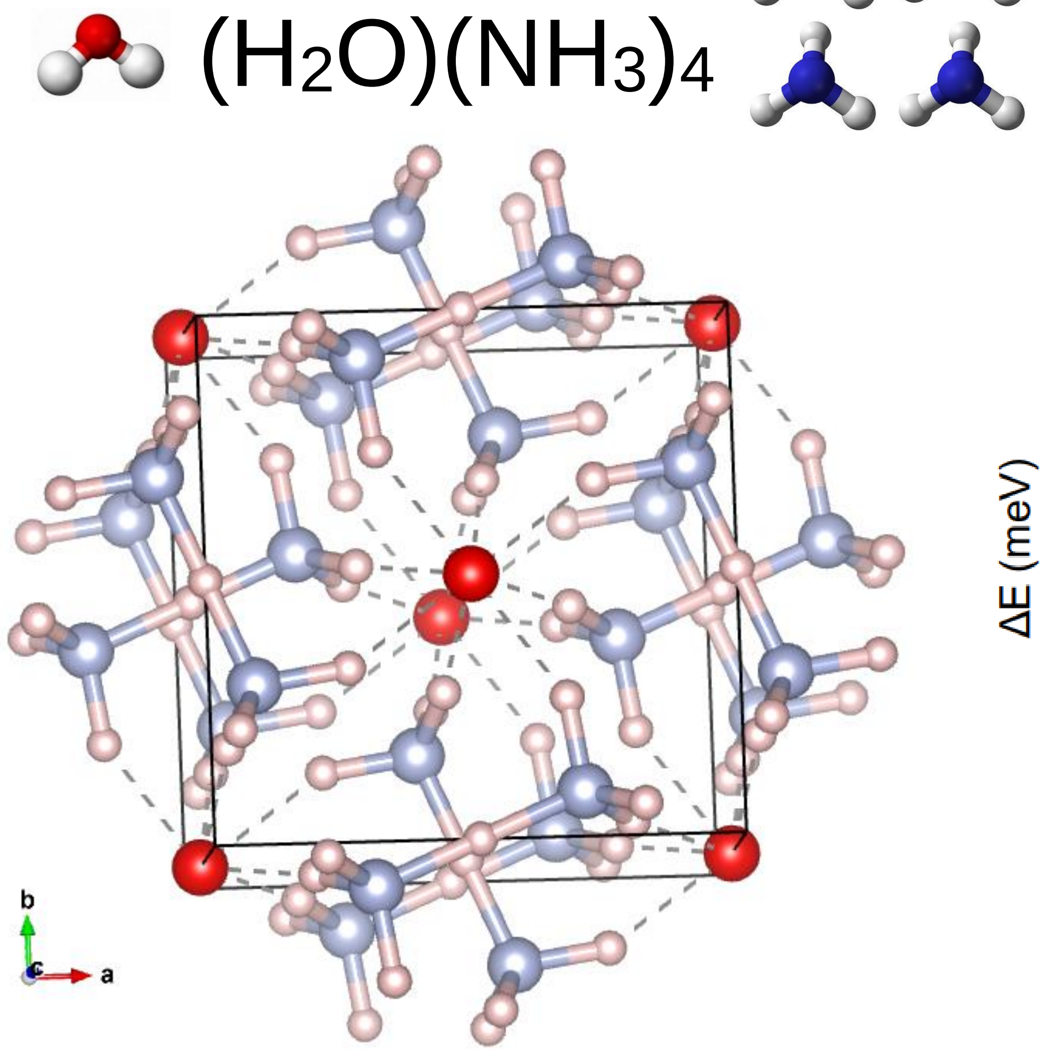
More ammonia-rich phases?

Ammonia Quarterhydrate

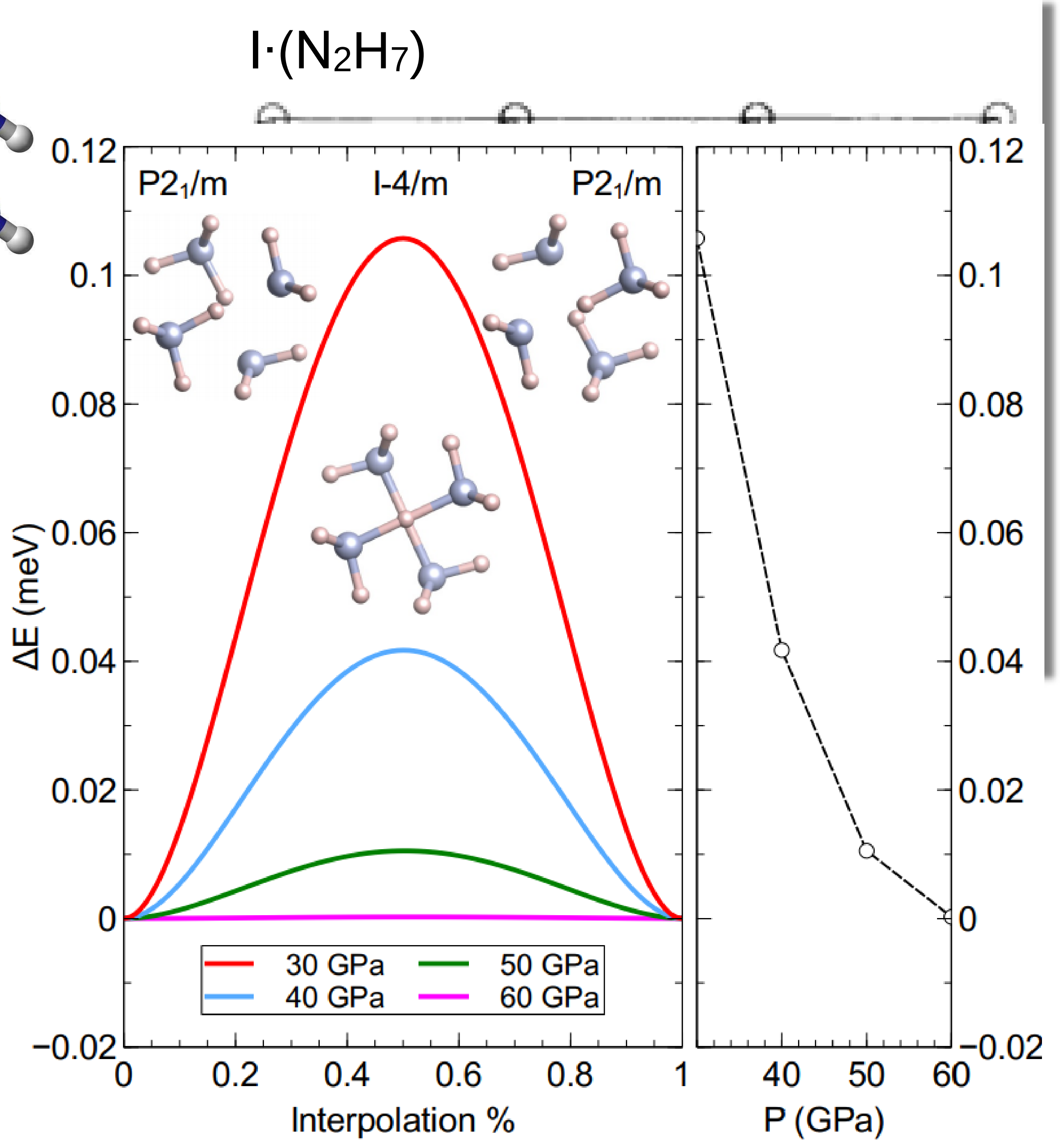


AQH

$(H_2O)(NH_3)_4$

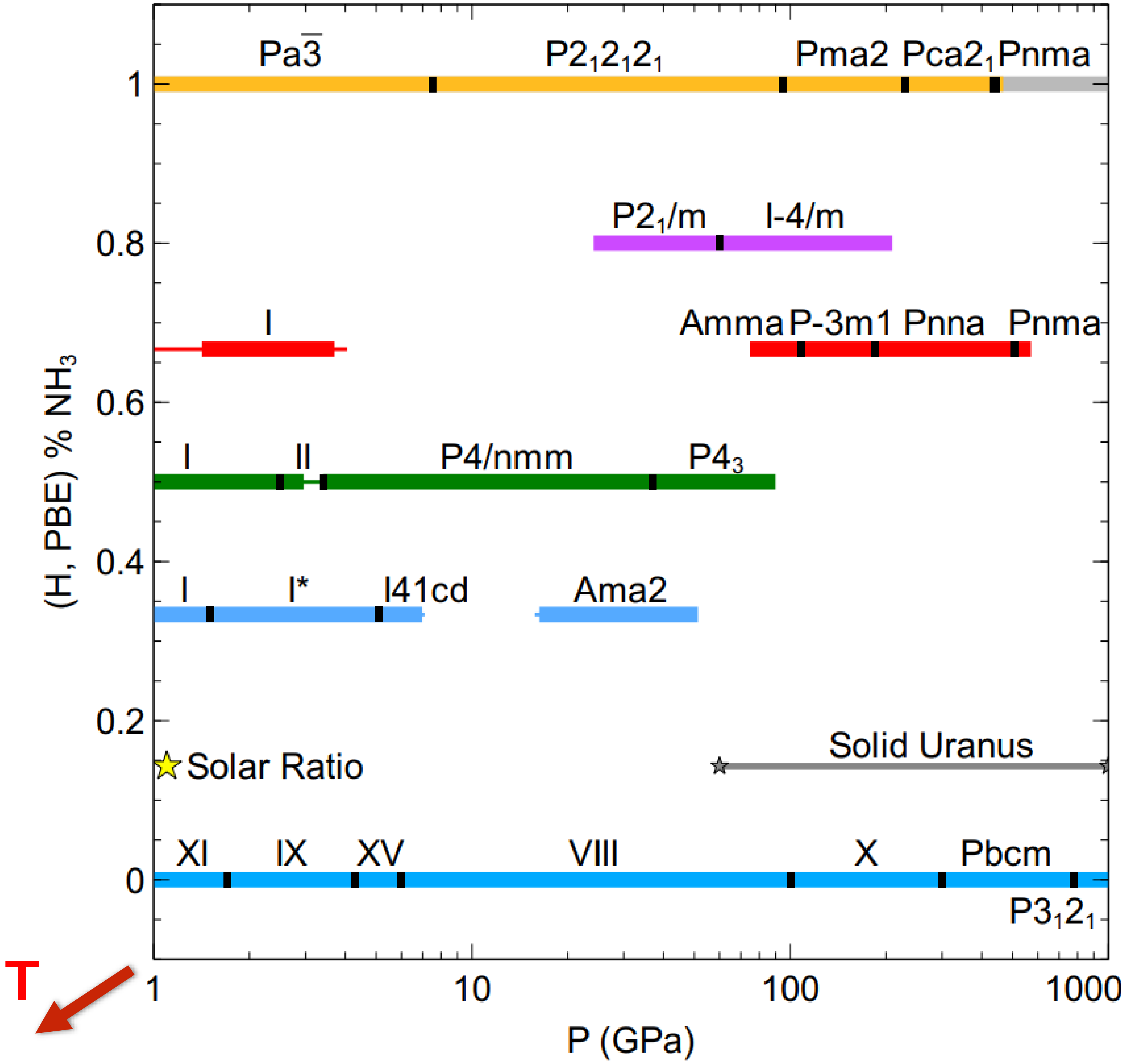


$O^{2-}(N_2H_7^+)_2$



Berthold et al, *Angew. Chem. Int. Ed.*, 1988.

Full NH_3-H_2O phase diagram



- AMH, ADH: decompose below 1 Mbar
- AHH, AQH: stable up to 5 Mbar

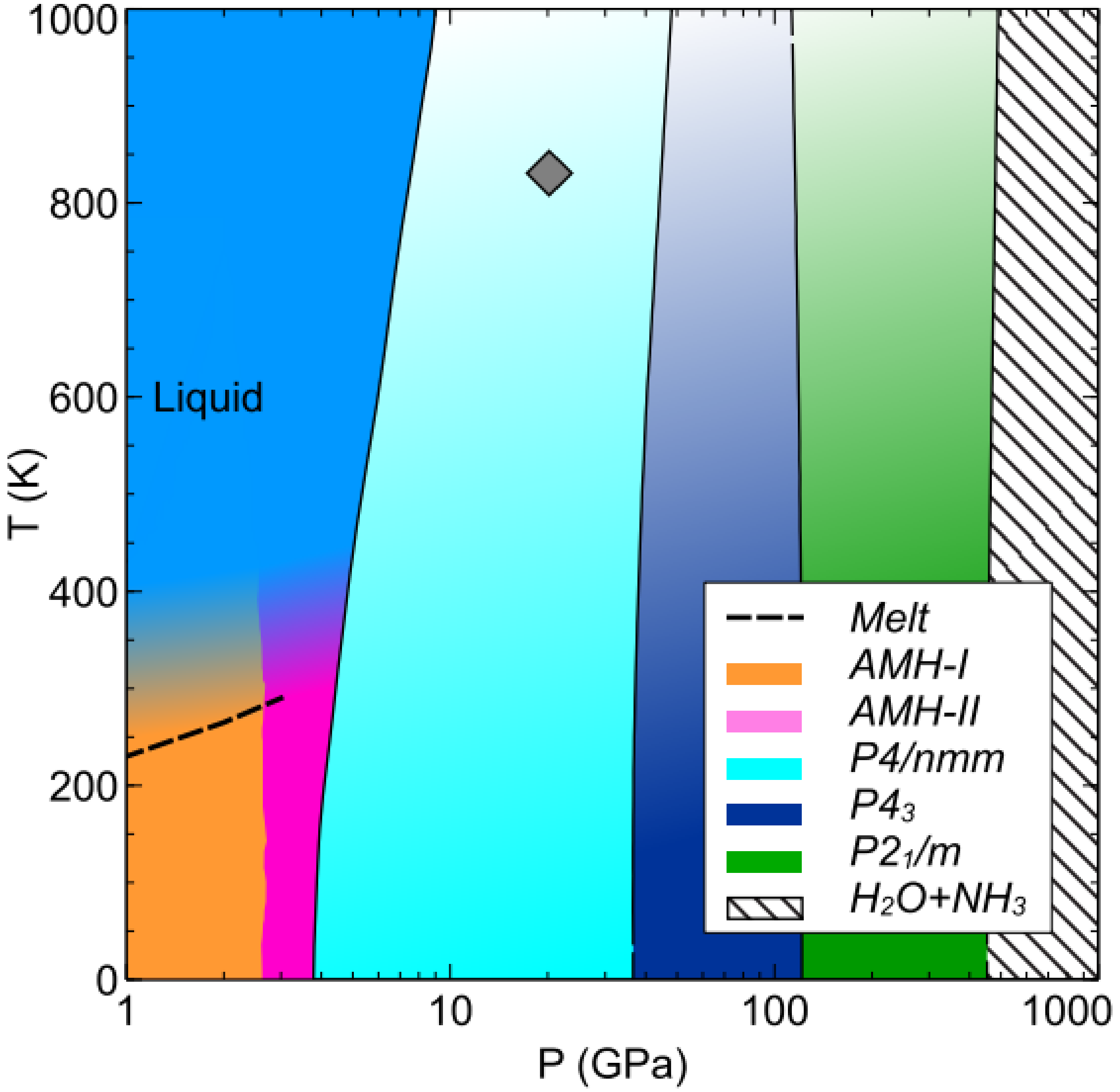
- Stabilization by water ionization

- High pressure favors mixtures with
  NH_3:H_2O ≥ 2

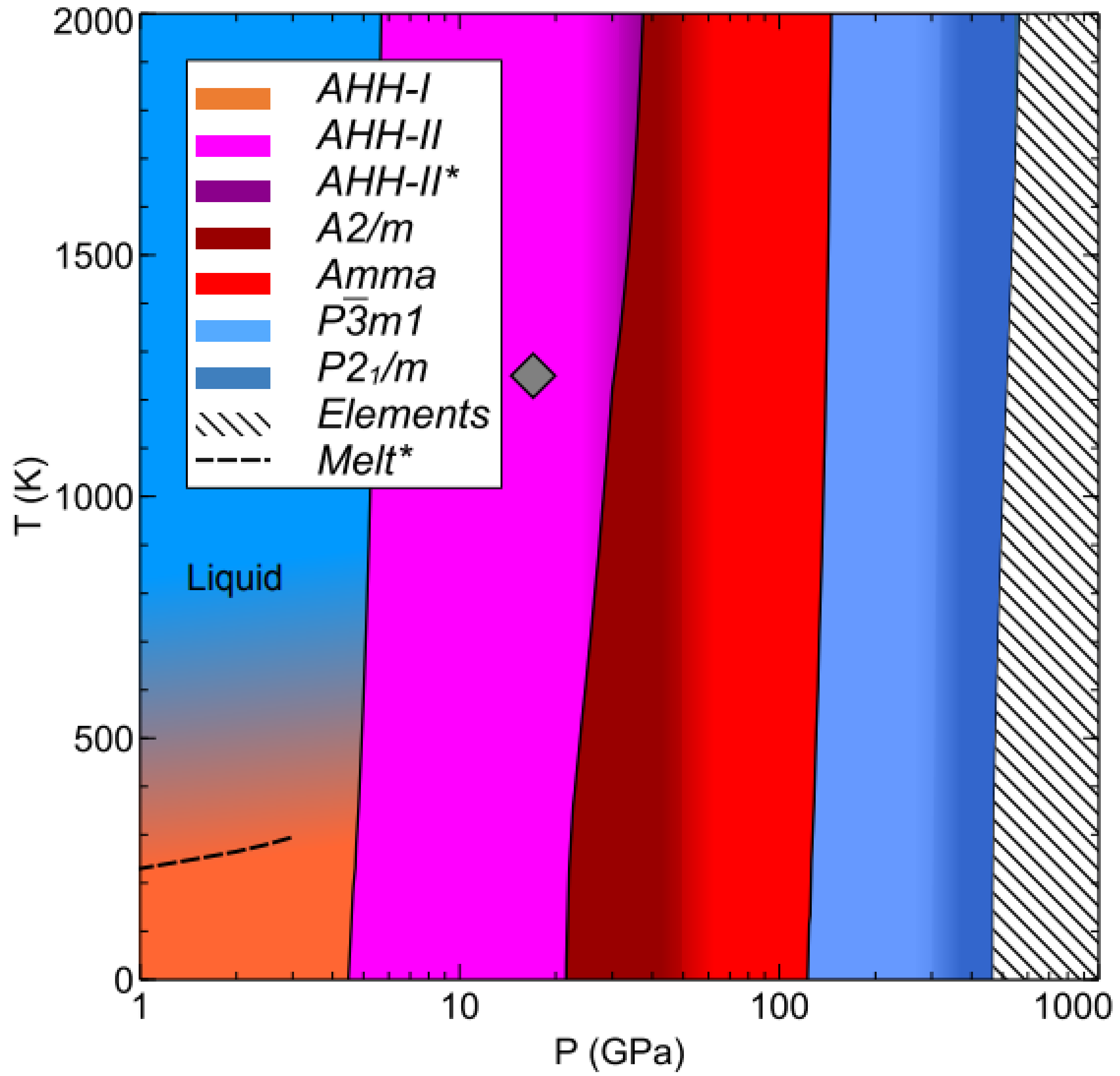
* PBE ground state results

V. Naden Robinson *et al.*, submitted.

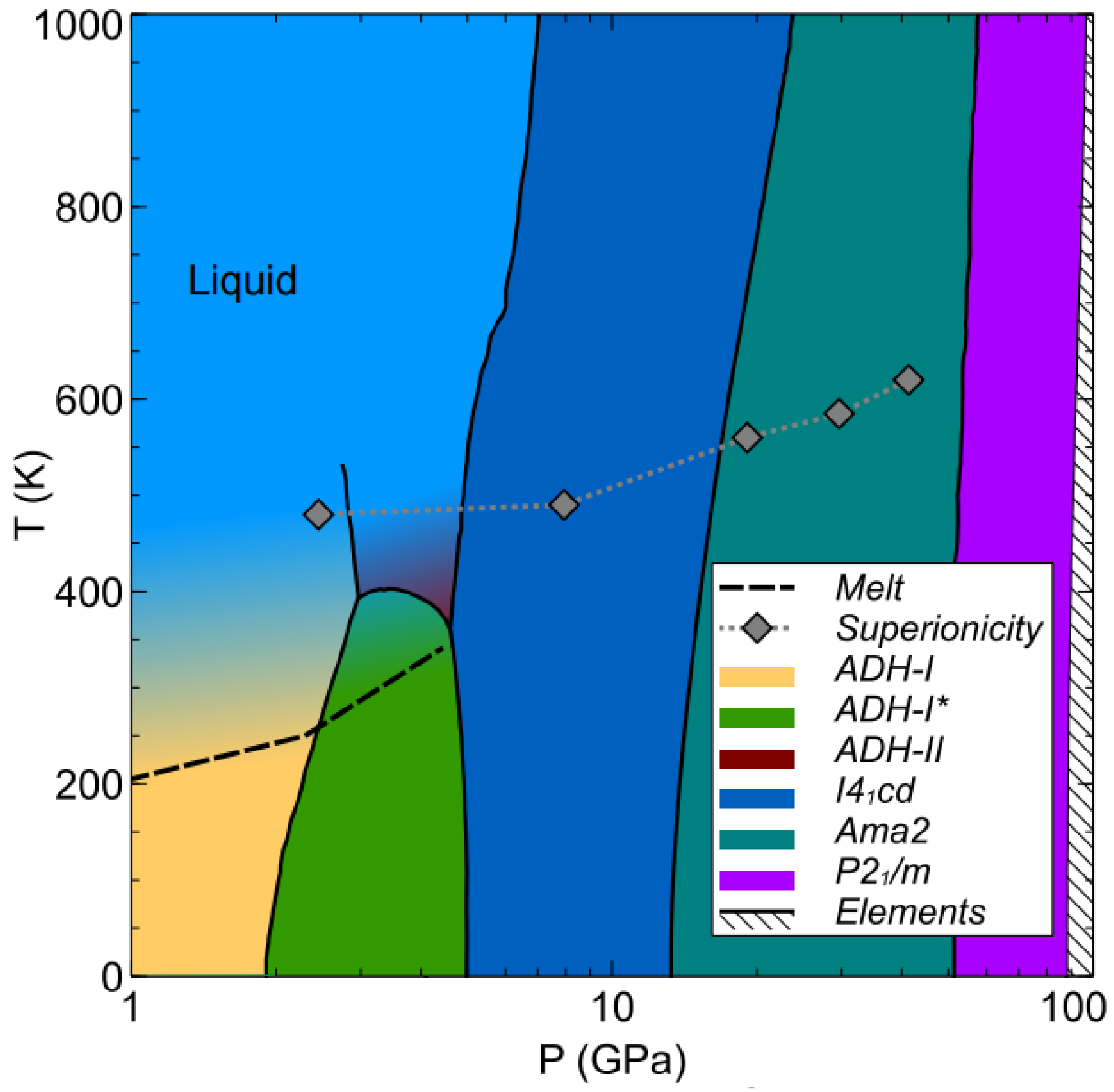
Finite Temperature



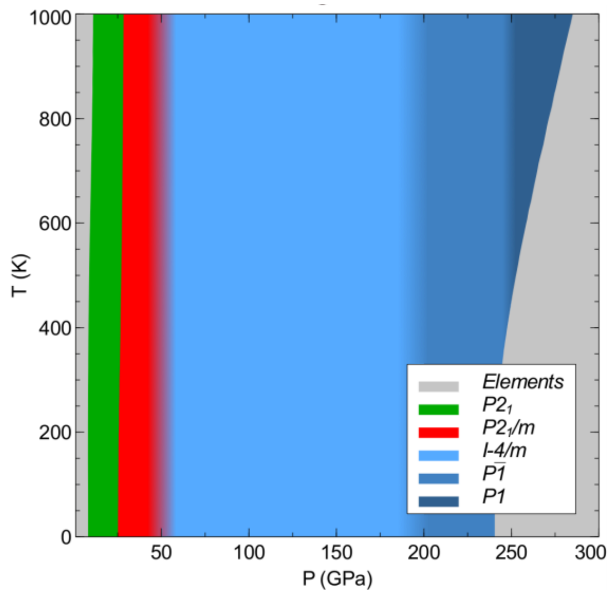
AMH [1:1]



AHH [2:1]



ADH [1:2]



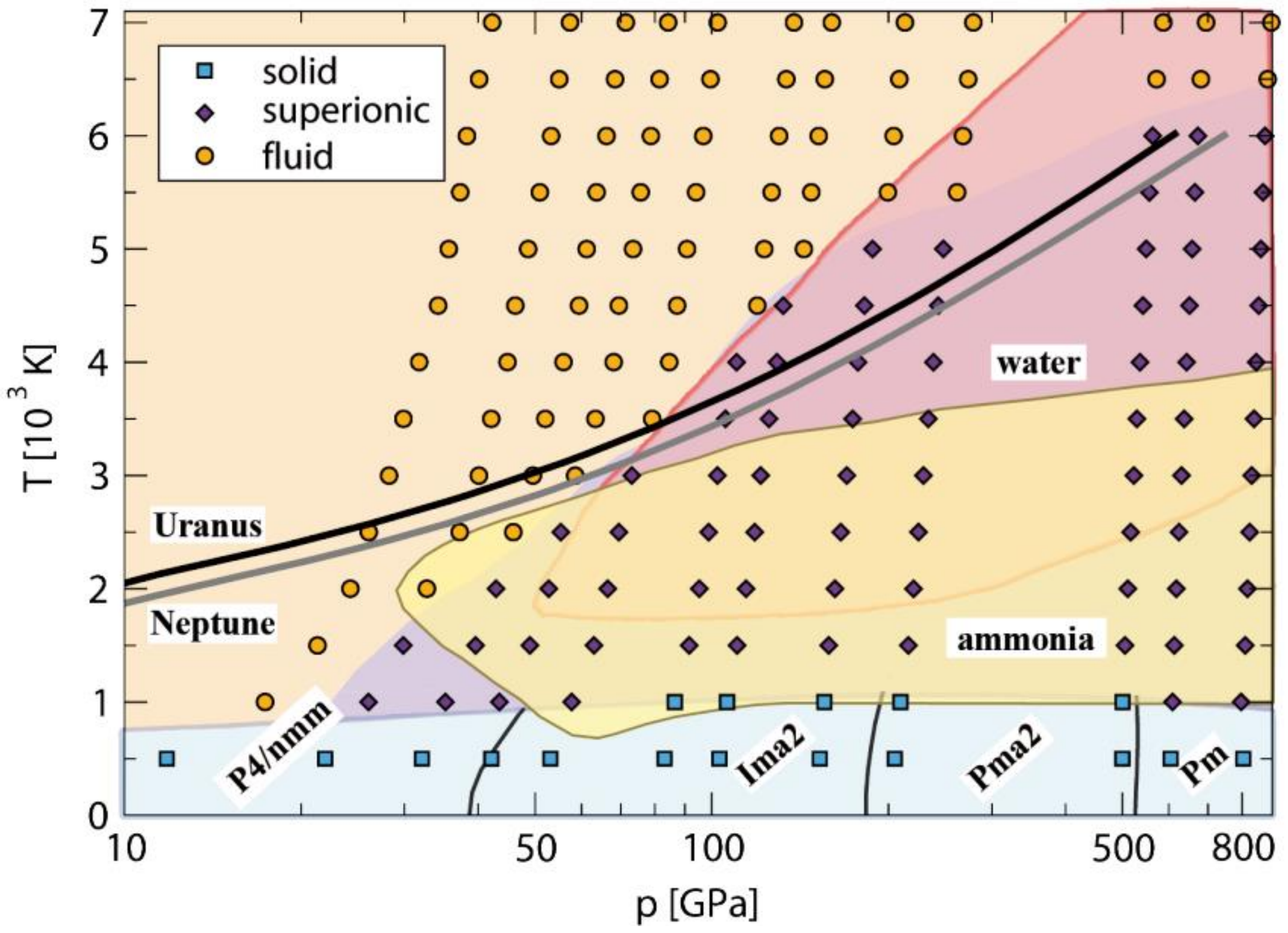
AQH [4:1]

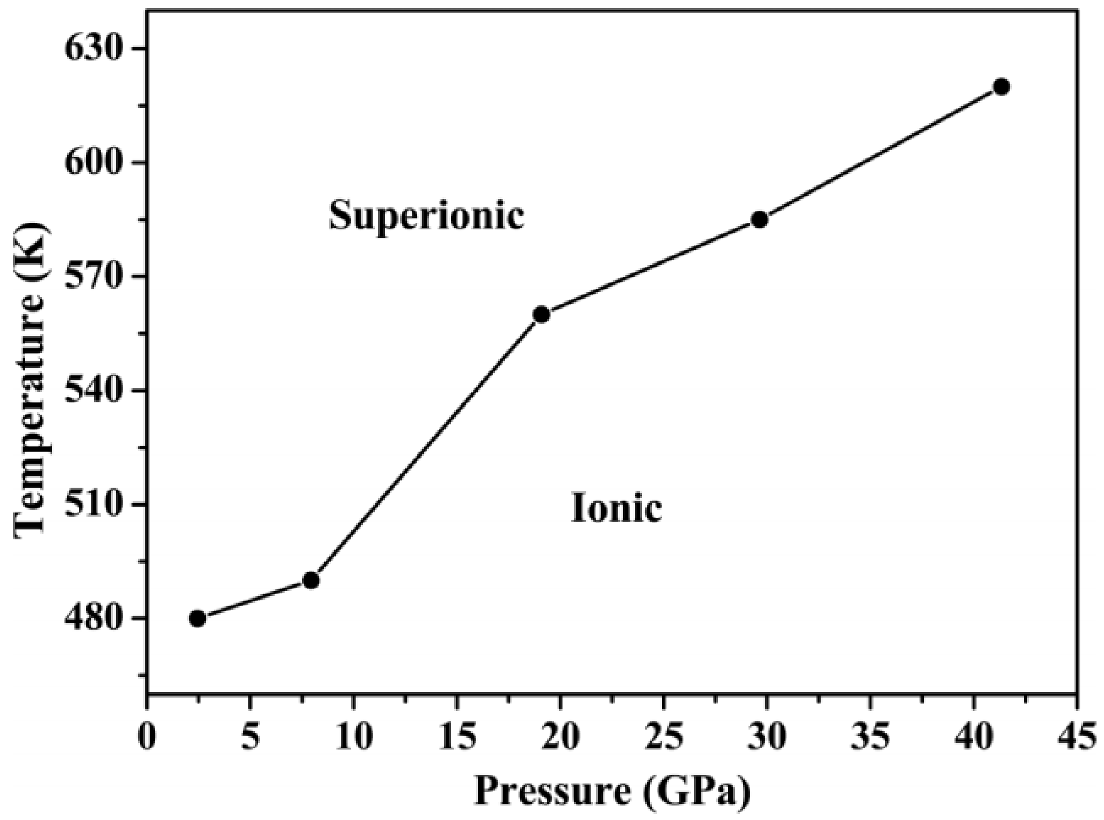
Harmonic approximation

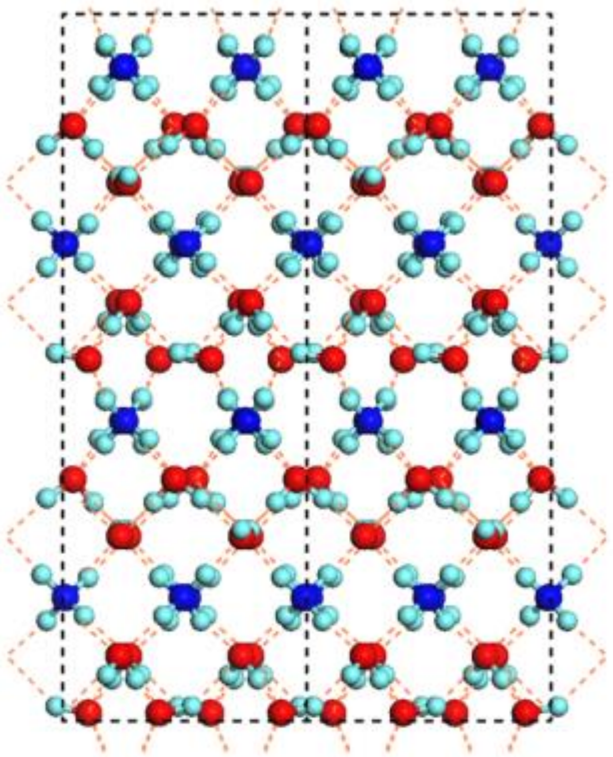
$$F(T,V) = E_0 - TS = E_0(V) + k_B T \int d\omega\, g(\omega) \ln\left[2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right]$$

