



Structural, vibrational and bonding properties of hydro-nitrogen solids under high pressure: An *ab-initio* study

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MS received 26 May 2016; revised 30 August 2016; accepted 31 August 2016

Abstract. Hydro-nitrogen solids are potential high energy density materials (HEDMs) due to high mass ratio of nitrogen which find wide range of applications as propellants and explosives. In the present work, we report the structural and vibrational properties of Tetramethyl Ammonium Azide (TMAA) and HydroZonium Azide (HZA) using density functional theory calculations by treating weak intermolecular interactions. The obtained ground state parameters using vdW-TS method are in good agreement with the experimental data. The pressure dependent lattice constants, compressibility and equation of state are discussed. The obtained equilibrium bulk moduli show the soft nature of these materials. The compressibility curves reveal that these compounds are highly compressible along crystallographic *a*-axis. We have also calculated the zone-center phonon frequencies and made a complete analysis of vibrational spectra at ambient as well as at high pressure. Contraction and elongation of C-H and N-H (NH₃ stretching) bonds under pressure lead to blue- and red-shift of the frequencies in the mid-IR region for TMAA and HZA compounds, respectively.

Keywords. Hydro-nitrogen solids; DFT; compressibility; Hydrogen bonding; IR spectra.

1. Introduction

It is a well-known fact that the chemical bonds are classified into primary (ionic, covalent and metallic) and secondary (σ -hole and hydrogen bonding) bonds. Strength of secondary bonds is approximately one tenth of the primary bonds. Even though, secondary bonds are weaker, they play significant role in determining the stability of molecular crystals. Therefore, chemical bonding (both primary and secondary bonds) is vital in understanding the nature of chemical reactions in any material, especially in energetic materials. Colton and Rabalais¹ reported that heavy metal azides are more covalent in nature when compared to alkali and alkaline-earth metal azides. Moreover, the ionic alkali metal azides (MN₃, M = Li, Na, K, Rb and Cs) are relatively stable when compared to heavy metal azides (M(N₃)₂, M = Cu, Hg and Pb) or hydrogen azide (HN₃) which are covalent in nature. Therefore, ionic and/or covalent bonding determines the stability and explosive nature of the inorganic azides. In addition, van der Waals (vdW) and hydrogen bonding are predominant in energetic molecular crystalline solids.

High energy density materials (HEDMs) became center of attraction due to their promising features in military and civil applications. High performance, insensitivity to external stimuli and eco-friendly nature are the ultimate goals in the field of energetic materials. The presence of hydrogen bonding plays a crucial role on the physical and chemical properties of an energetic material due to existence of strong intra- and intermolecular hydrogen bonding.²⁻⁴ It has been noticed that intermolecular hydrogen bonding in the solid phase can increase the efficiency and stability of HEDMs. The strong directional hydrogen bonding leads to an efficient packing in crystal structure resulting in high crystal density. Density (ρ) of a crystal is one of the most important factors to improve the performance of an explosive, since detonation pressure is proportional to ρ^2 and detonation velocity is proportional to ρ from Kamlet-Jacobs empirical equations.^{5,6} In addition, the presence of hydrogen bonding in planar layered energetic materials (for instance FOX-7, TATB and DAAzF) makes them insensitive, high performance and thermally stable.⁷⁻⁹

On the other hand, hydro-nitrogen solids (HNS) have received a lot of interest during the last half a decade for two reasons. 1) HNS can form polymeric nitrogen networks under extreme conditions and 2) they can also

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serve as model systems for studying the hydrogen bonding. In addition, understanding the high pressure behavior of HNS become an emerging field of research.¹⁰⁻¹⁶ A series of experimental^{15,16} and theoretical^{10-14,17,18} studies were reported to explore the electronic structure, mechanical, hydrogen bonding and possible structural phase transitions in HNS under hydrostatic compression. Ammonium Azide (AA) with nitrogen content of 93.3% by weight is proposed to form a polymeric nitrogen (which is a green high energy density material known till date) under extreme conditions.¹³ They also reported that hydrogen atoms play an important role to stabilize the polymeric nitrogen networks at ambient conditions.¹³ Tetramethyl Ammonim Azide (TMAA)¹⁹ and HydroZonium Azide (HZA)²⁰ are the HNS with 48.2% and 93.3% of nitrogen content by weight and they can also form an intermolecular hydrogen bonding networks. The presence of methyl group in place of hydrogen atom in AA¹⁵ reduces the nitrogen content by approximately 45% in TMAA.¹⁹ Therefore, investigation of structural and vibrational spectra under high pressure will be of interest in understanding the hydrogen bonding which further has strong impact on the performance and sensitivity of the explosive TMAA and HZA materials. The rest of the paper is organized as

follows: in section 2 we briefly describe the methodology of the calculations. Section 3 presents the results and discussion and finally section 4 summarizes the conclusions of the present study.

