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# Ammonium Azide under High Pressure: A Combined Theoretical and Experimental Study

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S *Supporting Information*

ABSTRACT: Efforts to synthesize, characterize, and recover novel polynitrogen energetic materials have driven attempts to subject high nitrogen content precursor materials (in particular, metal and nonmetal azides) to elevated pressures. Here we present a combined theoretical and experimental study of the high-pressure behavior of ammonium azide (NH_4N_3). Using density functional theory, we have considered the relative thermodynamic stability of the material with respect to two other crystal phases, namely, *trans*-tetrazene (TTZ), and also a novel hydronitrogen solid (HNS) of the form $(NH)_4$, that was recently predicted to become relatively stable under high pressure. Experimentally, we have measured the Raman spectra of NH_4N_3 up to 71 GPa at room temperature. Our calculations demonstrate that the HNS becomes stable only at pressures much higher (89.4 GPa) than previously predicted (36 GPa). Our Raman spectra are consistent with previous reports up to lower pressures and at higher pressures, while some additional subtle behavior is observed (e.g., mode splitting), there is again no evidence of a phase transition to either TTZ or the HNS.
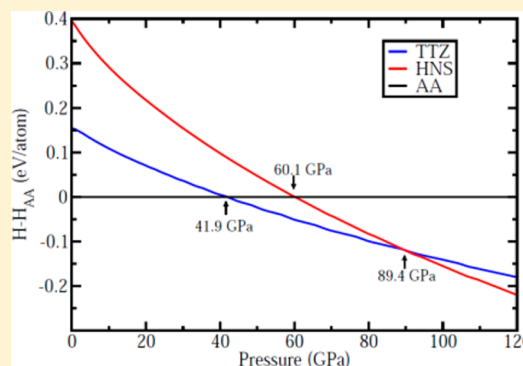
1. INTRODUCTION

Novel nitrogen compounds, N_n with n greater than three, have been of particular interest for the development of novel high energy density energetic materials with fast energy release.[1−6] This is because these single- and double-bonded "polynitrogens" are expected to decompose into familiar triply bonded diatomic nitrogen accompanied by the rapid release of enormous energy per unit mass. The origin of this energy is a substantial difference in strength of the N triple bond and that of single and double bonds, which are much weaker.[2] Many such materials have been predicted on the basis of theoretical calculations and include molecular (from N_3 up to N_{60})[7−15] and nonmolecular polymeric "cubic gauche" (cg-N) forms.[16−21] However, experimental progress in synthesizing novel forms of nitrogen, either pure or in compounds with other elements, has been slow. Recent examples include cg-N solid[3] as well as N_5^- and N_5^+ ions.[2] The exceptional properties of proposed polynitrogen energetic materials can be illustrated by comparing the predicted energy content of cg-N with a familiar explosive such as HMX (e.g., a 10-fold increase in detonation pressure; see the results of the calculations by H. Östmark presented by Christe[2]). However, such a comparison assumes that the density of cg-N, which was synthesized above 100 GPa and 2000 K, can be retained under ambient conditions. To date, the material has not been quenched, and no tests of energetic performance have been possible. Nevertheless, attempts to synthesize new nitrogen compounds under high pressure and temperature continue both experimentally and

theoretically. In particular, various workers have investigated the possibility that high nitrogen content precursor molecules rather than pure nitrogen might offer pathways to new polynitrogen compounds that involve less extreme conditions and are therefore more practical. One potential precursor is that containing the N_3^- anion, that is, the azide.[4,5]

