Diverse Chemistry of Stable Hydronitrogens, and Implications for Planetary and Materials Sciences

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Nitrogen hydrides, e.g., ammonia (NH₃), hydrazine (N₂H₄) and hydrazoic acid (HN₃), are compounds of great fundamental and applied importance. Their high-pressure behavior is important because of their abundance in giant planets and because of the hopes of discovering high-energy-density materials. Here, we have performed a systematic investigation on the structural stability of N-H system in a pressure range up to 800 GPa through evolutionary structure prediction. Surprisingly, we found that high pressure stabilizes a series of previously unreported compounds with peculiar structural and electronic properties, such as the N₄H, N₃H, N₂H and NH phases composed of nitrogen backbones, the N₉H₄ phase containing two-dimensional metallic nitrogen planes and novel N₈H, NH₂, N₃H₇, NH₄ and NH₅ molecular phases. Another surprise is that NH₃ becomes thermodynamically unstable above ~460 GPa. We found that high-pressure chemistry of hydronitrogens is much more diverse than hydrocarbon chemistry at normal conditions, leading to expectations that N-H-O and N-H-O-S systems under pressure are likely to possess richer chemistry than the known organic chemistry. This, in turn, opens a possibility of nitrogen-based life at high pressure. The predicted phase diagram of the N-H system also provides a reference for synthesis of high-energy-density materials.

Hydrogen is the most abundant, and nitrogen is the seventh most abundant element in the universe. Giant planets Uranus and Neptune are predominantly made of H, O, C and N. While the behavior of the H-O1 and C-O2 systems under pressure has been investigated in some detail, the N-H system remains largely unexplored. Ammonia (NH₃), an important compound in many branches of science and technology, was first proposed to exist in Uranus and Neptune by Ramsey3 and Bernal and Mussey4 in early 1950s, and further discussed by Stevenson and Bundy5,6. It is the only stable hydronitrogen at ambient conditions, and exists in a wide range of temperatures and pressures. Recent studies7–9 revealed that ammonia undergoes a series of phase transitions, including ionic disproportionation and return to non-ionic phase at megabar pressures. Ammonia is considered as a major component of the interiors of giant planets such as Uranus and Neptune under extreme pressure (up to 600 GPa) and temperature (2,000~7,000 K)10–14. What has not been properly explored is the full phase stability in the N-H system, including the possibility of decomposition of ammonia; it may well be that, instead of ammonia, very different molecules with different stoichiometries are actually present in planetary interiors.

All nitrogen hydrides, except ammonia, are metastable at ambient pressure. Due to the substantial energy difference between single and triple nitrogen-nitrogen bonds, nitrogen-rich hydronitrogens are potentially superior high-energy-density materials. However, large-scale synthesis of these materials is still problematic. Having

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a complete phase diagram for the N-H system is necessary for developing synthetic strategies, but such a phase diagram has not been determined. As a result, the high-pressure behavior, structures and stability of N-H phases are of great interest to both planetary and condensed-matter physics.

Extensive theoretical\textsuperscript{15-18} and experimental\textsuperscript{19} studies revealed exotic compounds appearing under compression, and exhibiting unique structures and properties different from usual compounds - see previous investigations of Na-Cl\textsuperscript{19}, Mg-O\textsuperscript{17}, B-H\textsuperscript{16}, H-O\textsuperscript{1} and Mg-Si-O\textsuperscript{18} systems. Considering the dramatically changed nature of nitrogen\textsuperscript{20-22} and the autoionization\textsuperscript{7} found in NH\textsubscript{3}, new hydronitrogen compounds are expected to be found.

