High pressure spectroscopic studies of hydrazine ($N_2H_4$)

Raja Chellappa$^1$, Dana Dattelbaum$^2$, Luke Daemen$^3$ and Zhenxian Liu$^4$

$^1$Los Alamos National Laboratory, Lujan Center, Los Alamos, NM 87544.
$^2$Los Alamos National Laboratory, Shock Physics, Los Alamos, NM 87544.
$^3$Los Alamos National Laboratory, Lujan Center, Los Alamos, NM 87544.
$^4$National Synchrotron Light Source, U2A Beamline, Upton NY 11973.

E-mail: $^1$raja@lanl.gov, $^2$danadat@lanl.gov

Abstract. Pressure-induced changes (up to 20 GPa) to the structure and bonding in hydrazine ($N_2H_4$) have been investigated using diamond anvil cell (DAC) with in situ Raman spectroscopy. Liquid hydrazine solidifies at 0.3 GPa into a crystalline phase and its structure was established using synchrotron x-ray diffraction (XRD) measurements. The high pressure phase is monoclinic ($P_{21}$) with a remarkable correspondence to the low-T monoclinic structure that is also seen in the similar Raman spectral features. With increasing pressure, the modifications to N-H…N hydrogen bonding is observed with emergence of new contacts beyond 5 GPa as well as appearance of new lattice modes. This is accompanied by small changes in the pressure dependency (dν/dP) of frequencies. Based on these observations, we conclude a sluggish phase transition in the 5-7 GPa range accompanied by selective strengthening and restructuring of hydrogen bonding network. Inelastic Neutron Scattering (INS) measurements performed in the 10-250 K range indicates that the order-disorder phase transition (observed in thin films at 175-80 K) driven by conformational changes is not observed in a bulk sample.

1. Introduction

Hydrazine ($H_2N-NH_2$) and its methylated derivatives are principal constituents of liquid rocket propellants due to their high energy density and insensitive reaction thresholds [1]. Hydrazine is also widely used in synthetic chemistry, explored as an alternative for fuel cell applications [2], and is expected as a photolytic product of ammonia in Jovian atmospheres [3]. Conformations and bonding in hydrazine is influenced by the electronic stabilization provided by hyperconjugation [$n(N)\rightarrow\sigma^*_{\text{NH}}$] interactions between the nitrogen lone pair $p$-orbital and the N-H $\sigma$ bond [4]. Studies in the gas phase point to the $C_2$-gauche conformation as the most stable while conformations in the condensed phases is not fully understood. At ambient pressure, liquid hydrazine freezes at 2 °C into a monoclinic structure ($C_{2h}^1 - P2_1/m$; $a = 3.56$ Å, $b = 5.78$ Å, $c = 4.53$ Å, $\beta = 109.5^\circ$, $V = 87.87$ Å$^3$, $Z = 2$) [5]. The earlier x-ray diffraction (XRD) studies suggested an eclipsed $C_N$ conformation for the molecule while neutron diffraction (partially refined) [6] and proton NQR measurements [7] favored a $C_2^1 - P2_1$ space group with either a $C_2$ or $C_{2h}$ staggered conformation. In the liquid phase, self-association and relatively strong N-H…N hydrogen bonding has been reported [8] and is evidenced by its physical properties (high boiling point: 113.5 °C, fusion enthalpy: $\Delta_fH = 12.5$ kJ/mol). However, further neutron
diffraction studies are necessary to establish conformation and precise hydrogen bonding distances in the solid phase.

The high P/T behavior of hydrazine is of interest to interpret its shock compression response/reactivity during impact that is relevant for fuel tank safety in space propulsion systems [9]. Further, as a simple molecule with N-H…N hydrogen bonding, it is of interest to understand the effects of compression on this intermolecular interaction [10]. The available shock compression studies of liquid hydrazine are inconclusive regarding detonability with early work pointing to shock initiation [9] while the recent studies point to lack of reactivity up to 21.4 GPa [11]. Our extensive work on shock-induced chemistry of simple molecular liquids suggests that shock-induced chemistry can be complicated with multiple reactions that possibly involve high P-T phase transitions [12, 13]. In this work, we have subjected hydrazine to pressures up to 20 GPa in a Diamond Anvil Cell (DAC) and investigated the effect of compression on hydrogen bonding and structure using Raman spectroscopy and synchrotron XRD. Inelastic Neutron Scattering (INS) measurements were performed in the 10-250 K range to confirm an order-disorder transition reported in literature [14].