There has been growing interest in the behavior of ammonium azide NH_4N_3,[22−27] some of which has been focused specifically on its behavior under high pressure.[22−25] Ammonium azide is particularly relevant in the present context thanks to its high nitrogen content (>90% by weight) and, upon full decomposition, is expected to yield only environmentally benign products. Furthermore, it has been specifically predicted to undergo a transition at 36 GPa to a high-energy density hydronitrogen solid (HNS) of the form $(NH)_4$.[22] This prediction has motivated recent high-pressure experimental efforts whose diagnostic was Raman scattering.[23] Medvedev et al. concluded that above 3 GPa and up to 55 GPa at room temperature ammonium azide is thermodynamically stable with no sign of a transition to the predicted hydronitrogen solid. Rather, their Raman spectra showed a polymorphic phase transition at 3 GPa. They named the phase "Phase II" to distinguish it from the lower pressure phase, "Phase I", which is stable to ∼3 GPa.[23,25] Medvedev et al. provided an extensive

summary of the Raman spectrum, its origins, and its dependence on pressure. Wu et al.[25] subsequently carefully analyzed the transition using a combination of X-ray diffraction and Raman spectroscopy. Our primary motivation here was to extend the previous measurements to higher pressures to investigate the possibility that the transition predicted by Hu and Zhang might indeed occur. We also revisit theoretically the previous prediction by carrying out density functional theory (DFT) calculations of the relative stability of the relevant phases.

2. THEORETICAL DETAILS

DFT Calculations of the Relative Thermodynamic Stability of Ammonium Azide, *trans*-Tetrazene (TTZ), and the Hydronitrogen Solid (HNS). The phase transition to a hydronitrogen solid that was predicted by Hu and Zhang would correspond to a radical chemical change and if it occurred would be expected to be clearly apparent in measured Raman spectra. Here we have reexamined the possibility of phase transitions of ammonium azide under high pressure by performing first-principles DFT calculations of the relative thermodynamic stability of ammonium azide and the two other crystal phases, the HNS[22] and *trans*-tetrazene[28] (TTZ) considered by Hu and Zhang[22] (Figure 1). The DFT
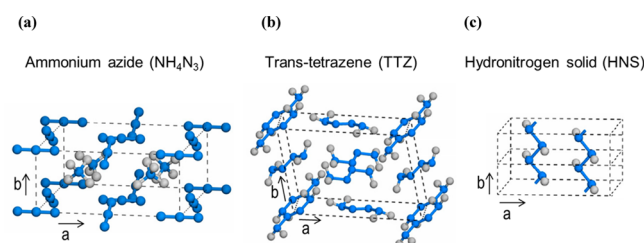

Figure 1. Crystal structures of (a) the molecular crystal ammonium azide (AA), (b) the molecular crystal trans-tetrazene (TTZ), and (c) the hydronitrogen solid (HNS). Blue spheres represent nitrogen, gray spheres represent hydrogen.

calculations employ the Perdew–Burke–Ernzerhoff (PBE) generalized gradient approximation (GGA) functional to DFT and the empirical dispersive correction by Grimme,[29] which takes into account long-range van der Waals (vdW) interactions. The HNS contains infinite 1-D zigzag nitrogen chains saturated by hydrogen, with repeated $(NH)_4$ units being arranged in a monoclinic unit cell having $P21/m$ space group[22] symmetry (Figure 1; we note that a somewhat similar structure was considered for LiN_3 by Prasad et al.[30]). TTZ is a molecular crystal containing vdW-interacting $(NH)_4$ molecules arranged in a unit cell with triclinic P-1 space group symmetry[1] (Figure 1).