2. Computational details

First principles calculations were performed with plane wave pseudo potential (PP) density functional package Cambridge Series of Total Energy Package (CASTEP).²¹ The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) parameterization was used for exchange-correlation functional.²² As the investigated materials are molecular crystals where vdW and hydrogen bonding interactions play major role in crystal binding, physical and chemical properties. Therefore, we have used semi empirical dispersion correction (vdW-TS) method proposed by Tkatchenko and Scheffler within PBE parameterization to capture intermolecular interactions.²³ We have used Vanderbilt type ultra-soft (US)²⁴ and Norm-conserving (NC)²⁵ PPs for treating electron-ion interactions. The USPPs were used to calculate the structural properties at ambient as well as at high pressure, while NCPPs have been used to calculate the pressure

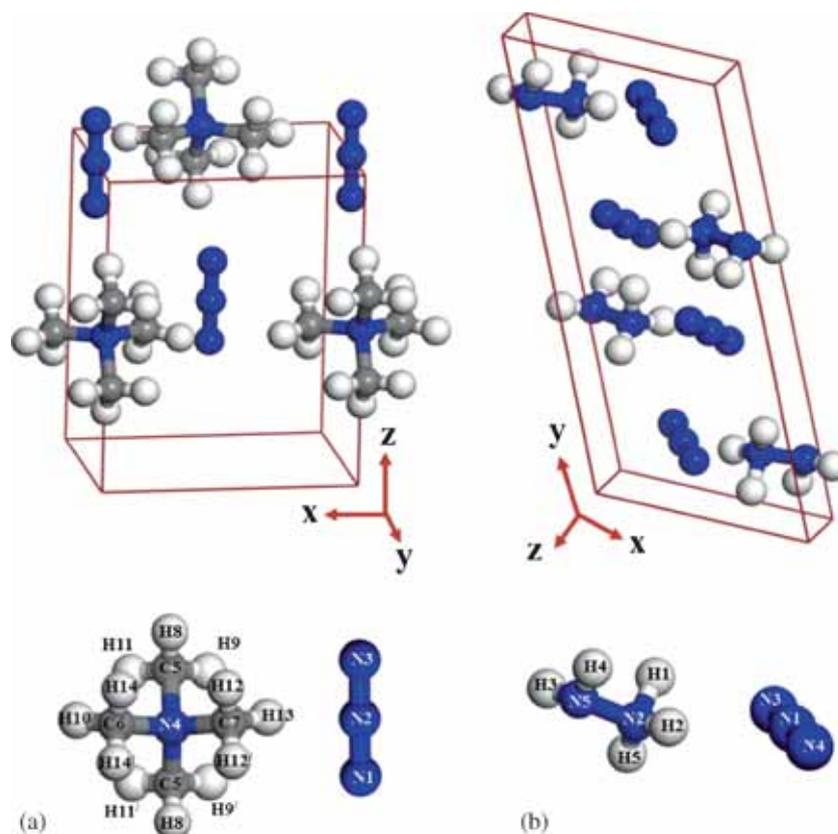


Figure 1. (a) Unit cell (top) and molecular structure (bottom) of TMAA (b) Unit cell (top) and molecular structure (bottom) of HZA.

Table 1. The calculated ground state structural properties of TMAA and HZA using vdW-TS method.

Compound	N(CH ₃) ₄ N ₃		N ₂ H ₅ N ₃		
	DFT (vdW-TS)	Expt ^a	DFT(vdW-TS)	Others ^b	Expt ^c
<i>a</i> (Å)	6.753 (−1.8%)	6.879	5.955 (5.1%)	5.9846	5.663
<i>b</i> (Å)	5.467 (−0.2 %)	5.479	12.148 (−2.3%)	12.1388	12.436
<i>c</i> (Å)	8.763 (−1%)	8.858	5.553 (0.8%)	5.5580	5.506
β (°)			117.68 (3.2%)	117.921	114.0
<i>V</i> (Å ³)	323.6 (−3.1%)	333.9	355.8 (0.4%)		354.17

^aRef. 19, ^bRef. 12, ^cRef. 20.

dependent zone center IR spectra of the HNS as they were well suited for lattice dynamical calculations. The plane wave cut-off energy of 600 eV for USPPs, 950 eV for NCPPs and k-mesh of 4×5×3 for TMAA and 5×2×5 for HZA according to Monkhorst-Pack grid scheme were used.²⁶ The self-consistent energy convergence was less than 5.0×10^{−6} eV/atom and maximal force between atoms was set to 0.01 eV/Å. The maximum displacement and stress were set to be 5.0×10^{−4} Å and 0.02 GPa, respectively. The vibrational spectra of TMAA and HZA were calculated using the linear response method within density functional perturbation theory.

