

Bibliographic project

Generation of optimized structures through Particle Swarm Optimization

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Repository: <https://github.com/antoinegs1r/ParticleSwarmOptimization>

Introduction

Novel phases in ammonia-water mixtures under pressure

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Crystal structure prediction in Saturn and Uranus' mantles

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Novel phases in ammonia-water mixtures under pressure

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While ammonia and water readily form hydrogen-bonded molecular mixtures at ambient conditions, their miscibility under pressure is not well understood, yet crucial to model the interior of icy planets. We report here on the behavior of ammonia-water mixtures under extreme pressure conditions, based on first-principles calculations of 15 stoichiometries in the pressure range of 1 atm–10 Mbar. We show that compression facilitates proton transfer from water to ammonia in all relevant mixtures. This favors ammonia-rich hydrates above 1 Mbar, stabilized by complete de-protonation of water and the formation of the unusual structural motifs $O^{2-}(NH_4)_2$ and $O^{2-}(N_2H_7)_2$. The hydronium cations persist to the highest pressures studied. We predict a new ammonia-rich 4:1-hydrate at intermediate pressures and find that by 5.5 Mbar, close to the core-mantle boundary of Neptune, all cold ammonia-water mixtures are unstable against decomposition into their constituents. Published by AIP Publishing. <https://doi.org/10.1063/1.5063569>

I. INTRODUCTION

Mixtures of molecular ices of water, ammonia, and methane (together with impurities and volatiles such as hydrogen or helium) make up a large proportion of the mantle regions of the “ice giants” Uranus and Neptune as well as large icy moons in our solar system and are presumed to feature prominently in the large number of Neptune-like exoplanets discovered by recent and ongoing astronomical observation campaigns.^{1,2} It is not clear how molecular ices organize themselves inside these planetary bodies—whether they form segregated layers with distinct chemical and density profiles or homogeneous mixtures corresponding roughly to the global composition ratio throughout. High pressure conditions (which reach hundreds of GPa, or several Mbar, inside ice giants) can, in general, favor unexpected chemical motifs and thus stabilize unusual compounds and stoichiometries, as found among prototypical mineral compounds^{3–10} as well as individual ices.^{11–16}

The molecular ices exhibit very different chemical responses to pressure: water ice forms a sequence of atomic networks above 65 GPa, where water molecules readily give up their protons to sit at the mid-points of nearest-neighbor O–O separations,^{13,14,17,18} while ammonia holds onto its protons much better and instead self-ionizes above 120 GPa into ammonium amide over a large pressure range before (in calculations) returning to packing of neutral molecules.^{15,16,19} The mixtures of the molecular ices can feature surprising pathways to stability under compression; for instance,

methane's solubility in water increases to about 40% at pressures as low as a few GPa,²⁰ which is largely unexplained. Mixtures of ammonia and water are of particular interest as they can form hydrogen-bonded networks. First-principles calculations have so far proven very useful in establishing or confirming the phase diagrams and properties of the individual ices and of a select few hydrate phases. Here, we present a computational study of the entire binary ammonia-water phase diagram that considers *all* mutual formation and decomposition reactions at various pressures and temperatures and also establishes which *new* hydrate stoichiometries should be stabilized under particular conditions.

II. COMPUTATIONAL METHODOLOGY

Solid crystalline structures were searched for using the particle swarm optimization algorithm as implemented in CALYPSO (crystal structure analysis by particle swarm optimization).^{21,22} Structure predictions were performed with up to 16 formula units of $(H_2O)_X(NH_3)_Y$, where X and Y are integers, and at 5, 10, 20, 30, 50, 80, and 100–1000 GPa in increments of 100 GPa. These searches were performed for the three canonical ammonia-water mixing ratios. At 50, 100, and 300 GPa, binary searches were performed to look for other stable mixing ratios. If a new mixing ratio was found to be stable, further searches were performed for this stoichiometry at relevant pressures. Structure predictions at pressures over 1 TPa and up to 5 TPa failed to find any structures stable against decomposition into NH_3 and H_2O . The predicted decomposition of NH_3 above 460 GPa was taken into account throughout.²³