Results

Stoichiometries and structures. Using the evolutionary algorithm USPEX\textsuperscript{23-26}, we have carried out structure and stoichiometry predictions in order to find all stable compounds (and their stability fields) in the N-H system (See Methods). Our calculations confirm that ammonia is the only stable hydronitrogen from ambient pressure to 36 GPa. Above 36 GPa, remarkably, a series of previously unknown compounds become stable, as shown in the pressure-composition phase diagram of the N-H system in Fig. 1. The detailed convex hulls at 60, 100, 200, 500, and 800 GPa are presented in Fig. 2. It needs to be emphasized that by calculating phonon dispersions, all the newly found compounds in this work are found to be dynamically stable in their corresponding stability field on the phase diagram (Fig. 1). Since zero-point energy can be a factor to affect the relative stability of structures, we have done zero-point energy calculations for N\textsubscript{2}H, NH, N\textsubscript{3}H\textsubscript{7}, NH\textsubscript{7} and NH\textsubscript{7}, and found out that the phase diagram shown in Fig. 1 does not change significantly. Therefore, in this work, the phase diagram of N-H is drawn without considering zero-point energy. We would like to leave more accurate phase diagram investigation of N-H at finite temperatures and with considering zero-point energy for further work.

We can classify these thermodynamically stable hydronitrogen compounds that we found into three types (See Table 1). (i) Infinite-chain polymeric hydronitrogens, including N\textsubscript{2}H, N\textsubscript{3}H, N\textsubscript{2}H and NH, with polymeric...
Chains featuring all-nitrogen backbones. (ii) Two-dimensional (2D) metallic $N_9H_4$ phase consisting of 2D nitrogen planes and $NH_4^+$ cations, interestingly, the 2D-nitrogen planes have not been reported in any other nitrogenous compounds before. (iii) Molecular compounds including $N_8H$, $NH_2N_3H_7$, $NH_4$, $NH_5$, and of course $NH_3$. Here, molecular (or molecular ionic) compounds are bonded by hydrogen bonds.

| Compounds   | Pressure(GPa) | Structure Type       | Subunits                  |
|-------------|--------------|----------------------|---------------------------|
| $N_2H$      | 50 – 54      | molecular            | $NH_3 + N_2$              |
| $N_3H$      | 51 – 80      | long-chain           |                           |
| $N_4H$      | 42 – 75      | long-chain           |                           |
| $N_9H_4$    | 50 – 60      | two dimensional      | $N_x^-$ plane + $NH_4^+$  |
| $N_5H$      | 60 – 260     | long-chain           |                           |
| $NH$        | 36 – >800    | (a) short chain ($P2_1/c$) | $N_xH_4$                  |
|             |              | (b) dimer+long-chain ($P1, C2$) | $N_xH_4^+ + \text{[long chain]}$ |
|             |              | (c) long-chain ($Fdd_2, Fdd_2$) | tetragonal spiral chain   |
| $NH_3$      | 200 – 780    | molecular            | $N_2H_4$ (hydrazine)      |
| $N_7H_5$    | 140 – >800   | (a) molecular/ionic  | $NH_3 + N_2H_4/NH_3^- + N_2H_5^-$ |
|             |              | (b) ionic ($P-3m1$)  | $N_5^- + N_2H_4^{2+}$      |
| $NH_4$      | 0 – 460      | molecular/ionic      | $NH_3/NH_3^- + NH_4^+$    |
| $NH_5$      | 50 – >800    | molecular/ionic      | $NH_3 + H_2/NH_3 + NH_4^+ + H^-$ |
| $NH_5$      | 55 – 100     | ionic                | $NH_3 + \text{[H3N...H...NH3]}^+ + H^-$ |

| Compounds   | Pressure(GPa) | Structure Type       | Subunits                  |
|-------------|--------------|----------------------|---------------------------|
| $N_8H$      | 50 – 54      | molecular            | $NH_3 + N_2H_4$            |
| $N_9H_4$    | 50 – 60      | two dimensional      | $N_x^-$ plane + $NH_4^+$  |
| $N_5H$      | 60 – 260     | long-chain           |                           |

Table 1. Chemical features of stable hydronitrogens.