3. Results and Discussion

3.1 Crystal structure and equation of state

TMAA¹⁹ crystallizes in the primitive orthorhombic crystal symmetry having space group *Pmn*2₁ with lattice parameters *a* = 6.879 Å, *b* = 5.479 Å, *c* = 8.858 Å, *V* = 333.9 Å³ and *Z* = 2, whereas AA¹⁶ crystallizes in the *Pmna* space group with lattice constants *a* = 8.93283 Å, *b* = 3.80848 Å, *c* = 8.6614 Å, *V* = 294.453 Å³ and *Z* = 4; consequently, TMAA is 15% loosely packed compared to AA. While HZA²⁰ crystallizes in the primitive monoclinic structure having space group *P*2₁/*b* with *a* = 5.663 Å, *b* = 12.436 Å, *c* = 5.506 Å, γ = 114.0°, and *Z* = 4. Liu *et al.*,^{7,8,12,17} investigated the structural, electronic and mechanical properties of HZA using vdW-TS method at ambient as well as at high pressure. In our previous study,¹⁴ we have also studied the structural and dynamical properties of AA using this method. Both of these studies reveal that vdW-TS method is good enough to reproduce the structural properties of HZA and AA which are closely comparable with the experimental data.^{16,20} Therefore, in the present study, we have also used the vdW-TS method to obtain the ground state structures by optimizing the lattice geometry and fractional co-ordinates

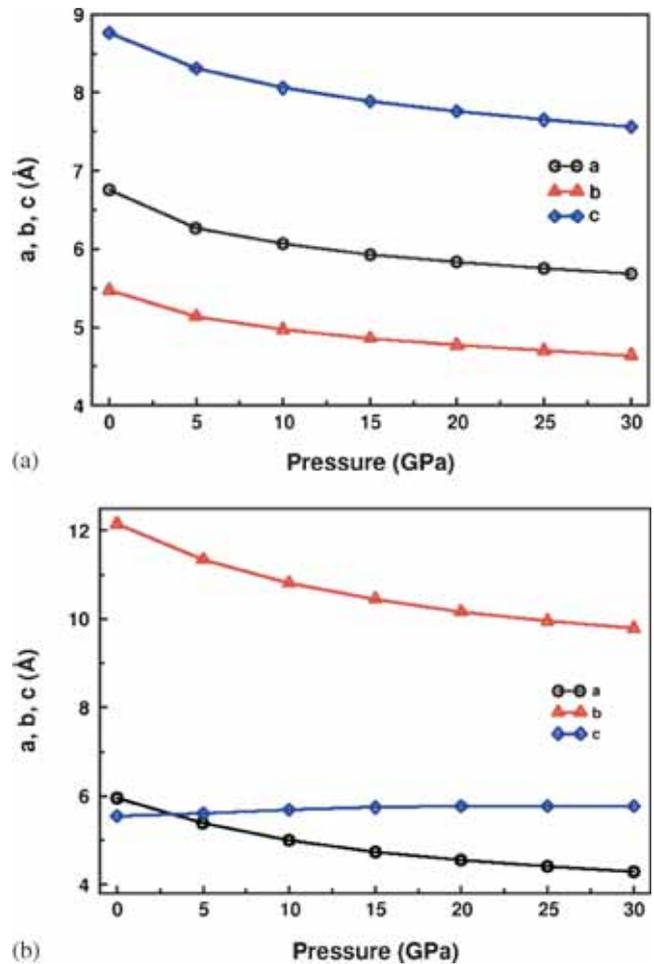


Figure 2. Calculated lattice constants of (a) TMAA (b) HZA as a function of pressure.

for the investigated compounds. The obtained equilibrium crystal structures along with molecular forms of cation and anions with their atomic labels are presented in Figure 1. The calculated lattice constants *a*, *b* and *c* are deviated by −1.8 % (+5.1%), −0.2 % (−2.3 %) and −1.0 % (+0.8 %) for TMAA (HZA) compound. Therefore, the resulting equilibrium volumes are different by −3.1% and +0.4% for TMAA and

HZA, respectively, when compared with the experimental results. Here “-” and “+” represent the under- and over-estimation of the calculated results when compared to experimental data.^{19,20} Also, the obtained ground state volume for HZA is in good agreement with previous theoretical studies by Liu *et al.*^{12,17} The calculated structural parameters are tabulated in Table 1 along with the experimental data^{19,20} and other theoretical calculations¹² for the studied compounds. Further, the optimized structures at ambient pressure were used to perform high pressure structural and vibrational properties of the two investigated compounds.