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Introduction

Crystal structure prediction requires sampling of multiple structures

Some existing methods:

- Monte Carlo
- Simulated annealing
- Minima/basin hopping
- Metadynamics
- Genetic algorithm

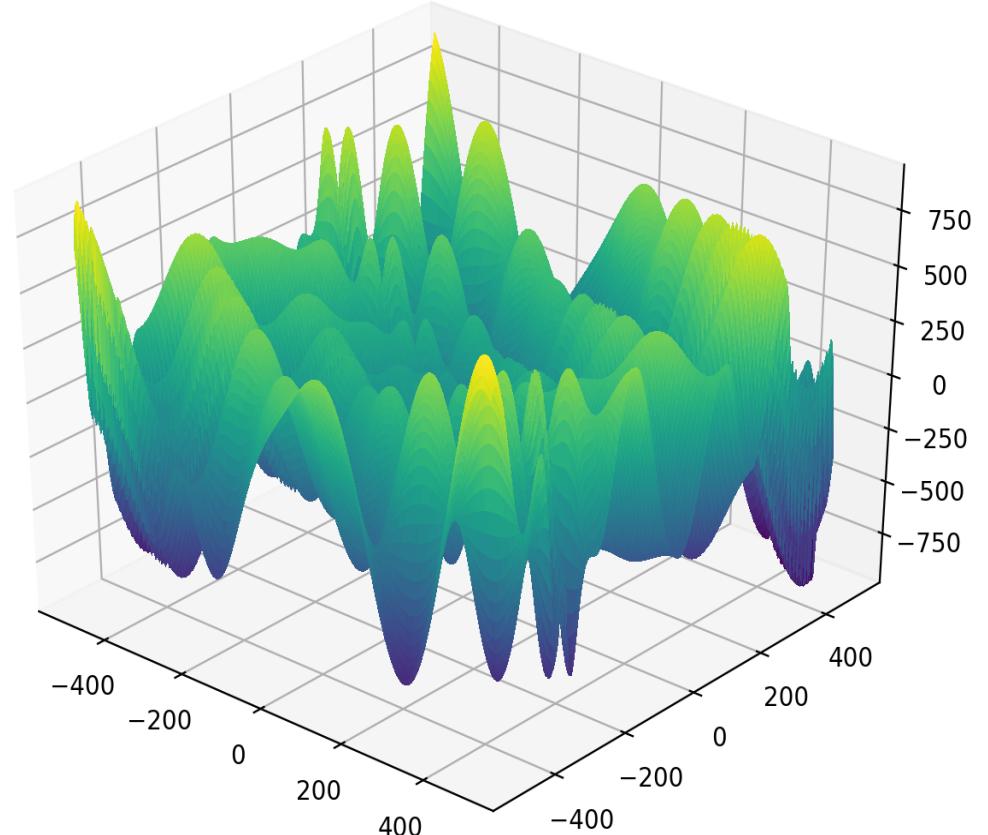


Figure 1: Eggholder function
(Nathan Rooy on [GitHub](#))

Introduction

Crystals in Saturn and Uranus:

- Presence of water ices and ammonia in similar quantities
- High pressures and temperatures

Problems using previous methods:

- High computational cost
- High energetic barriers to cross
- Has everything been sampled?
- Everything is unknown