Computing simple mixtures

- Crystal structure searches
- *Ab initio* MD based on ground state structures
- Observables: EOS, conductivities, viscosities







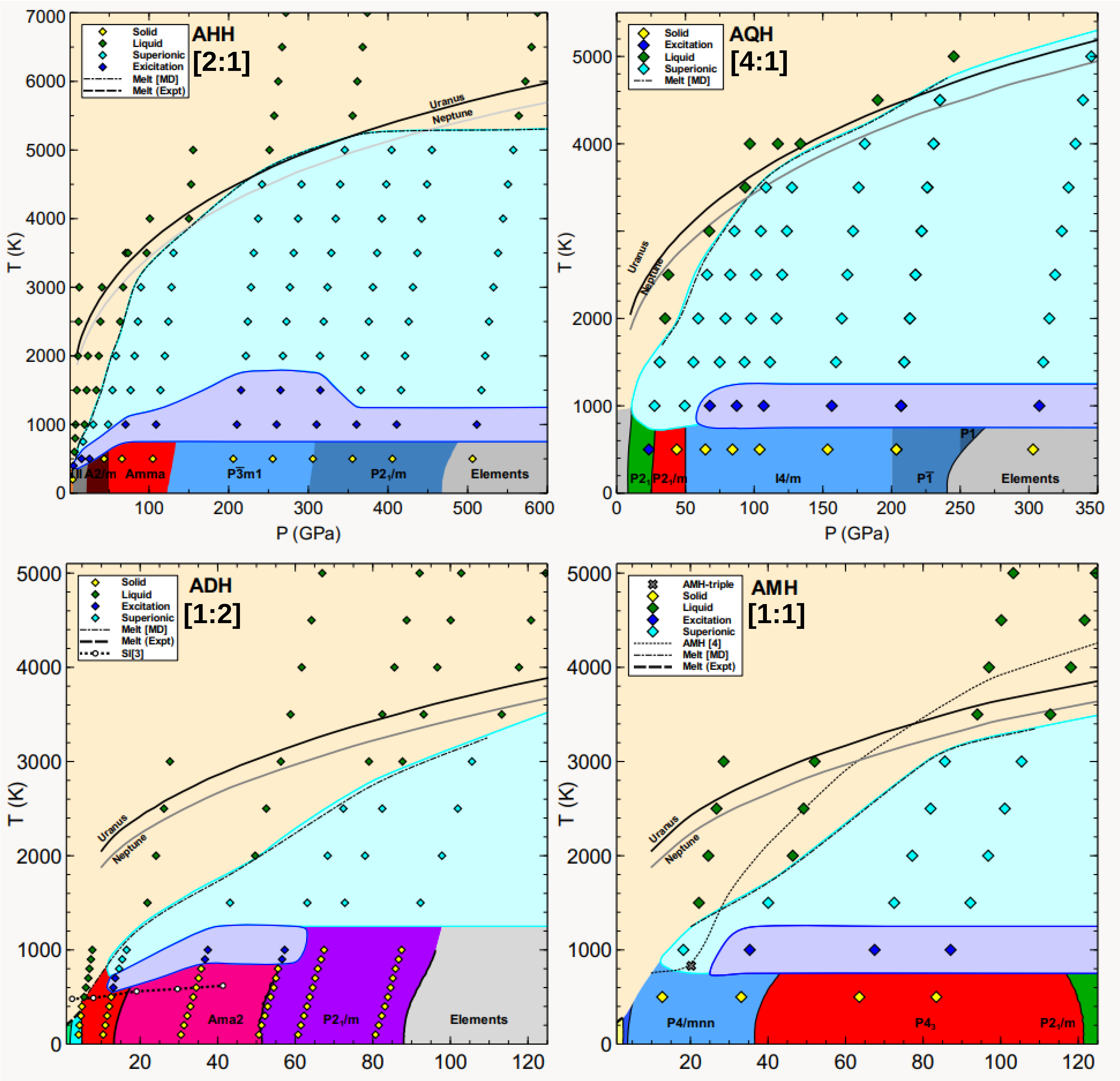
[1:1] $(H_2O)(NH_3)$

[1:2] $(NH_3)(H_2O)_2$

M. Bethkenhagen et al., *J. Phys. Chem. A*, 2015 **32 molecules**

X. Jiang et al., *Phys. Rev. B*, 2017. **384 molecules**

Phase Diagrams



NVT AIMD

CASTEP

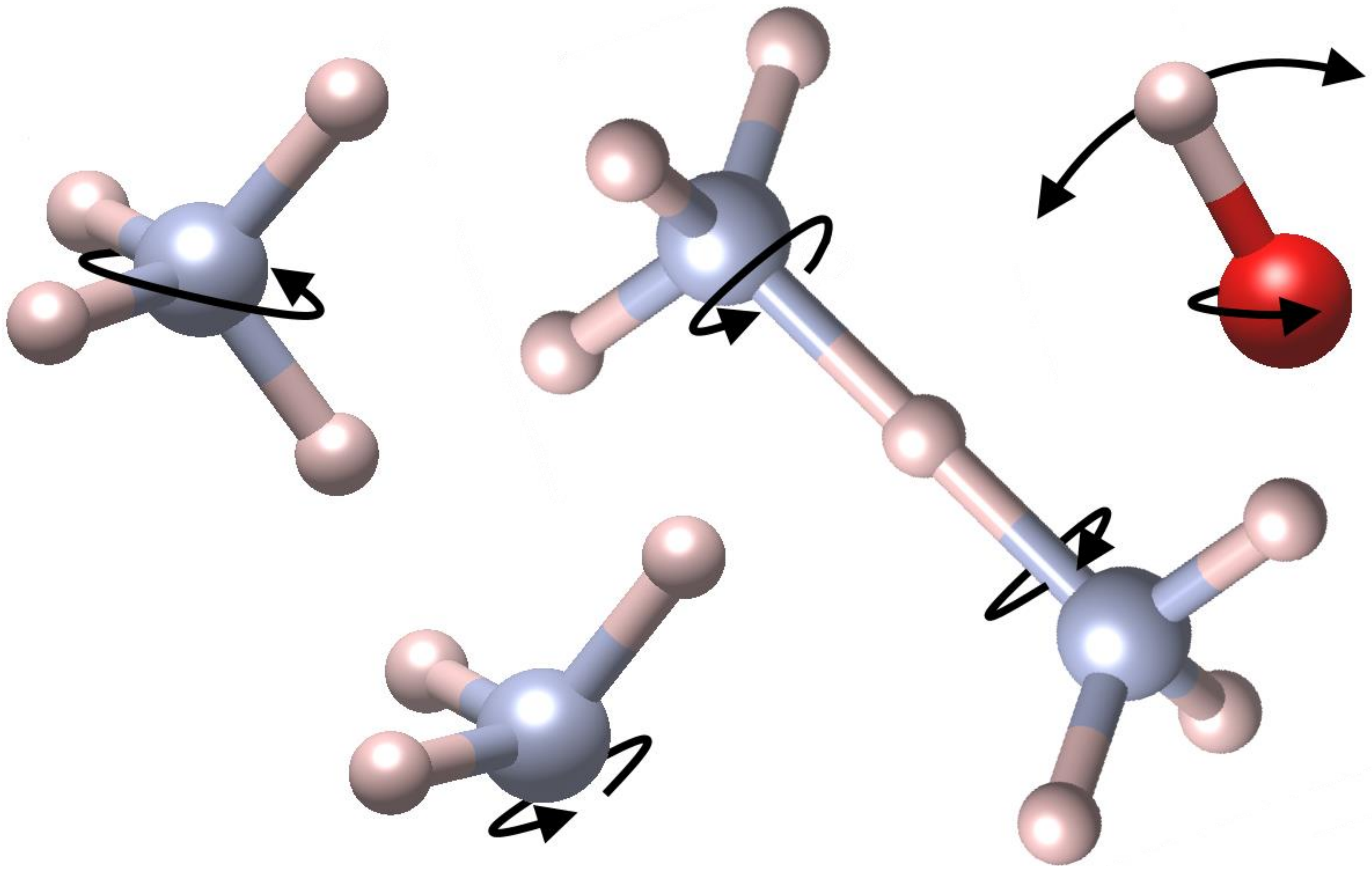
t_{total} = 1.53 ns

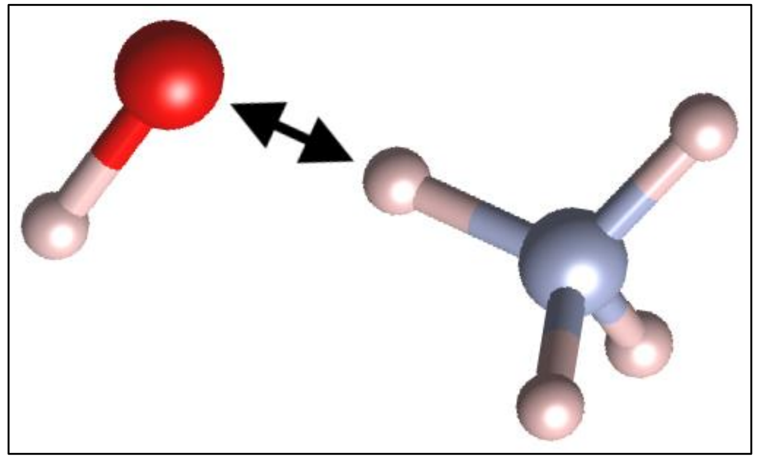
Up to:

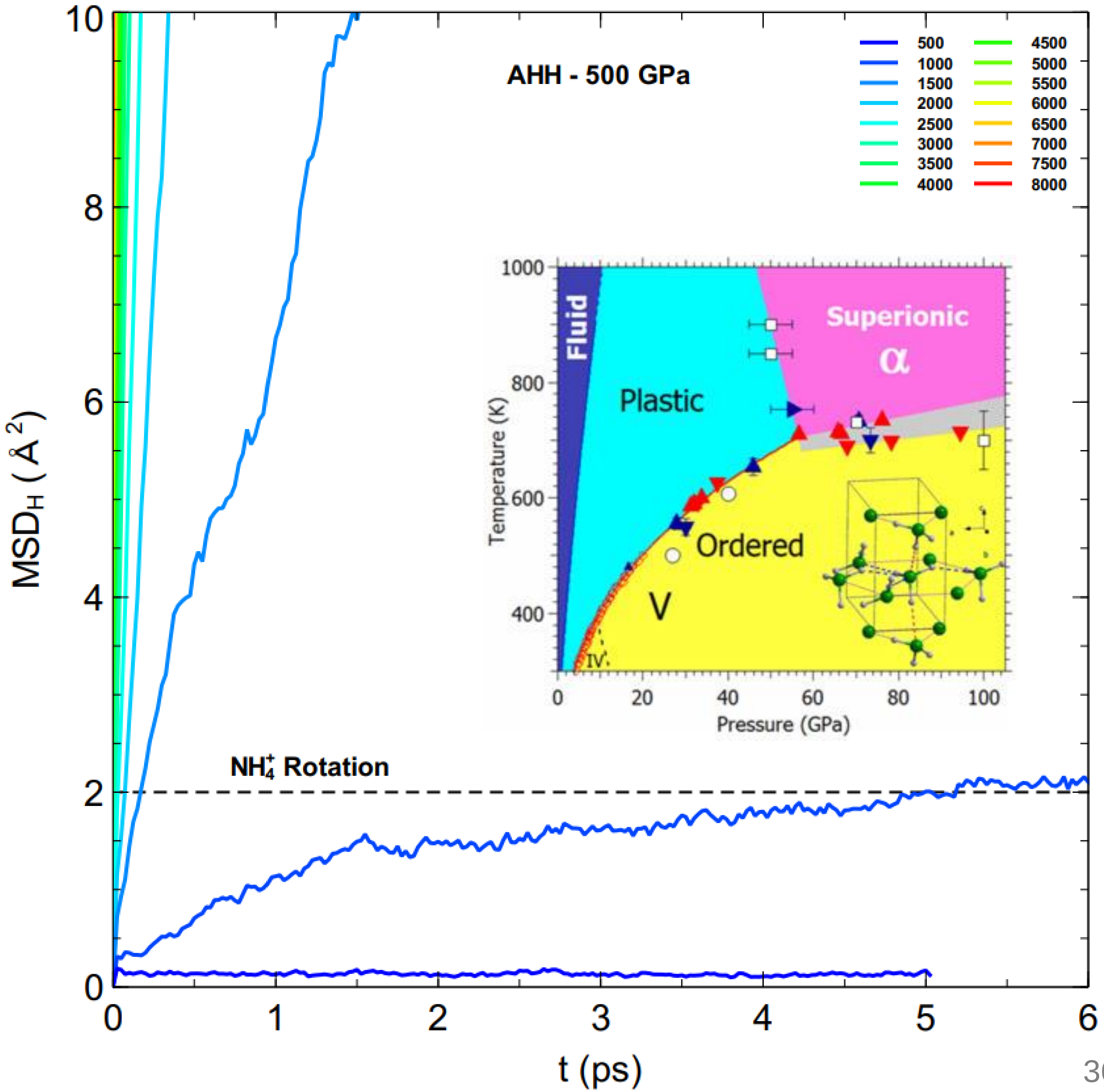
1280 atoms

384 molecules

Plasticity







AHH - 500 GPa
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
6000
6500
7000
7500
8000
Fluid
Plastic
Superionic
α
Ordered
V
IV
Temperature (K)
Pressure (GPa)
NH_4^+ Rotation
MSD_H ($Å^2$)
t (ps)
0
1
2
3
4
5
6
10
8
6
4
2

PHYSICAL REVIEW B **95**, 144104 (2017)

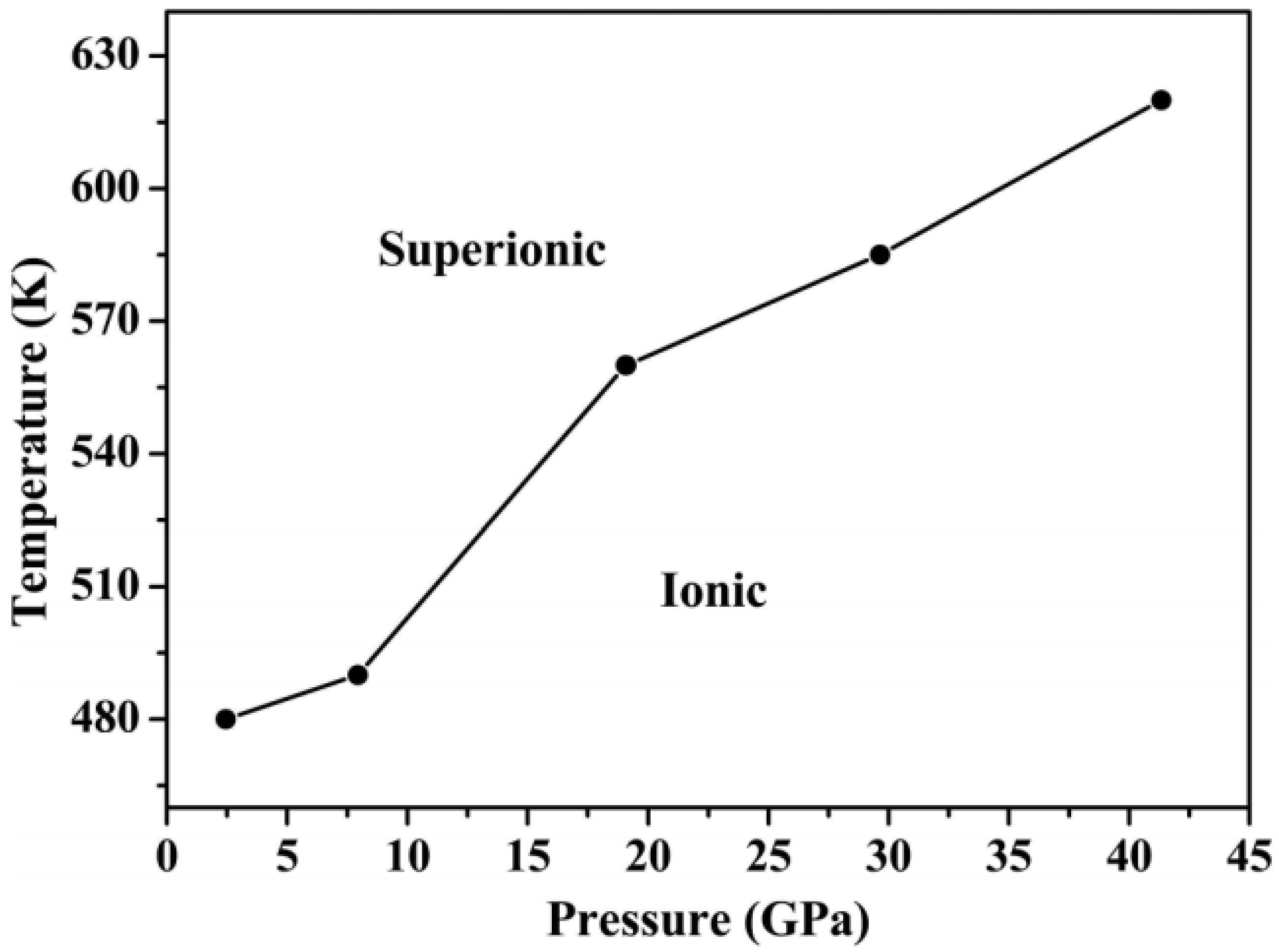
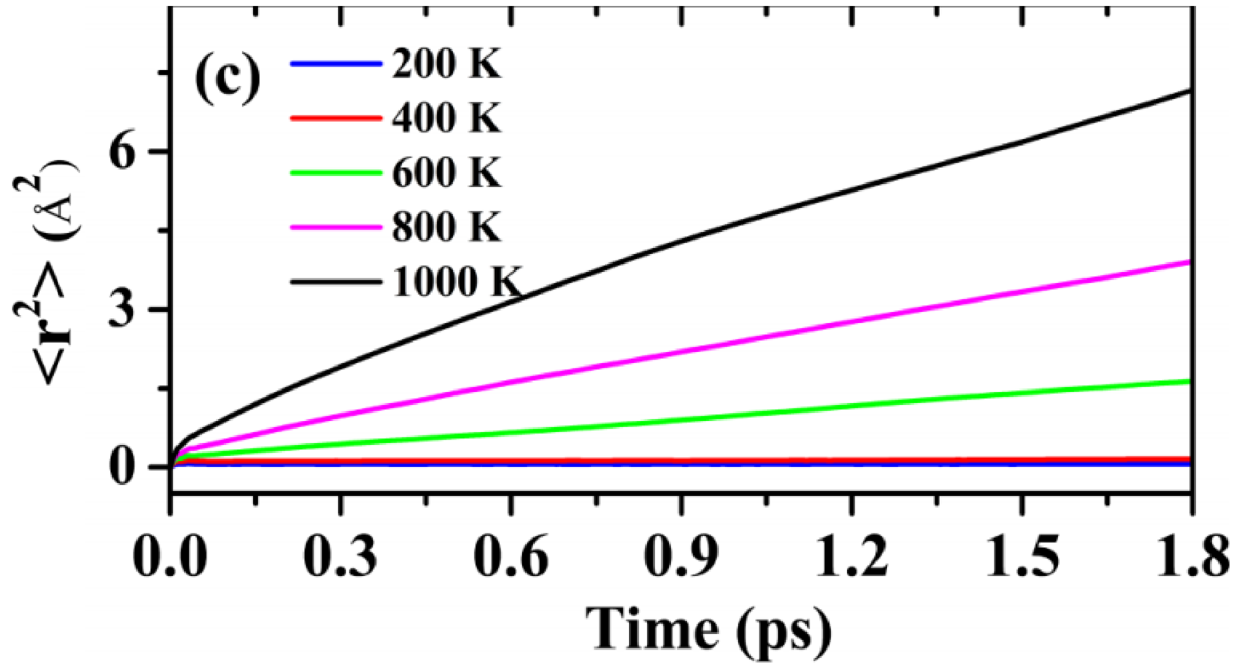
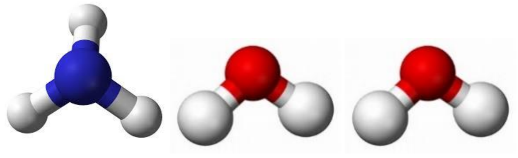


FIG. 7. P-T phase diagram of ionic and superionic ADH phases.

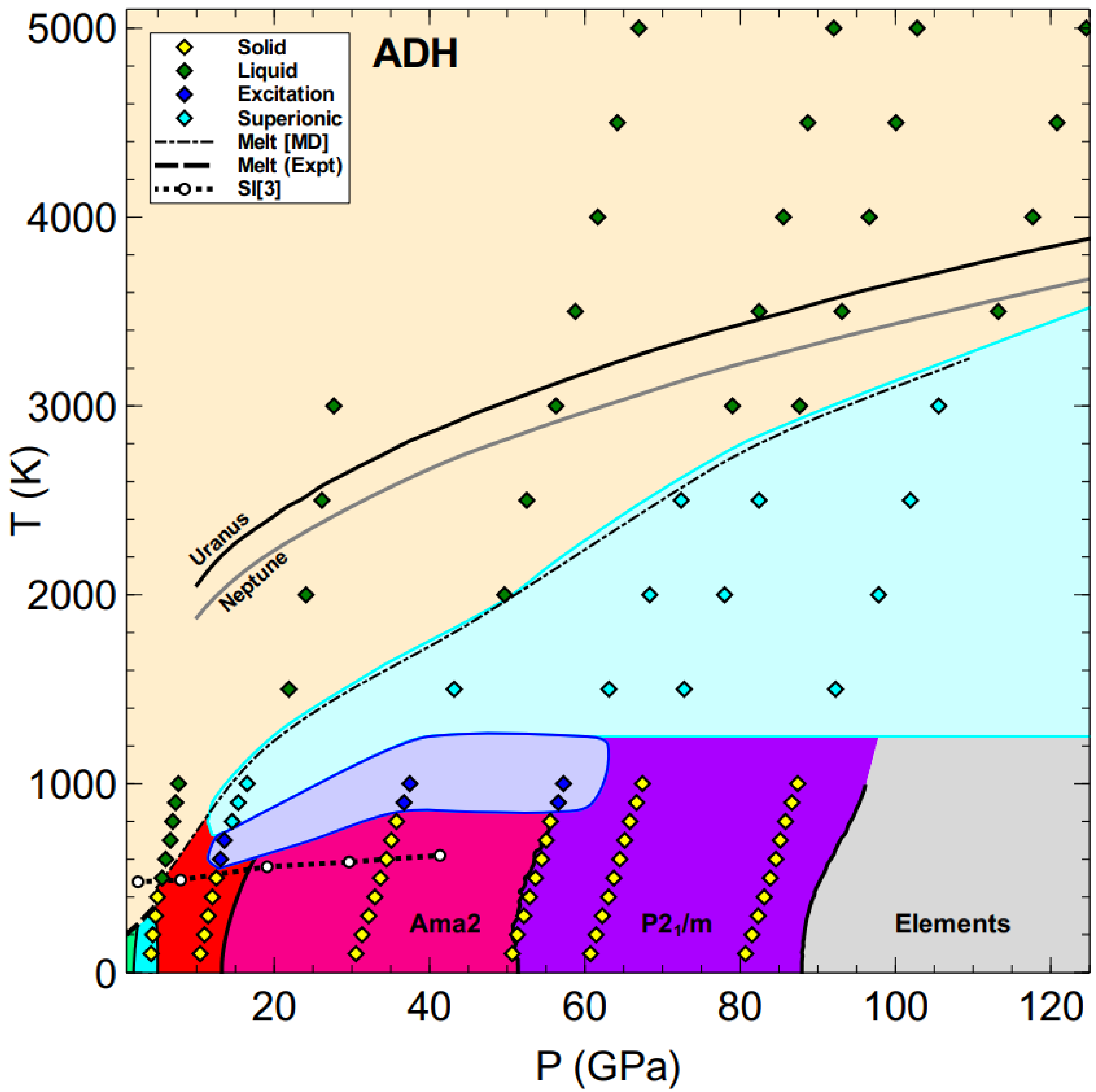


X. Jiang et al., *Phys. Rev. B*, 2017.

ADH [1:2]

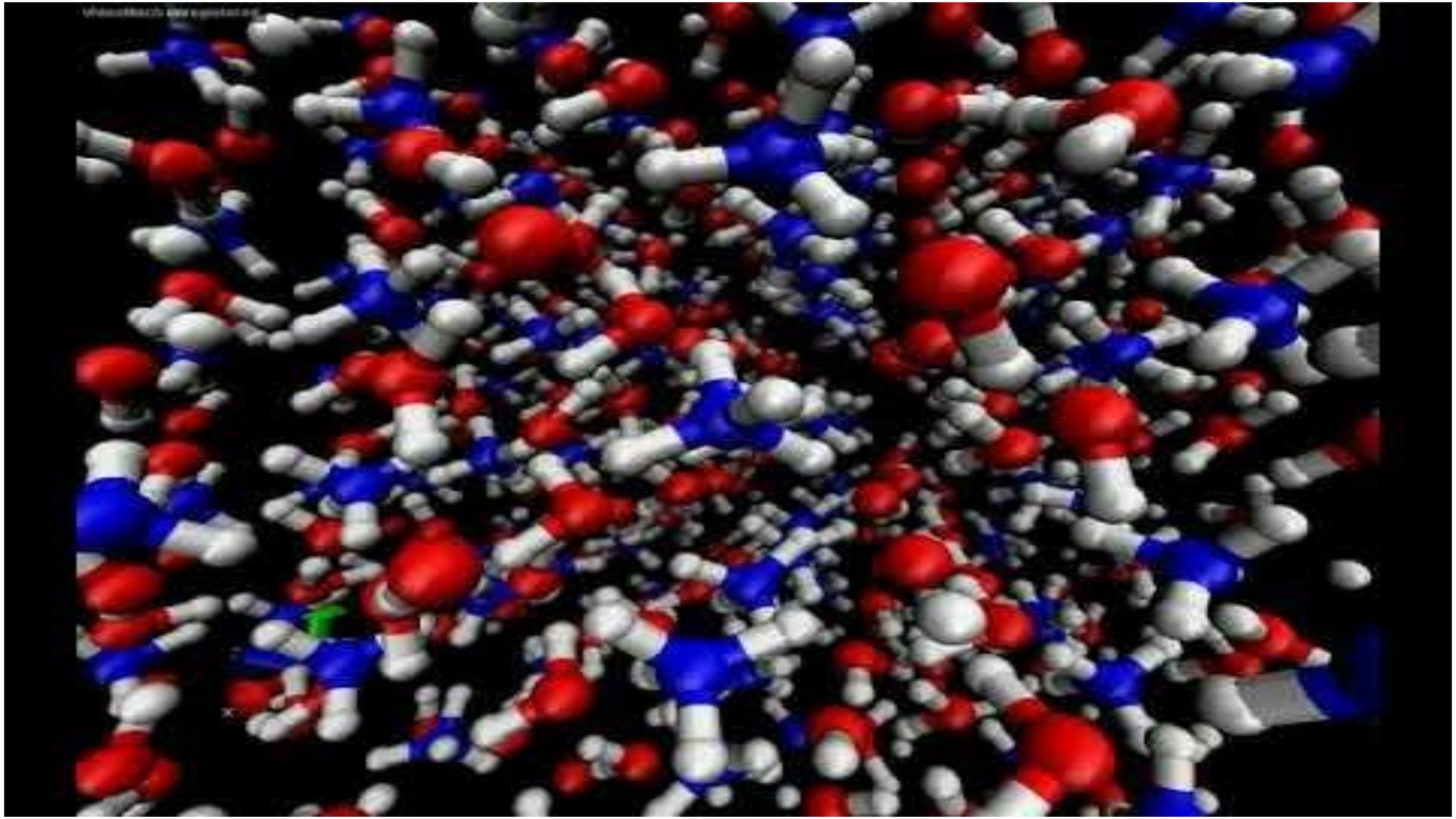


384 molecules



Plasticity

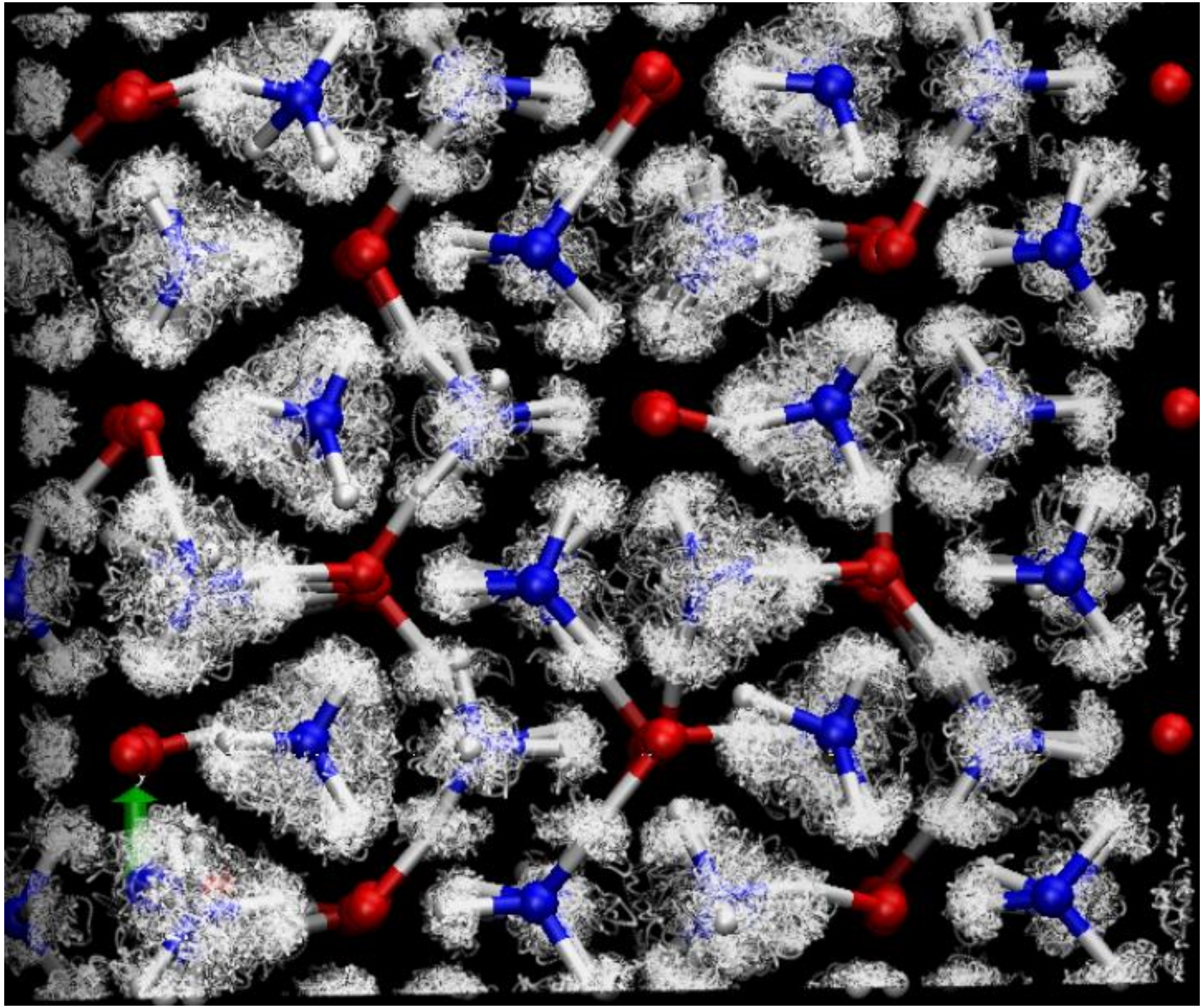
& double well



ADH[1:2] 10 GPa 700 K

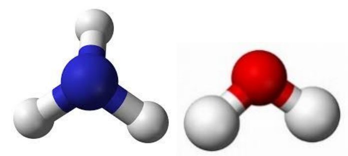
https://www.youtube.com/watch?v=dqizfwcwzvE