High pressure studies on structural properties of ionic molecular solids give a good insight into how pressure affects the weak intermolecular interactions in condensed matter. We have systematically investigated the structural properties of TMAA and HZA at zero Kelvin temperature under hydrostatic pressure up to 30 GPa in steps of 5 GPa. As illustrated in Figure 2, the calculated lattice constants are monotonically decreasing with pressure for the studied compounds. Except for the lattice constant *c* which is increasing with pressure and

these results are consistent with the previous theoretical calculations.¹² We could not see any discontinuity in the lattice constants under the studied pressure range of 0-30 GPa. Further, we have also calculated the axial compressibilities for the two compounds as depicted in Figure 3. It is found that the lattice of TMAA and HZA are the most and least compressible along *a*- and *c*-axes, respectively. When the calculated volumes are compared at 0 and 30 GPa (maximum pressure of the present study) pressures, the reduction in the volume is approximately 39% for both of the studied compounds as illustrated in Figure 4. In addition, we have also calculated the equilibrium bulk modulus (B_0) and its pressure derivative (B'_0) of these compounds by fitting the pressure-volume data to 3rd order Birch-Murnaghan equation of state.²⁷ The obtained B_0 (B'_0) values were found to be 15.2 GPa (5.9) and 22.0 GPa (4.1) for TMAA and (HZA), respectively. The obtained B_0 (B'_0) value for HZA is consistent with the previously calculated value of 24 GPa (5.1).¹² The results indicate that these materials are softer than AA whose B_0 value is 27.6 GPa.¹⁴

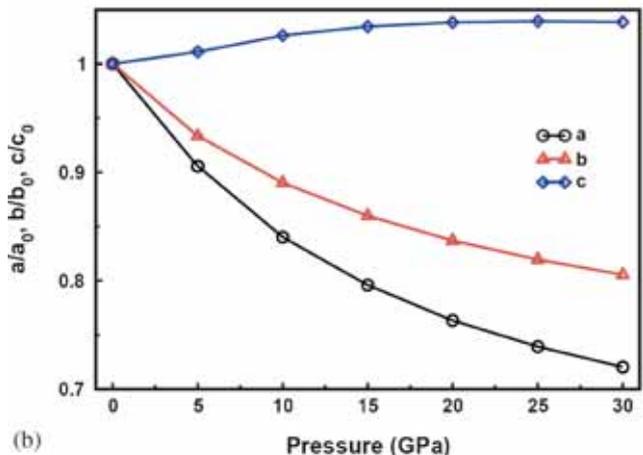
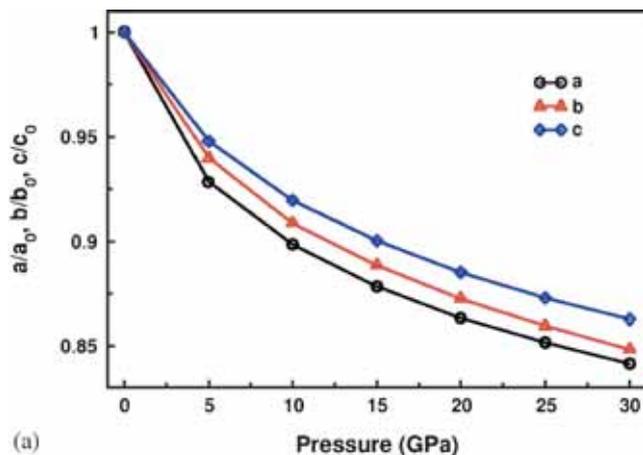


Figure 3. Calculated normalized lattice constants of (a) TMAA and (b) HZA compounds.