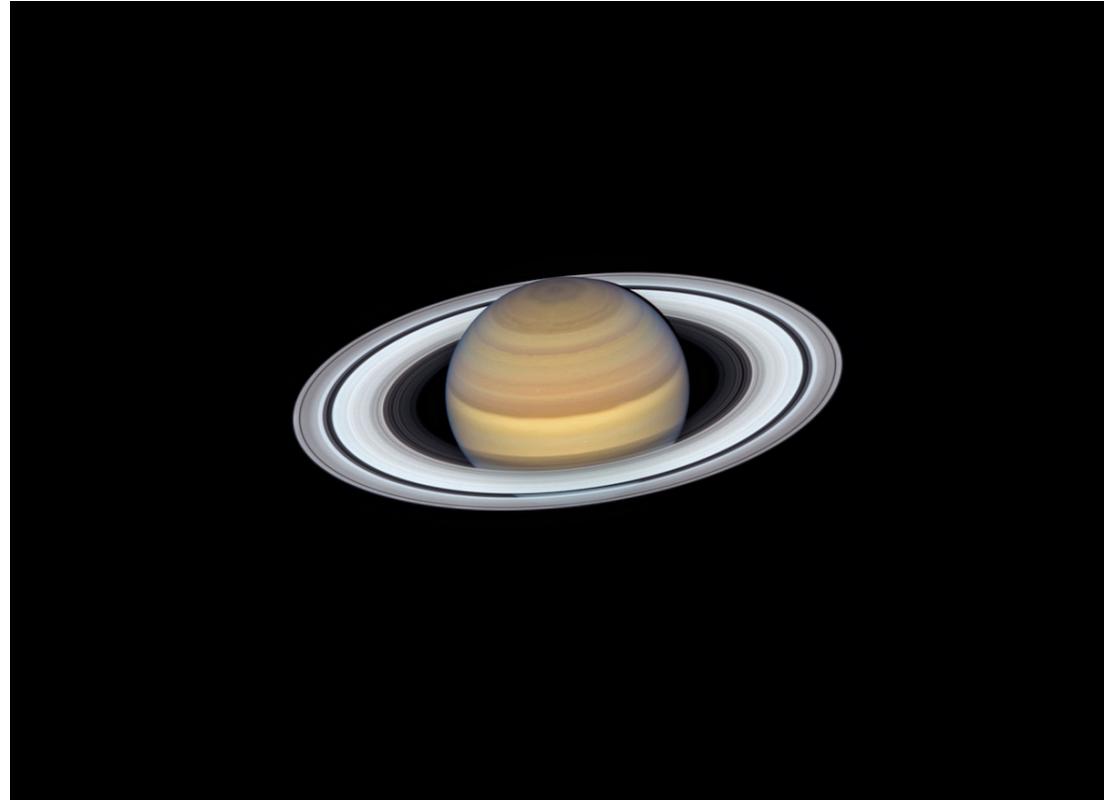


Figure 2: Saturn by Hubble telescope
([Nasa](#), September 2019)

Particle Swarm Optimization (PSO)

Population-based optimization algorithm based on behaviors of birds in a flock



Figure 3: Bird flock, by P. D. van de Velde

$$v_{i,j}^{t+1} = \omega v_{i,j}^t + c_1 r_1 (\text{pbest}_{i,j}^t - x_{i,j}^t) + c_2 r_2 (\text{gbest}_{i,j}^t - x_{i,j}^t)$$