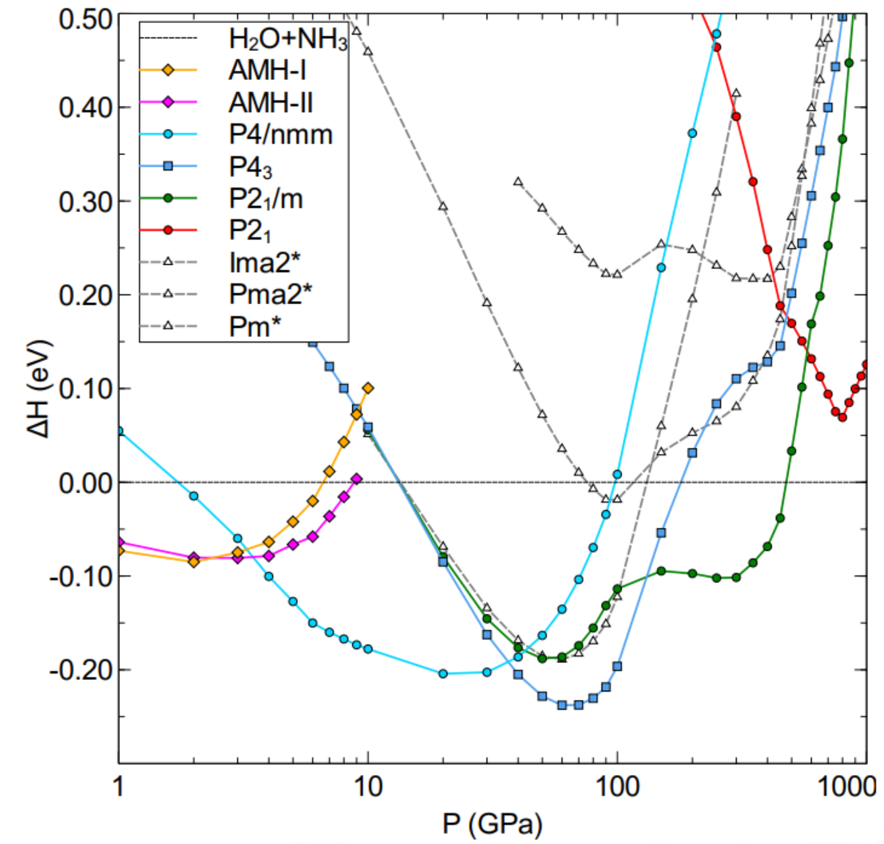
Plasticity



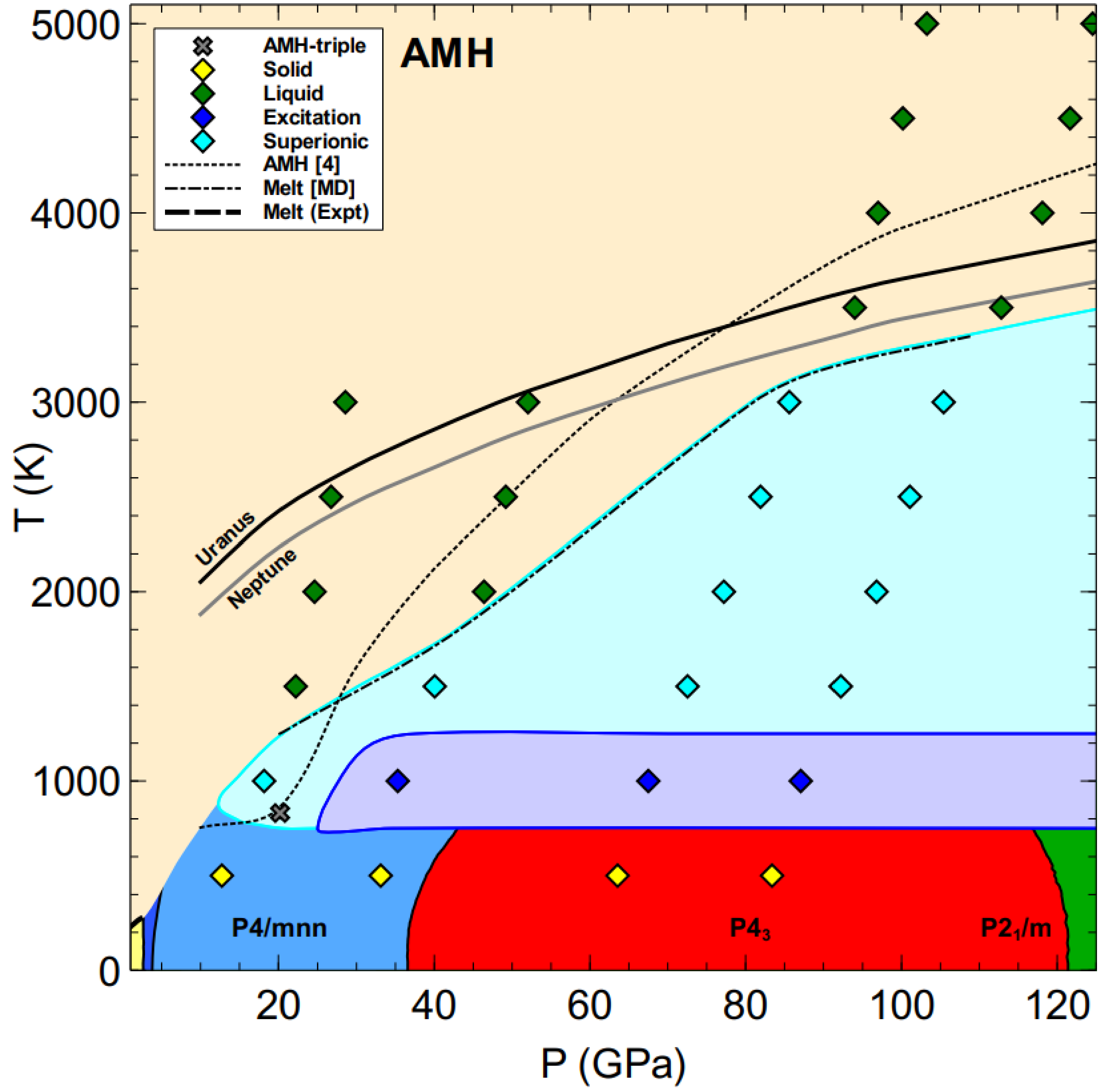
AHH[2:1] 500 GPa 1000 K

AMH [1:1]

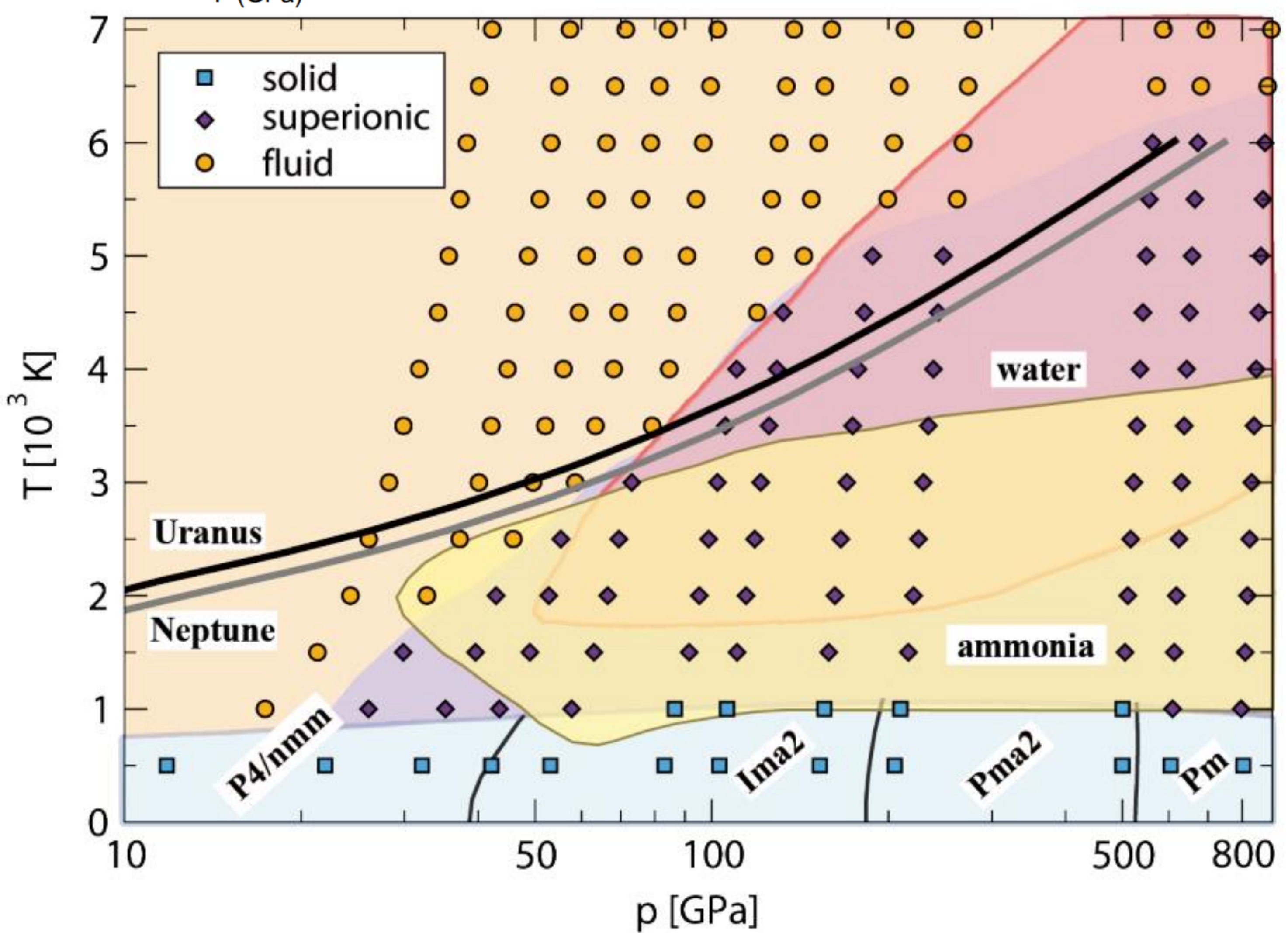




144 molecules



32 molecules



M. Bethkenhagen et al., *J. Phys. Chem. A*, 2015

Full NH_3-H_2O phase diagram

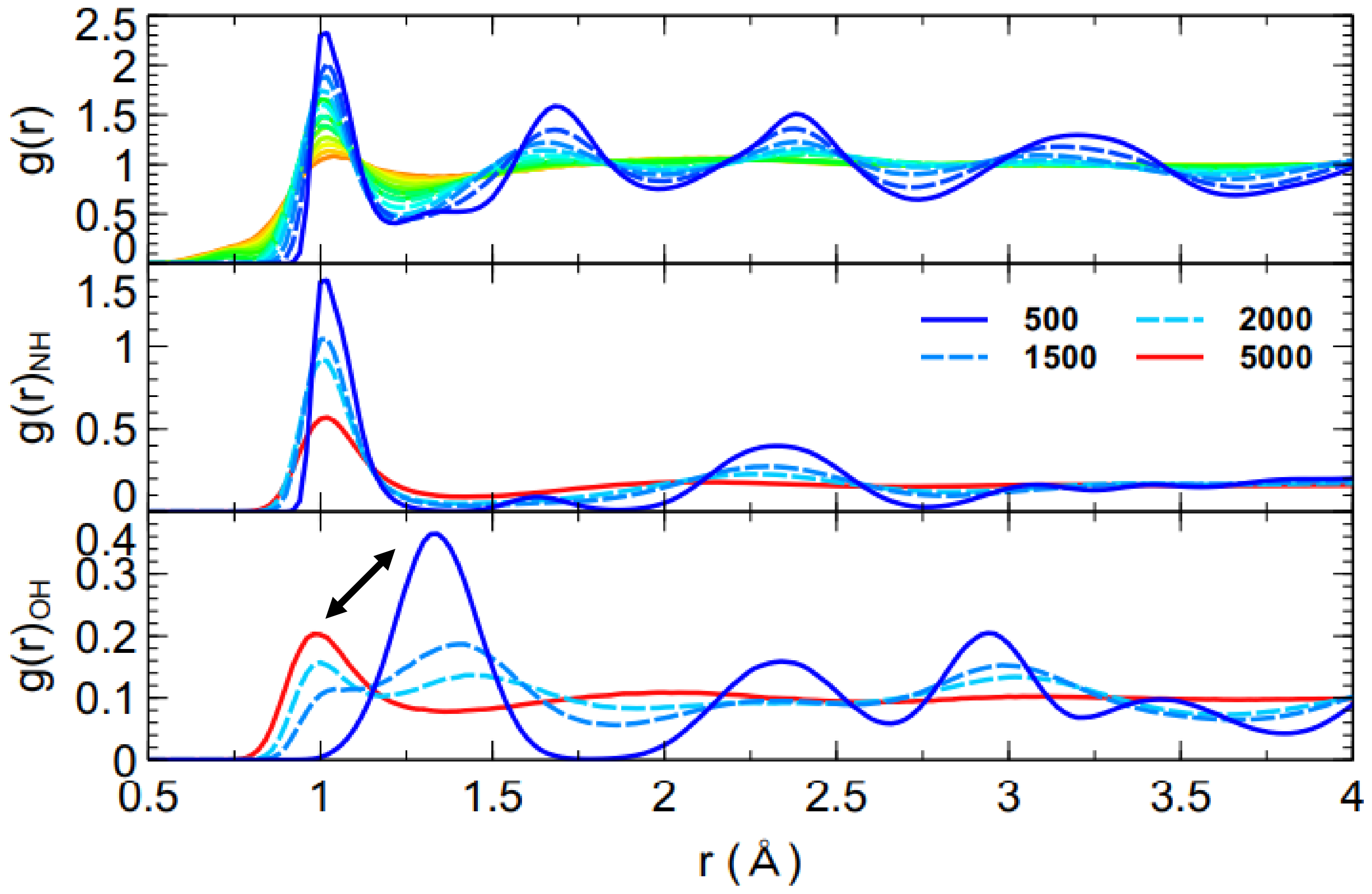
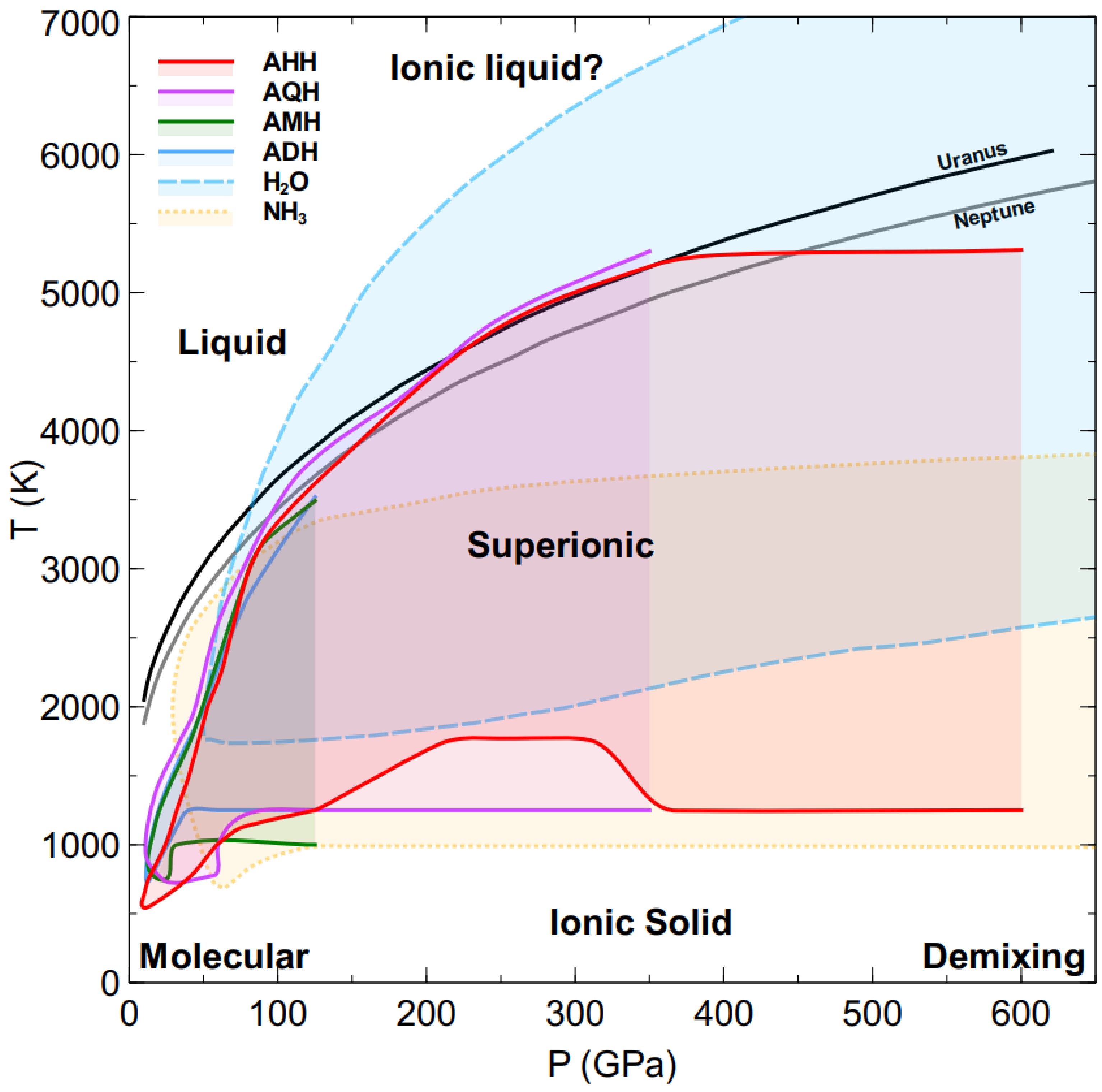
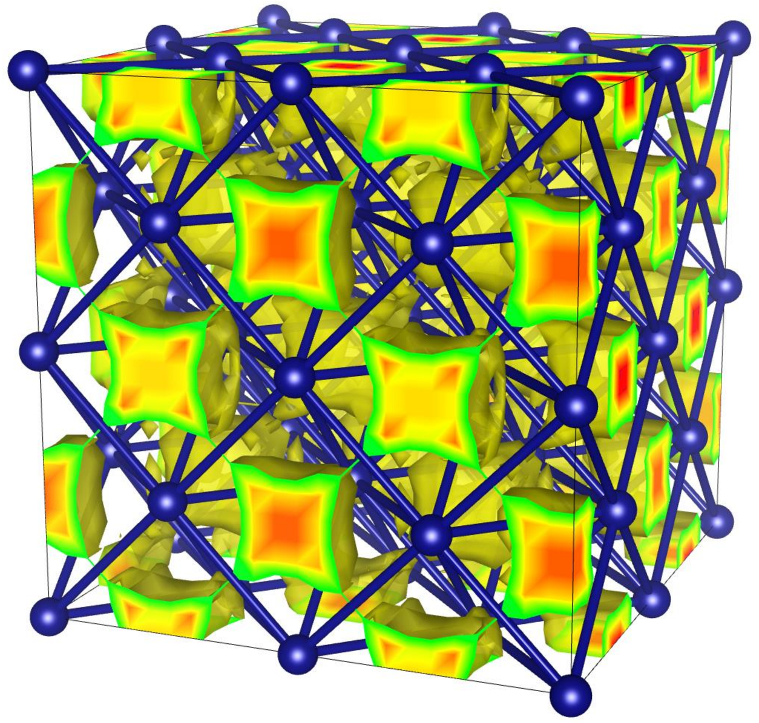
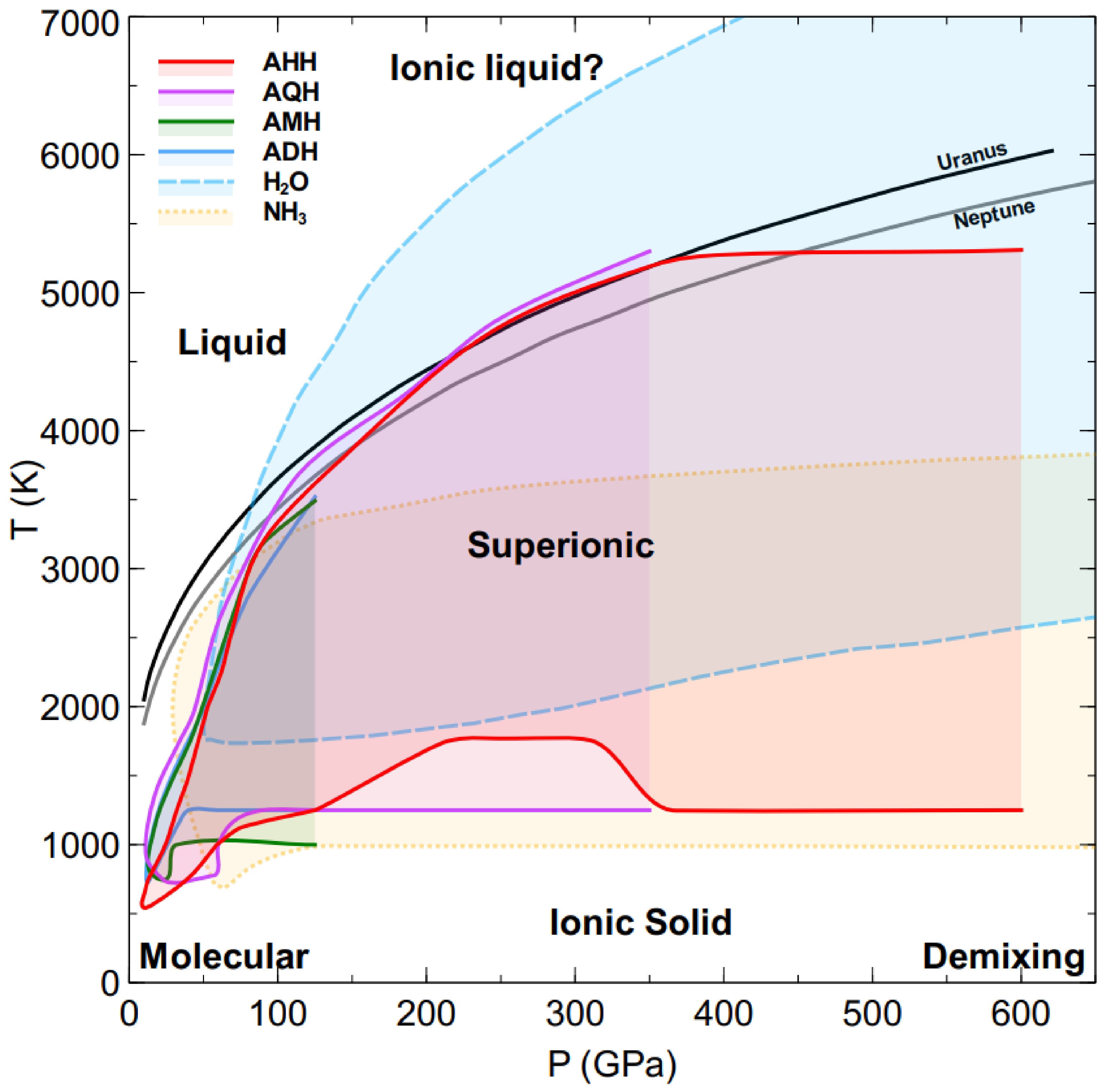


Figure 6.18 *RDF's and PDF's for AHH at 100 GPA where dashed lines indicate the superionic phase.*



Full NH_3-H_2O phase diagram

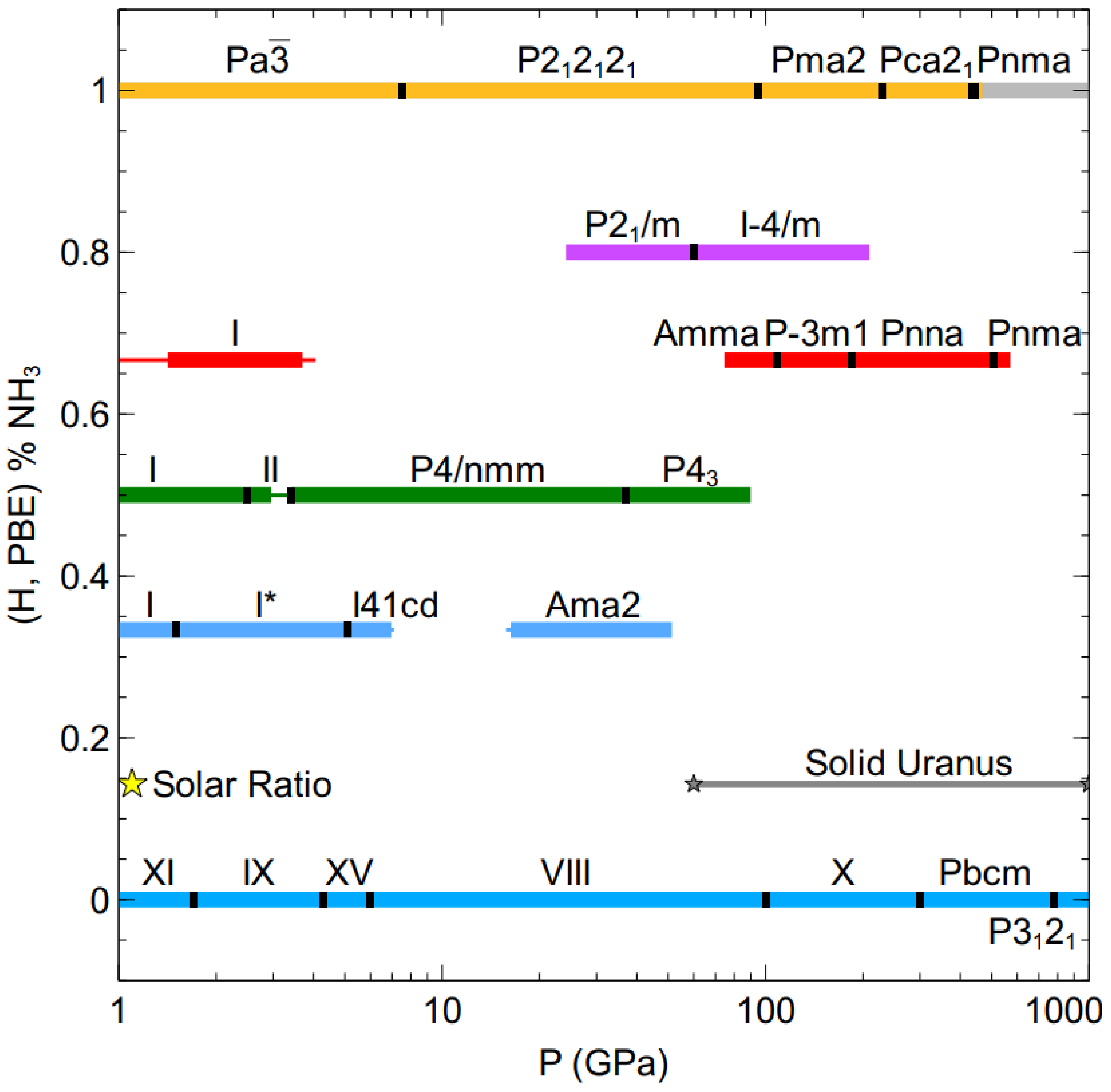


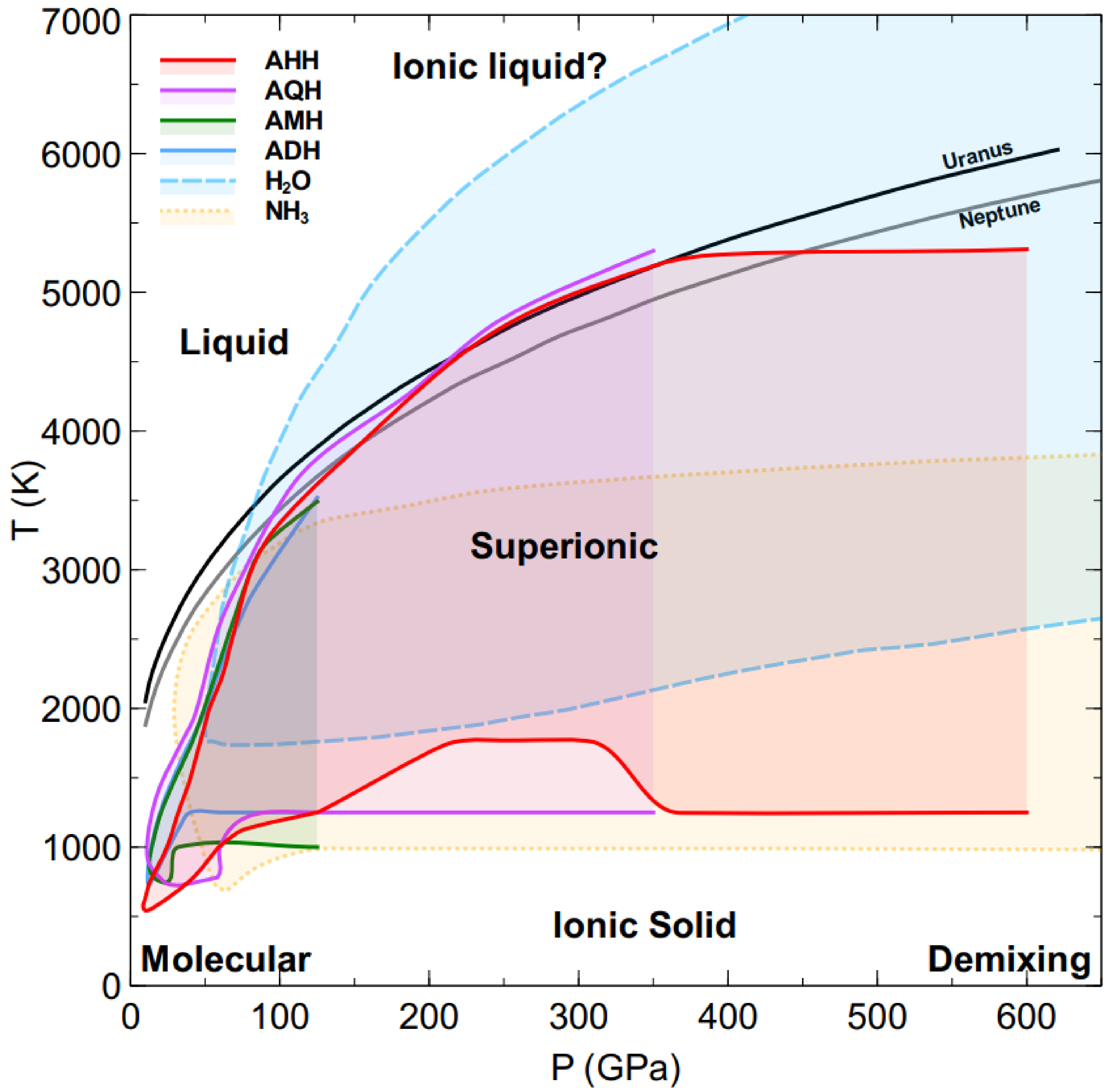


Superionic to superionic phase change in water: Consequences for the interiors of Uranus and Neptune

Hugh F. Wilson, Michael L. Wong, Burkhard Militzer Phys.Rev.Lett. 110 (2013) no.15, 151102