One-dimensional polymeric hydronitrogens. We have found that, except $N_9H_4$ and $N_5H$, nitrogen-rich hydronitrogens ($N_xH, x \geq 1$) are more prone to adopt polymeric structures with N-backbones. The $N_9H_4$, $N_5H$ and $N_4H$ compounds are predicted to be stable at 51–80 GPa, 42–75 GPa and 60–260 GPa, respectively. The ground state of $N_4H$ has a $Cmc2_1$ structure, containing four zigzag nitrogen chains ($N$-chains) in the unit cell, with pairs of nearest N-chains linked by hydrogen bonds, see Fig. 3(a). Here, we use $\text{[long chain]}$ to represent the monomeric unit in the polymeric chain of $N_4H$. The delocalized nitrogen-nitrogen bonds run along the zigzag chain, and have the same length of 1.28 Å at 60 GPa. Instead of a zigzag chain, the most stable $N_3H$ structure has space group $P2_1/c$ and is composed of distorted arm-chair monomers $\text{[long chain]}$, see Fig. 3(b). These chains are connected with each other through H-bonds to form a layered structure. The $P2_1/c$ phase of $N_4H$
becomes thermodynamically stable at ~60 GPa, and its structure consists of two $\text{N}_2\text{H}_2^+$ monomers in the unit cell, see Fig. 3(c). At 200 GPa, the lengths of single N-N bonds in this polymer are 1.27 and 1.28 Å, and the double N=N bond is slightly shorter (1.24 Å). The smallness of the difference hints at a possible bond resonance along the chain. The doubly-bonded nitrogen atoms form weak asymmetric hydrogen bonds with nearby chains. Before the symmetrization of hydrogen bonds occurring at $\sim$280 GPa, $P_{21}/c$-$\text{N}_2\text{H}$ undergoes a spontaneous decomposition at $\sim$260 GPa. All these polymeric structures are metallic as a result of bond resonance and electronic delocalization along the nitrogen backbone.

With the equal ratio of nitrogen and hydrogen, the NH compound is predicted to be stable in a huge pressure range, from 36 GPa to at least 800 GPa. The $P_{21}/c$ structure is more stable than the one predicted in the work of Hu & Zhang. This phase consists of two tetrazen N$_4$H$_4$ molecules in the unit cell. At 55 GPa, $P_{21}/c$-$\text{NH}$ undergoes a phase transition to an ionic structure with $P1$ symmetry. As shown in Fig. 3(d), the ionic structure is composed of $\text{N}_2\text{H}_5^+$ cations arranged in hydrogen-bonded layers, alternating with layers of infinite chains $\text{N}_4\text{H}^-$. The unit cell contains 6 NH formula units: $\text{N}_2\text{H}_5^+$ group and $\text{N}_4\text{H}^-$ from the polymeric chain. At $\sim$180 GPa, all hydrogen bonds become symmetric and the space group raises to $C2$. Both $P1$ and $C2$ are only nominally ionic, because they are metallic and metals have very efficient screening of ionic interactions by the electron gas. Above $\sim$220 GPa, the ionic NH phases become less stable than an $Fdd2$ structure which is made of tetragonal spiral chains, as shown in Fig. 3(e). Similar square chains have been reported in group VI elements under pressure, e.g. sulfur-II phase and the $I_4/\text{amd}$ phase of oxygen at pressure around 2 TPa. The $Fdd2$-NH is predicted to be a wide-gap semiconductor (4.8 eV at 400 GPa). In contrast to the strongly localized electrons found in the $I_4/\text{amd}$-oxygen structure with isolated chains, $Fdd2$-NH has asymmetric hydrogen bonds between the square chains. $Fdd2$ transforms to an $Fddd$ structure upon hydrogen bond symmetrization at 460 GPa. For
both these orthorhombic phases symmetry breaking leads to two non-equivalent N-N bond lengths in the chain -e.g. 1.25 and 1.34 Å in \( F_{ddd} \)-NH at 460 GPa. The different lengths of the N-N bonds come from the distortion of the square spirals, caused by their packing and hydrogen bond pattern. The \( F_{ddd} \)-NH remains stable up to at least 800 GPa.

2D-polymeric hydronitrogen. Distinct from the polymeric chain structures, we also discovered an exotic stable nitrogen-rich compound \( \text{N}_9\text{H}_4 \). Its structure has \( \text{Ccc}_2 \) symmetry, and is composed of negatively-charged 2D nitrogen planes and \( \text{NH}_4^+ \) cations. \( \text{Ccc}_2\text{-N}_9\text{H}_4 \) was predicted to be thermodynamically stable in a narrow pressure range 50–60 GPa. As shown in Fig. 3(f), the 2D nitrogen plane is a loose structure due to the hexagonal star-shaped holes decorated by 18 additional nitrogen atoms. Parallel stacking of the nitrogen planes creates infinite channels in the perpendicular direction, and \( \text{NH}_4^+ \) cations are located along these channels. The electrons in the plane are delocalized, as a result this compound is metallic with a flat band crossing the Fermi level. (See more details about properties of \( \text{N}_9\text{H}_4 \) in Supplementary Information).