The relative enthalpies of TTZ, and the HNS referenced to the enthalpy of the NH_4N_3 crystal are shown as a function of pressure (Figure 2). Our calculations predict the following sequence of phase transitions: NH_4N_3 to TTZ at 41.9 GPa (36 GPa[22]) and TTZ to the HNS at 89.4 GPa (75 GPa[22]). The values in parentheses are the transition pressures reported by Hu and Zhang,[22] the differences being due to the inclusion of vdW interactions in our calculation. We also point out that the transition at 36 GPa that was predicted in the previous work is actually the transition[31] to TTZ and not the HNS. Therefore, we do not expect to see evidence in our measured Raman spectra of a transition to the HNS because it should occur only
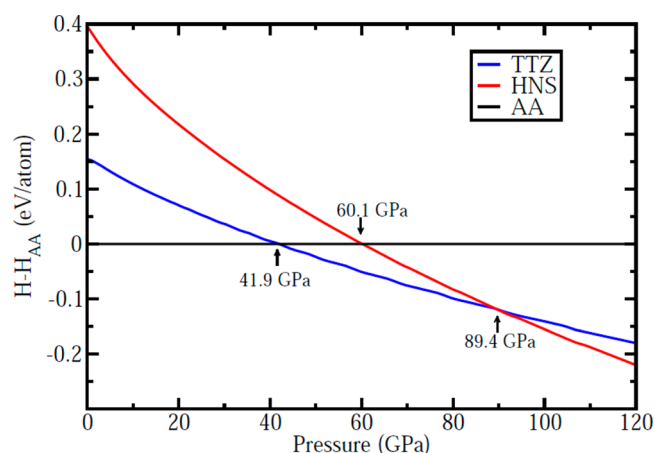

Figure 2. Relative enthalpy of TTZ and HNS compared to ammonium azide (AA). The transition pressure between each pair of phases is displayed in the plot.

at pressures substantially higher than those reached in the experiment (71 GPa). Our spectra also show no evidence of a transition to TTZ. (See later.) In this case, however, the predicted pressure at which TTZ becomes relatively stable is substantially less than the highest experimental pressure; it would seem that in this case at least there is a large energetic barrier separating the two crystal phases. Alternatively, phase II, which is known from experiment to occur above 3 GPa, may in reality simply be more stable than TTZ in this pressure range.

3. EXPERIMENTAL DETAILS

Raman measurements were taken in a diamond anvil cell (DAC) equipped with "ultra-low" fluorescence diamonds (Almax) or type-II artificial diamonds (Sumitomo) of tip dimension 300 or 200 μm, respectively. The gasket material was rhenium; it was preindented and then cut using electric arc discharge machining[32] to form a sample cavity whose dimensions depended on the desired pressure range (~100 μm diameter with a preindent to ~45 μm for the highest pressure experiments). The pressure medium was argon. The NH_4N_3 sample (prepared for these experiments at LLNL), in the form of a fine grain white polycrystalline powder and a small ruby chip, was lightly compacted into the sample cavity under dry nitrogen gas. Over a period of approximately 5–10 min, the solid ammonium azide sample would decompose into previously observed products such as presumably hydrazoic acid in the gas phase[33] to the point where perhaps 20% of the sample cavity was filled with remaining solid NH_4N_3 starting material. At this point, the cavity was sealed. In one of the experimental runs the trapped material was subsequently characterized using FTIR spectroscopy (Figure S1 of the Supporting Information and corresponding discussion). The diamond cell was then placed in liquid argon. After ~10 min the cell was opened and then resealed to introduce and trap the argon. The small ruby chip (<10 μm) was used to determine pressure. Raman spectra from the azide were collected within 30–50 um of the ruby chip.

The Raman measurements were made using an excitation wavelength of 632.8 nm (1.96 eV). Laser power reaching the DAC was ~4 mW or less. Spectra were recorded on a 300 lines/mm ("low resolution") and an 1800 lines/mm ("high resolution") grating. Narrow spectral artifacts were removed before further analysis. All quantitative results were obtained

from high-resolution spectra in the frequency range of ∼100 to 3200 cm^{-1}. The instrument was approximately calibrated using emission lines from a neon standard lamp. Instrumental nonlinearity across most of the spectral windows was assumed to be small, and we did not correct for either frequency or intensity. In the range of 2800 to 3150 cm^{-1}, where our system sensitivity decreased relatively rapidly, we did correct for intensity. Measurement precision was expected to be 1 to 2 cm^{-1}.