Full NH_3-H_2O phase diagram

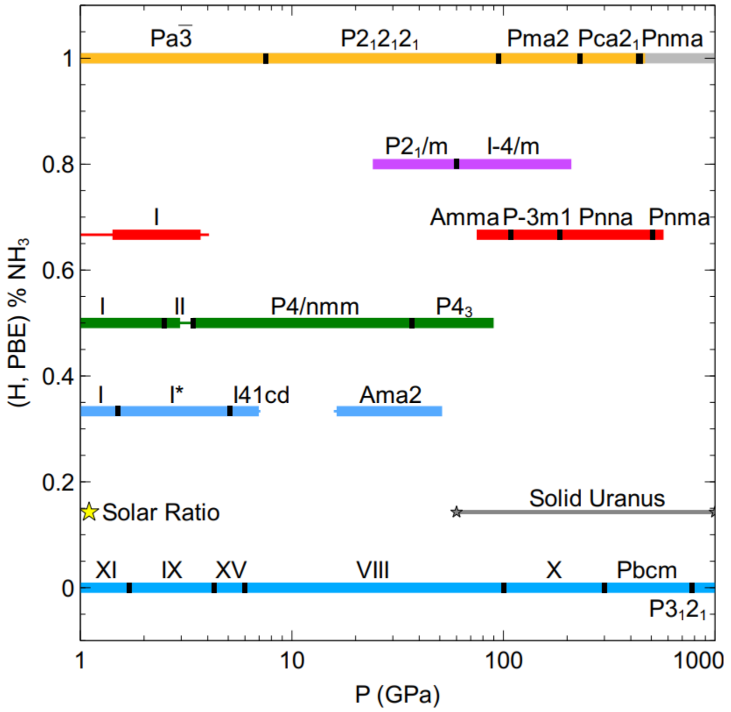


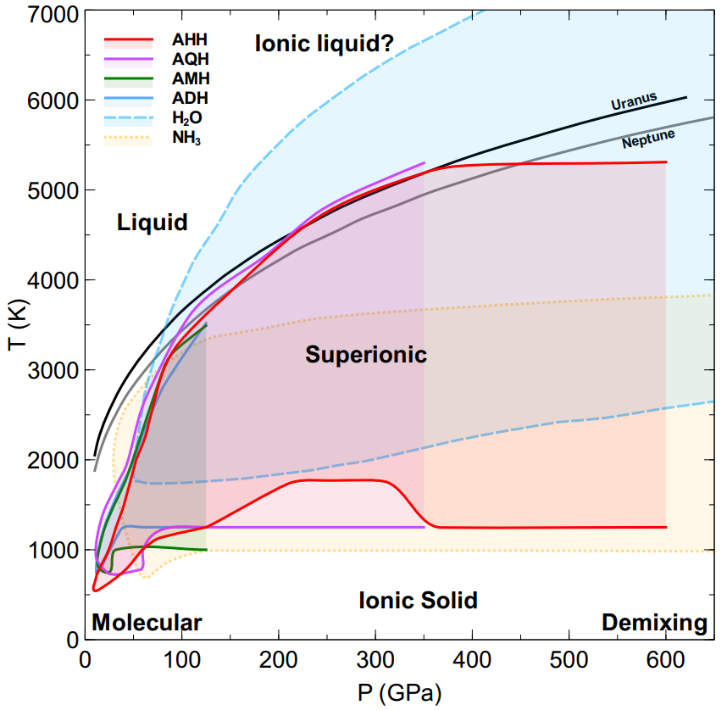


Summary & Acknowledgements

Ammonia-water mixtures

- **AHH**: sequence of fully de-protonated, ionic structures
  DMA approximants
  Change in superionicity?
- **AMH**: updating high-pressure evolution
  H-bond network topologies
- Full binary H_2O-NH_3 phase diagram
  New quarter-hydrate, **AQH**
  Ammonia-rich phases favored
- **Superionic**, **plastic**, and **melt** lines categorized for all mixtures





Supervisor

Andreas Hermann

Collaborators

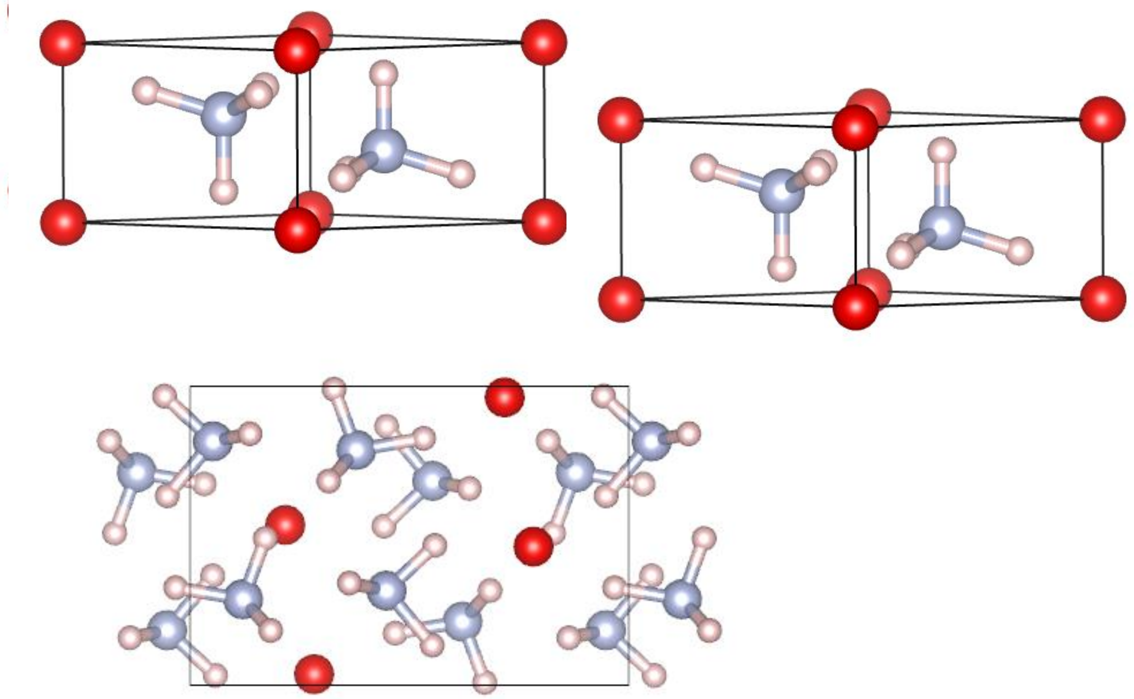
Yanchao Wang
Yanming Ma
Miriam Marquez

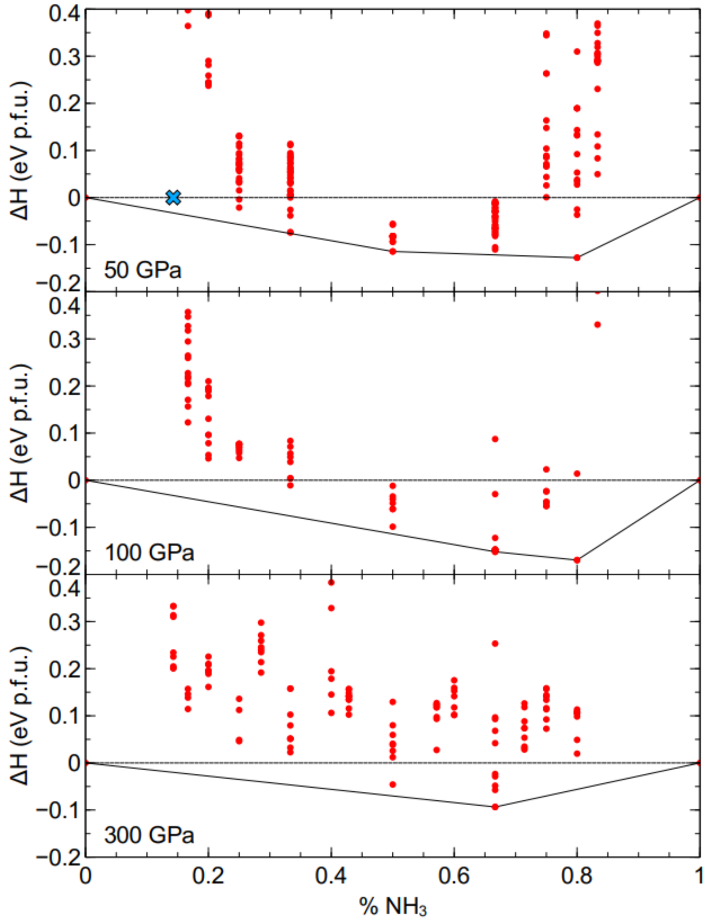
Jacob F. Christiansen

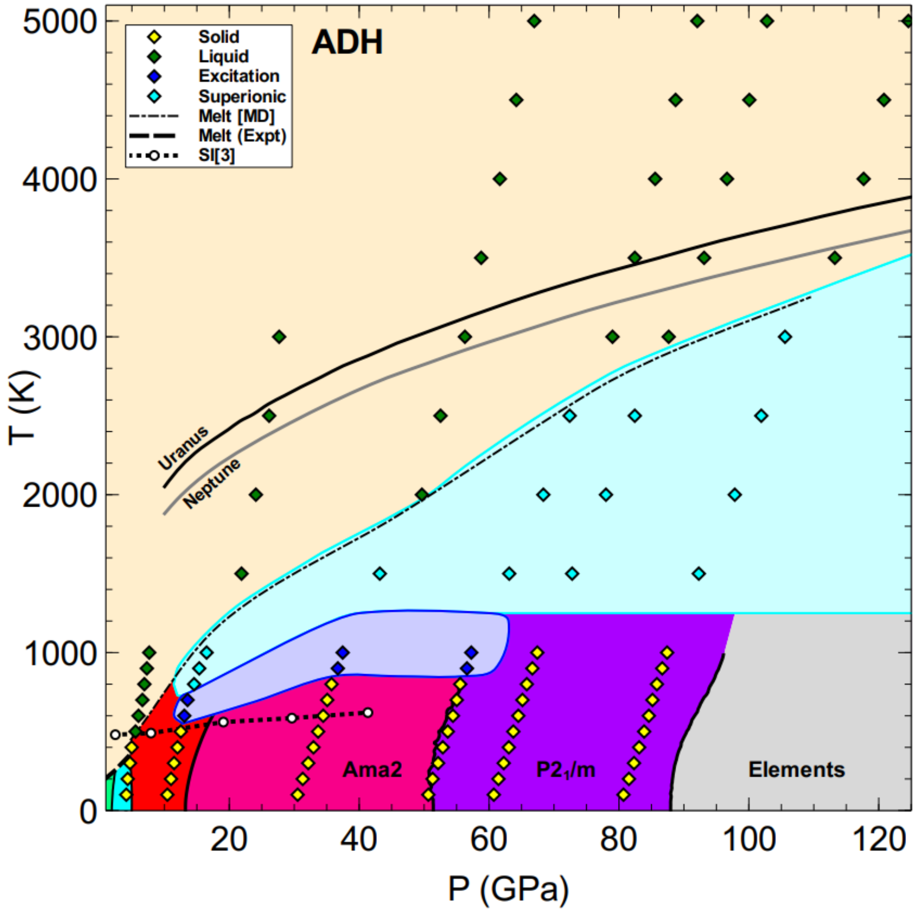
Funding & Computing

Research Structure

Crystal Structure Searching → Stable Mixture Stabilities → Finite Temperature MD

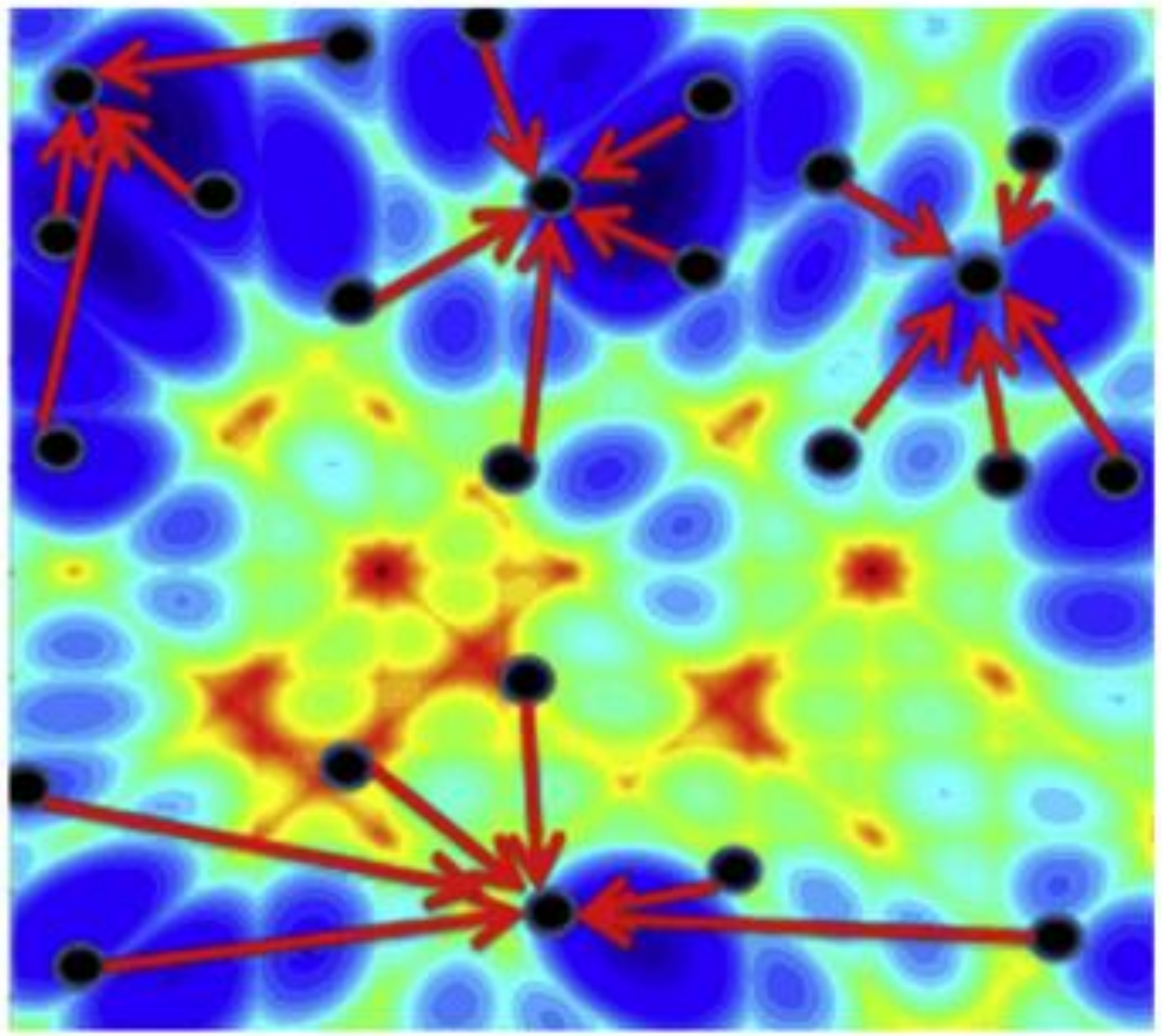


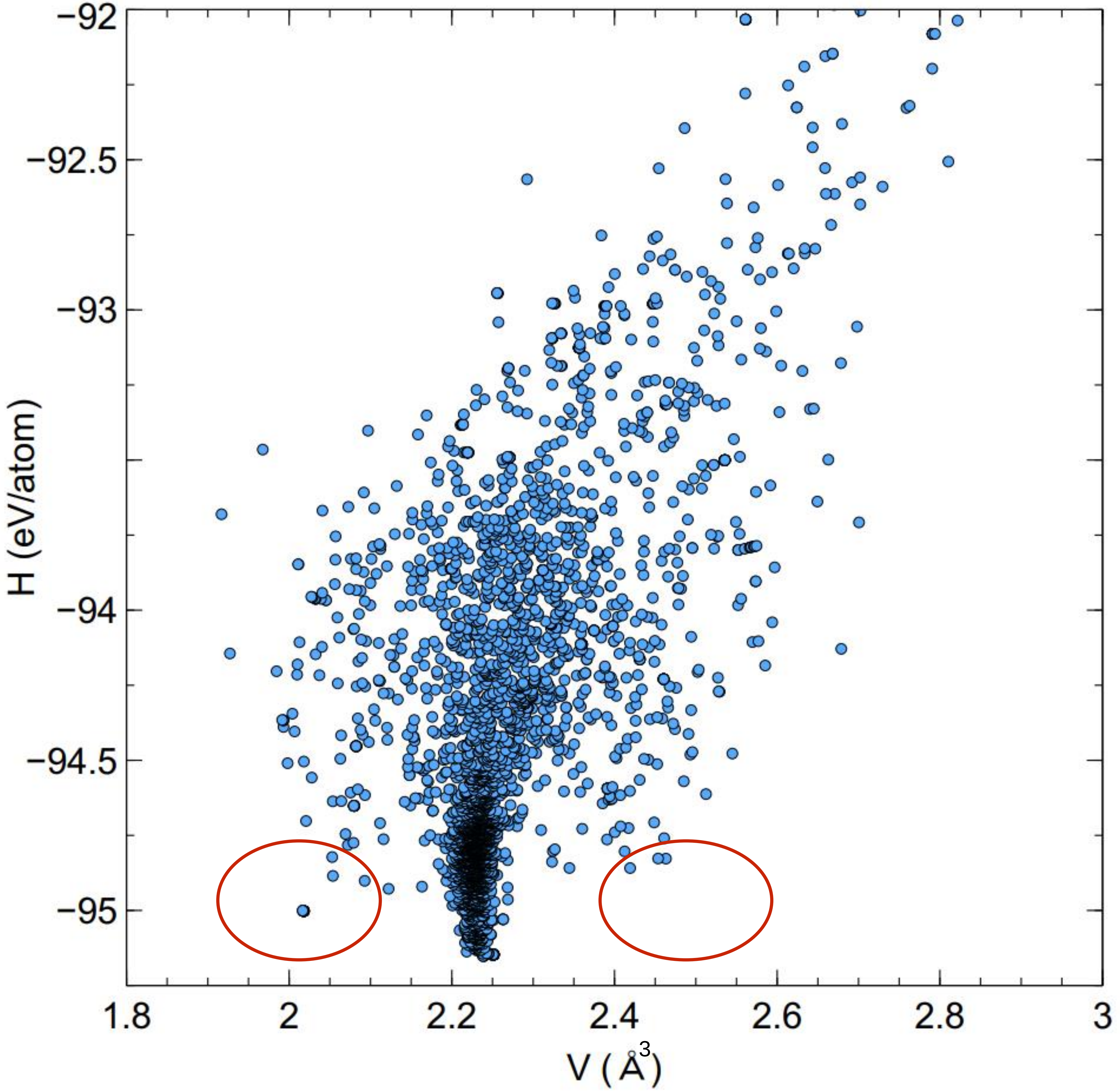




Crystal structure prediction

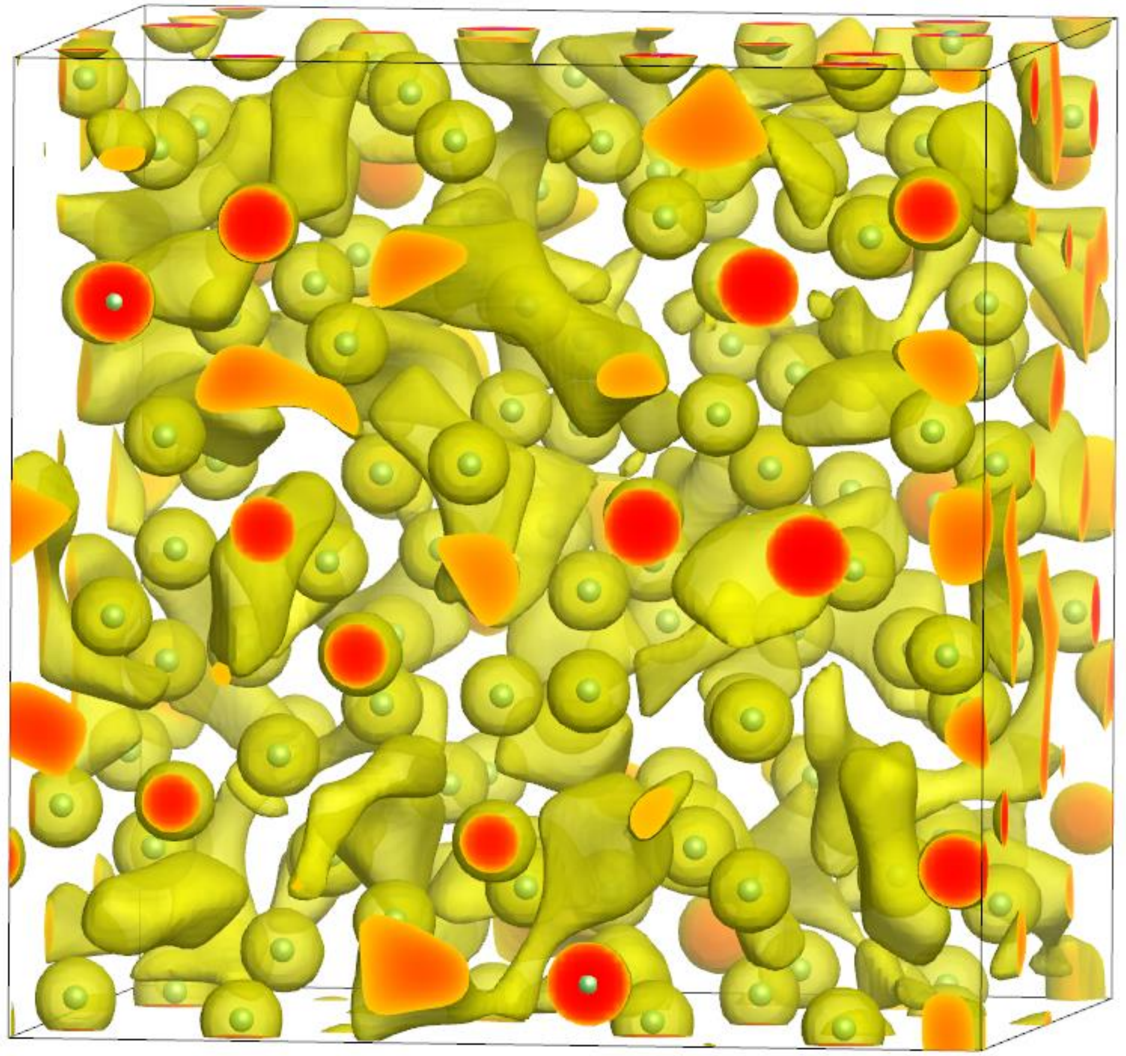
- Particle-swarm optimization
- CASTEP total energy calculations
- Up to four formula units, 200,000 + structures
- Pressures 5, 10, 20, 30, 50, 80, 100 … 1000 GPa



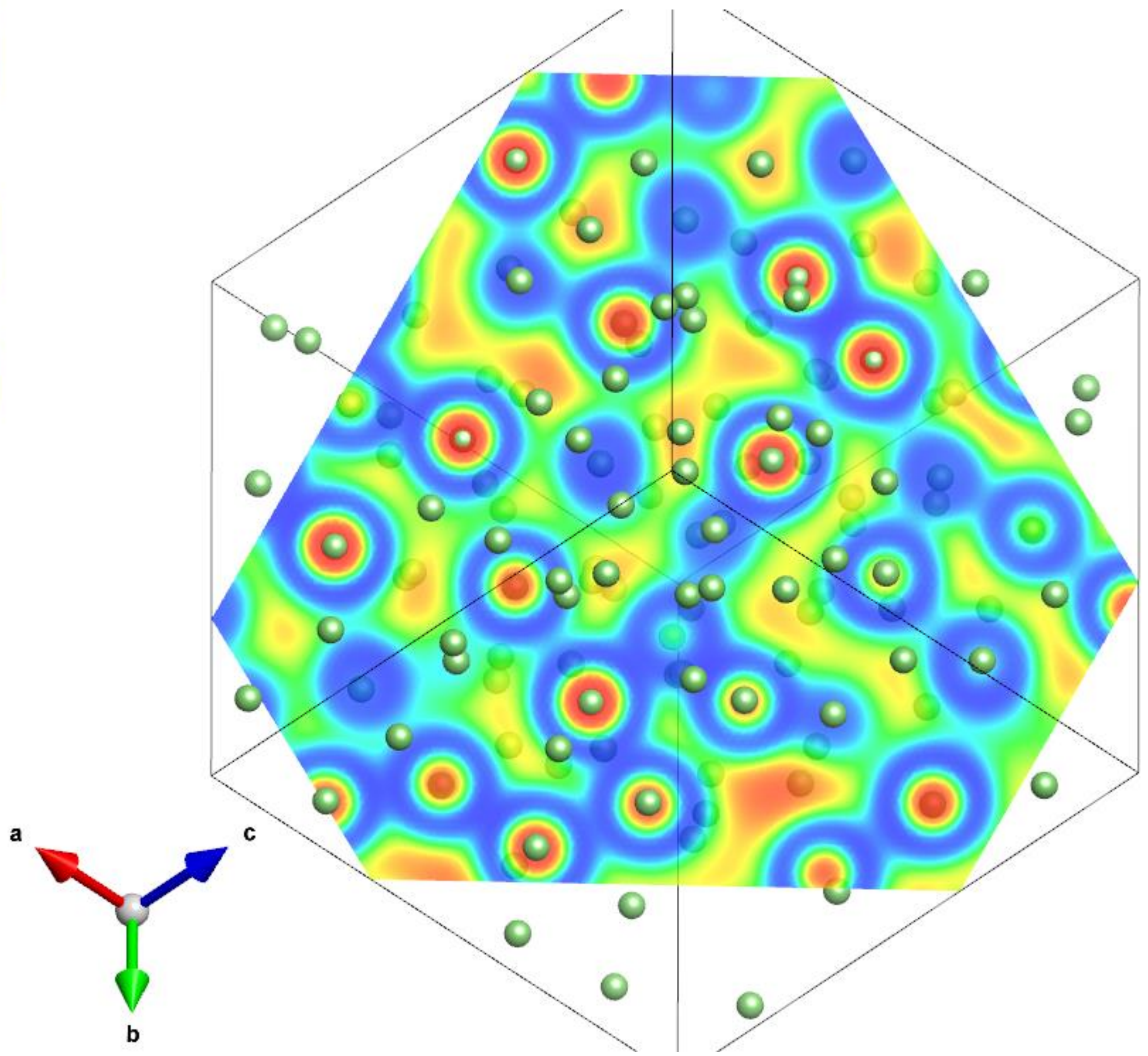


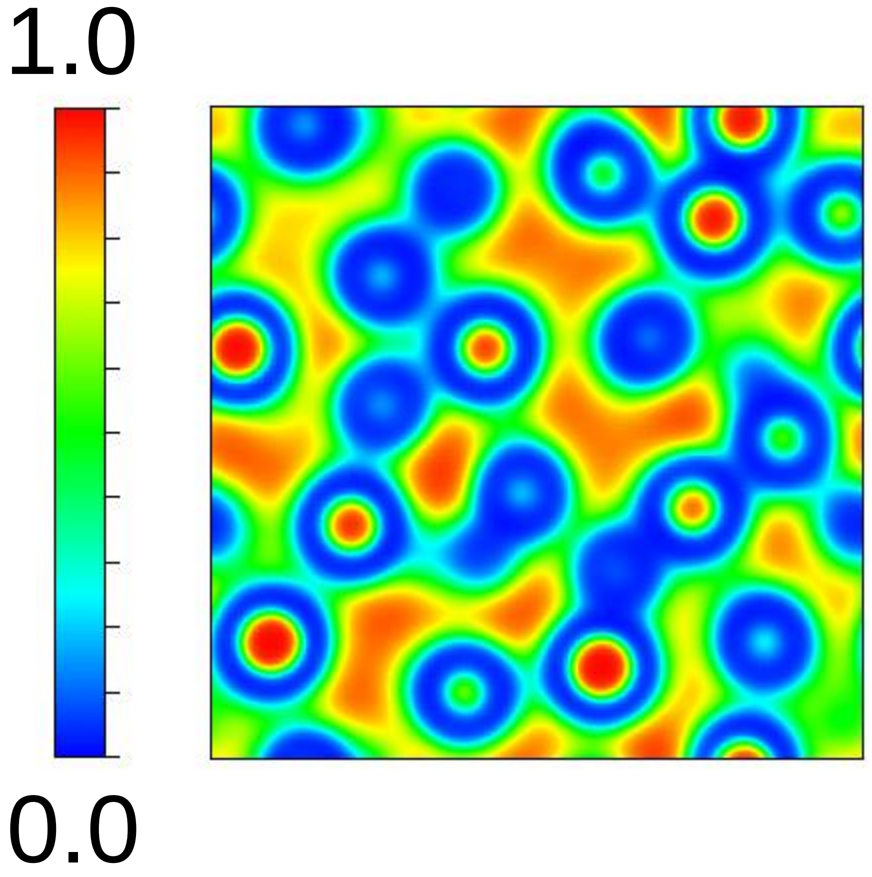
-92
-92.5
-93
-94
-94.5
-95
H (eV/atom)
1.8
2
2.2
2.4
2.6
2.8
3
V (Å^3)

Liquid Electrides



Li [90 GPa, 1500 K]