Molecular hydronitrogens. \( \text{N}_8\text{H} \) is found to be stable around 50 GPa, and adopts a very unusual molecular structure with four pentazole (\( \text{N}_5\text{H} \)) and six nitrogen (\( \text{N}_2 \)) molecules in the unit cell. (See more details about \( \text{N}_8\text{H} \) structure in Supplementary Information).

Hydrogen-rich hydronitrogens, instead of polymeric structures, have hydrogen-bonded molecular structures. The \( \text{NH}_4 \) phases, containing a higher hydrogen ratio than \( \text{NH}_3 \), are found to be thermodynamically stable above ~50 GPa, and remain stable at least up to 800 GPa. At pressures above 50 GPa, \( \text{NH}_4 \) first adopts a host-guest structure of \( \text{Pc} \) symmetry with the structural formula (\( \text{NH}_3 \))\({}_2\text{H}_2 \). Other host-guest structures, adopting \( \text{P}2_1/\text{c} \) and \( \text{I}4/\text{m} \) symmetries, have very close enthalpies to this structure below 80 GPa (See more details about these \( \text{NH}_4 \) structures in Supplementary Information). Accurate fixed-composition crystal structure predictions for \( \text{NH}_4 \) show that above 52 GPa, \( \text{C}2/\text{c} \) structure is located in the global minimum of the energy landscape for \( \text{NH}_4 \), and other structures with close enthalpies are structurally similar to the \( \text{C}2/\text{c} \) structure. In all host-guest structures, \( \text{H}_2 \) molecules are captured in hydrogen-bonded frameworks formed by \( \text{NH}_3 \) molecules. In the pressure range 85–142 GPa, the ionic \( \text{P}1-\text{NH}_4 \) phase is more stable than host-guest molecular structures. In the unit cell of this low-symmetry ionic phase, as shown in Fig. 4(a), every eighths ammonia molecule reacts with an \( \text{H}_2 \) molecule to form the \( \text{NH}_4^+ \) cation and \( \text{H}^- \) anion. The distance of \( \text{H}^- \) anion and the nearest hydrogen of the \( \text{NH}_4^+ \) cation is 1.13 Å at 100 GPa. Above 142 GPa, the ionic phase undergoes a reentrant transition to the same \( \text{C}2/\text{c} \) host-guest structure again, thus returning to structures consisting of neutral \( \text{NH}_4 \) and \( \text{H}_2 \) molecules. Hydrogen-bond symmetrization was not observed in all stable \( \text{NH}_4 \) phases up to 800 GPa.

Figure 4. The proposed structures of \( \text{NH}_4 \), \( \text{NH}_5 \) and \( \text{N}_3\text{H}_7 \). The small pink spheres indicate hydrogen atoms and the blue large spheres are nitrogen atoms. The nitrogen atom in \( \text{NH}_4^+ \) cation and the \( \text{H}^- \) anion are noted with green and aqua spheres, respectively. (a) Phase transition sequence from host-guest \( \text{Pc} \rightarrow \text{host-guest C}2/\text{c} \rightarrow \) Partially ionic \( \text{P}1-\text{NH}_4 \) phases. In host-guest structure of \( \text{C}2/\text{c}-\text{NH}_4 \), the hydrogen molecules are captured in the channels formed by \( \text{NH}_3 \) molecules. In the partially ionic \( \text{P}1-\text{NH}_4 \) structure, the \( \text{NH}_4^+ \) cation is close to the \( \text{H}^- \) anion. (b) The ionic \( \text{C}2/\text{c} \) \( \text{NH}_5 \) phase, with symmetric hydrogen bonds in \( [\text{H}_2\text{N}--\text{H}--\text{NH}_3^-]^- \) units and \( \text{H}^- \) anions. (c) Phase transition sequence molecular \( \text{P}1 \rightarrow \text{ionic C}2 \rightarrow \text{ionic P}-3\text{m}1 \).
With the 1:1 ratio of H, and NH₃, several NH phases are also found to be thermodynamically stable or nearly stable around 55–100 GPa. The ionic C2/c phase (See Fig. 4(b)) has the lowest enthalpy at pressures below 162 GPa. In the unit cell of C2/c-N₃H, there are two [H₃N···H···NH₃]⁺ units and two H⁺ anions. At pressure above ~162 GPa, C2/c-N₃H phase transforms into metastable ionic P2 and Amn₂ structures, then adopts a P2₁/c structure containing alternating layers of NH₃ and N₂H₄ molecules above ~363 GPa. (See more details about NH₃ high pressure phases in Supplementary Information).