4. RESULTS

We carried out multiple experimental runs ranging in pressures from 1 to 71 GPa. Raman spectra obtained in different spectral regions and associated quantities are shown in the Figures: ∼ 100 to 700 (Figure 3), 1350 to 1550 (Figure 4), 1600 to 2250
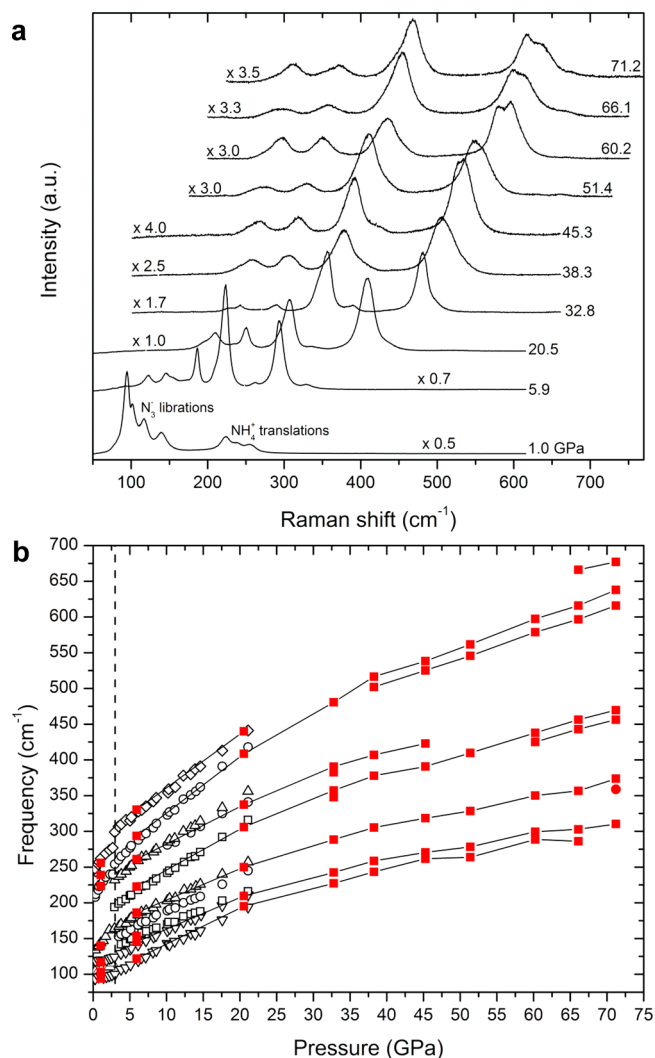

