

Ab-initio studies of ammonia-water mixtures at icy planet mantle conditions

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Abstract

The interiors of icy planetary bodies contain large amounts of mixtures of the molecular ices of water, ammonia, and methane. To develop a detailed picture of these bodies' interiors it is crucial to understand how these compounds interact at extreme pressure and temperature conditions. We present here results combining electronic structure total energy calculations, crystal structure prediction methodology, and ab-initio molecular dynamics (MD), to study the phase evolution of ammonia-water mixtures under pressure. We show that ammonia-rich hydrates are preferred above 100 GPa, and discuss MD results on four different stoichiometric ammonia-water mixtures up to 500 GPa and 5000 K. We find the presence of superionic regions, where protons move freely in heavy nuclei lattices, analyse their diffusive properties and bond lifetimes, and establish their melting lines.

1. Introduction

Accurate models of the interior structure of planetary bodies, in our or other solar systems, are key to understanding their formation and many of their properties. For instance, the stratification (or lack thereof) of molecular mixtures inside icy planets' mantles influences their luminosity and cooling rates; and the presence (or not) of water stored inside rocky planets' mantles influences their convection rates, the magnitude of plate tectonics and presence of surface water. But direct measurements of planetary interiors are virtually impossible and laboratory experiments are difficult, which is why accurate computer simulations can make important contributions.

Amongst mixtures of planetary ices, ammonia-water compounds are arguably of the most chemical interest, because they can form fully connected $\text{HOH} \cdots \text{NH}_3$ and $\text{H}_2\text{NH} \cdots \text{OH}_2$ hydrogen bonded

networks. Three stoichiometric mixtures exist in nature and close to ambient conditions: ammonia monohydrate (AMH, $\text{NH}_3:\text{H}_2\text{O}=1:1$), ammonia dihydrate (ADH, 1:2) and ammonia hemihydrate (AHH, 2:1). These mixtures have been studied experimentally up to 10's of GPa in pressure, and rich phase diagrams have been uncovered [1]. Computational studies have pushed individual mixtures to much higher pressures, to investigate their structural evolution and behaviour at elevated temperatures [2].

Here, we use density functional theory (DFT) to determine the electronic structure of a variety of stoichiometric ammonia-water binary mixtures, across a range of pressures up to 1 TPa, which enables us to compare their relative stability and trends in formation and decomposition under various conditions. We utilise the particle swarm optimisation method as implemented in the CALYPSO package [3] in conjunction with the CASTEP total energy software suite [4] to sample the crystalline configurational landscape and determine promising structural candidates for each stoichiometry at given pressure conditions.

These candidate structures form the basis to develop low-temperature phase diagrams of binary ammonia-water mixtures based on enthalpic relations, while MD calculations are used to probe the onset of superionicity and full melting in these compounds.

2. Results

While the cosmic abundance ratio of ammonia to water is roughly 1:7, we find that relative modest compression favours the formation of ammonia-rich hydrate compounds, in particular the 2:1 AHH phase [5]. In Figure 1 we summarise the results from a large set of crystal structure prediction runs at 300 GPa, by showing the relative formation enthalpies of a large set of stoichiometric binary mixtures. The convex hull of these data points (shown as the solid line) indicates all

stable phases. At 300 GPa, only a single ammonia-water mixture, AHH, should be stable against decomposition.

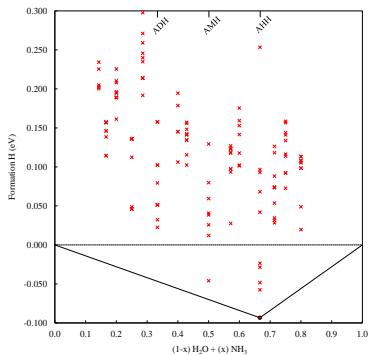


Figure 1: Convex hull construction of the formation enthalpies of the best ammonia-water mixtures found at 300 GPa.

We argue that this is due to energetically favourable de-protonation of water molecules under pressure, with the simultaneous formation of ammonium NH_4^+ ; this, in AHH, leads to the transformation from a hydrogen-bonded molecular mixture to a fully ionic compound. A dominant high-pressure phase of AHH has the archetypal CdI_2 ionic structure type, and is shown in Figure 2. The picture of different molecular entities is supported by a detailed analysis of the topologies of the electronic charge density and the electron localisation function (ELF), which probes covalent bonding.

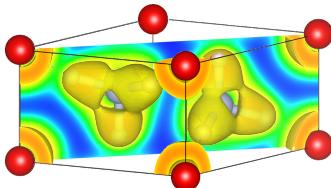


Figure 2: Electron localization function (ELF) isosurfaces and contours in the $P3m1$ phase of AHH at 300 GPa, outlining the presence of isolated oxygen O^{2-} anions in a matrix of NH_4^+ cations.

The significant stabilisation of solid ionic structures under pressure has consequences for the high-pressure

stability of ammonia-water mixtures – pushing the pressure of eventual decomposition into individual ices beyond 500 GPa – and the high-temperature behaviour of the mixtures: in ammonia-rich hydrates that support full de-protonation of water, the onset of superionicity (where protons become diffusive in a solid heavy ion lattice) is shifted to higher temperatures than in e.g. the 1:1 AMH compound. We will discuss the resulting P-T phase diagrams of the different relevant mixtures.

3. Summary

In this contribution we show that ammonia-water mixtures undergo a series of interesting phase transitions under pressure, leading to the stability of unusual ammonia-rich hydrates at pressures present inside the lower mantles of large icy planets. Their stabilisation is aided by the formation of ammonium oxides, and we present detailed analyses of the chemical bonding, vibrational properties, and high-temperature behaviour of the relevant phases.

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