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Abstract

High pressure \textit{ab initio} evolutionary structure searches resulted in a hydronitrogen solid with a composition of (NH)\textsubscript{4}. The structure searches also provided two molecular isomers, ammonium azide (AA) and trans-tetrazene (TTZ) which were previously discovered experimentally and can be taken as molecular precursors for high pressure synthesis of the hydronitrogen solid. The computed pressure versus enthalpy diagram showed that the transformation pressure to the hydronitrogen solid is 36 GPa from AA and 75 GPa from TTZ. Its metastability was analyzed by the phonon dispersion spectrum and room-temperature vibrational density of state together with the transformation energy barrier back to molecular phases at 298 K. The predicted energy barrier of 0.21 eV/atom means that the proposed hydronitrogen solid should be very stable at ambient conditions.

(Some figures in this article are in colour only in the electronic version)
metallic hydride of oxygen and fluorine [27]. Based on the hydrogen bonding in the ice structure, Bucknum further suggested that the three-dimensional hydronitrogen lattices could be accessible at room temperature by cold compression of the non-metallic salt ammonium azide in a diamond anvil cell. However, recent high pressure experiments on sodium azide and lithium azide have shown that high temperature is necessary for the transformation from azide ions to large nitrogen clusters and the subsequent formation of polymeric nitrogen networks [28, 29]. Furthermore, polymeric nitrogen simulations have shown that the lowest enthalpy polymeric nitrogen phase at ambient conditions is a zigzag chain (zzc-N) in a one-dimensional structure instead of three-dimensional cg-N [7]. This nitrogen zigzag chain is analogous to polyacetylene with alternating single and double bonds between nitrogen atoms. Like the nitrogen zigzag chain, a one-dimensional hydronitrogen solid can be naturally constructed by chemically activating nitrogen double bonds and adding hydrogen atoms on unsaturated nitrogen single bonds, where the hydrogen bonding of N–H···N is much weaker than that of O–H···O in the ice. It is therefore questionable that the three-dimensional hydronitrogen lattices would be as stable as the ice at ambient conditions.

In this paper, we report \( \text{ab initio} \) evolutionary simulations [30] to search for the lowest enthalpy structures of hydronitrogen systems at zero temperature and different pressures; these searches were carried out without any experimental information. The evolutionary simulations were conducted using the code developed in-house which was successfully applied to the first-principles density functional theory (DFT) study of the high pressure molecular \( \zeta \) phase of nitrogen [31]. Initially we took eight nitrogen and eight hydrogen atoms in unit cells. The size of the genes was 20. The structure searching convergence criteria was that the lowest energy structure was the same for three consecutive generations. In the present work, the VASP package [32] was mainly employed in \( \text{ab initio} \) evolutionary structure searches while the SIESTA code [33] was used for pressure versus enthalpy diagrams, equation of state and molecular dynamics calculations. All calculations were based upon first-principles DFT within the generalized gradient
Figure 3. Phonon dispersion spectrum and vibrational density of state for \( P2_1/m \) hydronitrogen solid; (a) phonon dispersion at high frequencies, (b) phonon dispersion at lower frequencies and (c) the room-temperature vibrational density of state calculated from velocity autocorrelation functions of molecular dynamic simulations at 300 K and 0 GPa.

approximation (GGA) \[34\]. For the SIESTA calculations, the Troullier–Martins norm-conserving pseudopotential \[35\] was utilized with the nitrogen reference configuration of \([\text{He}]2s^22p^3\) along with corresponding numerically doubled \{s, p_x, p_y, p_z\} orbitals plus d-type polarization orbitals. The cutoff radius was 1.24 Å for nitrogen and 1.25 Å for hydrogen. A 20.0 Å cutoff was employed for the \( k \)-point sampling in structure optimization calculations. The metastability energy barrier for the transformation of the hydronitrogen back into molecular precursors at ambient conditions was calculated using GAMESS \[36\] at the same GGA and 6-31G(d, p) basis set level theory.

In the pressure range 30–100 GPa for structure searches, three structures of hydrogen–nitrogen systems were remarkably uncovered, namely a new optimized structure of the \((\text{NH})_4\) hydronitrogen solid and an ambient pressure structure of ammonium azide (AA) and trans-tetrazene (TTZ) as shown in figure 1. Note that AA and TTZ are molecular crystals experimentally discovered previously \[37, 38\]. The \((\text{NH})_4\) hydronitrogen solid features one-dimensional nitrogen single-bonded and hydrogen-capped nitrogen zigzag chains with a monoclinic \( P2_1/m \) space group. At 0 GPa, the unit cell vector lengths of this hydronitrogen solid are \( A = 8.5935 \) Å, \( B = 2.3167 \) Å and \( C = 3.0021 \) Å with lattice angles \( \alpha = 90.0^\circ \), \( \beta = 105.74^\circ \) and \( \gamma = 90.0^\circ \), respectively. The four nitrogen atom positions can be recovered with two Wyckoff positions 2e, namely (0.8130, 0.2500, 0.6888) and (0.7005, 0.7500, 0.5944) and by their symmetry. In the same way, the four hydrogen atomic positions are given by two Wyckoff positions 2e (0.8509, 0.2500, 1.0525) and (0.6627, 0.7500, 0.2307). The nitrogen single-bond length is 1.486 Å while it is 1.051 Å for the hydrogen–nitrogen one. The dihedral angle for \( \text{N–N–N–H} \) is about 75.28°. The density of the hydronitrogen solid is thus about 1.734 g cm\(^{-3}\) based on its structure information. Clearly, its structure is different from the ones proposed by Bucknum. Like polymeric nitrogen phases whose stability depends on the repulsion of electron lone pairs, the structural configuration of this hydronitrogen solid allows electron lone pairs of neighboring nitrogen atoms to separate from each other as far as possible and therefore offers a lower enthalpy for its stability. From the calculations at higher pressures, the enthalpy of this hydronitrogen solid is much lower than those of molecular ones seen in figure 2, indicating that they can be synthesized under high pressure starting from AA or TTZ molecular precursors. Based on the calculated pressure versus enthalpy diagram and equations of state, the predicted transformation pressure for the hydronitrogen solid is about 36 GPa from AA and 75 GPa from TTZ.