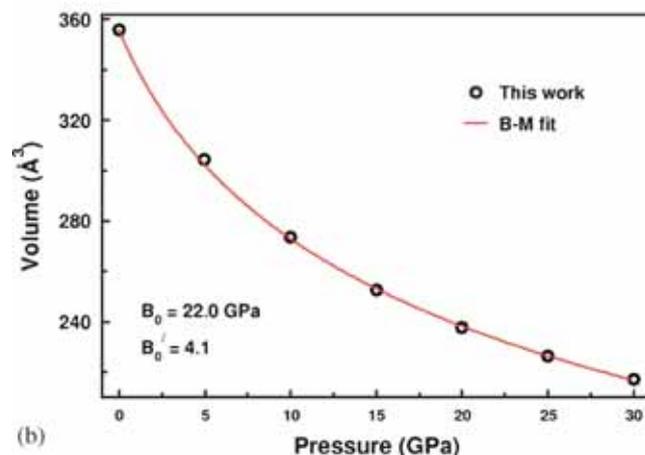
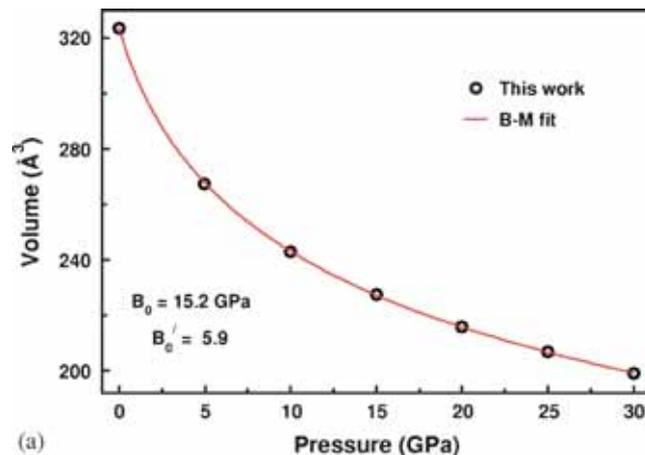


Figure 4. Calculated equation of state for (a) TMAA and (b) HZA compounds.

3.2 Vibrational properties

Energetic materials exhibit complex vibrational structures with strong hydrogen bonding networks in the crystalline environment. The vibrational modes of these materials are mixed with intra- and inter-molecular character thereby providing information regarding molecular structures, chemical bonding and changes in the circumstances. To have a fundamental knowledge on the vibrational spectra and bonding properties of these complicated structures, it is necessary to investigate the lattice dynamical properties using IR and Raman spectroscopic techniques.

In the present study, a detailed analysis of the vibrational spectra and their complete assignments have been made at ambient as well as at high pressure. As discussed in section 3.1, single crystal X-ray diffraction studies disclose that TMAA and HZA compounds crystallize in the primitive orthorhombic ($Pmn2_1$) and monoclinic ($P2_1/b$) structure having four molecules per unit cell (or 40 atoms per cell) resulting in the 120 vibrational modes, which are further classified into 3 acoustic and 117 optical modes. According to the group theory analysis of the $Pmn2_1$ and $P2_1/b$ space groups, the symmetry decomposition of the modes are $\Gamma_{\text{tot}}^{\text{TMAA}} = 34B_1 \oplus 26B_2 \oplus 34A_1 \oplus 26A_2$, $\Gamma_{\text{tot}}^{\text{HZA}} = 30B_u \oplus 30A_u \oplus$

Table 2. The calculated zone-center vibrational frequencies and their assignments for TMAA at vdW-TS equilibrium volume using NCPP approach at ambient pressure.

Mode	Frequency (cm ⁻¹)	Assignment
M120-M105	3097-3058	C-H Asym str
M102-M97	2985-2956	C-H Sym str
M96, M95	1886, 1855	N=N Asym str
M94-M71	1502-1379	C-H Scissor
M70-M65	1276-1261	C-H Wagg
M64, M63	1206, 1206	N-N Sym Str
M62-M53	1173-1036	C-H Wagg + Twist
M52-M47	930-913	C-H Twist + C-N Asym str
M46, M45	732, 728	N-(CH ₃) ₄ Sym str
M44-M41	604-603	N=N=N (N ₃) Bend
M40-M33	443-360	N(CH ₃) ₄ Scissor
M32-M23	355-284	CH ₃ Rot
M22-M4	151-34	N(CH ₃) ₄ & N ₃ Rot and/or Trans (lattice modes)

Table 3. The calculated zone-center vibrational frequencies and their assignments for HZA at vdW-TS equilibrium volume using NCPP approach at ambient pressure.

Mode	Frequency (cm ⁻¹)	Assignment
M120-M117	3271-3263	NH ₂ Asym str
M116-M113	3142-3127	NH ₂ Sym str
M112-M108	3064-2758	NH ₃ str
M107, M106	2752, 2747	NH ₃ Asym str
M105 & M104, M103	2711 & 2705, 2661	NH ₃ Str & NH ₃ Sym str
M102, M101	2613, 2612	NH ₃ str
M100-M97	1900-1883	N=N=N (N ₃) Asym Str
M96-M94	1686-1662	NH ₃ Scissor & Twist
M93	1647	NH ₃ Scissor & Twist + NH ₂ Scissor
M92	1645	NH ₃ Scissor & Twist
M91-M85	1636-1590	NH ₃ Scissor & Twist + NH ₂ Scissor
M84-M81	1552-1539	NH ₃ Wagg
M80-M77	1441-1427	NH ₃ & NH ₂ Twist
M76-M73	1318-1287	NH ₃ Wagg & Twist + NH ₂ Wagg
M72-M69	1246-1245	N=N=N (N ₃) Sym Str
M68-M61	1188-1113	NH ₃ Wagg & Twist + NH ₂ Twist
M60-M57	969-962	N-N Str + NH ₃ & NH ₂ Wagg
M56-M41	654-507	NH ₃ & NH ₂ Rot + N=N=N Bend
M40-M4	343-47	N ₂ H ₅ & N ₃ Rot and/or Trans (lattice modes)