2. Experimental

Liquid hydrazine (Sigma Aldrich, 99%) was loaded in DACs with 300 µm diameter culets in stainless steel gaskets with sample chamber dimensions of 100-130 µm diameter and 50-60 µm thickness. Ruby chips/balls or Au powder were used as internal pressure markers [15, 16]. Raman spectra were measured using a customized micro-Raman system using a Newport Excelsior-532 nm laser with the beam focused to 20 m (< 5 mW) to avoid any laser-induced damage. The spectral resolution was 1.5 cm\(^{-1}\) with a SP-2556 spectrograph and a Spec-10:100 BR/LN CCD detector (Princeton Instruments). Synchrotron XRD measurements were performed at HPCAT, 16-IDB beamline at the Advanced Photon Source, Argonne National Laboratory with \(\lambda = 0.3679\) Å and \(\lambda = 0.6199\)Å with x-ray beam dimensions of ~10 x 10 \(\mu\)m FWHM. Characteristics of the diffraction experiment were calibrated with a CeO\(_2\) standard. INS measurements were performed at the Filter Difference Spectrometer (FDS) at Lujan Center, LANSCE [17].

3. Results and Discussion

Liquid hydrazine was sealed in a DAC and was observed to crystallize into a high pressure solid phase (denoted as HZ-I) at 0.3 GPa. Over-pressurization of liquid phase was observed to occur in some starting samples with the solid phase appearing at pressures as high as 2.4 GPa. This behavior is analogous to the severe undercooling (40 K or more) exhibited during low-T crystallization [7]. In order to interpret the effect of compression on hydrogen bonding in hydrazine, we first determined the structure of the high pressure solid phase to contrast with the low-T solid phase using synchrotron XRD. Since XRD is not a suitable probe for determining ‘H’ atom positions, we also obtained INS spectra, sensitive to vibrational modes involving motion of protons, to gain insights into the conformational aspects.

3.1. Crystal Structure of High Pressure Solid Phase

Synchrotron XRD data at 0.3 GPa (\(\lambda = 0.3679\)Å) was indexed using the Crysfire suite [18] and the space group identified by systematic extinctions. The Lebail refinement of the profile \((C_2^2-P2_1; a = 3.500\) Å, \(b = 5.724\) Å, \(c = 4.479\) Å, \(\beta = 110.255^\circ, V = 84.215\) Å\(^3\), \(Z=2\)) is given in figure 1(a) [19]. The high pressure HZ-I phase (0.3 GPa, 298 K) is isostructural with the low-T solid phase (258 K) with a similar unit cell size and confirmed by a striking resemblance of spectral features. The experimentally determined low-T structure with available atomic coordinates [6, 7] is shown in figure 1(b) with the independent molecule possessing a staggered \(C_2\) conformation. It is noted that preliminary DFT calculations allowing the parent low-T structure to relax resulted in a molecular geometry identical to the gas phase \(C_2\)-gauche conformation. As expected, the N-H…N hydrogen bonding network in the
low-$T$ solid [$d (N\cdots H) < 2.6 \text{ Å}$] is extensive (for clarity, some N$\cdots$H contacts are not shown) and the high pressure HZ-I phase is expected to possess a similar 3D network.

**Figure 1.** (a) Structure of low-$T$ solid phase showing extensive hydrogen bonding [$d (N\cdots H) < 2.6 \text{ Å}$]. (b) Lebail fit of the synchrotron XRD pattern of high pressure HZ-I phase at 0.3 GPa.

**Figure 2.** Compilation of INS spectra at selected temperatures. No major changes are observed in the lattice vibration region ($< 400 \text{ cm}^{-1}$) indicating that the monoclinic phase is stable in the 10-250 K range. The gradual smearing of intensities is due to the increasing contribution from the thermal vibrations.

### 3.2. INS Spectra from 10-250 K

INS measurements can provide insights into conformations, molecular motions, and the role of hydrogen bonds in driving modifications. This is particularly useful for hydrogen-rich compounds such as hydrazine since the most intense bands in INS spectra arise from vibrations large displacements of the H atoms (hindered rotations, torsion, wagging, rocking etc.). Previous studies on thin-film or aerosol phases of hydrazine indicate a disorder-order transition at 175-180 K and possibility of forming amorphous hydrazine phases with extended N-H$^-$N network is intriguing. INS spectra at selected temperatures are shown in figure 2. A total of 21 lattice vibrational modes and 17 internal modes could be resolved and have been assigned based on available spectroscopic data. As noted below, factor group analysis predicts a total of 33 optical modes ($\Gamma$ point) and INS measurements reveal vibrational modes that are not limited by the first Brillouin zone. Theoretical modeling of the INS spectra will provide further insights into conformations of hydrazine molecule. Our temperature dependent INS spectra provide evidence that the order-disorder transition observed in thin films is not observed in a bulk crystalline sample.