Chemically this hydronitrogen is an isomer of the molecular AA and TTZ structure. The simulations of transformation from AA and TTZ were performed. The results showed that a hydronitrogen chain can be formed following a pressure path in which TTZ was compressed up to a target pressure starting from its \( 2 \times 2 \times 2 \) supercell structure at 0 GPa pressure. At 220 GPa target pressure, the bond length of the azo \( \text{N}=\text{N} \) groups in TTZ molecules started to increase and hydronitrogen chains were formed with hydrogen migration from amino \( \text{NH}_2 \) groups of TTZ. This pressure was far above the predicted equilibrium transformation pressure since there is a large barrier to separate this hydronitrogen solid from the molecular TTZ phase. High temperature would be necessary to overcome this large barrier and first-principles simulations at 120 GPa and 2000 K starting from TTZ revealed the formation of hydronitrogen fragments, thus indicating
hydrogen migration from amino groups of TTZ. In the simulations starting from AA, the formation of hydronitrogen fragments was also observed but they were always mixed with ammonia NH$_3$ or hydrazoic acid HN$_3$ molecules which prevent further transformation to hydronitrogen fragments.

The simulations for the stability of the hydronitrogen solid at ambient conditions were performed in three steps. First, each atom was displaced in a $2 \times 2 \times 2$ 64-atom supercell randomly by a maximum of 5% of the bond length deviation in each Cartesian direction. An enthalpy minimization on the randomly displaced system was carried out with a target pressure of 0 GPa. Second, a finite-temperature molecular dynamic simulation was conducted with a target pressure of 0 GPa and a target temperature of 300 K. Third, a phonon dispersion calculation with a $3 \times 3 \times 3$ supercell and 30 $k$ points was made. All these simulations showed that the hydronitrogen solid is metastable at ambient conditions. Figures 3(a) and (b) show the phonon dispersion spectrum and figure 3(c) provides the room-temperature vibrational density of state for the $P\overline{2}_1/m$ structure. The fact that there are no negative frequency modes from the phonon dispersion spectrum establishes the metastability of the hydronitrogen solid. The room-temperature vibrational density of state further demonstrates the metastability at ambient pressure and temperature. To estimate energy barriers between the hydronitrogen solid and the molecular precursors, a transformation path was optimized at 298 K using GAMESS at the GGA [34] and 6-31G(d, p) level theory. This transformation path consists of isomers, AA, TTZ, (NH)$_4$ solid, and molecular A and B structures together with transition states TS-1, TS-2 and TS-3, which were obtained from geometry optimization calculations. The vibration analyses of these isomers and transition states except the (NH)$_4$ solid were performed at the same theory level to verify whether it is a minimum or a transition state on the potential energy surfaces. In this path, the hydrogen migration reaction from the hydronitrogen solid undergoes a 0.21 eV/atom energy barrier shown in figure 4, which is in good agreement with previous studies for N$_4$H$_4$ isomers [39]. Such a high energy barrier means that the hydronitrogen solid will be much more stable at ambient conditions.

Finally, electronic band structures of the hydronitrogen solid from ambient pressure to 230 GPa were also calculated and the derived energy gaps were about 2.8 eV at 0 GPa and about 1.2 eV at 230 GPa, as seen in figure 5. The insulating property of the hydronitrogen solid is preserved at both ambient and high pressures. In comparison with the metallic polymeric nitrogen zigzag chain structure [7], it shows that the hydrogen bonding that caps nitrogen in the hydronitrogen solid is strongly localized even at higher pressures.

In conclusion, we have conducted extensive studies on hydronitrogen systems using high pressure ab initio evolutionary structure searches. A $P\overline{2}_1/m$ hydronitrogen solid
with the composition (NH)4 was proposed. Its structure, stability, electronic structure and pressure versus enthalpy diagram were predicted using first-principles simulations. The predicted equilibrium transition pressures from molecular AA and TTZ are about 36 GPa and 75 GPa, respectively. A 0.21 eV/atom energy barrier at ambient conditions is also predicted that prevents transformations of the hydronitrogen solid back to their molecular precursors and therefore ensures its metastability at ambient conditions.

References