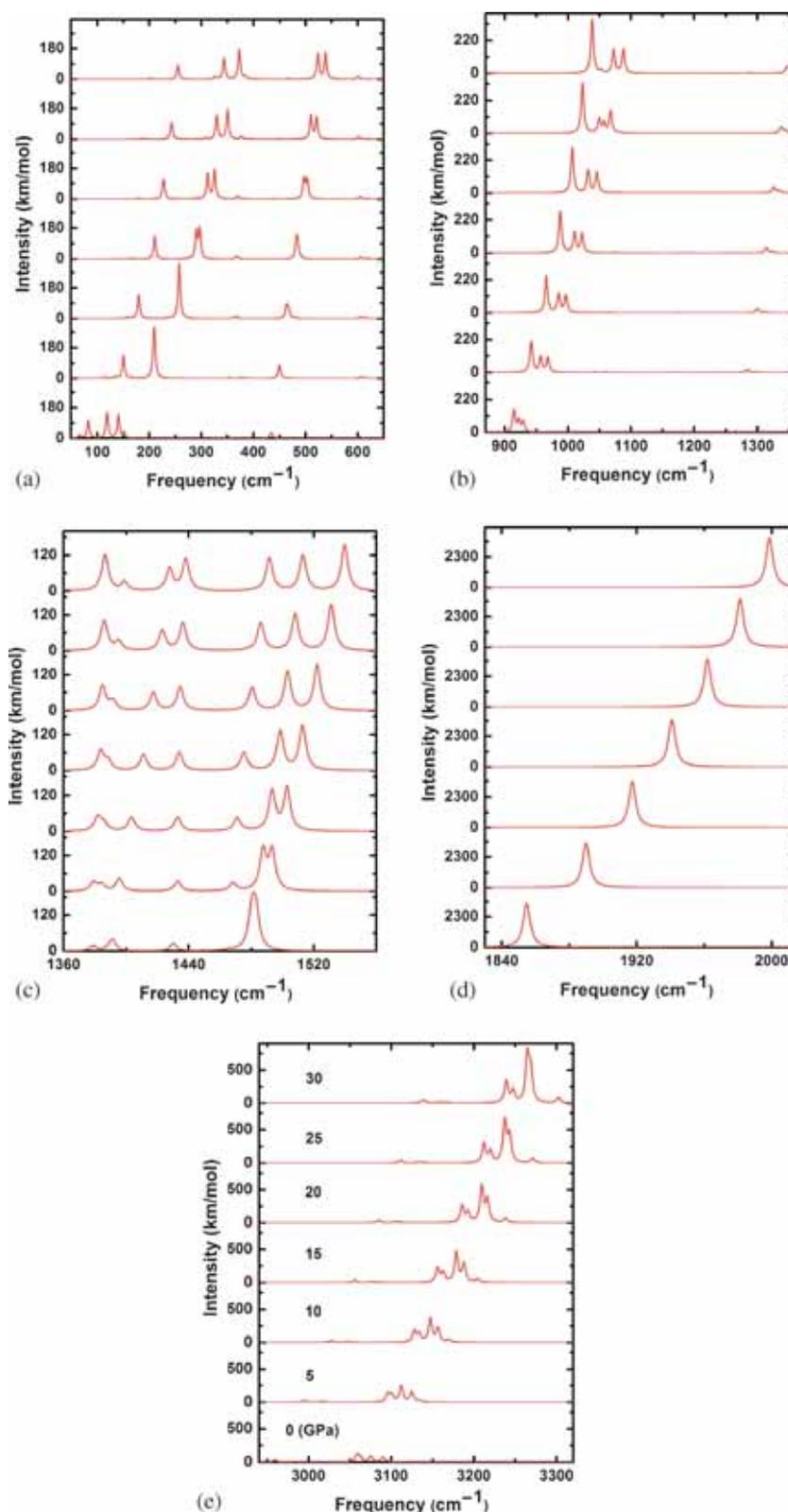


Figure 5. Calculated IR spectra (a) lattice modes (b, c) bending modes of $N(CH_3)_4$ (d) asymmetric stretching of N_3 (e) C-H symmetric and asymmetric stretching modes of TMAA as a function of pressure.