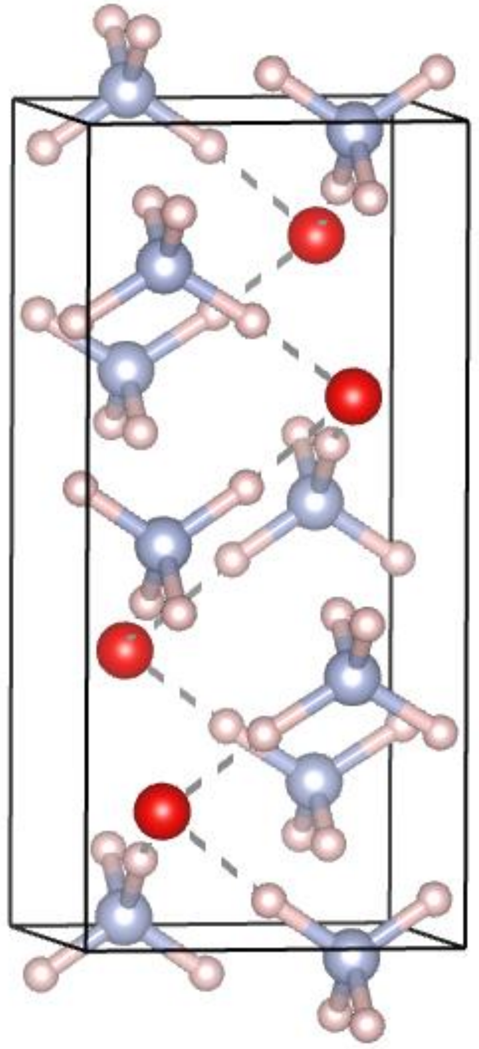




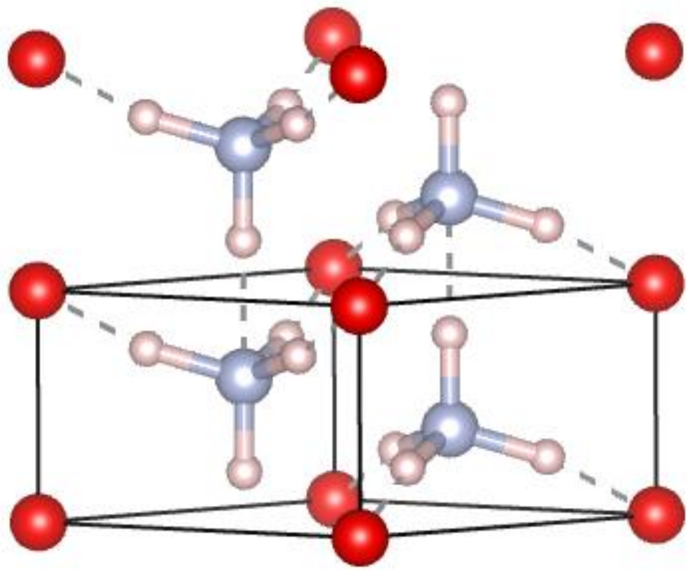
AHH phase evolution

H_2O		OH^-	O^{2-}				
AHH-I	AHH-II	ps-DMA	*Amma*	*P-3m1*	*Pnna*	*Pnma*	H_2O+NH_3

P [GPa] 5.5 23 65 110 180 505 540



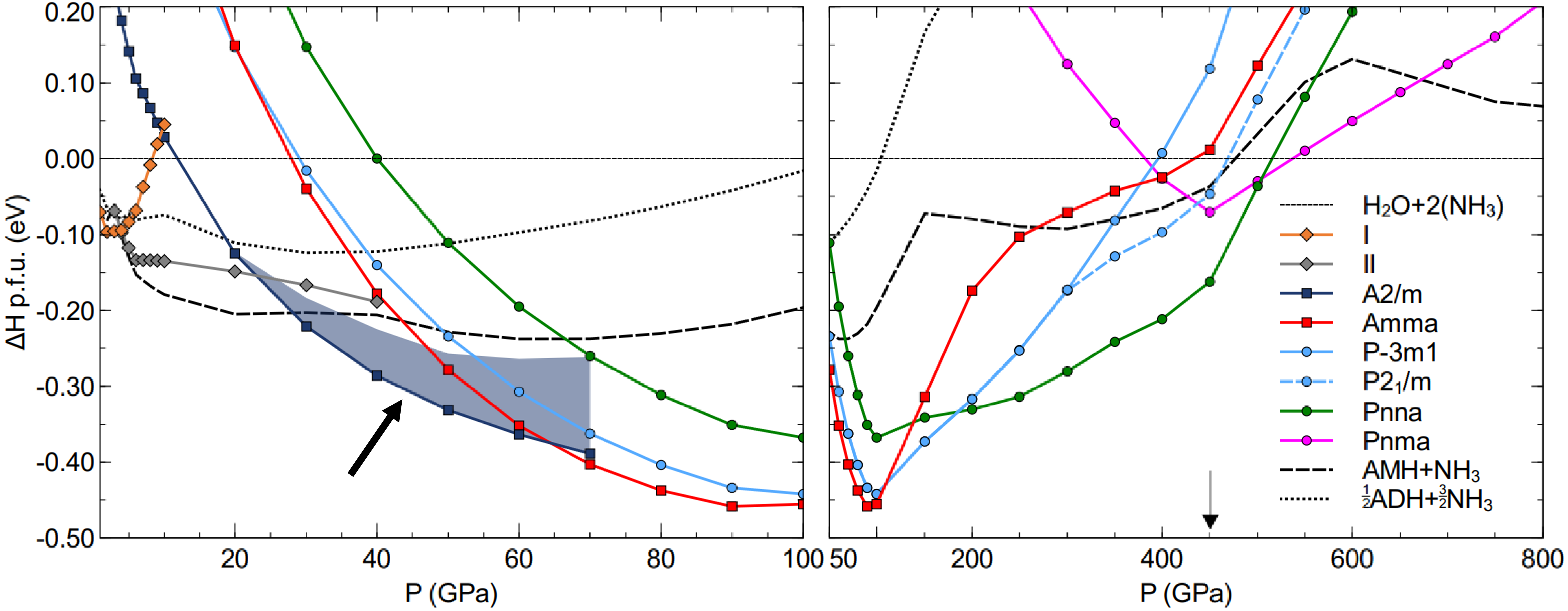
Amma



P-3m1

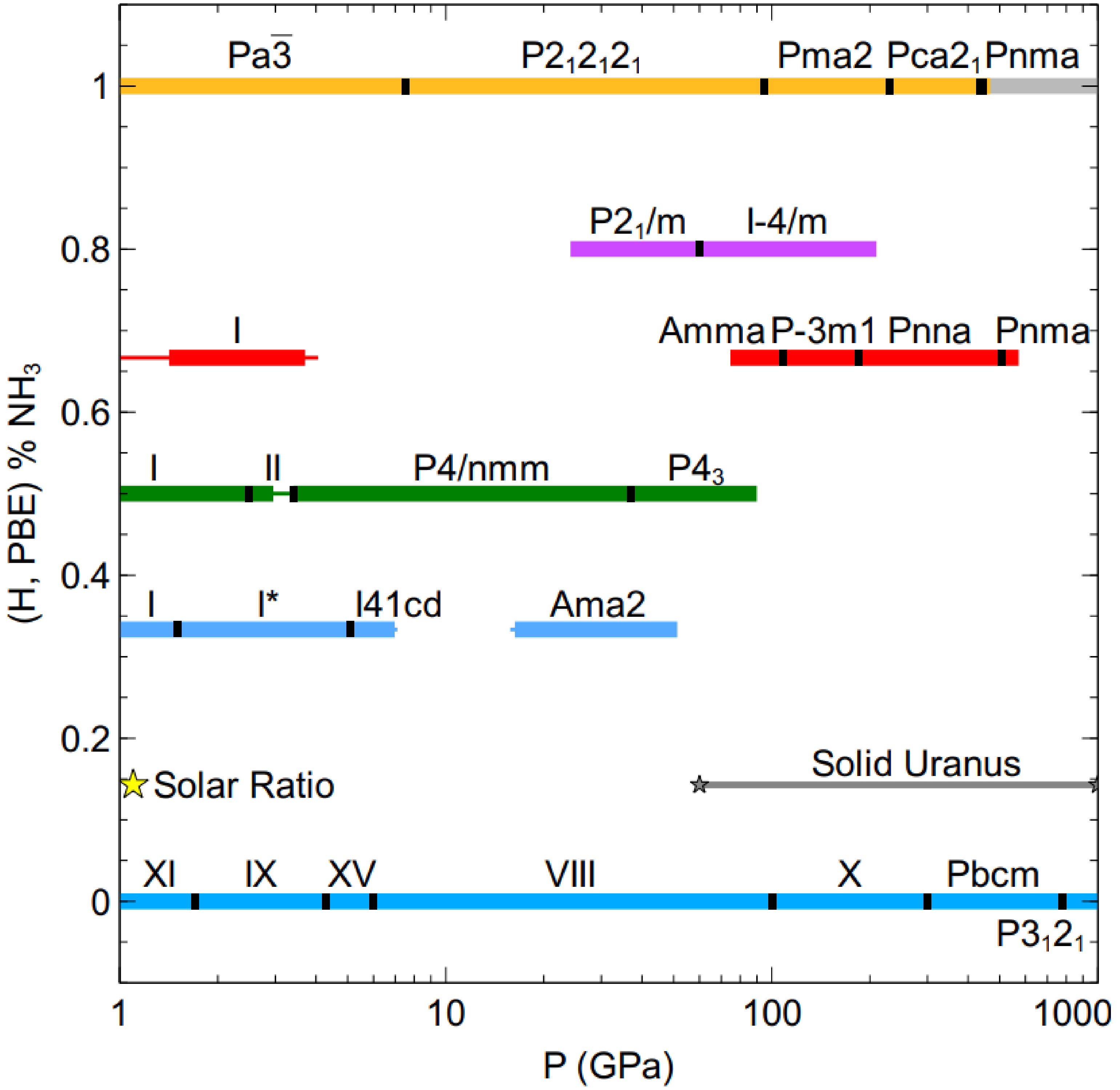
Above 65 GPa:
- Fully deprotonated water molecules
- Ionic structures $O^{2-}(NH_4^+)_2$

Disordered region

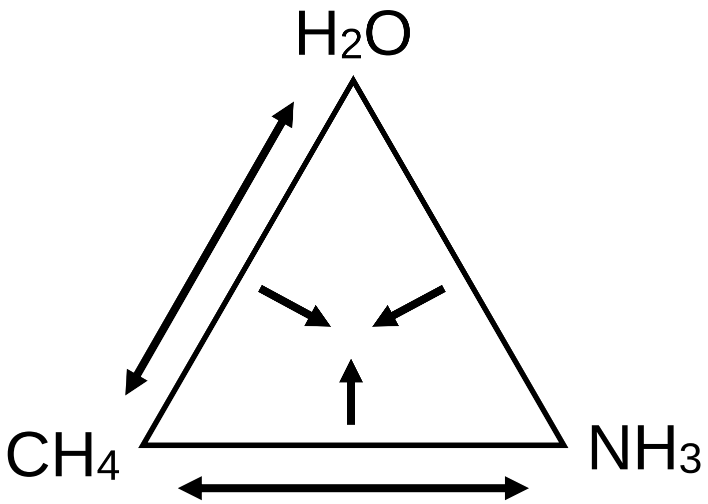


V. Naden Robinson *et al.*, *Proc. Natl. Acad. Sci.*, 2017.

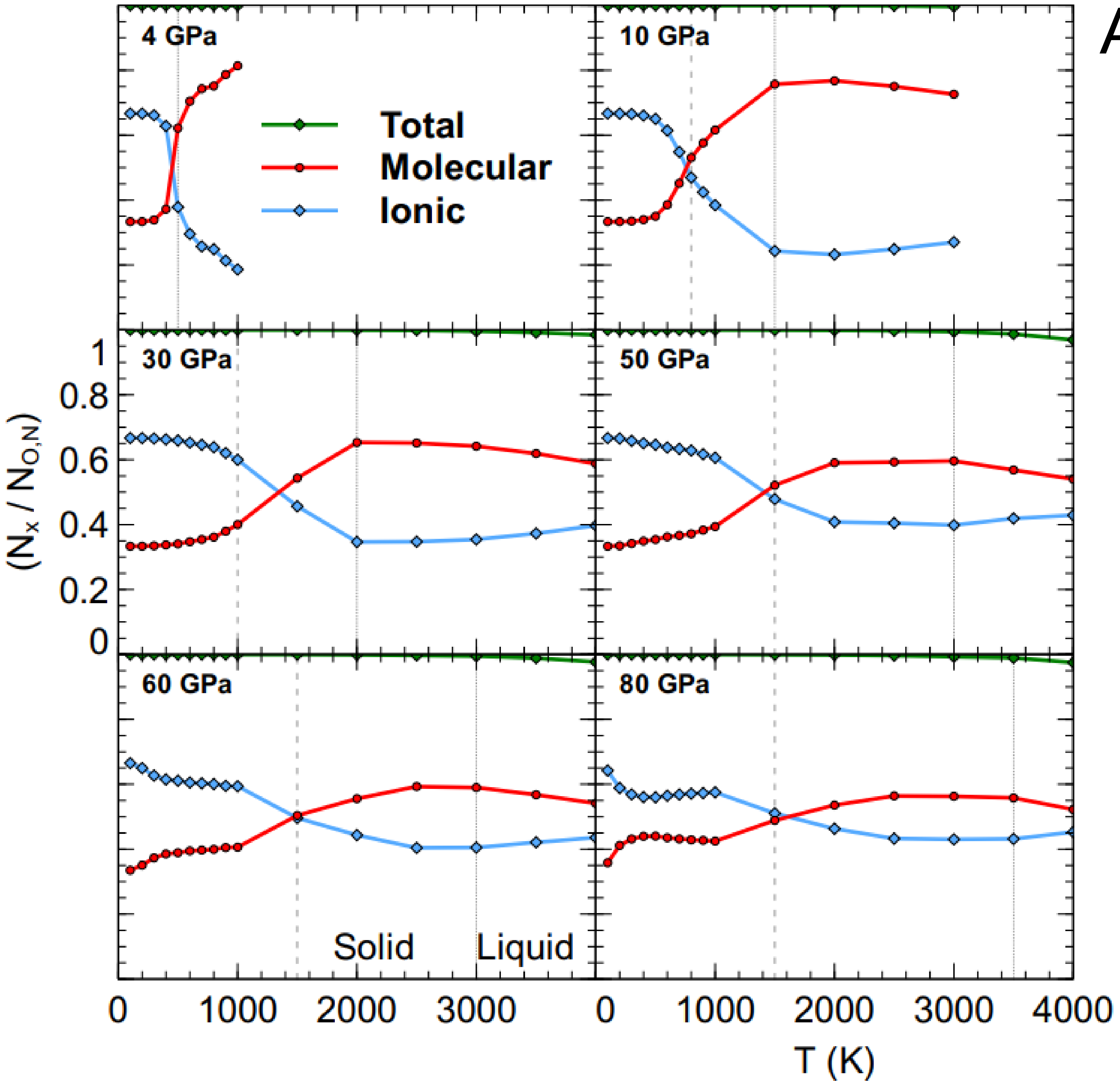
What next?



- Independent of XC functional
- IR and Raman Spectroscopy
- Heat these up
- Low pressure regime
- (Superionic) Alloys in the Icy Planets



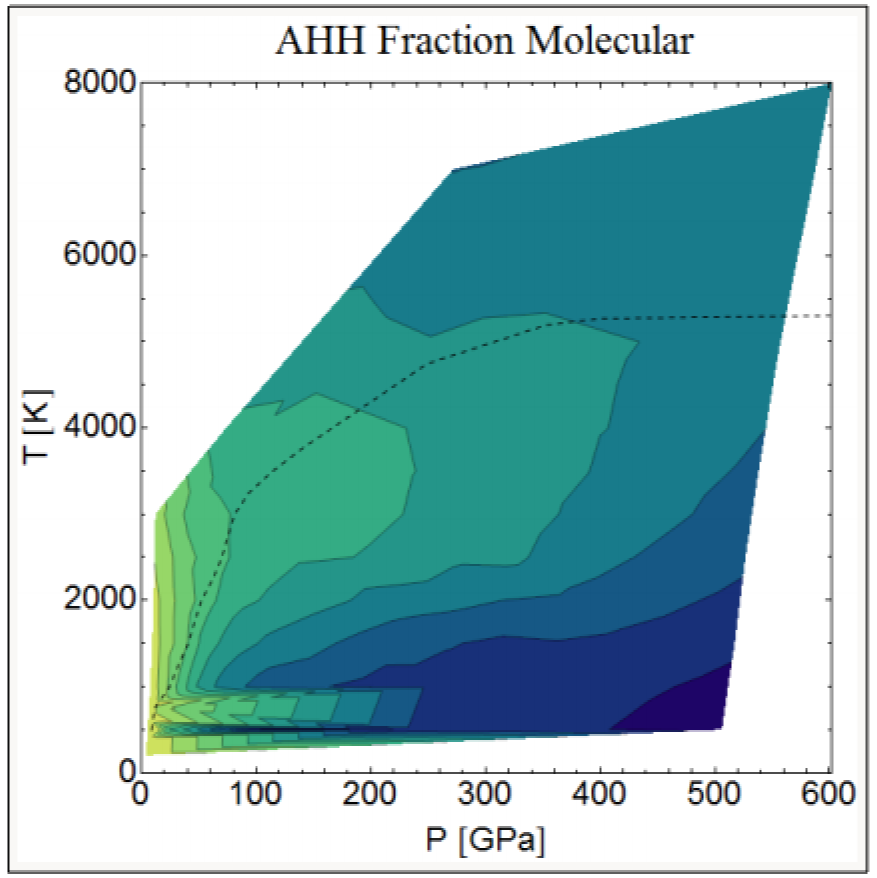
What's inside?

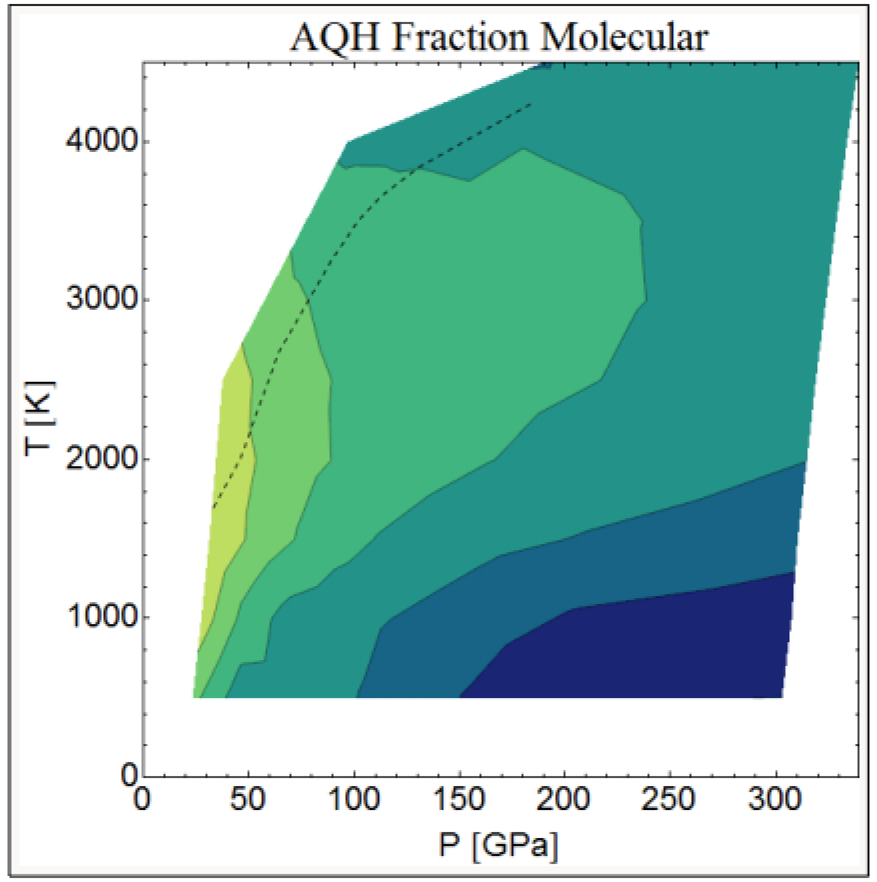


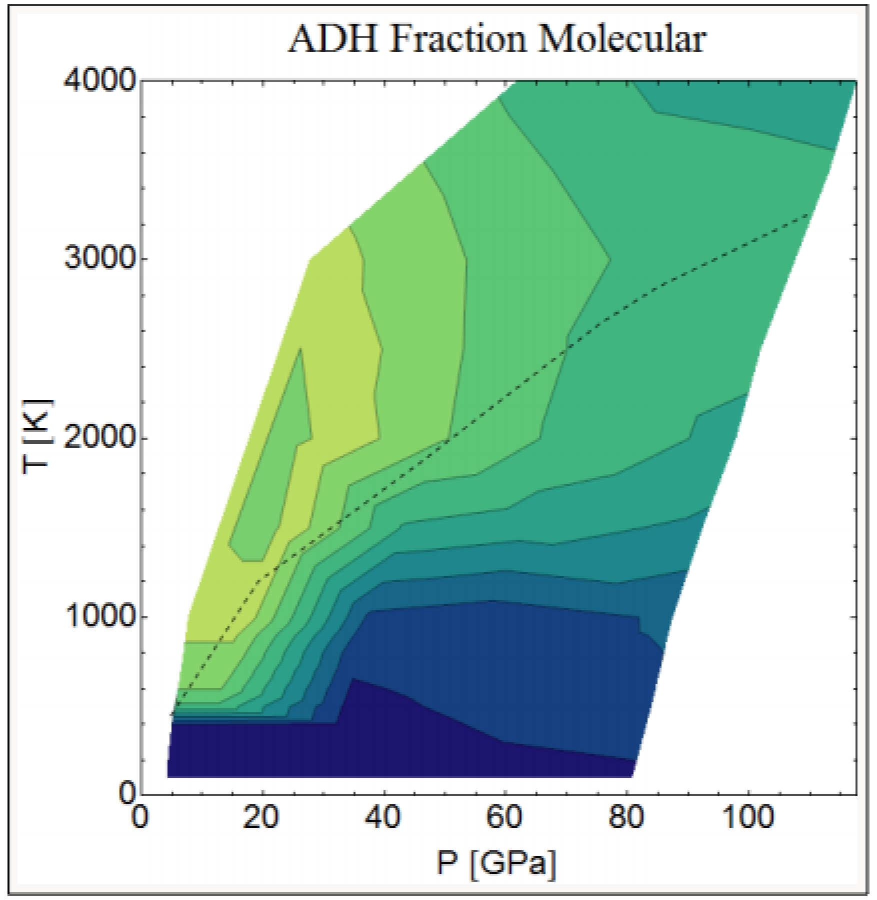
ADH [1:2]