Figure 3. (a) Raman spectra of NH$_4$N$_3$ measured in the frequency range of ∼100 to 700 cm^{-1}. External (lattice) mode region. Pressures range from ∼1 to 71 GPa and are indicated. Measured spectra are displaced vertically and scaled to permit comparison. The observed bands are assumed to have their origin in librational and translational modes consistent with the assignments of Medvedev et al.[23] (b) Measured frequencies versus pressure of the bands shown in panel a. The vertical dashed line in panel b at 3 GPa delineates the approximate transition pressure[23] from phase I to phase II. Open symbols are data obtained by Medvedev et al.[23,24]
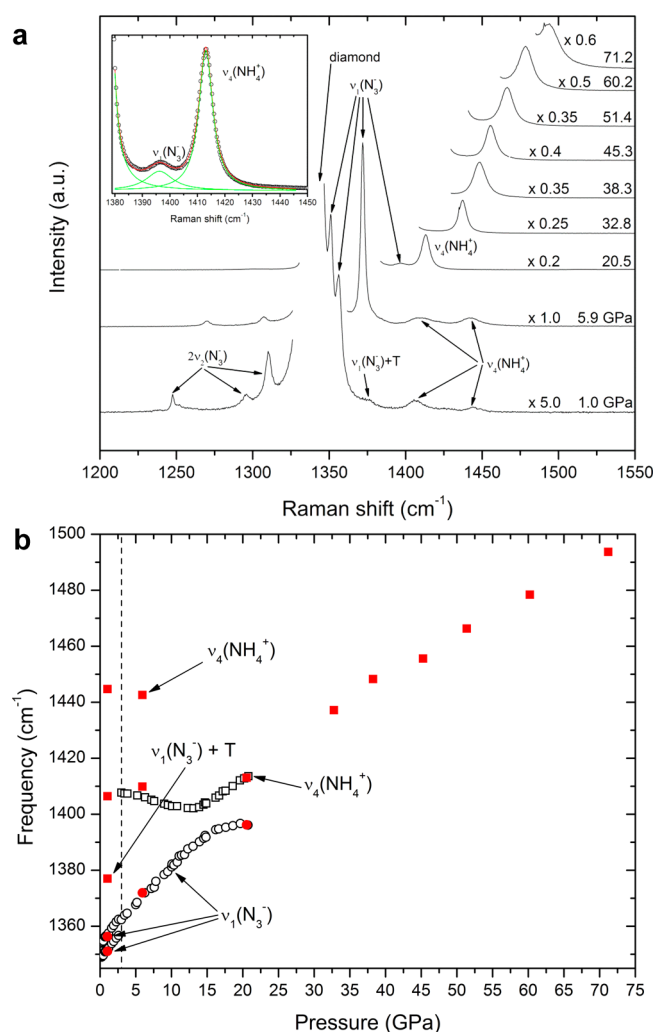

Figure 4. (a) Raman spectra of NH$_4$N$_3$ measured in the frequency range of ∼1350 cm^{-1} to 1550 cm^{-1}. Pressures are indicated in GPa. Measured spectra are displaced vertically and scaled to permit comparison. Band origins are labeled according to the assignments of Medvedev.[23] Inset: fit to bands due to the azide stretch and ammonium ion bending modes at 20.5 GPa. (b) Measured frequencies of most of the bands shown in panel a. The vertical dashed line at 3 GPa delineates the approximate transition pressure[23] from phase I to phase II. Open symbols are data obtained by Medvedev et al.[23,24]

(Figure 5), and 2800 to 3150 cm^{-1} (Figure 6). (Examples of spectra acquired using the 300 lines/mm grating are shown in the Supporting Information, Figure S2, each of which simultaneously cover most of the relevant spectral range.) Data at 5.9 and 20.5 GPa and at 1 and 38.3 GPa were obtained in separate runs; the rest were obtained in a single run. Overall behavior did not differ between runs, but frequencies and line widths for at least some features showed small but clear differences at similar nominal pressures.

We discuss our observations for each spectral window below. Medvedev et al. (2011),[23] and Medvedev et al. (2012)[24] used Raman spectroscopy to study NH$_4$N$_3$ at room temperature under high pressure in a silicone oil pressure medium. They provided quantitative results for some of the measured bands up to ∼11 and ∼21 GPa, respectively. We compare our results to theirs where possible.