At about 140 GPa, a previously unreported remarkable compound with the composition N₃H₂ is also found to be thermodynamically stable. For N₃H₂, we have predicted several thermodynamically stable phases with the structural sequence P1 → P2 → P₃m1 → P2₁/m1 → P2₁/m-1 upon increasing pressure (See Fig. 4(c) for the first three structures). At 140–200 GPa, P1-N₃H₂ adopts a stable molecular structure, consisting of one ammonia (NH₃) and one hydrazine (N₂H₄) molecules in the unit cell. At 200 GPa, P1 undergoes a spontaneous molecular-to-ionic transition, resulting in a layered C2 structure. In this process, ammonia and hydrazine molecules react to form the NH₃⁺ (amide) anions and N₃H⁺ (hydrazinium) cations, respectively. The N₃H⁺ ions are in a parallel arrangement and connected by symmetric H-bonds. At 300–380 GPa, complicated ionic N₃H₇ structure of P-3m1 symmetry becomes stable. As shown in Fig. 4(c), in this unique structure, the trigonal unit cell has two neutral ammonia molecules, one N₃⁻ anion, one [N₃H₉]₂⁺ cation and one [N₄H₈]⁺ unit (net formula N₃H₄⁺, the red H symbols indicate that such hydrogen atoms are symmetrically hydrogen-bonded and shared with neighbor N₃H₈⁺ units). This is the only structure with bare nitrogen anions observed among the newly proposed nitrogen hydrides. The nitride anion N₃⁻ is surrounded by 12 hydrogen atoms from NH₃ molecules and N₃H₈⁺ cation, with distances of 1.32 and 1.38 Å at 380 GPa. Then, at pressure above 380 GPa, the trigonal N₃H₂ phase will give way to another two P2₁/m type ionic structures, consisting of NH₃⁺ anions and N₃H⁺ cations again. They have different packing patterns from the ionic C2 structure (named P2₁/m-I and P2₁/m-II N₃H₂ by stability sequence upon increasing pressure, respectively (See Supplementary Information for more details).

With pressure increasing, our calculation confirmed that NH₃, above 36 GPa, undergoes phase transformations from hydrogen-bonded molecular P2₁/2₂ structure to layered ionic Pmna and Pcn₂ phases, and then returns to Pmna structures consisting of neutral NH₃ molecules at very high pressure²⁸. However, NH₃, the only thermodynamically stable hydronitrogen compound at ambient conditions, is surprisingly predicted to decompose into N₂H₄ and NH₃ at ~460 GPa at zero temperature. For NH₃, the dense molecular hydrazine phase was also predicted to be stable and have a C2/c symmetry at ~200–780 GPa, which is consistent with Zhang's work²⁹. The C2/c structure of NH₃ consists of hydrazine molecules, forming both symmetric and asymmetric hydrogen bonds with each other.