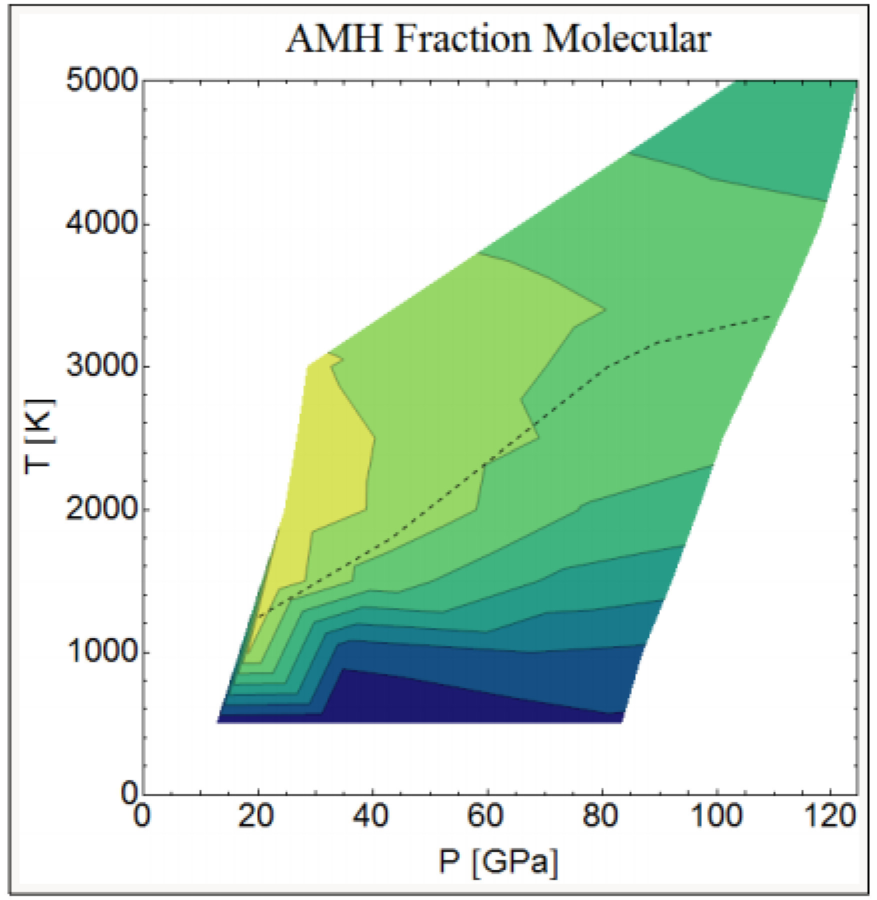
r_{cut}= 1.15 Å

Molecular Nature

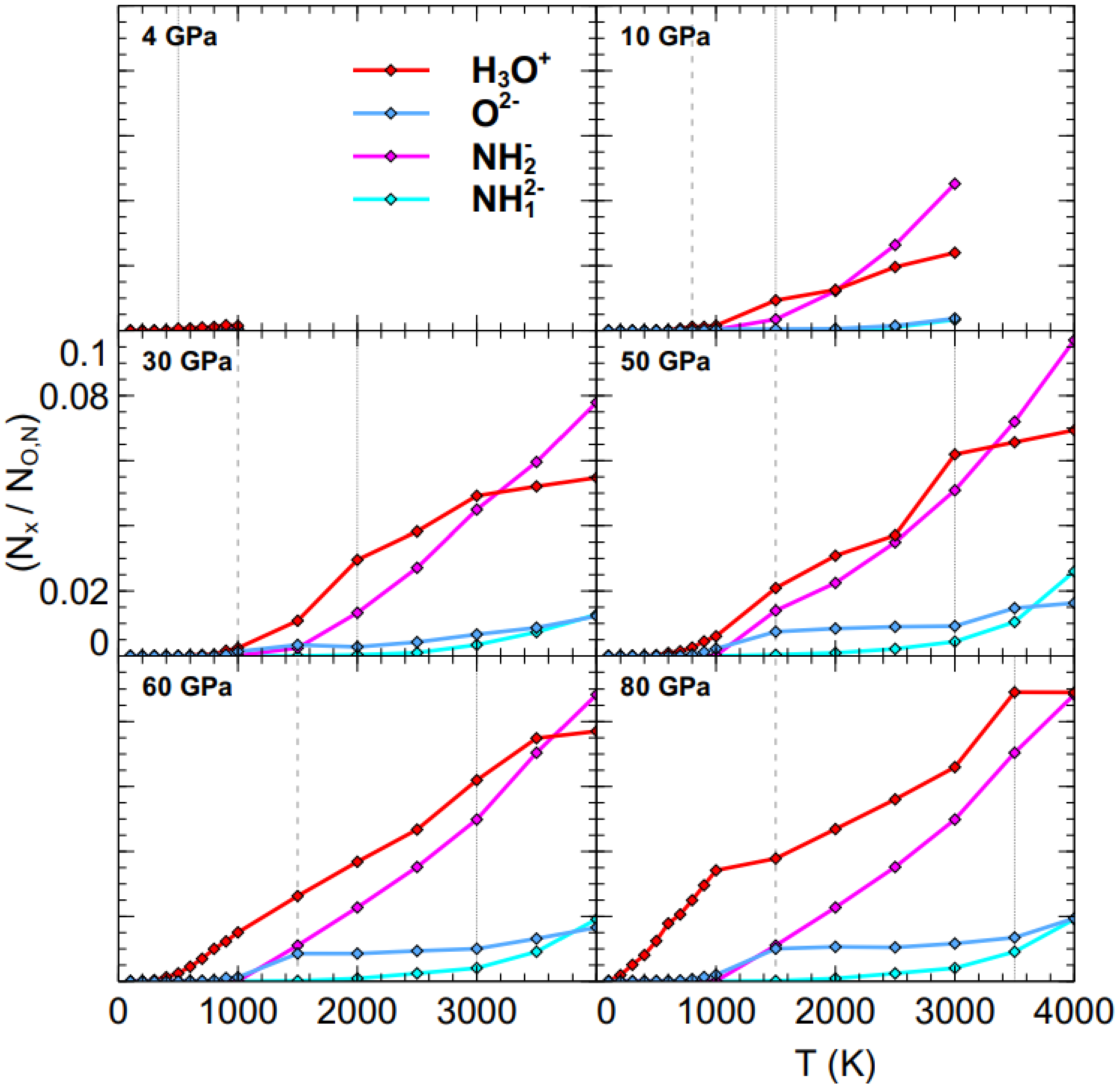


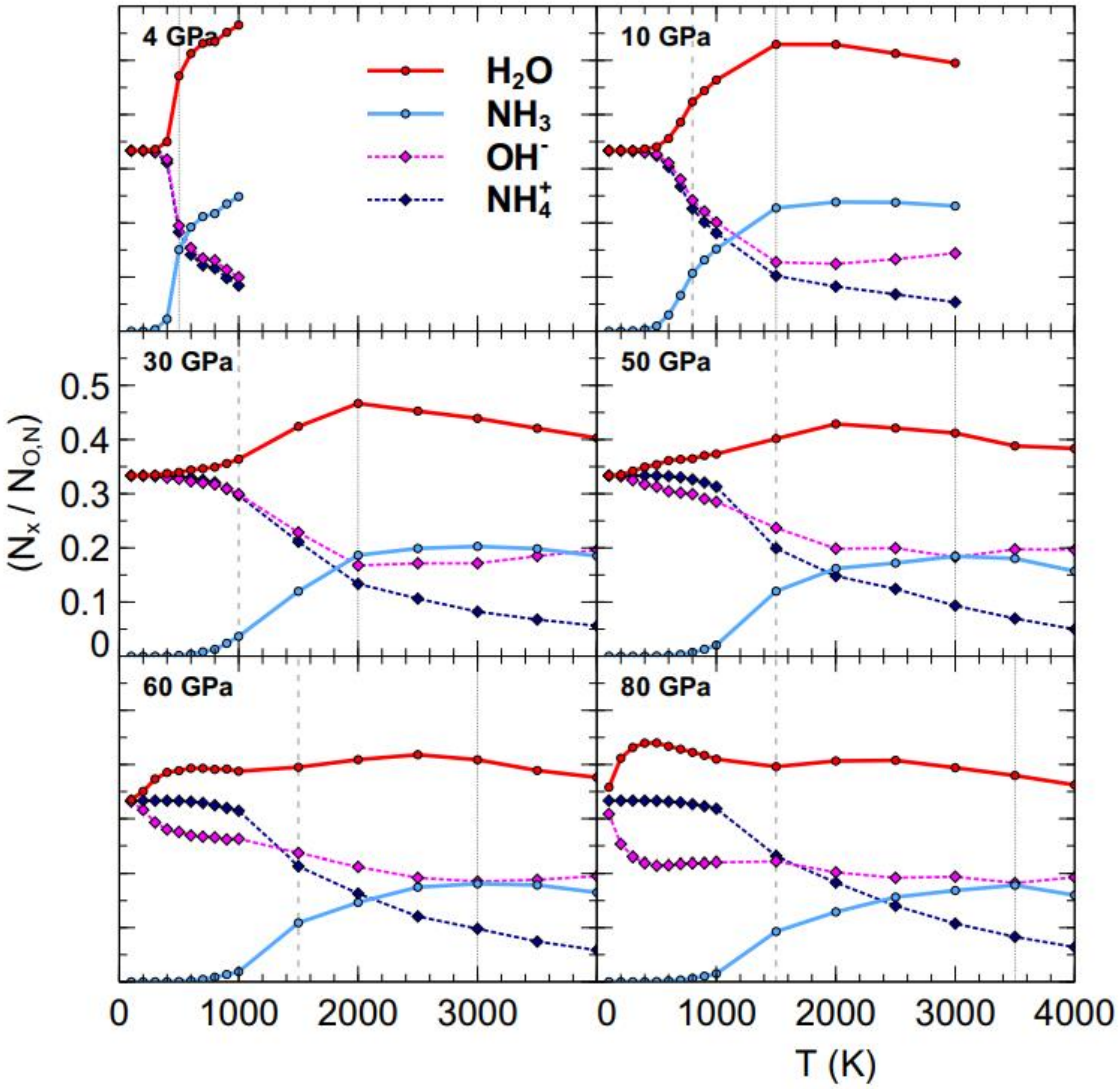






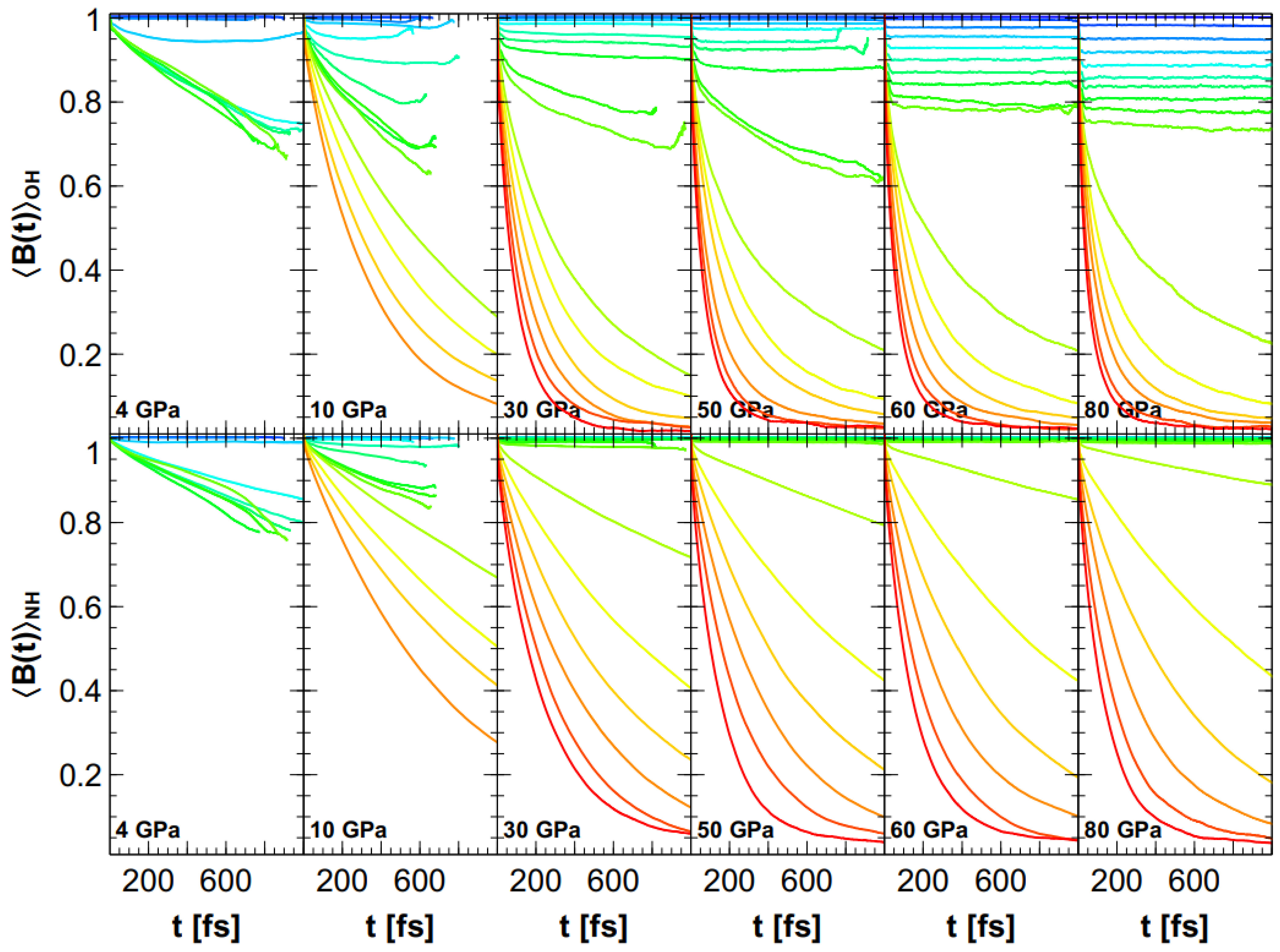
Unit types





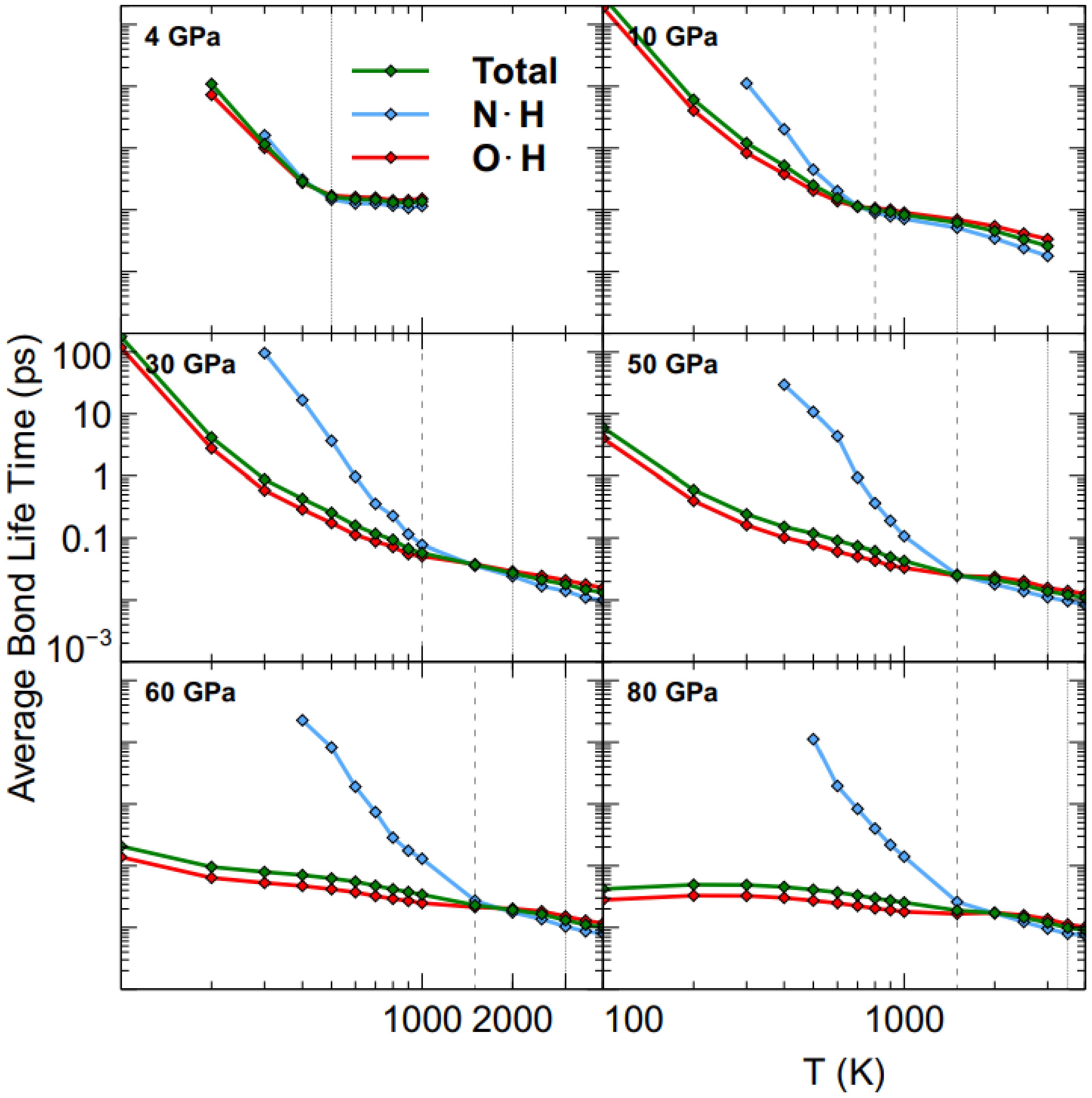
ADH [1:2]

BAC



⟨B(t)⟩OH
⟨B(t)⟩NH
1
0.8
0.6
0.4
0.2
4 GPa
10 GPa
30 GPa
50 GPa
60 GPa
80 GPa
200 600
t [fs]

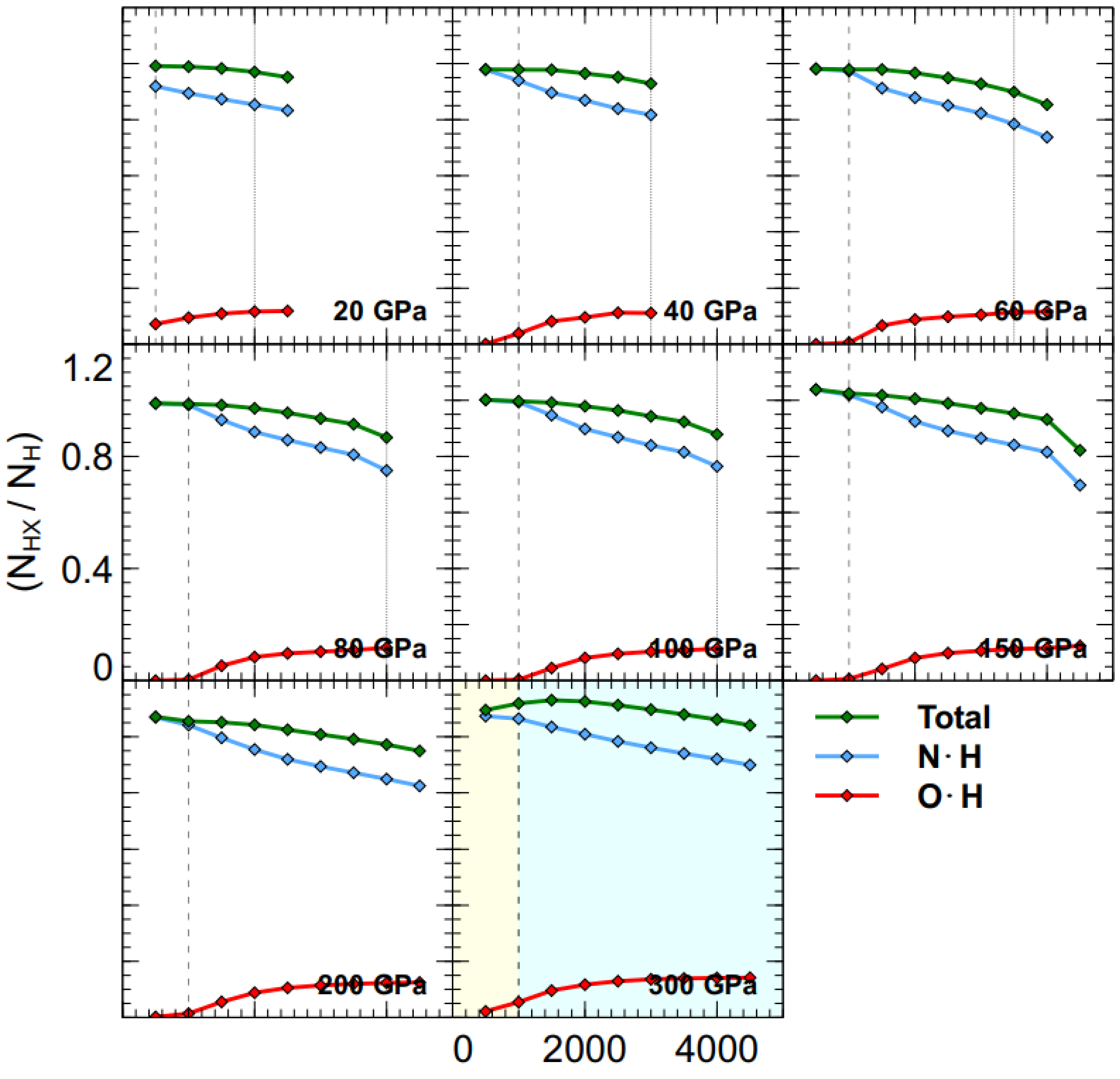
Bond life times



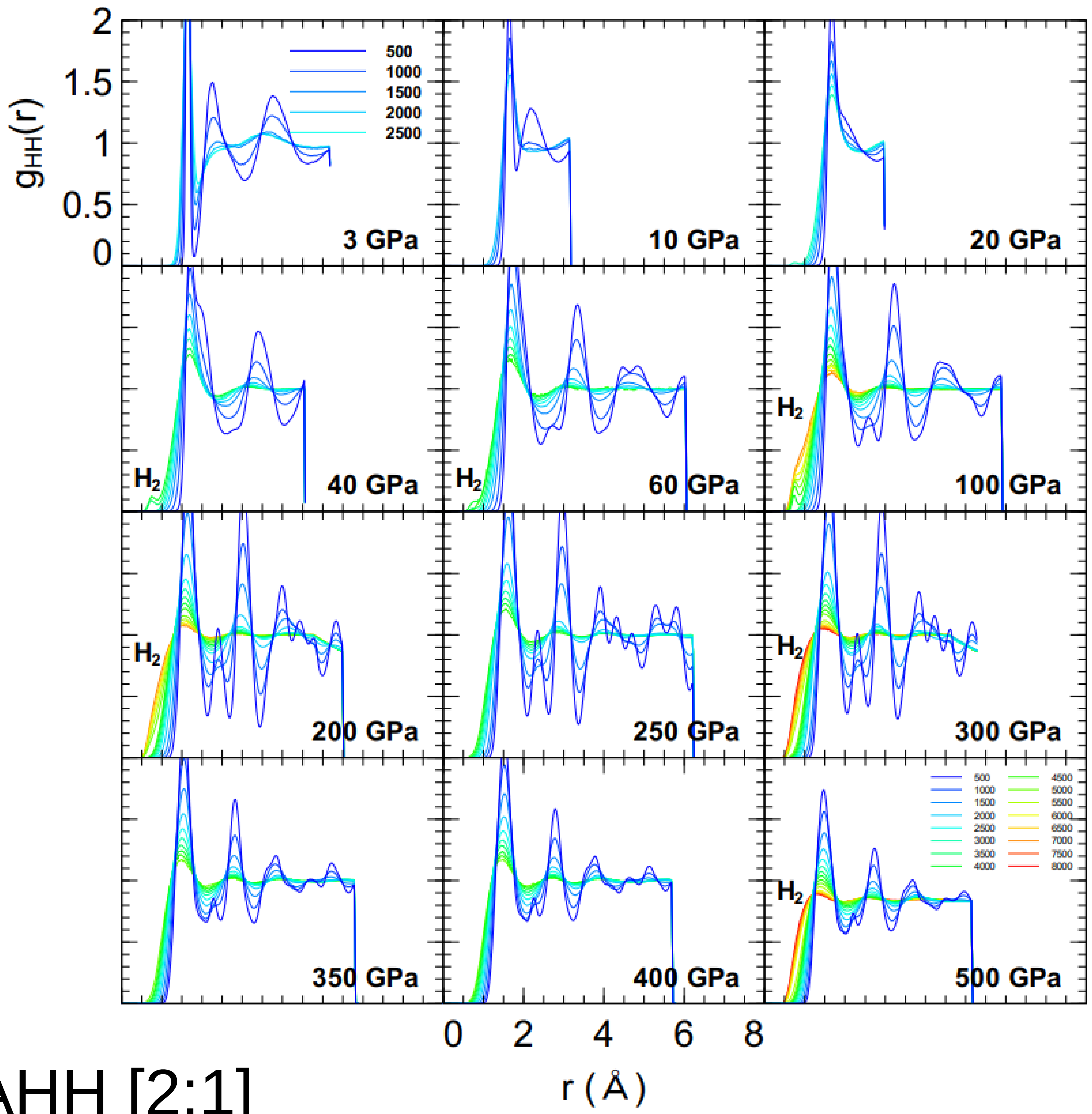
ADH [1:2]

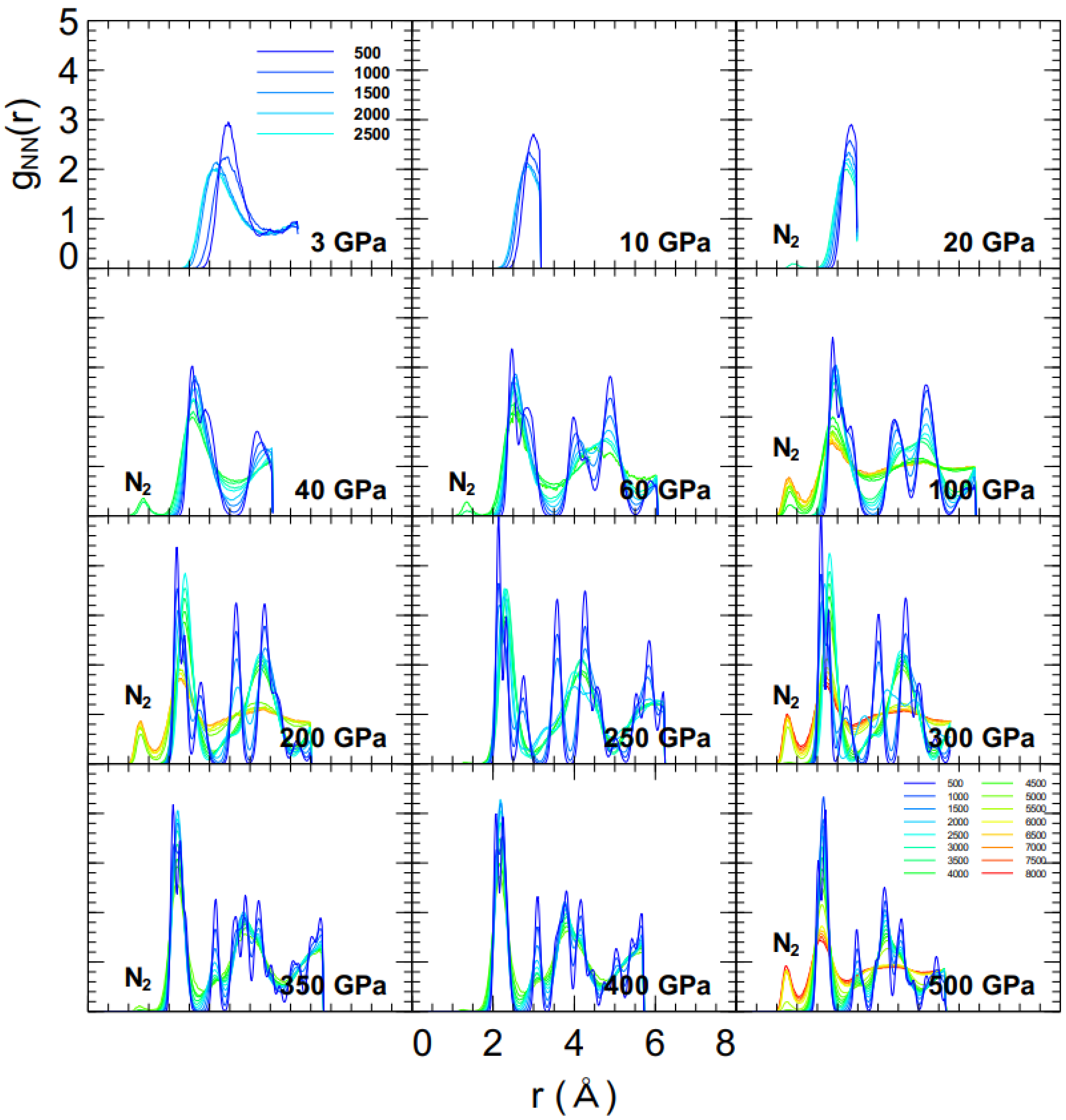
Number of O/N-H bonds

AQH [4:1]



Decomposition chemistry H_2, N_2, NO

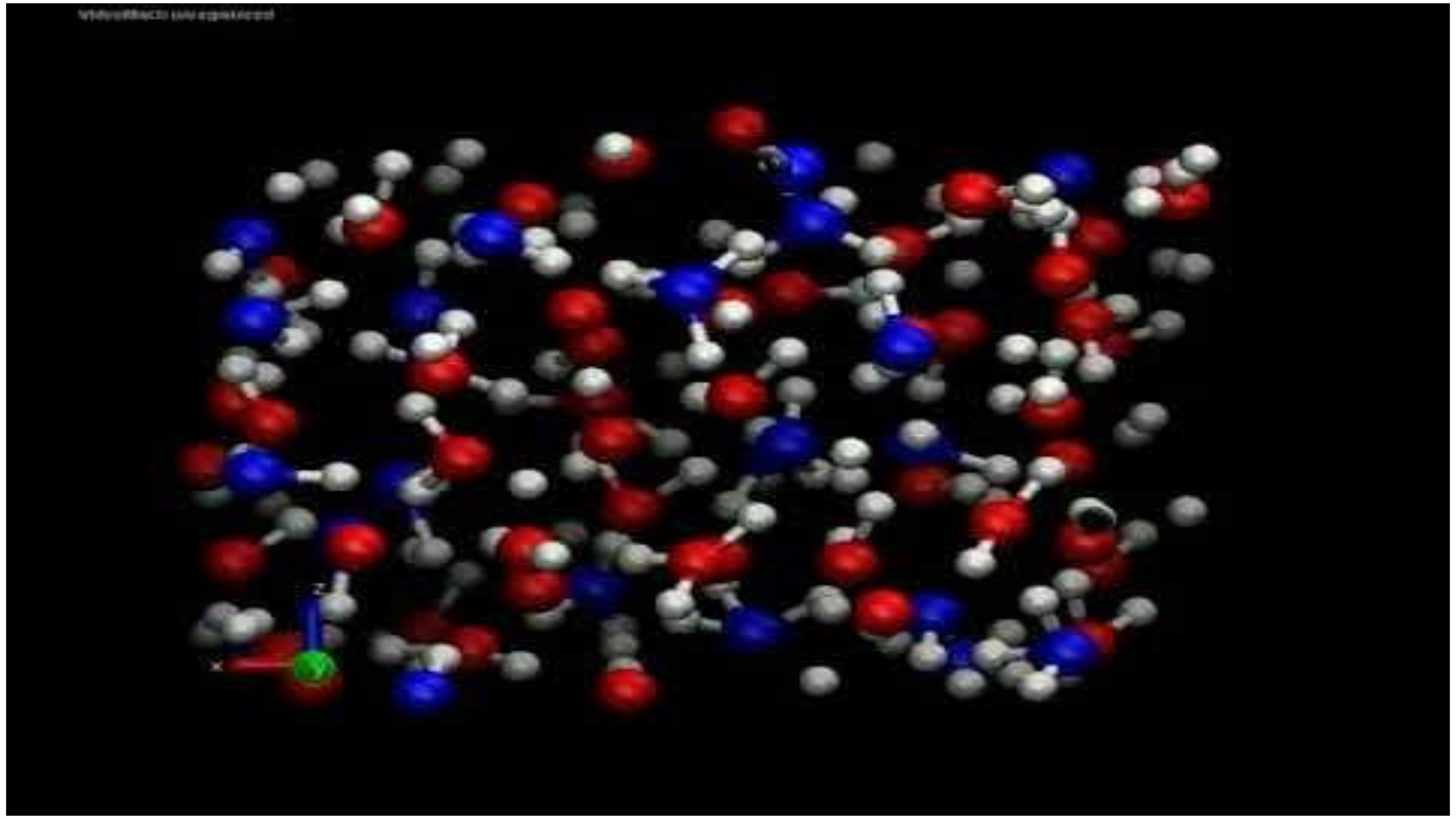


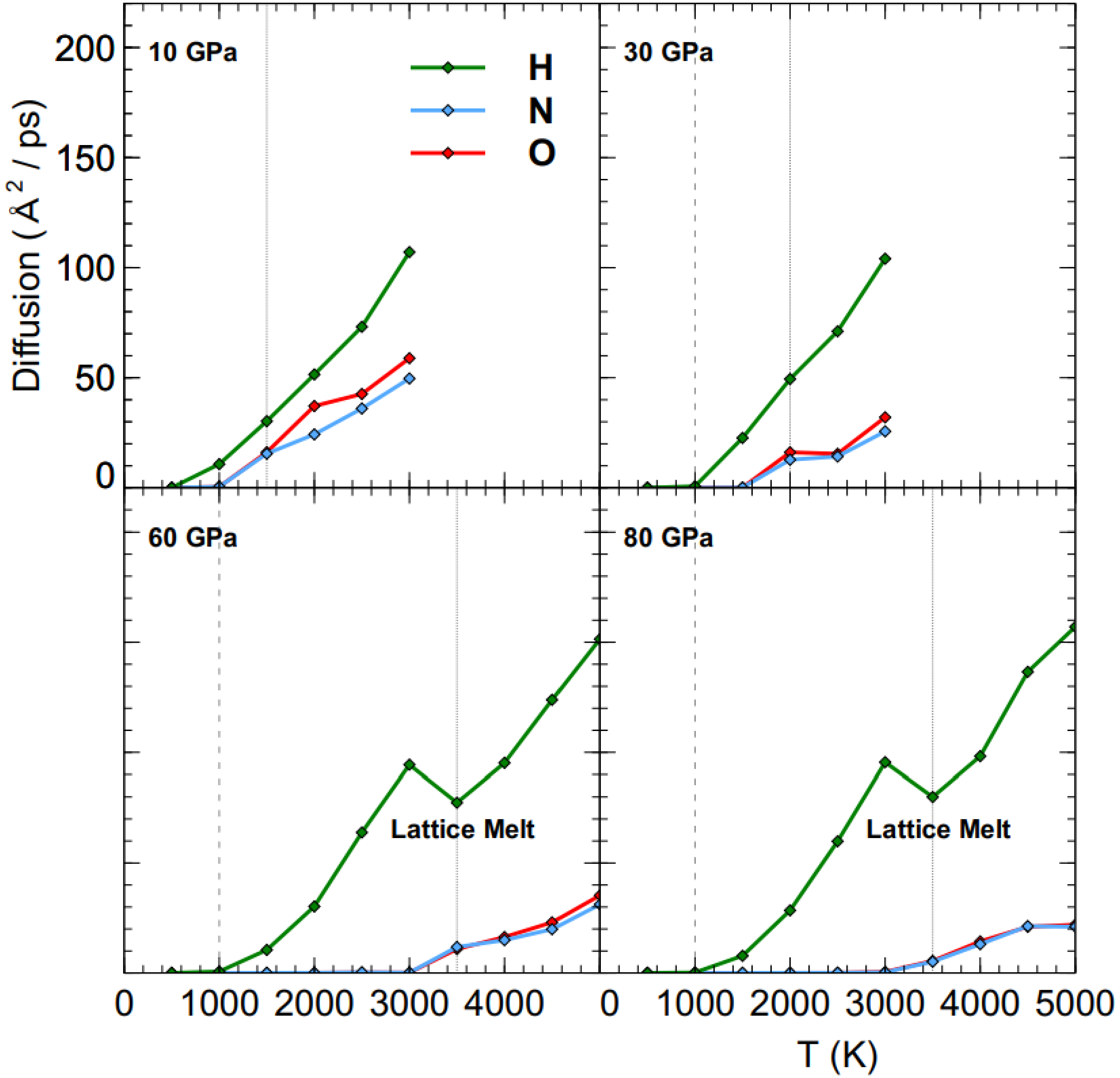


AHH [2:1]

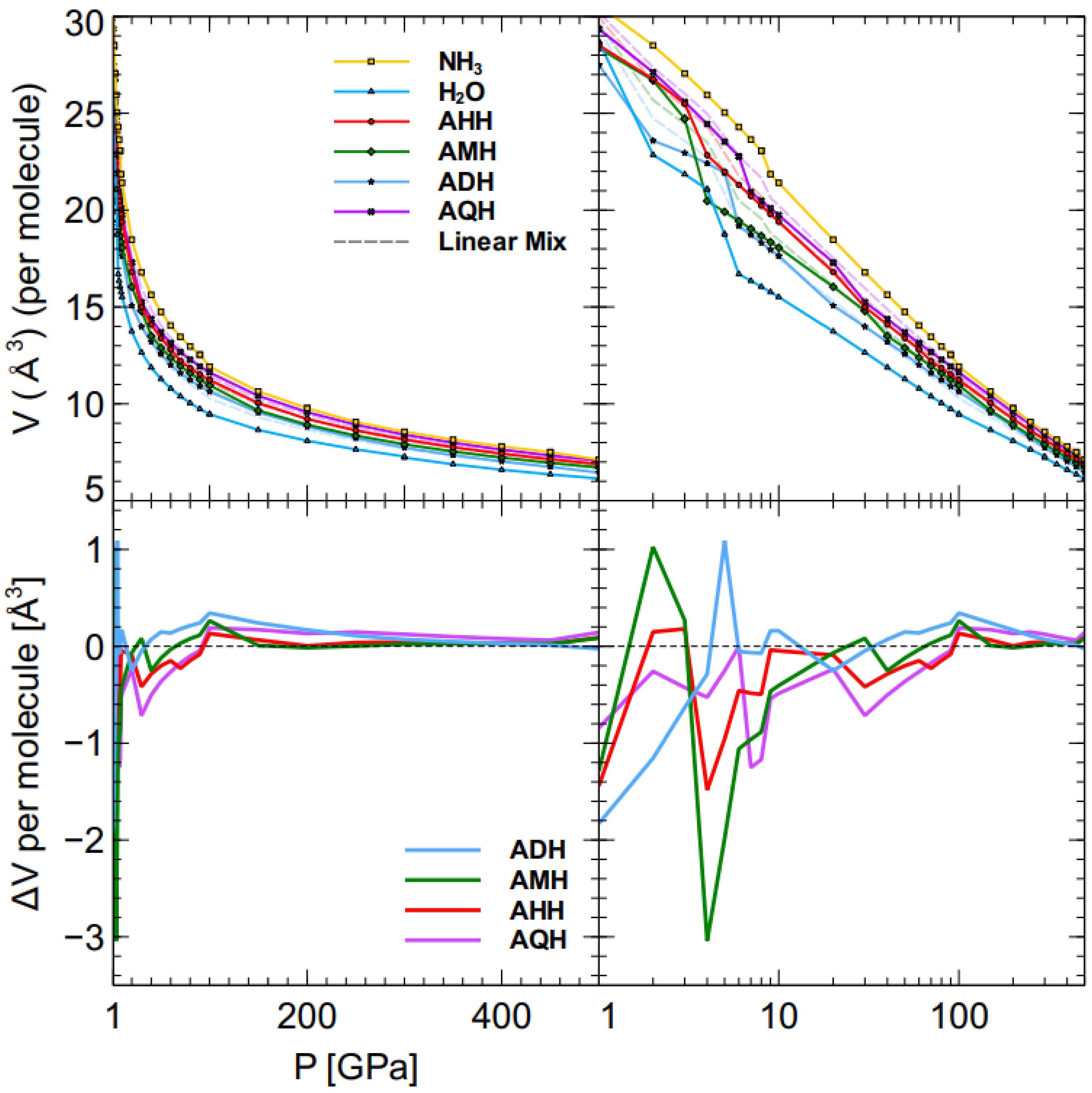
Diffusion differences

AMH [1:1]