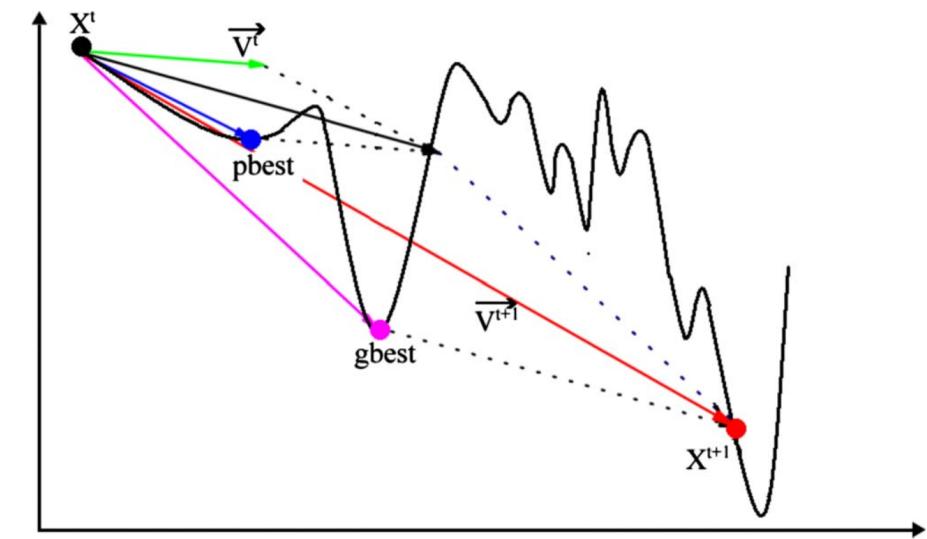


Figure 4: PSO principle, by Wang et al.

How does it work?

1. Generation of one random structure per symmetry
2. Local optimization of every structure
3. Exclusion of similar structures (*through bond characterization matrix*)
4. Generation of new structures by PSO, using personal and flock's histories (global best minimum **gbest** and personnal best minimum **pbest**)
5. Repetition of the three last steps until convergence (difference between two consecutive minimal values less than a defined epsilon)