a. Spectral Region 100−700 cm^{-1} (Lattice Modes). Figure 3a shows the evolution of the measured Raman spectra
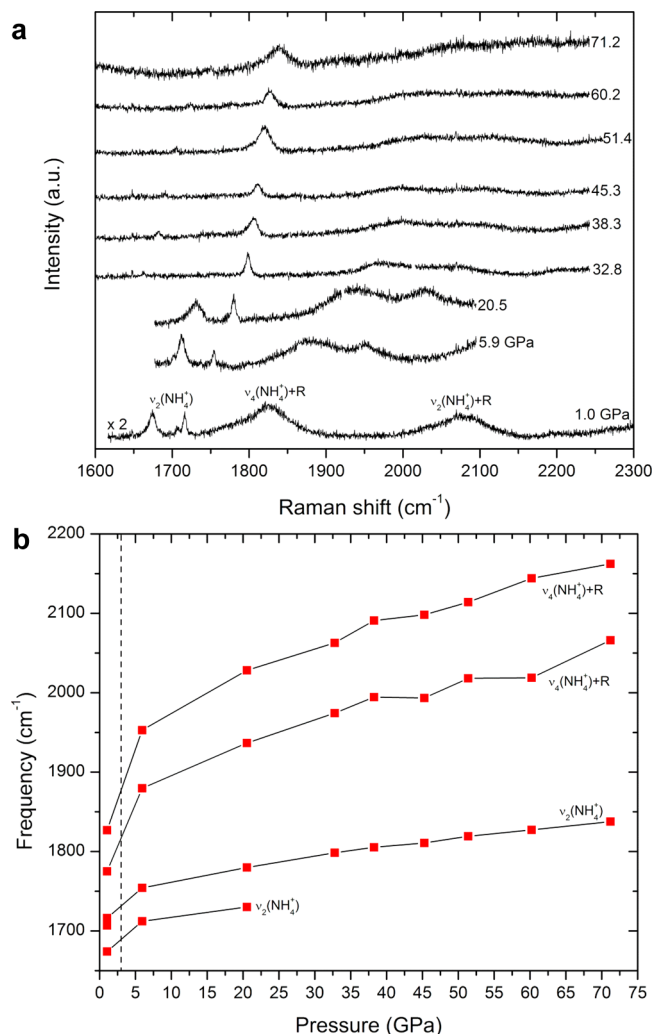
Figure 5. (a) Raman spectra of NH_4N_3 measured in the frequency range of ~1600 to 2300 cm^{-1}. Pressures are indicated in gigapascals. Measured spectra are displaced vertically to permit comparison. Band origins are labeled according to the assignments of Medvedev. (b) Measured frequencies of the indicated bands of panel a. The vertical dashed line at 3 GPa delineates the approximate transition pressure[23] from phase I to phase II.

Figure 6. (a) Raman spectra of NH_4N_3 measured in the frequency range of ~2800 to 3150 cm^{-1}. Pressures are indicated in gigapascals. Measured spectra are displaced vertically to permit comparison. Band origins are labeled according to the assignments of Medvedev. (b) Measured frequencies of the indicated bands of panel a. The vertical dashed line at 3 GPa delineates the approximate transition pressure[23] from phase I to phase II. The dashed red lines are linear fits. The gray data are exactly twice the frequency of the $\nu_4(NH_4^+)$ mode shown in Figure 4b. Open squares are data obtained by Medvedev et al.[23]

with pressure in the range of frequencies associated with lattice modes. We observe a profound, but expected, change in the spectrum between 1 and 5.9 GPa and attribute this to the phase I → phase II transition reported by Medvedev et al.[23] and which occurs at ~3 GPa.

Above that pressure range the spectrum evolves smoothly up to the highest pressure achieved of 71 GPa, and there is no sign of a substantial physical or chemical transition. However, above ~35 GPa, the most intense band, probably due to an ammonium ion translational mode (compare with the assignment given by Medvedev et al.[23] for phase I), begins to broaden and then split. Above 60 GPa, the band is clearly composed of (at least) two components. This behavior was reproducible as we observed it in three different runs. Medvedev et al.[23] shows one spectrum in this range at 55 GPa; the mode in question does not appear split but might be relatively broadened.