**Discussion**

Our theoretical calculations indicate that the N-H system exhibits rich chemistry under pressure. The infinite long-chain polymeric structures are widely found in nitrogen-rich hydronitrogen compounds, and are thermodynamically stable above 42 GPa. They could potentially serve as good high-energy-density and fuel materials due to the substantial energy difference between the single/double and triple nitrogen-nitrogen bonds. The nitrogen backbone evolves with increasing hydrogen concentration. With the "antiseds" technique (See Methods), we found that metastable nitrogen phases containing zigzag N-chains have competitive enthalpies (~0.03 eV/atom higher at 60 GPa) to the molecular states and the singly bonded cg-N structure at 40–70 GPa, and they are more energetically favorable than arm-chair-shaped and other N-chains (See Fig. S5 in Supplementary Information). A low hydrogen content stabilizes these chains and does not change much of the packing pattern of the chains and the electronic properties of the resonant N-N bonds. The lowest-enthalphy structures of metastable N₃H₂ and stable N₃H₃ phases contain infinite zigzag N-backbones. (See more details about these two compounds in Supplementary Information) With higher hydrogen content, the zigzag N-backbone become unstable in N₃H, N₂H and NH phases. These long-chain polymeric hydronitrogen compounds would be an interesting alternative to commonly used high-energy-density materials. Compared to pure polymeric nitrogen (cg-N phase), layered P2₁/c N₃H is stable at pressures above ~42 GPa, i.e. at pressures lower than the stability pressure of cg-N (~56 GPa). Hydrazoic acid (N₃H) may be an even better precursor for synthesizing long-chain polymers. With hydrazoic acid, the layered P2₁/c N₃H can be formed at as low as 6.0 GPa (See Table 2). The VC-NEB³⁰ calculation indicates that the phase transformation from hydrazoic acid to P2₁/c N₃H has an energy barrier of ~0.25 eV/atom at 10 GPa, (See

| Reaction | Pressure [GPa] | ∆V |
|---------|---------------|----|
| N₃H (HA⁺) → N₃H (long-chain) | 6.0 | 7.58 |
| N₃H₂ + N₃H (HA) → 5NH (dimer=long-chain) | 12.1 | 10.9, 9.81** |
| N₃H₂ + N₃H(P₄,2₂₁₂) → 4NH (dimer=long-chain) | 32.5 | 6.26 |
| N₃H₂ + 5N₃H(P₄,2₂₁₂) → 4N₃H (long-chain) | 37.3 | 18.5 |

Table 2. Chemical reactions to synthesis high-energy-density hydronitrogen at ΔH = 0. *HA short for Hydrazoic Acid. **With C2 and P2₁-N₃H₂ phases, respectively.
Fig. 5), and occurs in several stages. In the first stage, some H-bonds between HN₃ molecules break, making the molecules free to rotate (as shown in Fig. 5 from Image-1 to Image-5). After adjusting directions of HN₃ molecules (Image-5 to Image-18), metastable short N-chain molecules (Image-21 and Image-27) appear during the transition, new nitrogen-nitrogen bonds appear, eventually leading to infinite polymeric chains (Image-30). The energy barrier of first stage with rotation of the HN₃ molecules is around 0.15 eV (from Image-1 to Image-19), and approximately equals to the barrier of the second stage (nitrogen-nitrogen bond formation). The transition should happen easily in liquid hydrazoic acid. Mixture of hydrazine and hydrazoic acid is an alternative precursor, with polymerization estimated to happen at ∼13 GPa (See Table 2).

Isoelectronic to oxygen, (NH) units generally serve as analogs of group VI elements in these polymeric chain structures. Besides the square-spiral chain in high-pressure phases found in NH, the monoclinic N₃H phase can be considered as an analogue material of sulfur nitride (SN)ₙ₃⁴ or (ON)ₙ₃⁵,₃⁶ polymers. The proposed nitrogen oxides (ONNO)ₙ chain oligomer also has comparatively strong N=N bonds. The monoclinic N₃H phase is a metallic polymer as the Fermi level is crossed by anti-bonding π* bands (See Fig. S4 in Supplementary Information), which is similar to the first known metallic polymer (SN)ₙ₃⁷ as a superconductor with T_c = 0.26 K. All our 1D long-chain hydronitrogen compounds containing delocalized nitrogen bonds are metallic. Our calculations reveal that N₅H (at 55 GPa) and N₇H (at 60 GPa) are superconductors with T_c = 2.6 and 7.8 K (with the value of μ* = 0.13), respectively. In contrast, N₉H₄ phase is not a superconductor.