$30A_g \oplus 30B_g$ for TMAA and HZA, respectively. The optical modes B_1 , B_2 , and A_1 are both IR and Raman

active whereas A_2 mode is purely Raman active for TMAA. While A_u and B_u are IR active, A_g and B_g are

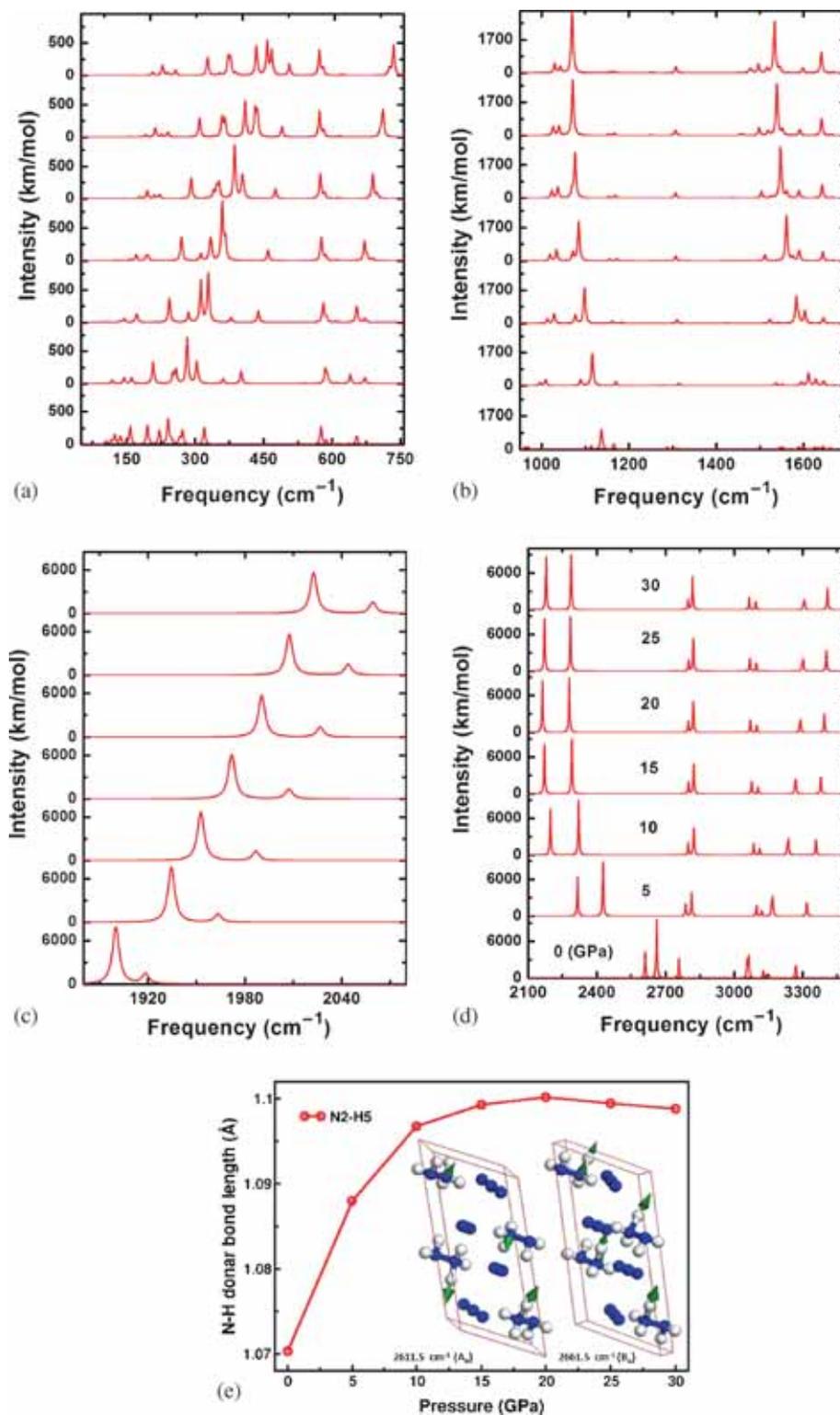


Figure 6. Calculated IR spectra (a) lattice modes (b) N-H bending modes of NH₃ & NH₂ (c) asymmetric stretching of N₃ (d) N-H symmetric and asymmetric stretching modes and (e) N-H donor bond length of NH₃ unit from N₂H₅ cation of HZA as a function of pressure.

Raman active modes for HZA. The calculated optical modes and their vibrational assignments corresponding to each vibration are given in Tables 2 and 3 for TMAA and HZA, respectively, at ambient pressure.