Figure 3b shows measured frequencies versus pressure. Frequencies were obtained by assuming Lorentzian line shapes and linear backgrounds. (Figure S3 in the Supporting Information shows as an example the fit to the spectrum
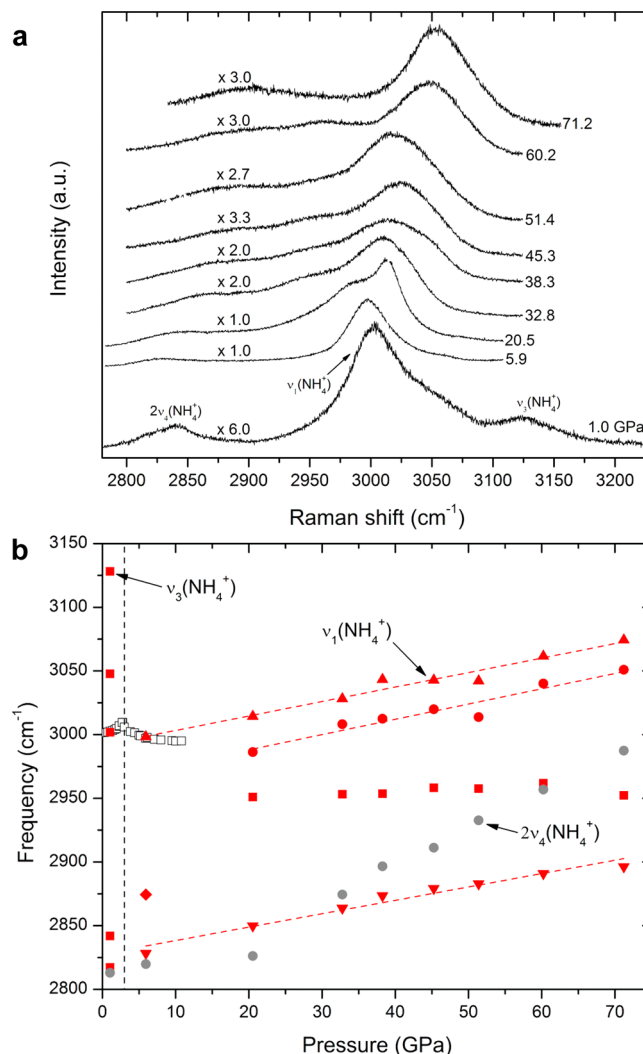
recorded at 71.2 GPa.) In several cases, in both this spectral range and others, fits were not definitive; some modes were clearly asymmetric, and it was not obvious how many distinct bands were involved. Also, a few very weak bands were not fitted and their frequencies were merely estimated. The overall behavior was, however, quite clear. In the pressure range of overlap, we find good agreement between our results and those of Medvedev et al. There are a few small, and we presume insignificant, discrepancies. In phase I, we observe a small additional feature in the NH_4^+ translational bands (at 239 cm^{-1} at 1 GPa) not reported by Medvedev et al. This feature is not reported by Iqbal and Malhotra either[34] in their 1-bar study although the mode they observed at 205 cm^{-1} appears slightly asymmetric and may possibly contain a higher frequency component. In phase II, Medvedev et al. report a weak mode with a frequency of ~155 cm^{-1} at 3.5 GPa (circles in Figure 3b). A weak band in this range is likely present in our low-

pressure spectra, but we did not attempt to track it. Similarly, Medvedev reports another weak mode that has a frequency of 355 cm^{-1} at 21 GPa (up triangles).

b. Spectral Region 1350−1550 cm^{-1} (Azide Symmetric Stretch and Ammonium Ion Bending Modes). This spectral region is dominated by the ν_1 symmetric stretching mode of the N_3^- anion and the ν_4 HNH angle bending mode of the NH_4 cation (Figure 4). We observe that the former is split by ~5 cm^{-1} due to the azide ion occupying nonequivalent crystal sites, as noted by Medvedev et al.[23] At low pressures, additional bands are visible, for example, a shoulder at between ~1370 and 1380 cm^{-1} (assigned to a combination of ν_1 and translational modes[23]). We also note lower frequency bands in the range of 1250−1310 cm^{-1} in our lowest pressure spectrum (1 GPa, phase I), which are consistent with those measured by Medvedev et al. They were assigned to overtones of the azide bending modes, ν_2, with an intensity derived from ν_1 due to Fermi resonance. As pressure increased above 20.5 GPa, we tracked only a single band due to the $\nu_4(NH_4^+)$ mode.