Multiple stable stoichiometries exist in hydrogen-rich hydronitrogens at pressure. These hydronitrogens form molecular crystals at low pressure, and then tend to undergo auto-ionization under moderate compression, except NH₅ (See Table 1). The structures of these compounds show various characteristics and are quite different from each other. N₅H₅, NH₇ (and NH₉) can be considered as binary NH₅ + N₅H₇ and NH₇ + xH₂ compounds, respectively. Therefore, in general, high-pressure hydrogen-rich hydronitrogens tend to contain molecules and molecular ions.
It is predicted that hydrogen-rich hydronitrogens remains stable to extremely high pressures, NH3 and NH2 become unstable and decompose (into NH and N2H) or into NH and N2H4) at 480 and 780 GPa, respectively; and NH2 and N2H4 are thermodynamically stable at least up to 800 GPa. In contrast, methane (CH4) was predicted to dissociate into ethane (C2H6), butane (C4H10), and finally, diamond plus hydrogen at 287 GPa2.

NH3 and NH2 undergo a molecular \( \rightarrow \) ionic \( \rightarrow \) molecular phase sequence under pressure, which is very similar to NH3. The auto-ionization process also occurs in N2H4, which remains in the ionic phase at least up to 800 GPa. In contrast, C-H compounds have non-polar non-ionic structures, and the high energy cost of proton transfer in H2OO39 prevents auto-ionization until extremely high pressure (~1.4 TPa)39. Our calculation revealed that the energy cost of proton transfer from H2 to NH3 molecule and from NH3 to N2H4 molecule is ~0.7 eV and ~1.0 eV, respectively, while it costs ~0.9 eV40 to form NH2- ions in NH3. Therefore, NH3 + xH2 compounds would undergo auto-ionization at a lower pressure (NH4 at ~85 GPa and NH3 at ~42 GPa) than pure NH3 (at ~90 GPa). Due to high cost of proton transfer, auto-ionization phenomenon was not observed in any stable H2O-H2 compounds1. Calculations show that auto-ionization happens at ~200 GPa in N3H7, higher in NH3 (90 GPa), due to the higher proton transfer energy cost, and survives up to at least 800 GPa. The pV term in the free energy plays an important role in deterring the phase transition sequence at high pressure. Under pressure, stable NH3 and NH3-xH2 guest-host phases are more packing-efficient than the volume of NH3 free energy plays an important role in deterring the phase transition sequence at high pressure. Under pressure, stable NH3 and NH3-xH2 guest-host phases are more packing-efficient than the volume of NH3.

Conclusions

We have extensively explored the nature of hydronitrogen compounds up to ultrahigh pressures. It turns out that unusual compounds, such as N2H, NH, N2H4, NH3, NH2, NH2-NH4, NH3, NH2, and NH3 are stable under pressure. These compounds possess intriguing crystal structures and remarkably novel, exotic properties. Three main features can be concluded, 1) the (NH) unit behaves similarly to its isoelectronic analogs, oxygen (also the sulfur) atoms, 2) molecular hydronitrogens are mainly composed of H2, NH3, N2H4 molecules and corresponding ions, 3) auto-ionization is common in N-H molecular phases due to the low energy cost of the proton transfer between the H2, NH3, N2H4 molecules.

Our investigation opens ways for designing synthesis of novel high-energy-density polymeric hydronitrogens. It is clear that starting with metastable precursors (such as N2H4, NH3) should lower polymerization pressure (compared to the lowest pressure of thermal dynamic polymeration, 42 GPa). We experimented with different mixtures of N2H4, NH3, and N2 give bulk NH3 or NH3 compositions. We found that using N2 in the precursor mixture does not give good results. Instead, pure N2H4 and NH3, or their mixtures can polymerize already at near-ambient conditions. For planetary interiors (where H/N > 1), we expect the presence of N-containing molecular ions at all pressures above ~55 GPa in NH3. This means a much thicker layer with ionic conductivity than previously thought, which will affect models of planetary magnetic fields (which are generated by convection of electrically conducting layers). High-pressure chemistry of hydronitrogens uncovered here has greater diversity than hydrocarbons.