The program then returns the configuration associated to the lowest energy

Trial over a basic 2D function

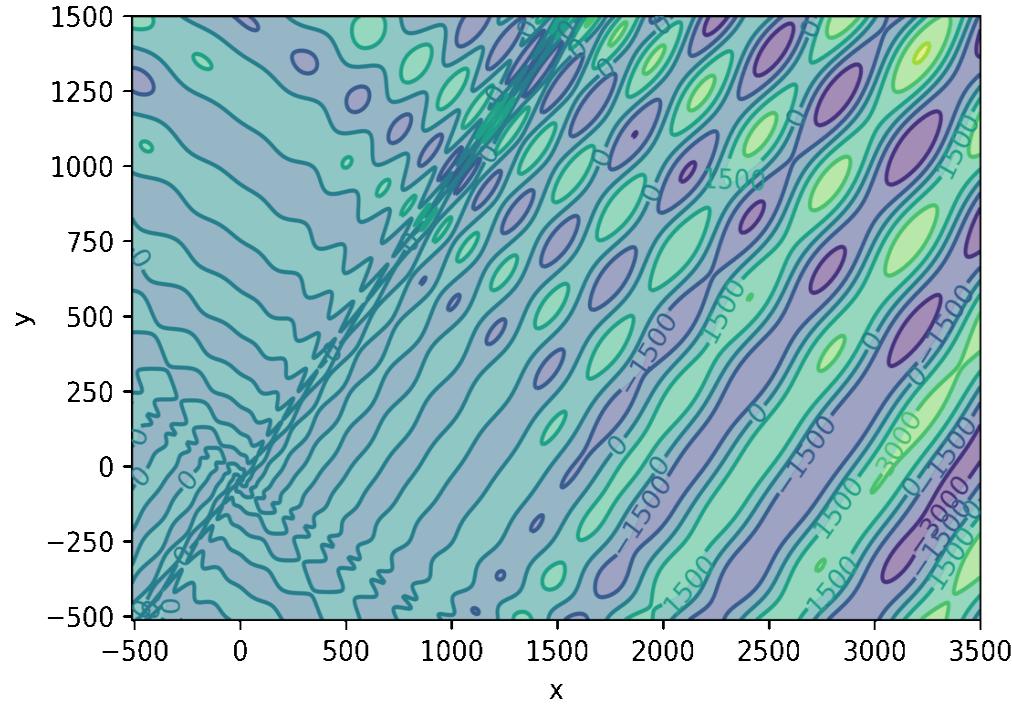


Figure 5: Global minimum over time

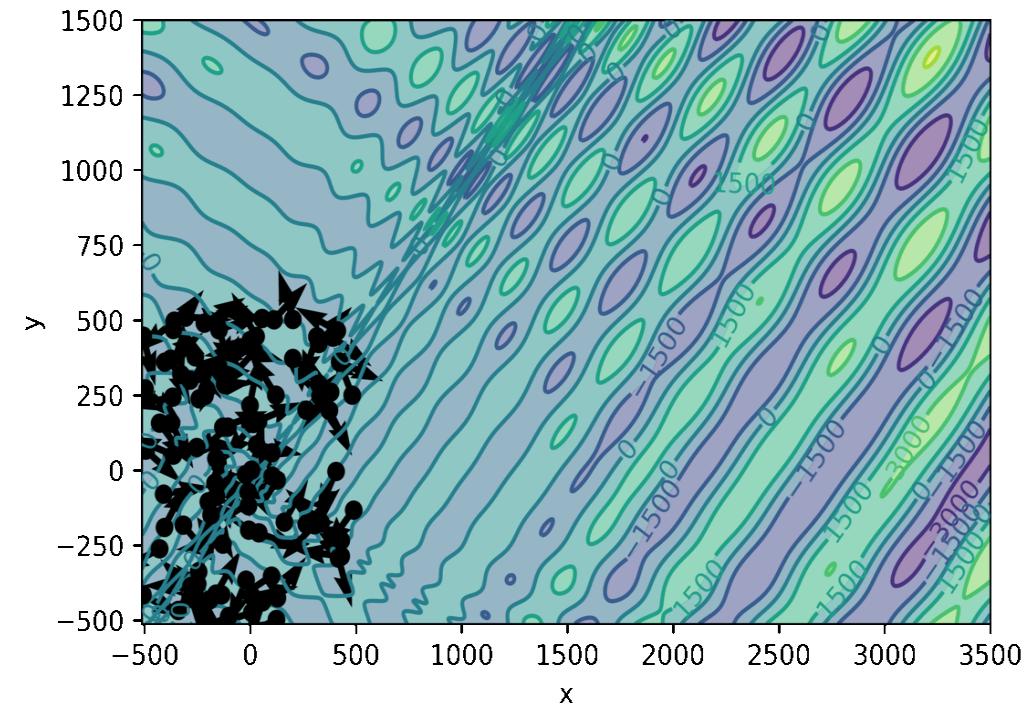


Figure 6: Evolution of particles over time

PSO for crystal structure prediction

Results from previous studies

Three stable mixtures were found

- AMH \rightarrow $(\text{H}_2\text{O})(\text{NH}_3)$
- ADH \rightarrow $(\text{H}_2\text{O})_2(\text{NH}_3)$
- AHH \rightarrow $(\text{H}_2\text{O})(\text{NH}_3)_2$

For each mixture, various phases depending on pressure (see Figure)