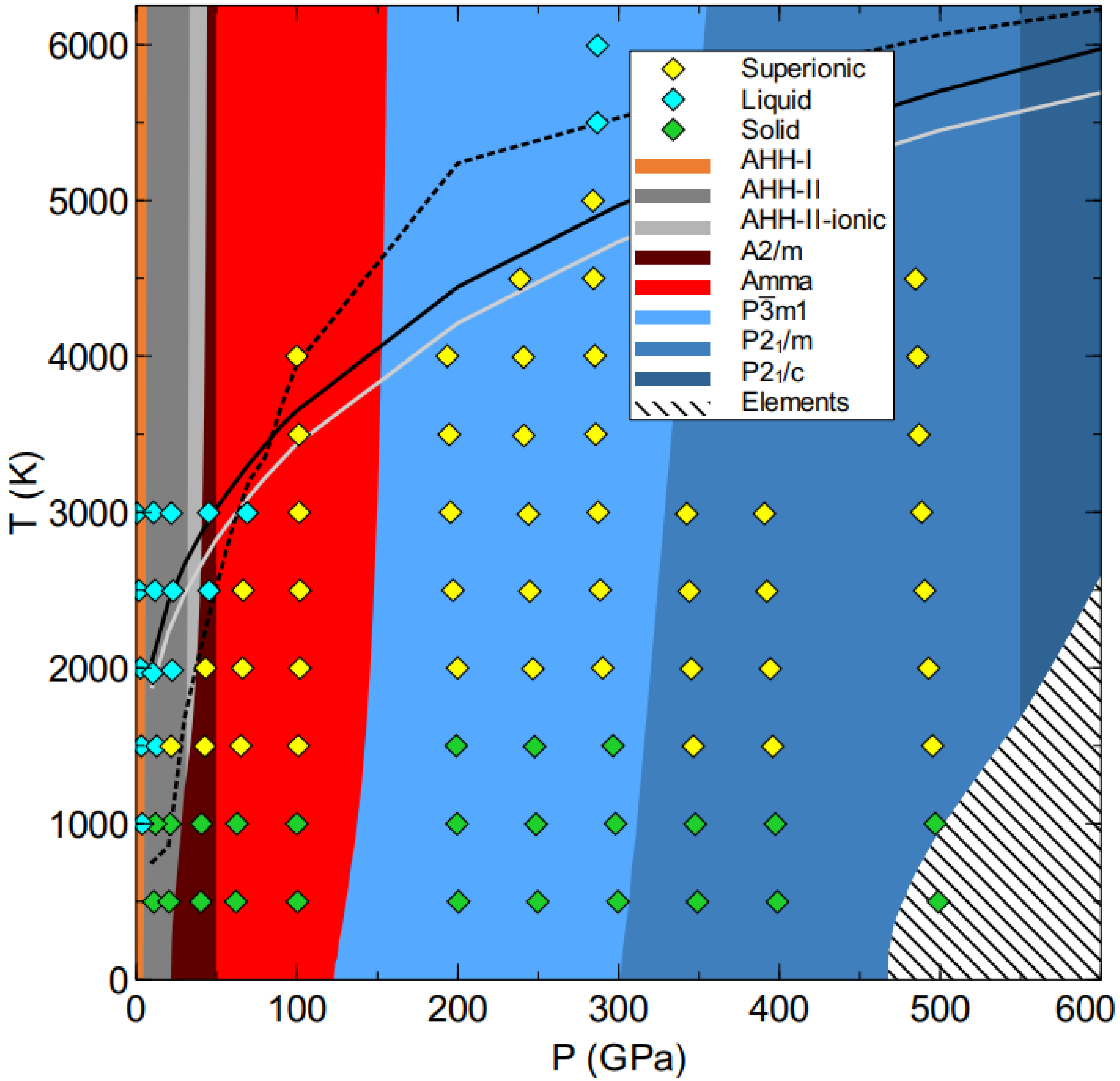


Equation of State

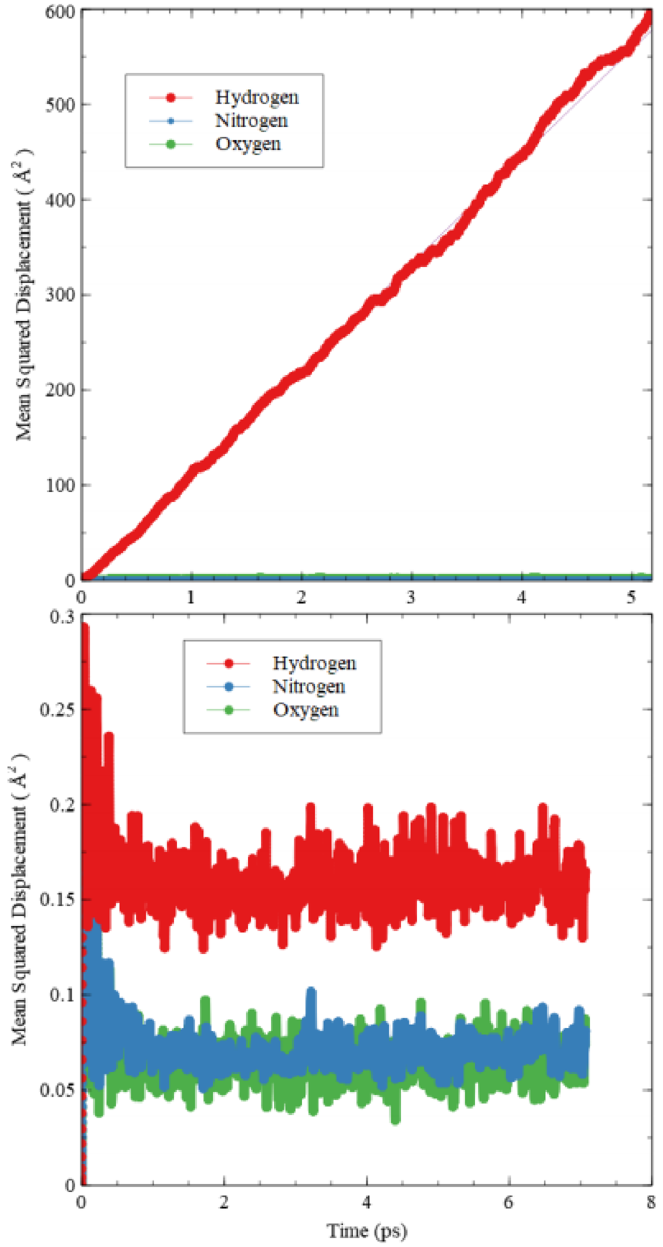


Preliminary data on superionicity

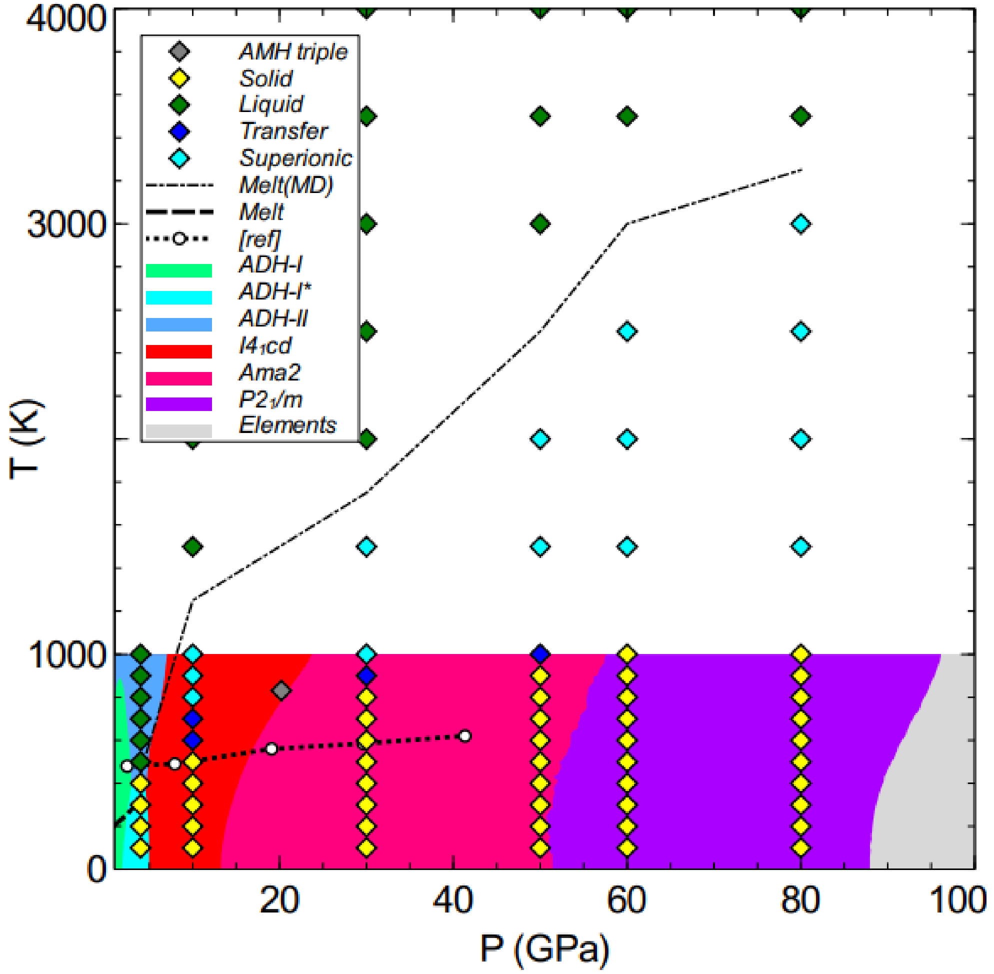
Ab-initio MD on AHH phases



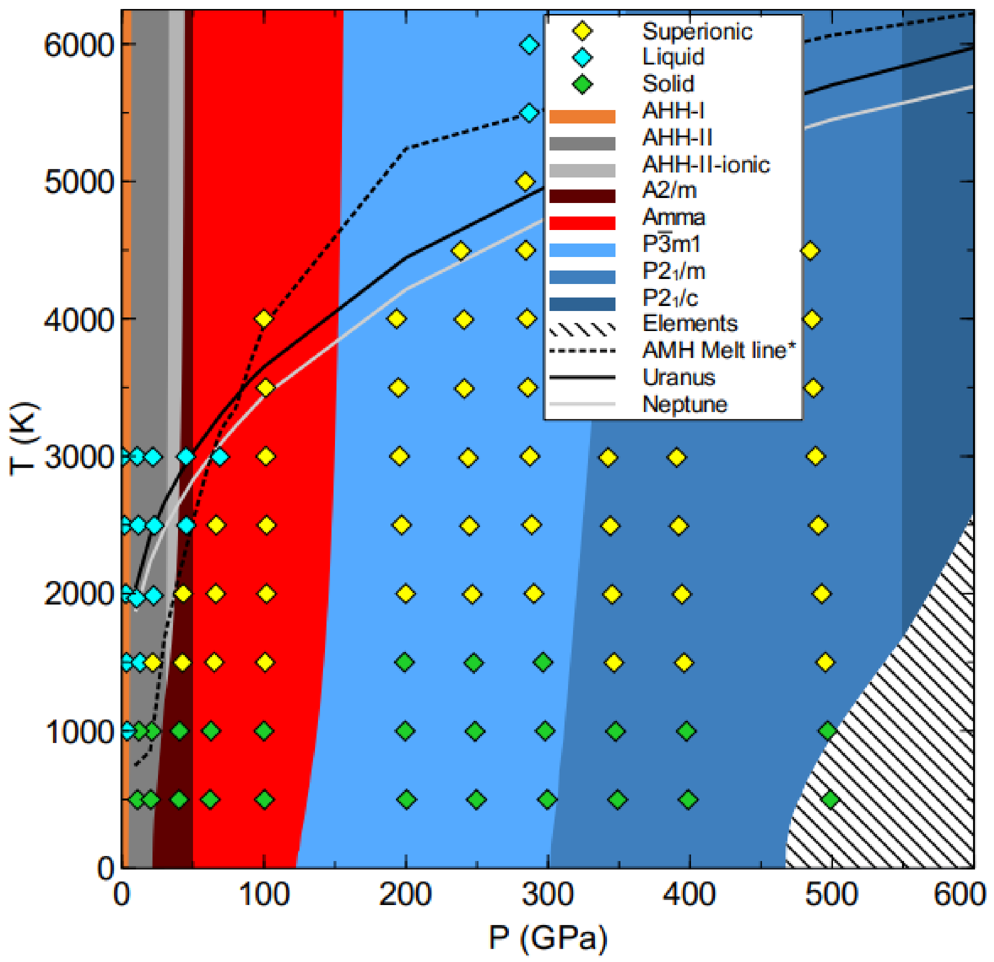
Superionicity (WIP)



Thanks to Jacob F. Christiansen

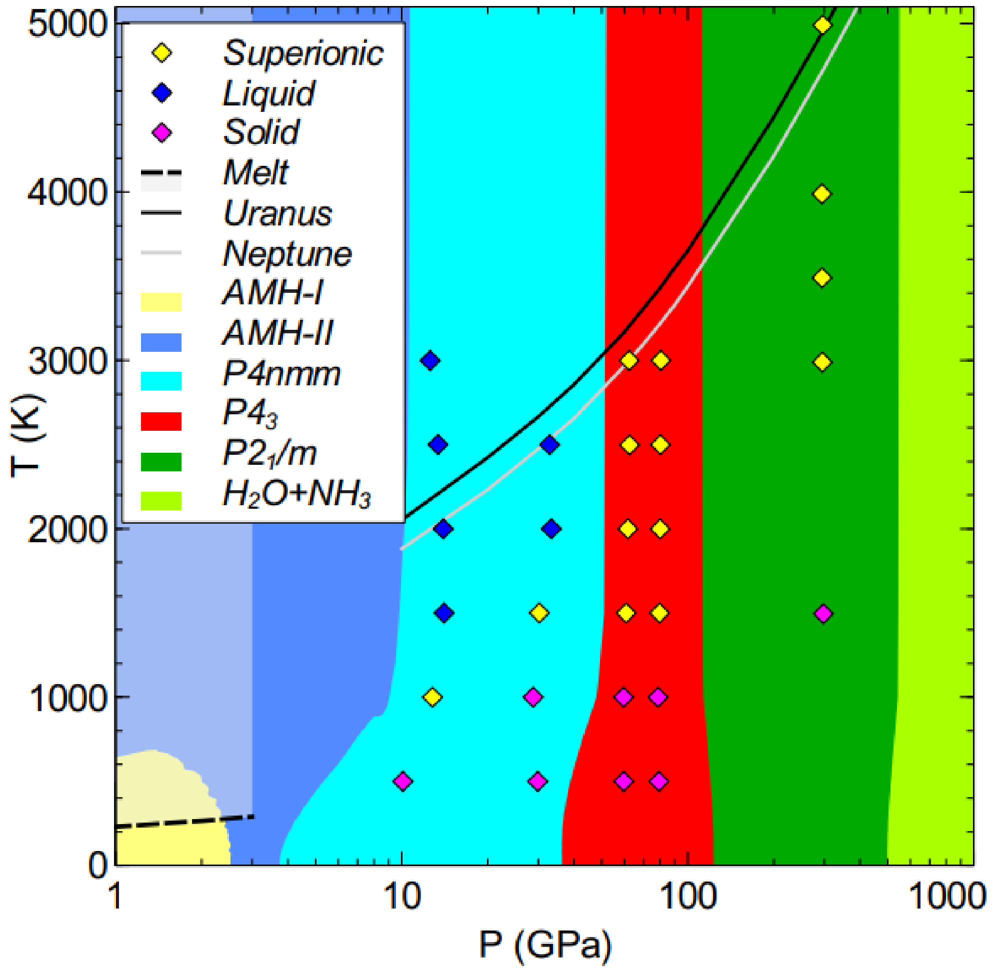


ADH

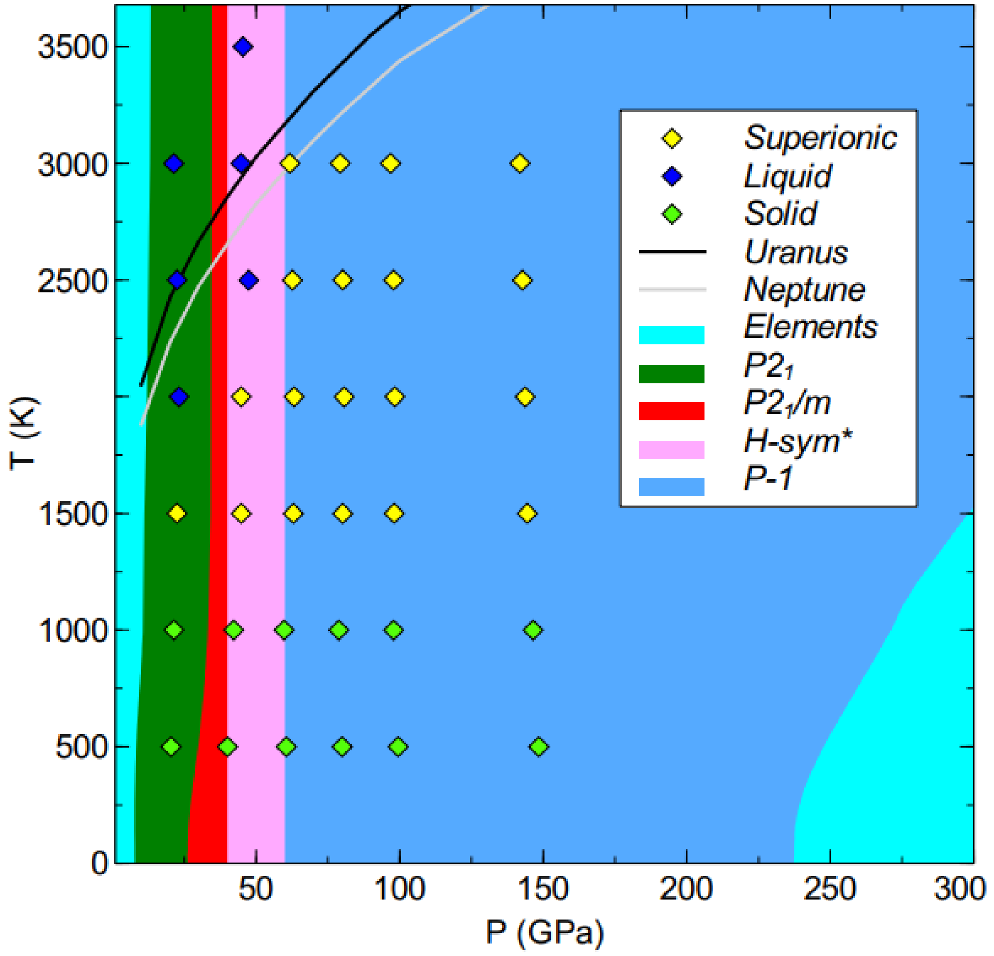


AHH

AMH

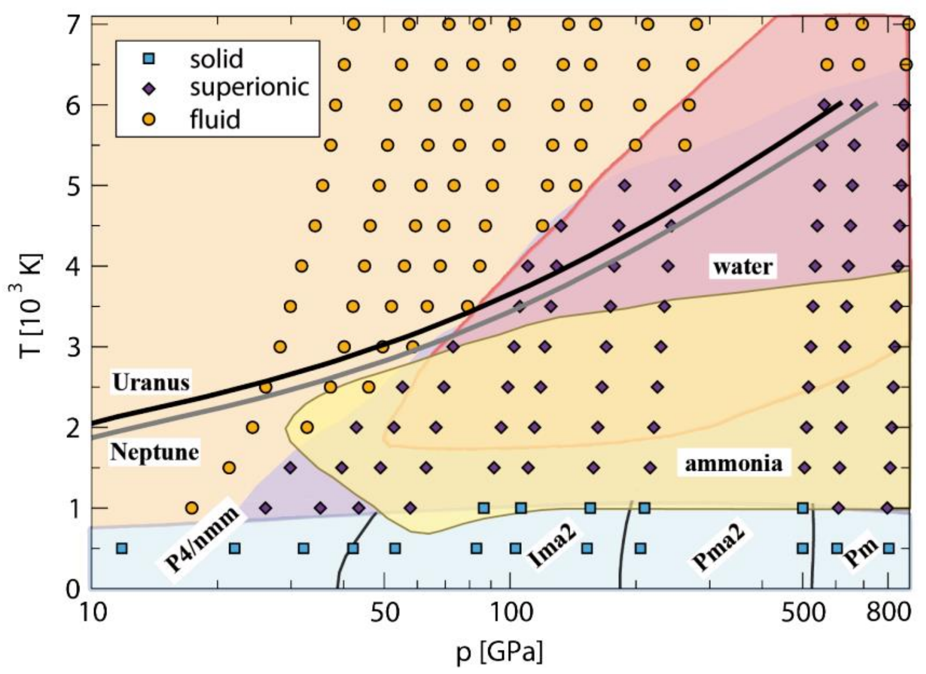


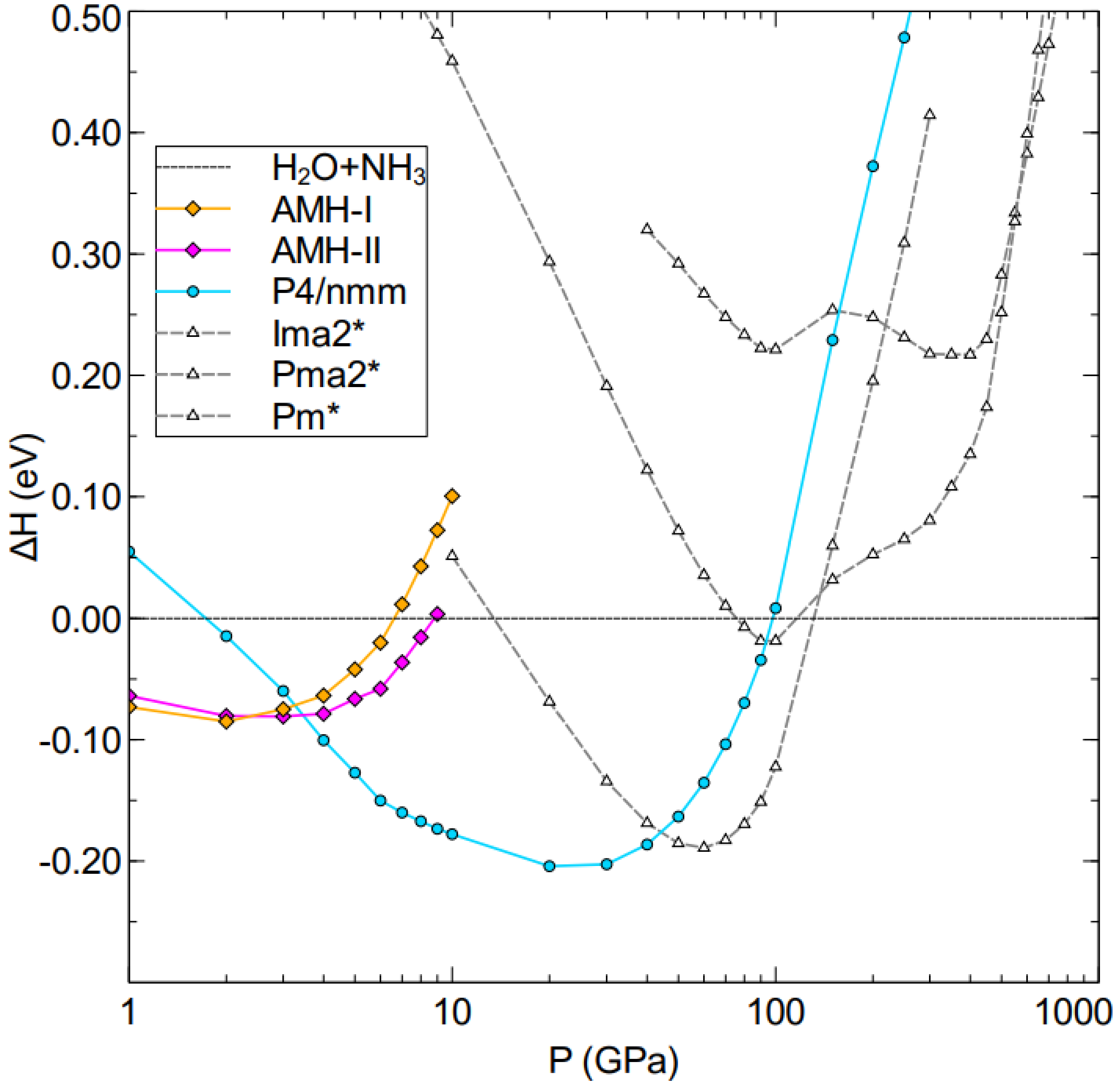
AQH



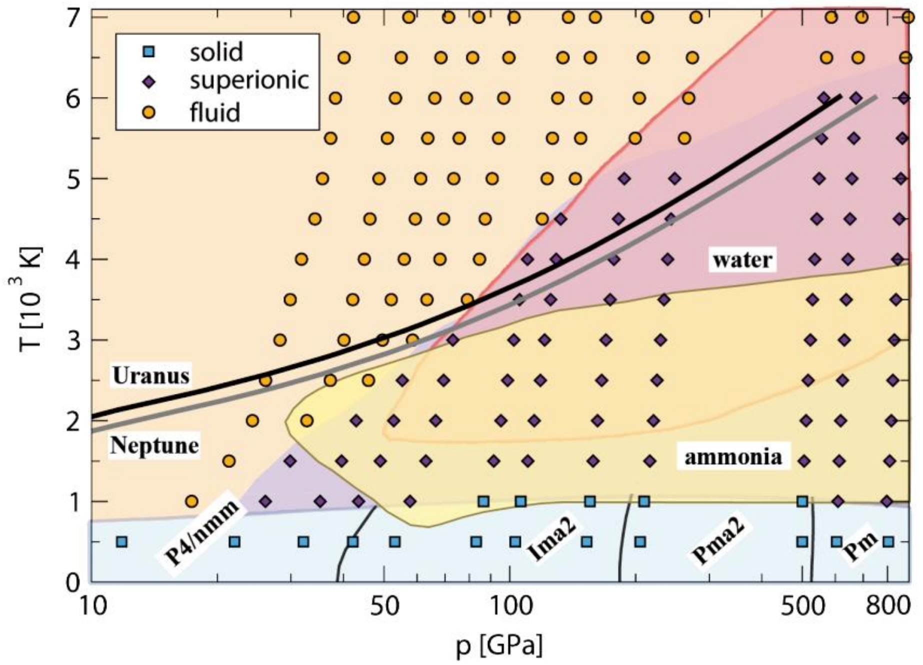
Revisiting AMH

No stable phases at high pressures?

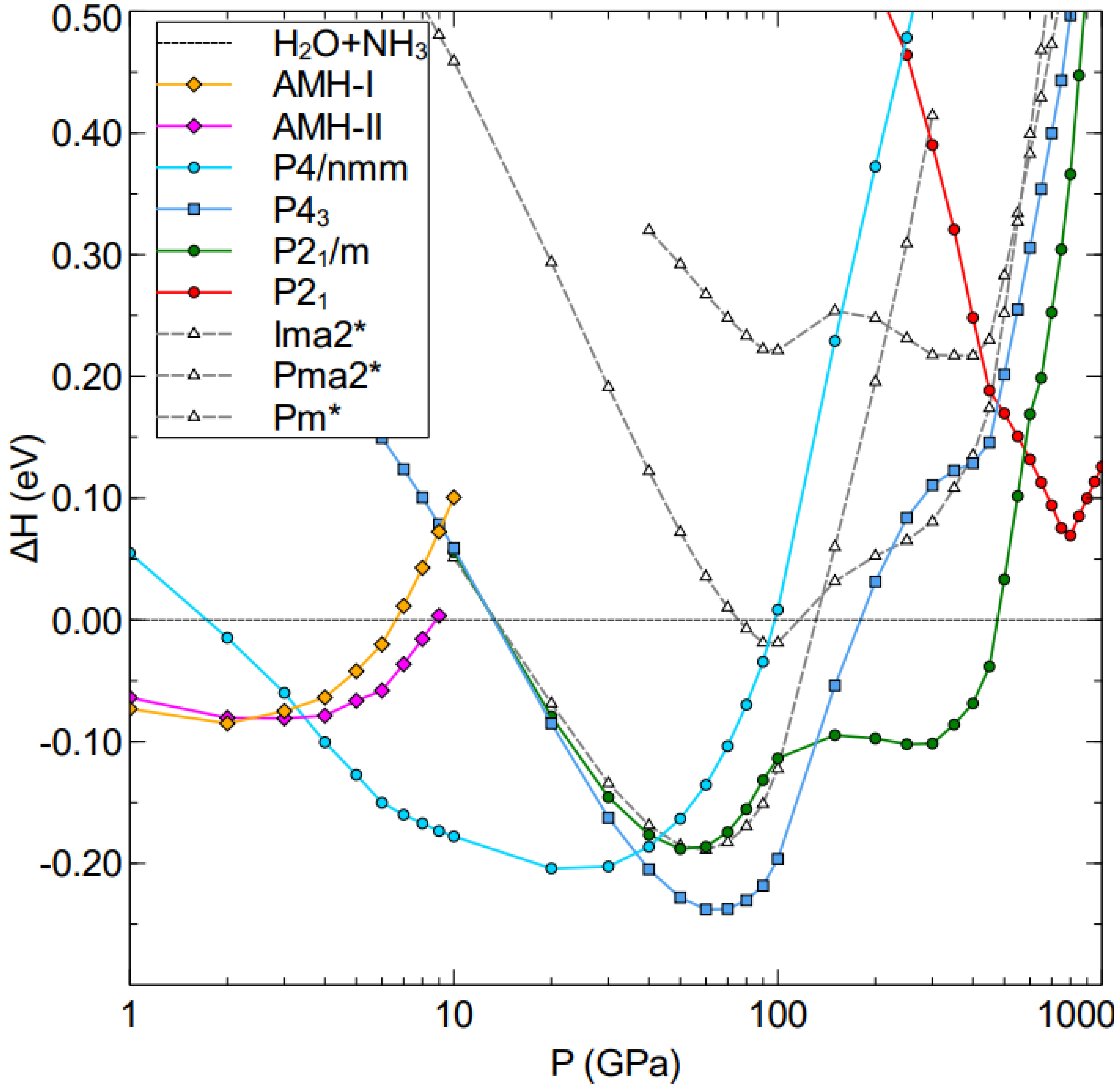




AMH structure searching

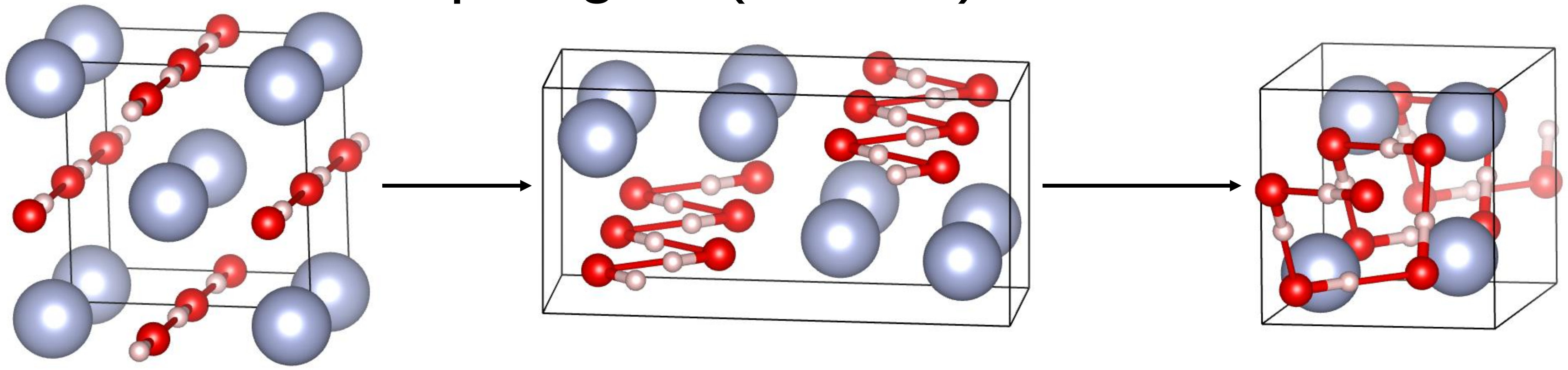


Phase	Stable to
AMH-I	2.5GPa
AMH-II	3.5GPa
P4/nmm	35GPa
P4₃	140GPa
P2₁m	470GPa



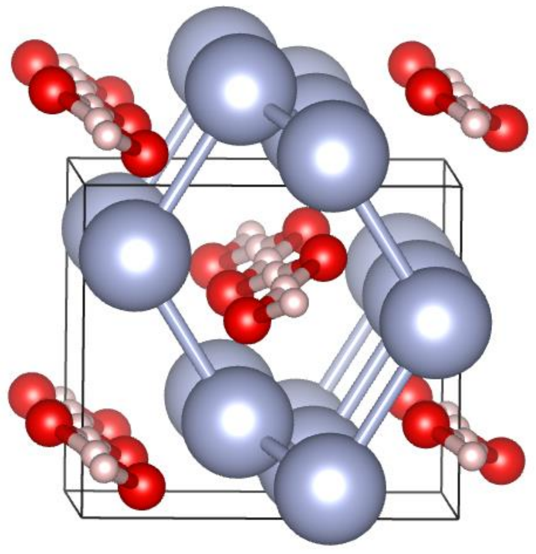
AMH high-pressure phases

H-bond chain topologies (70GPa)



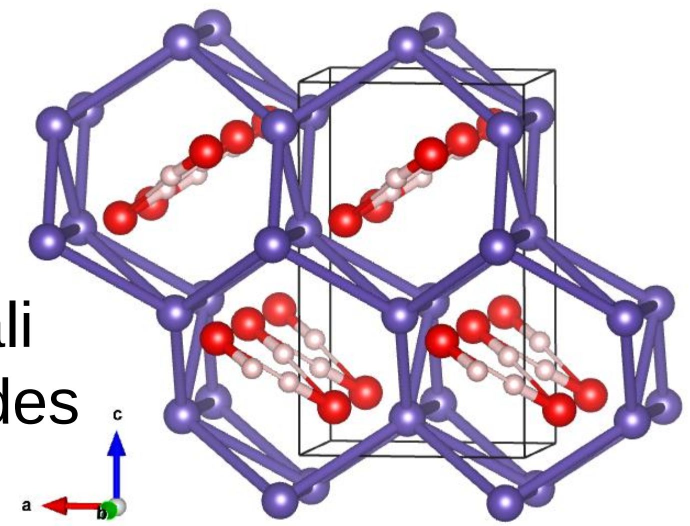
P4/nmm (2012) *Ima2 (2015)* *$P4_3$ (2017)*

H-bond symmetrisation (140 GPa)