3.3 IR spectra under pressure

Hydrogen bonding has strong implications on IR spectra of hydrogen-bonded solids. IR and Raman spectroscopic

studies are used to study the effect of pressure and possible structural phase transformations in materials. In the Raman spectroscopic study, a pressure induced polymorphic phase transition was observed in AA which is due to modification in the strength of the hydrogen bonding at the transition pressure ~ 3 GPa.¹⁵ Reynolds and Sternstein²⁸ reported the effect of high pressure (up to ~ 2.5 GPa) on the IR spectra of oxalic acid, polyvinyl alcohol, nylon 6-6 and other materials and found that red-shift in O-H and N-H stretching frequencies and changes in the intensity of CH₂ bands. Hamann and co-workers compared the IR spectra of various hydrogen bonded solids at ambient as well as at 4 GPa pressures, and they found that stretching frequencies decrease and bending frequencies increase with pressure. The exception to this rule is shown by compounds with strong and symmetrical hydrogen bonding, whose stretching frequencies increase with increasing pressure.²⁹⁻³⁵ Joseph and Jemmis³⁶ made a consolidated description for strengthening and/or weakening of hydrogen bonding based on red-/blue-shift of stretching frequencies. Owing to the presence of hydrogen bonding, it can be expected that the N-H strengthening frequency decreases (red-shift) with increasing pressure and this red-shift leads to strengthening of hydrogen bonding.²⁸ In addition, our previous^{37,38} studies on hydrogen bonded systems, and those of Pravica *et al.*,³⁹ suggest that the red-/blue-shift in the mid-IR frequencies stabilizes/destabilizes the system under high pressure. Therefore, in the present study, we have also calculated the IR spectra under pressure up to 30 GPa to get spectroscopic picture of the hydrogen bonding for the TMAA and HZA compounds under hydrostatic compression.

As illustrated in Figure 5, for TMAA, the obtained lattice modes are due to rotational and/or translational motion of both cation (N(CH₃)₄) and/or anion (N₃) and they are increasing with pressure. The strong lattice translation and N(CH₃)₄ wagging modes lift the degeneracy as a function of pressure as shown in Figure 5a. The vibrational modes corresponding to C-H wagging, twisting and scissoring modes show blue-shift with increasing pressure. The asymmetric stretching modes of azide (N=N=N) ions are hardening with pressure. As depicted in Figure 5e, the C-H asymmetric and symmetric stretching modes show blue-shift under pressure which is due to decrease in the bond length of C-H bond with increasing pressure, which is commonly seen in case of improper hydrogen bonded systems.^{40,41} While in the case of HZA, the calculated lattice modes are due to rotational and/or translational motion from both hydrazonium (N₂H₅) and/or azide (N₃) ions and they are increasing with pressure. The vibrational modes

corresponding to NH₃, NH₂ wagging, twisting and scissoring show a red-shift with pressure. The asymmetric stretching modes of azide (N=N=N) ions are hardening with pressure, similar to TMAA. Also, the intense vibrational modes such as 2611.5 and 2661.5 cm⁻¹ in the NH₃ stretching region (see Figure 6d) show large red-shift as a function of pressure due to increase in the N₂-H₅ bond length as a function of pressure, as illustrated in Figure 6e. Whereas, the asymmetric N-H stretching modes from NH₂ group show blue-shift which is due to contraction in the N-H bond under the studied pressure range. In addition, the degeneracy of NH₃ and NH₂ stretching modes is lifted due to strong coupling between NH₃/NH₂ and N₃ units which further strengthens the hydrogen bonding in HZA as a function of pressure.

4. Conclusions

In summary, we have investigated the high pressure behavior of hydro-nitrogen solids, namely TMAA and HZA molecular crystals, using van der Waals density functional theory calculations. The calculated ground state structural properties using vdW-TS method are in good agreement with experimental data when compared to the standard PBE-GGA functional. We could not see any discontinuity in the calculated lattice constants indicating that TMAA and HZA are structurally stable under the studied pressure range. Our calculations clearly show the anisotropic compressibility of the materials and both of these lattices are found to be more compressible along crystallographic *a*-axis. The obtained equilibrium bulk moduli 15.2 GPa for TMAA and 22 GPa for HZA show the soft nature of these materials. In addition, we have also calculated the vibrational spectra of TMAA and HZA and assigned all the vibrational modes. Contraction and elongation of C-H and N-H bonds under pressure lead to blue- and red-shift in the mid IR region for TMAA and HZA, respectively.

Acknowledgements

NYK and BMA would like to thank DRDO for funding through ACRHEM and CMSD, University of Hyderabad for providing computational facilities.

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