Medvedev et al.[24] discuss an interesting resonant coupling that occurs for the modes near 1400 cm^{-1}, $\nu_1(N_3^-)$, and $\nu_4(NH_4^+)$, respectively. The modes appear to be crossing but instead bend away from each other (Figure 4b). At the same time, the intensity of ν_4 grows, while that of ν_1 shrinks. Once again we find that our data at 5.9 and 20.5 GPa are in good agreement with these lower pressure results, and we find a smooth extension of the $\nu_4(NH_4^+)$ frequency up to 71 GPa. We also note that the width of the band nominally associated with an NH_4^+ bending mode shows a substantial increase in width at a similar pressure to that at which the splitting of the translational mode just discussed begins to occur.

c. Spectral Region 1700−1900 cm^{-1} (Ammonium Ion Bending Modes). In this frequency range, the spectra are mostly much weaker than those in the other ranges. Nevertheless, a number of bands are observable (Figure 5a). These are assigned to NH_4^+ bending modes and combinations with torsional motion of the ammonium ion.[23] Above 20.5 GPa, the spectrum is dominated by a band whose origin is assumed due to an $\nu_2(NH_4^+)$ bond bending mode. After an initial rather sudden increase in frequency (presumably associated with the phase I → phase II transition), the frequency-dependence on pressure of the various bands is essentially monotonic (Figure 5b). Figure S4 in the Supporting Information shows as an example the fit to the spectrum recorded at 20.5 GPa.

d. Spectral Region 2800−3150 cm^{-1} (N−H Stretching Modes). In this frequency range, the spectrum is dominated by bands due to the symmetric and asymmetric N−H stretching modes, $\nu_1(NH_4^+)$ and $\nu_3(NH_4^+)$, respectively. There are, however, other contributions, for example, due to an overtone of $\nu_4(NH_4^+)$ apparently.[23] In general, the evolution of the spectrum with pressure (Figure 6a) is complicated, and attempted fits assuming Lorentzian line shapes are once again not definitive. (Figure S5 in the Supporting Information shows as an example the fit to the spectrum recorded at 51.4 GPa.) Nevertheless, a monotonic increase in the $\nu_1(NH_4^+)$ frequency above 20.5 GPa is clear (Figure 6b). As shown by Medvedev et al., the frequency of this mode first increases up to the phase I → phase II transition before decreasing. On the basis of their results and ours, the frequency passes through a minimum between 10 and 20 GPa. This behavior implies that hydrogen bonding first decreases in strength up to the phase I to phase II transition,[24] then possibly increases up to a maximum between

10 and 20 GPa (corresponding to the minimum in the ν_1 frequency), before once again beginning to weaken. It is, however, difficult to make definite conclusions in this spectral range due to the complexity of the measured spectra and the well-documented failure of first-principles DFT to provide a quantitative description of hydrogen bonding in the condensed phase.

At the higher range of the pressures studied here, the efficacy of the pressure medium needs to be considered. While argon is a relatively good (i.e., soft) medium at low pressures, it becomes substantially harder at higher pressures. We found that in some cases measured frequencies and widths showed small but clear differences between runs at nominally similar pressures and attributed this to the different distribution of stresses obtained in each load. While experimentally more challenging, a medium such as neon would be preferable. Therefore, the role of the pressure medium in the observed splitting and broadening is currently unclear.

5. CONCLUSIONS

Raman spectra of ammonium azide have been measured up to 71 GPa. We observe previously unreported behavior including mode splitting and broadening. However, the transition to HNS predicted by Hu and Zhang to occur at moderate pressures above 36 GPa has not been detected in our experiments. Moreover, we reexamined the prediction by Hu and Zhang using DFT calculations and found that such a transition would happen at much higher pressures exceeding nearly 90 GPa.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

FTIR spectrum of ammonium azide near 1 bar is shown and discussed. Additional low-resolution Raman spectra at various pressures are also shown. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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