We remind that at normal conditions, the only thermodynamically stable compound of carbon and hydrogen is methane (CH4), all the other hydrocarbons being metastable and kinetically protected by high energy barriers. Here we have uncovered unique structural diversity among THERMODYNAMICALLY STABLE hydronitrogens. N-H bonds are directional covalent bonds (just like C-H), which should also lead to high energy barriers and ubiquitous metastability. If one includes metastable hydronitrogens, and adds other elements (such as O, S, smaller amounts of C), the diversity will most likely exceed the diversity of organic chemistry. This invites the question whether nitrogen-based (rather than carbon-based) life is possible in the interiors of gas giant planets. Briefly, we see the following conditions as necessary for emergence of life: (1) great structural and chemical diversity based on a small number of chemical elements (C-H-O or N-H-O), (2) abundance of metastable compounds with long lifetimes, (3) chemical reactions for energy production, (4) reversible reaction for storing/releasing energy (similar to the function of ATP in carbon-based life), (5) a molecule that can be used as information matrix (analogous in its function to DNA). For nitrogen-rich compounds, condition (1) is clearly satisfied. Condition (2) is also likely satisfied at not very high temperatures. Energy source and storage can be related to metastable compounds -e.g. oxidation of hydronitrogens for energy production, and polymerization/depolymerization of hydronitrogens for energy storage. As for condition (5), it is too early to say which N-based molecules could be suitable -the main conditions seem to be 1D or 2D polymeric nature and aperiodicity. Nitrogen-based life could be possible, but the likelihood of this is highly limited due to high temperatures in these planets’ interiors, which could make lifetimes of metastable compounds too short. Given the abundance of N, H, O, C in giant planets, and high pressures in their interiors, we expect great diversity of molecular species there.

Methods

Crystal structure prediction. Crystal structure prediction was performed using the variable-composition evolutionary algorithm USPEX15,23–26. A number of studies illustrate the power of the USPEX method16,17,19. Calculations for the N-H system were performed at various pressures in the wide range of 0–800 GPa.

Given the dramatically changed behavior of nitrogen under pressure and a wide pressure range of our investigation, we performed a number of different types of predictions with USPEX. We ran variable-composition predictions for N-H, N-NH and NH-H systems with up to 32 atoms per unit cell. Given molecular nature of all stable and nearly stable compounds in hydrogen-rich hydronitrogens, we also did structure prediction for the packing of well-defined NH3 and H2 molecules (rather than N and H atoms), by applying the specially designed constrained global optimization algorithm29, considering structures with up to 24 molecules (i.e. up to 96 atoms) per primitive unit cell. These calculations were run together in a global coevolutionary search with exchanging good (stable and some metastable) structures between different runs. This coevolutionary method is very efficient.
and has been implemented on top of the USPEX code. When performing prediction for metastable nitrogen structures containing zigzag N-chains, we applied the antiseeds technique, which was adopted to search for all low-enthalpy structures based on zigzag N-chains.

**DFT calculations.** The underlying *ab initio* structural relaxations and electronic structure calculations in USPEX were carried out using the all electron projector augmented wave (PAW) method as implemented in the VASP code. The plane-wave cutoff energy of 800 eV and dense Gamma-centered k-point meshes with a resolution better than 2π × 0.05 Å were adopted, and ensured high-quality results. After identifying the most stable compositions and several candidate structures, we relaxed them at numerous pressures in the range of 0–800 GPa with higher PAW potentials, in which the core radius equals 0.42 and 0.58 Å for hydrogen and nitrogen, respectively. An extremely high cutoff energy of 1400 eV was used for these relaxations and calculations of enthalpies of reactions and phase diagram. In addition, phonon dispersions throughout the Brillouin zone were derived using the finite-displacement approach as implemented in the Phonopy code. Superconducting Tc was calculated in QUANTUM ESPRESSO, with ultrasoft potentials using 40 Ry plane-wave cutoff energy.

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**Author Contributions**

G.-R.Q. and H.Y.N. contributed equally to this work. A.R.O. designed research, G.-R.Q., H.Y.N., C.-H.H., Q.F.Z. and H.-Y.Z. performed simulations, G.-R.Q. and H.Y.N. analyzed data, G.-R.Q., H.Y.N., A.R.O. and C.-H.H. wrote the manuscript.

**Additional Information**

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