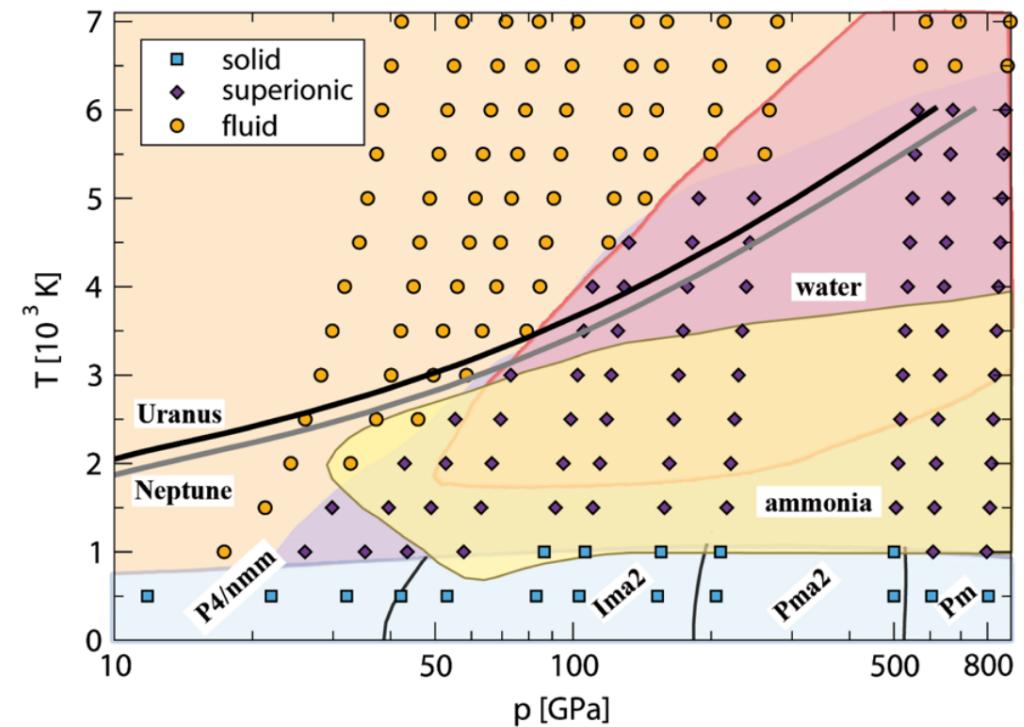


Figure 7: Phase diagram determined by Bethkenhagen et al. (using genetic algorithm)

PSO for crystal structure prediction

Using PSO, authors were able to show that new structures might be more stable

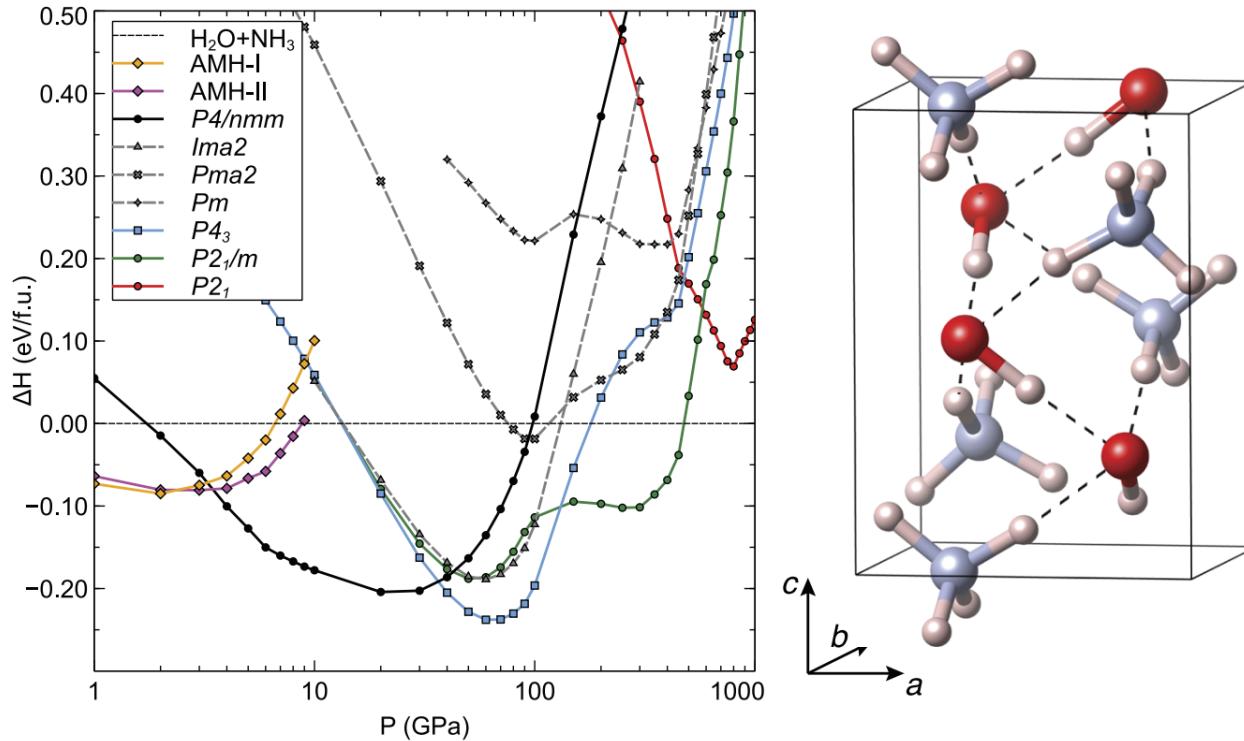


Figure 7: Relative enthalpies of AMH structures

PSO for crystal structure prediction

Authors also discovered the existence of another mixture : AQH \longrightarrow $(\text{H}_2\text{O})(\text{NH}_3)_4$