$P2_12_12_1$

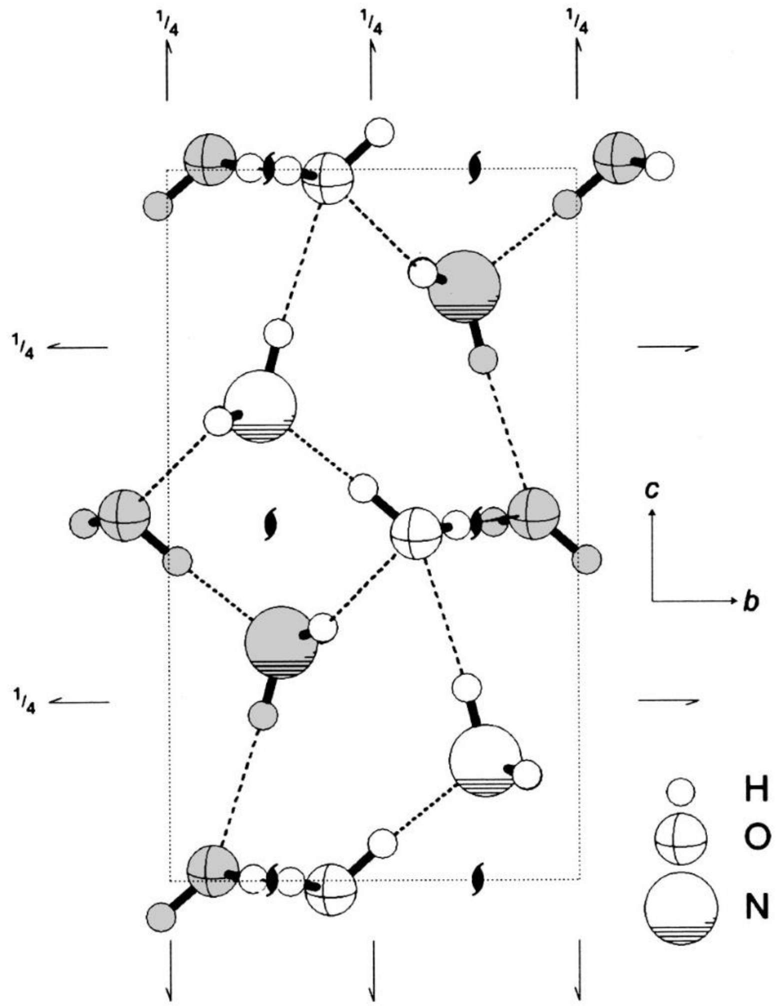
C.f. alkali hydroxides



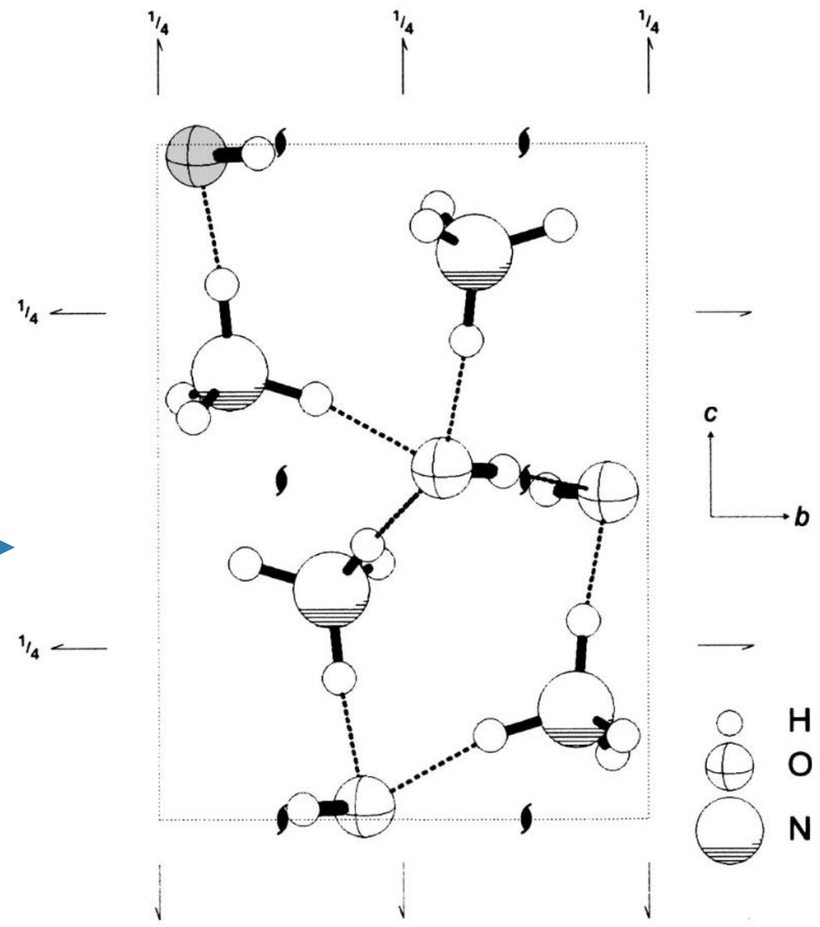
LiOH, CsOH

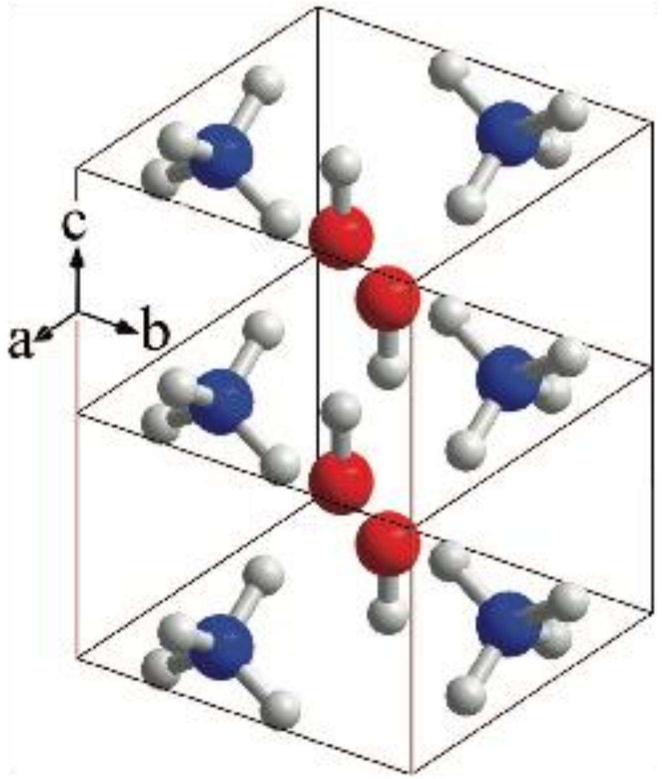
Ionic phase transitions

$$H_2O + NH_3 \rightarrow OH^- + NH_4^+$$



~5GPa



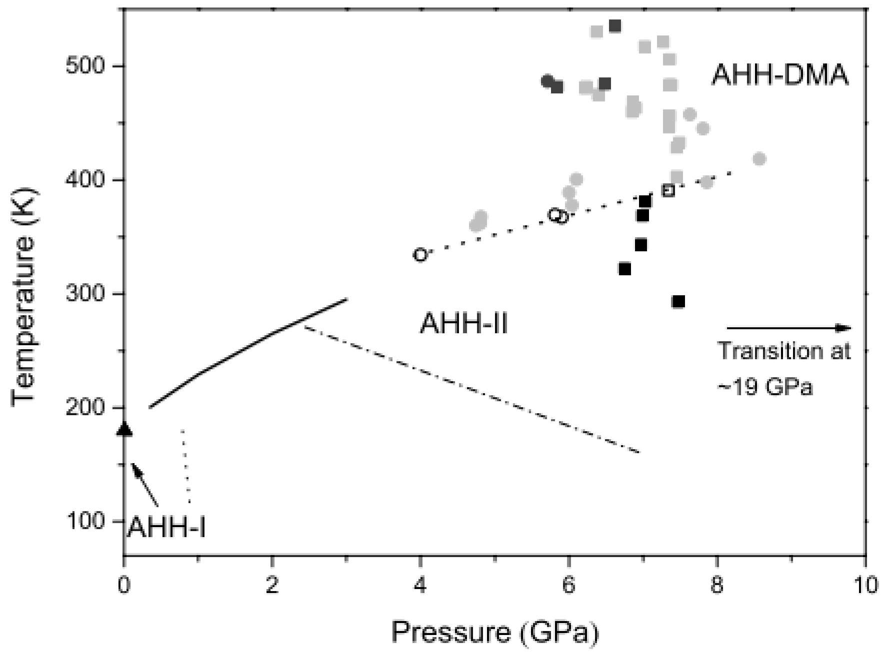


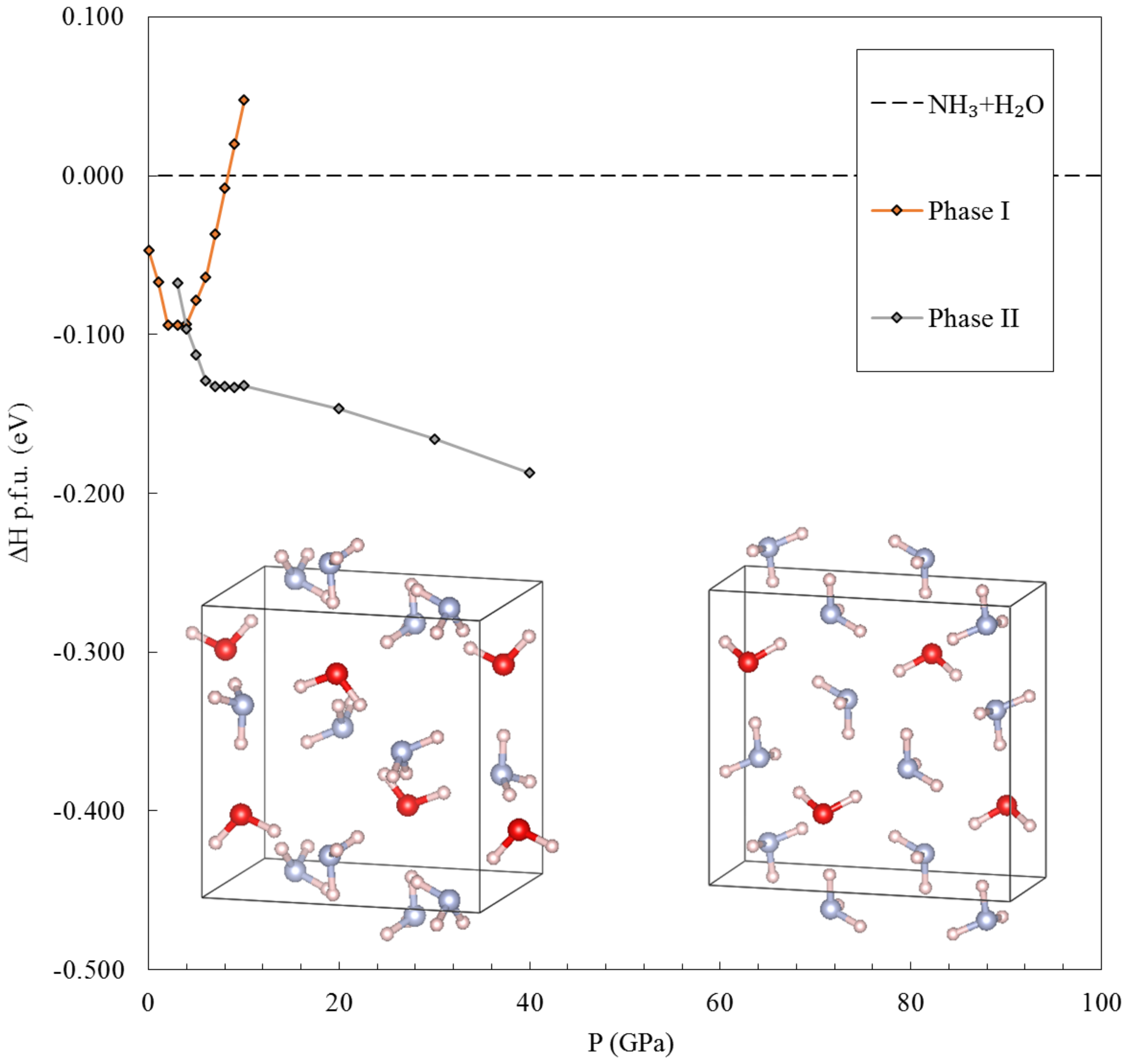
AMH-I

A.D. Fortes et al., *J. Chem. Phys.* 2001.
G.I.G. Griffiths et al., *J. Chem. Phys.* 2012.

Ammonia hemihydrate

$(H_2O)(NH_3)_2$ — molecular phases

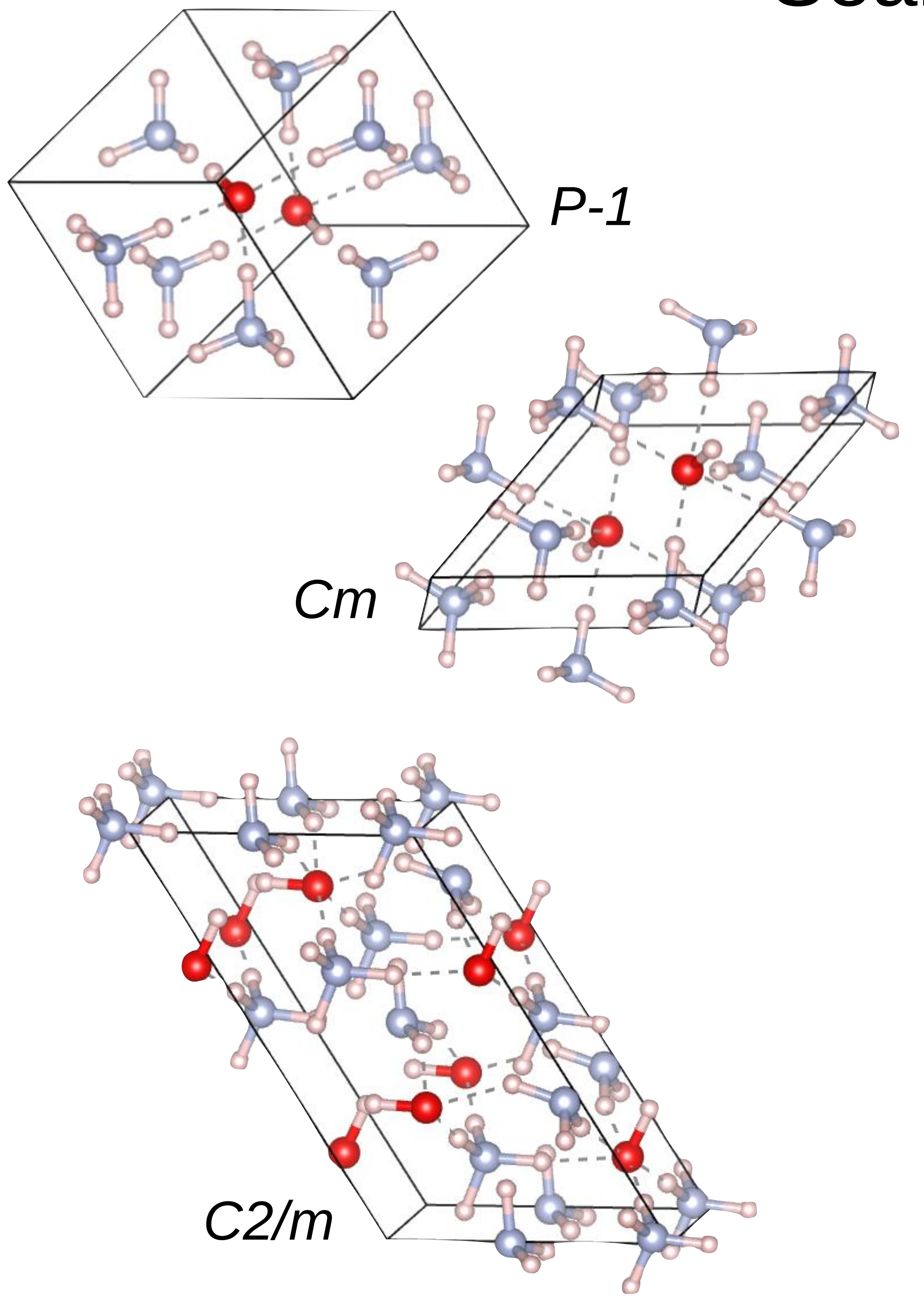


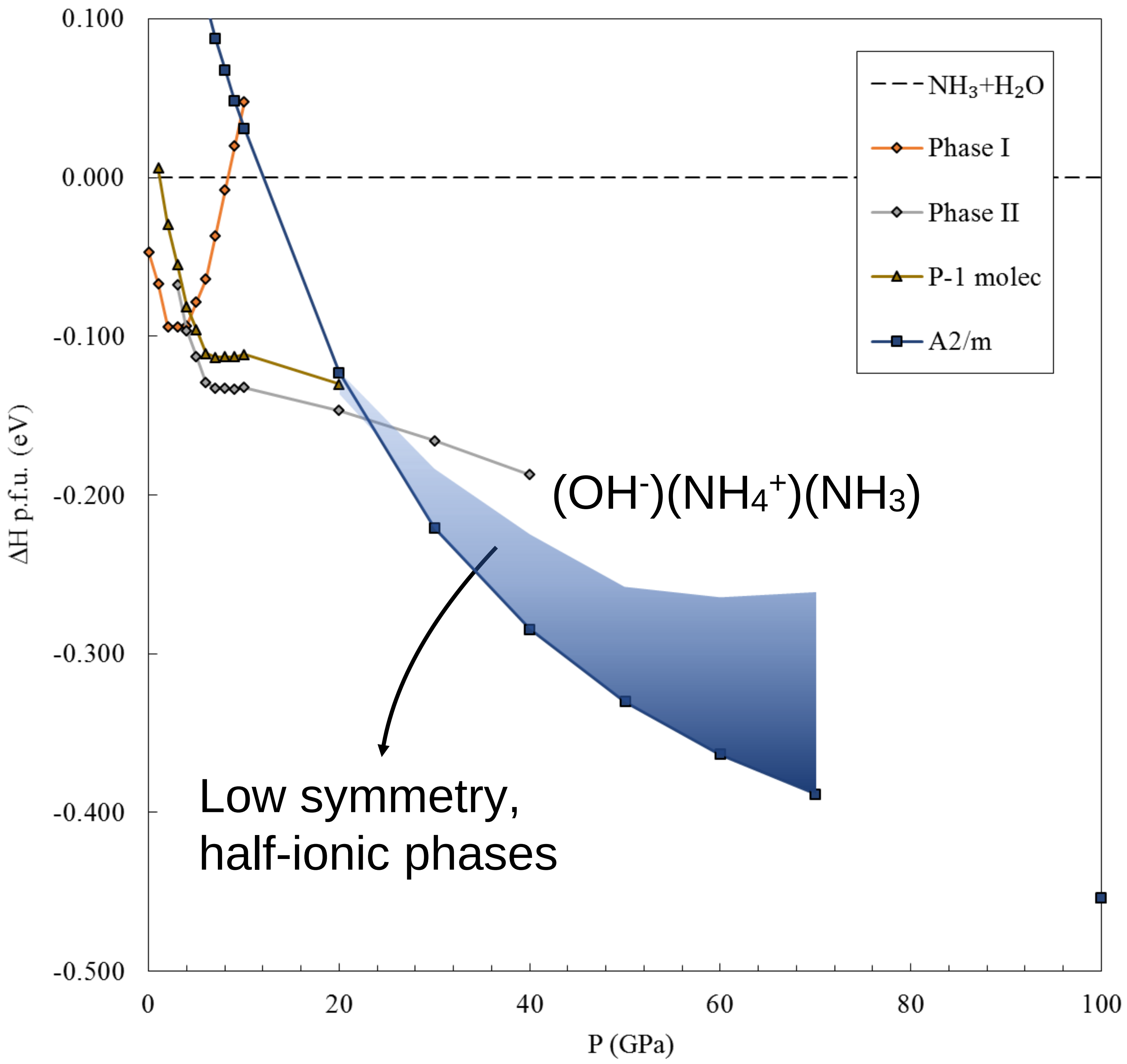


- CASTEP code
- PBE functional
- 1000 eV cutoff
- Ultrasoft PP
- $r_{O,N}$=1.2Å, r_H=0.6Å

Ammonia hemihydrate

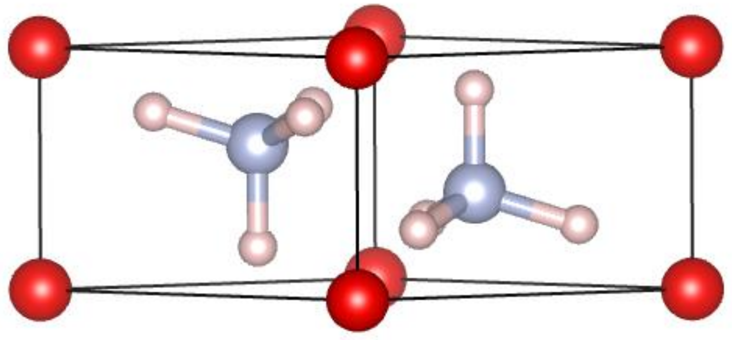
Searching for disorder





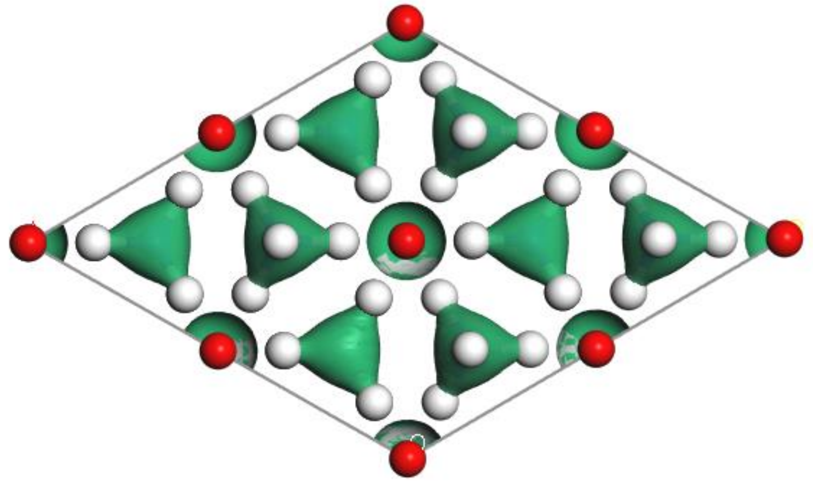
Full ionisation of water

Ionic structures…

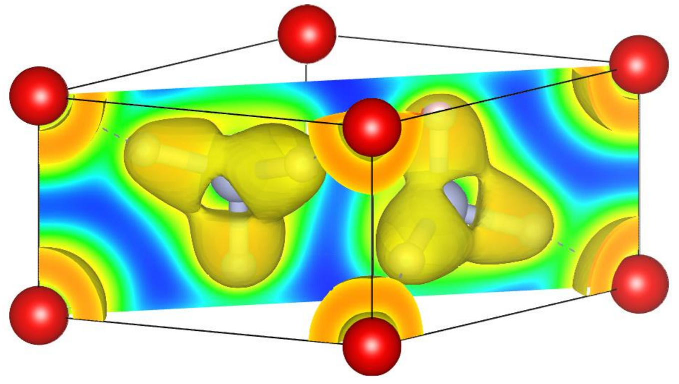


AHH-P-3m1

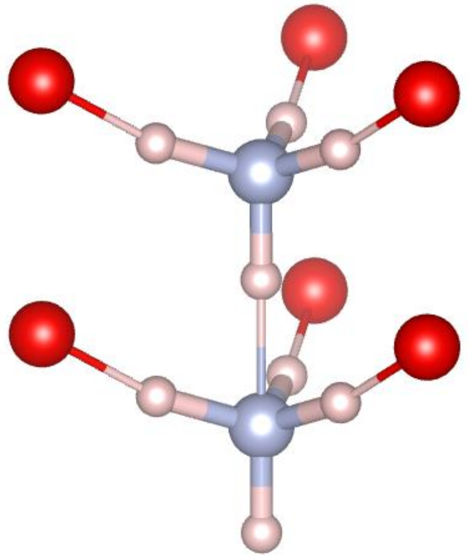
Charge density:

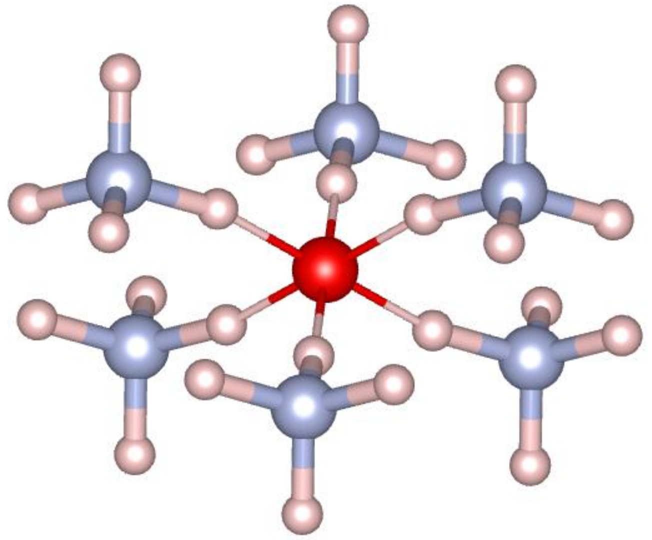


Electron Localization Function (ELF):



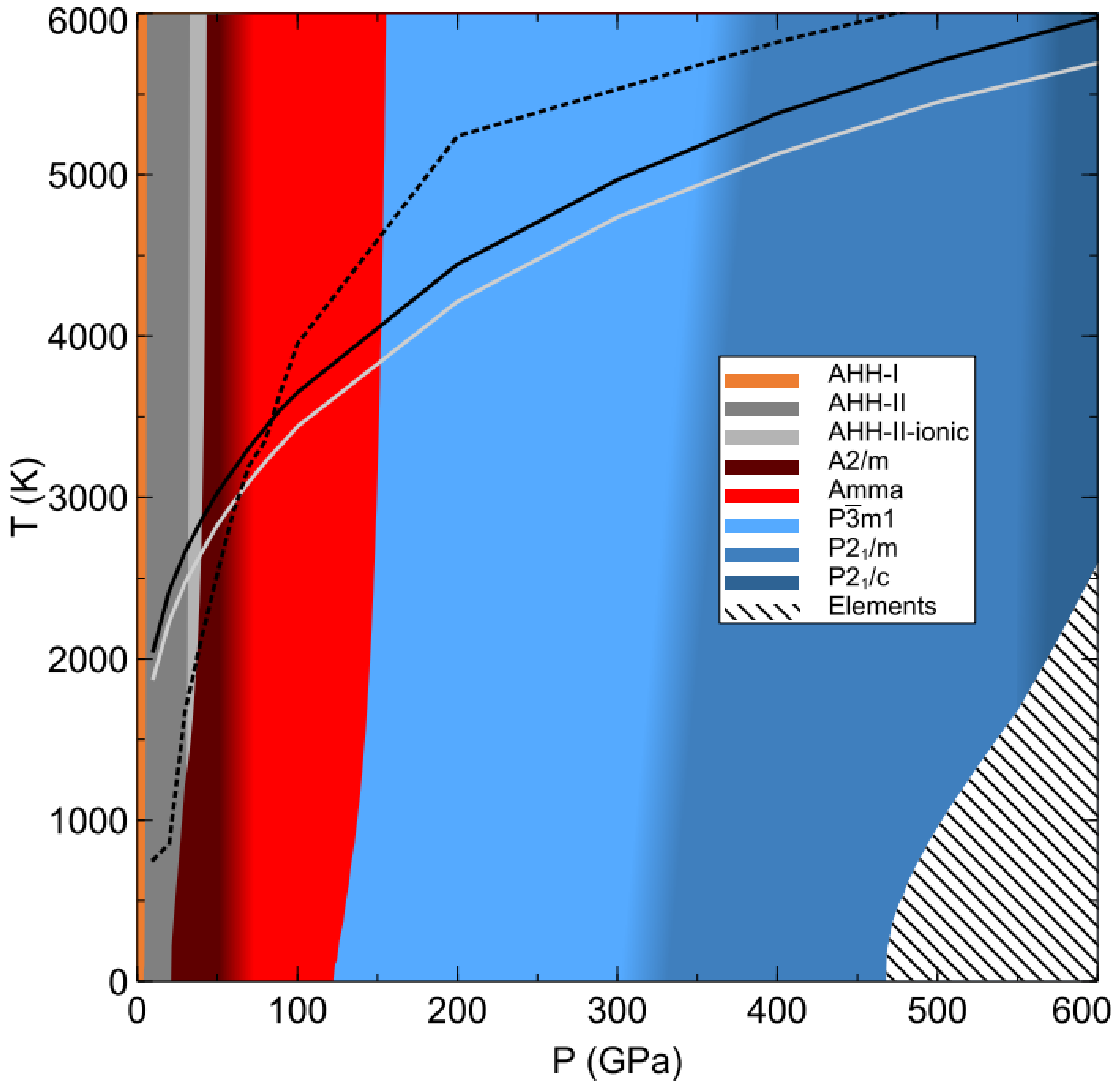
…and hydrogen bonding





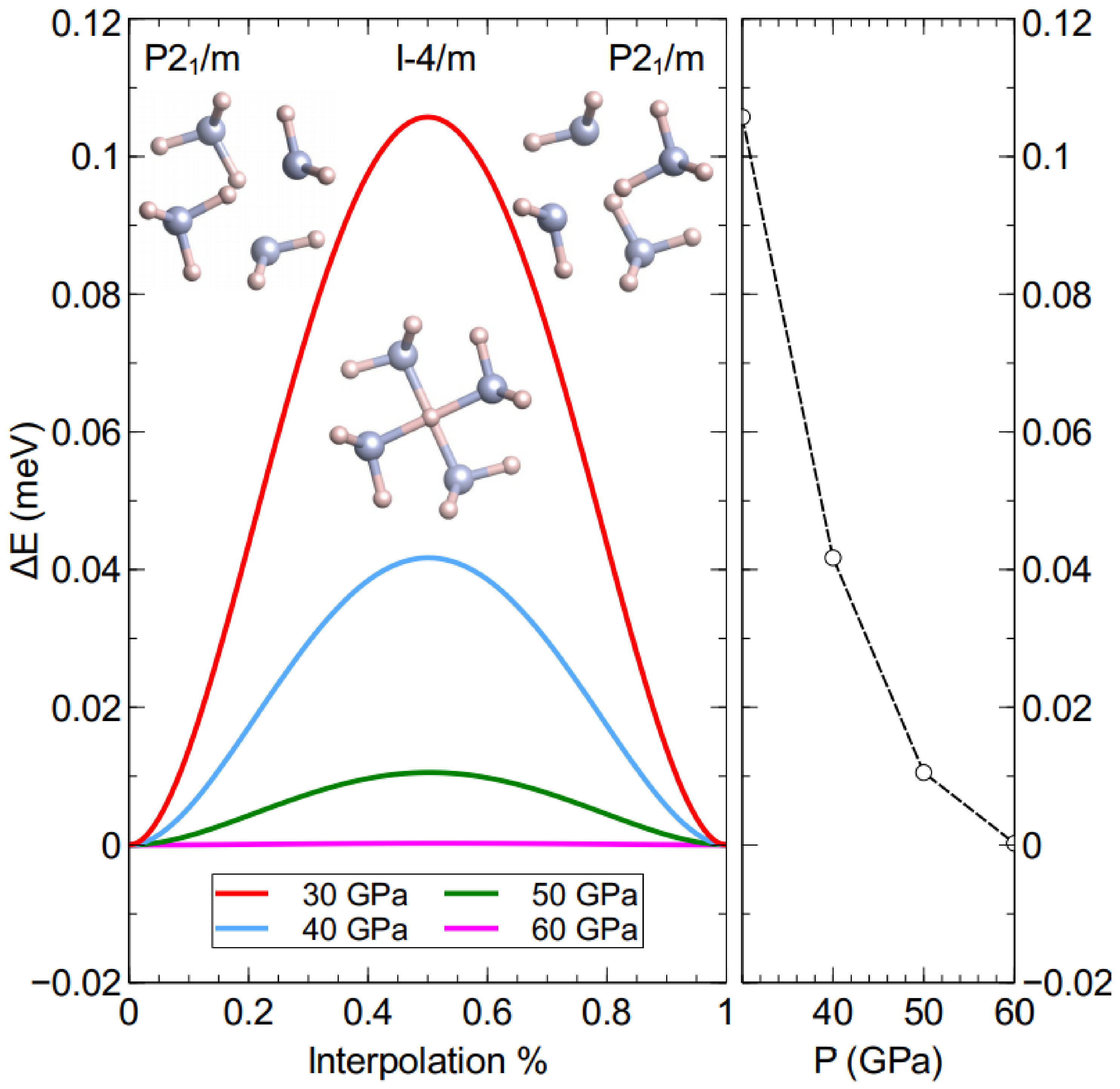
Finite temperature stability

Harmonic approximation



$$F(T,V) = E_0 - TS = E_0(V) + k_B T \int d\omega g(\omega) \ln\left[2\sinh\left(\frac{\hbar\omega}{2k_B T}\right)\right]$$

AQH h-bond Symmetrization



ISIS – AMH DMA formation