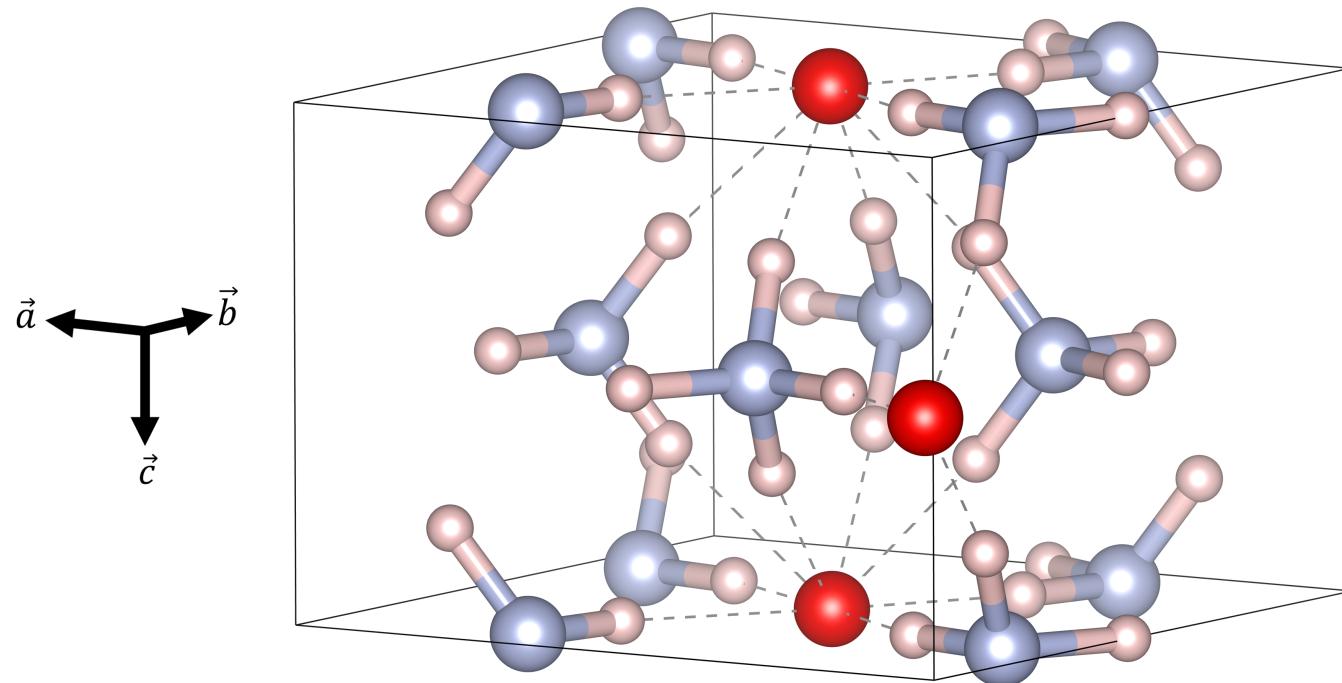


Figure 8: AQH- $P2_1/m$ structure at 40 GPa

Elaboration of final phase diagram

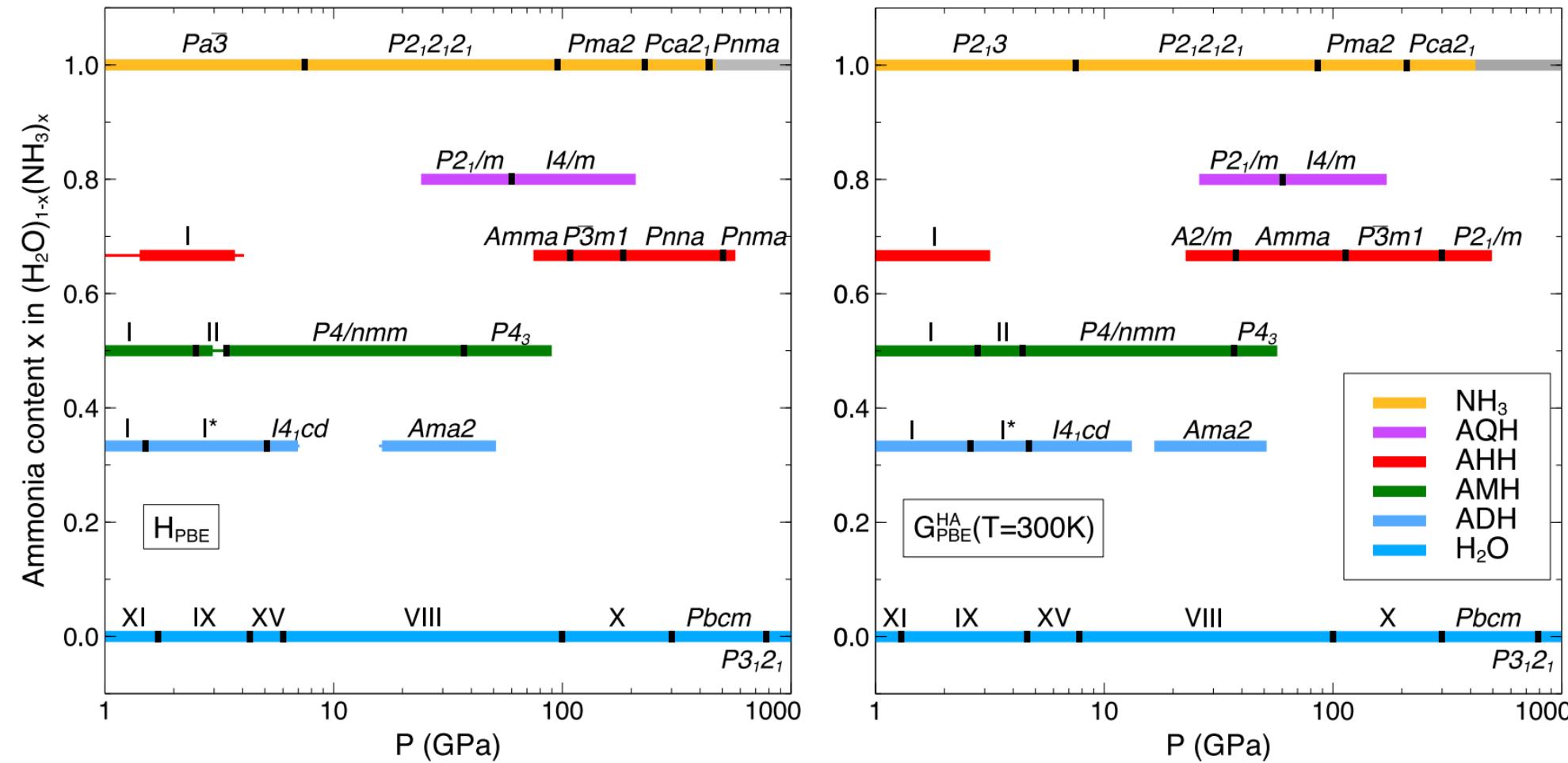


Figure 9: Phase diagram for binary ammonia-water mixtures as a function of pressure

Conclusion

- Discovery of a new phase and new stable structures using Particle Swarm Optimization
- Techniques implemented in the algorithm by Wang et al. (symmetry constraints, bond characterization matrix), make it possible to **reduce the number of iterations**
- PSO seems like a good method for this study case
- But will certainly not become the gold standard
 - Dynamics are not implemented
 - When starting point is given, some techniques might be faster