### 3.3. Raman Spectroscopy

#### 3.3.1. Mode Assignments.

Factor group analysis predicts a total of 33 optical modes that are both IR and Raman active ($\Gamma = 17A + 16B$), which comprises of lattice librational ($\Gamma_{\text{lib}} = 3A + 3B$), translational ($\Gamma_{\text{trans}} = 2A + B$), and the internal ($\Gamma_{\text{int}} = 12A + 12B$) vibrations of the $N_2H_4$ molecule ($C_2$ point group). The three acoustic vibrations are translational in character and given by ($\Gamma_{\text{acoustic}} = A + 2B$). As summarized in table 1 and annotated in figure 3, at 1.4 GPa, we observe 7 lattice modes (translational:
T, librational: L) at 101 (T), 108 (L), 134 (L), 144 (T), 193 (L), 232 (T), and 301 (L) cm$^{-1}$. In the internal mode region, we observed 10 modes with several weak signatures observed in the low-$T$ solid [20] could not be resolved. Further, vibrations in the vicinity of $\sim$1300 cm$^{-1}$ are masked are by the intense diamond signature. Notable features of the spectra include the intense rocking mode, $\rho$ (NH$_2$) at 892 cm$^{-1}$, $\nu$ (N-N) stretching mode at 1117 cm$^{-1}$, symmetric $\nu$$_s$(NH$_2$) stretching at 3167 cm$^{-1}$ (sh. 3188 cm$^{-1}$), and the antisymmetric $\nu$$_a$(NH$_2$) mode is observed at 3305 cm$^{-1}$. The $\delta$(NH$_2$) bending modes are observed weakly at 1607 cm$^{-1}$ and 1664 cm$^{-1}$.

3.3.2. Effect of Compression. Changes to Raman spectra are discussed by considering two pressure regimes I ($<5$ GPa) and II ($>5$ GPa). With an increase to 2.4 GPa, the lattice modes exhibit interesting behavior with several modes shifting to lower frequencies (table 1). The low frequency doublets at (102, 108) cm$^{-1}$ and (137, 142) cm$^{-1}$ are seen at 113 cm$^{-1}$ (T) and 131 cm$^{-1}$ (L). The 193 cm$^{-1}$ (L) and 231 cm$^{-1}$ (T) modes (at 1.4 GPa) shift to lower frequencies to 185 cm$^{-1}$ and 224 cm$^{-1}$ (at 2.4 GPa), respectively. With the exception of $\delta$(NH$_2$), $\nu$$_d$(NH$_2$) modes that show a small red shift, all the internal modes move to higher frequencies at 2.4 GPa. It is unclear if the unusual softening of the lattice modes is related to a structural transition especially due to lack of related changes in the internal modes and further XRD measurements are on-going. In the 2.4-5.5 GPa range, all the Raman-active modes shift to higher frequencies with pressure with the exception of $\delta$(NH$_2$) (-1.7 cm$^{-1}$/GPa) and $\nu$$_s$(NH$_2$) (-4.7 cm$^{-1}$/GPa). Typical of molecular crystals, modes affected the most by the changes in intermolecular distances (lattice modes) shift with a larger $d\nu/dP$ slope when compared to internal modes (table 1).

In the 4.8-20 GPa range (II), several changes to Raman spectra are observed beginning at 4.8 GPa with the splitting of the $\nu$$_a$ (NH$_2$) mode that now appears as a doublet at 3309 and 3316 cm$^{-1}$. The weak shoulder peak to the $\nu$ (N-N) stretching mode could not be resolved while a weak shoulder peak (1122 cm$^{-1}$) emerges that is associated with the intense $\nu$ (N-N) stretching mode. In the lattice mode region, two librational modes emerge at 6.9 GPa (322 cm$^{-1}$) and at 8.2 GPa (203 cm$^{-1}$) that continue to increase in intensity with pressure (figure 3). The pressure dependence of frequencies ($d\nu/dP$) shows...
no anomalies with only small changes in relative slopes. It is noted that several modes lose intensity beyond 10 GPa.

Table 1. Assignment of Raman modes and their pressure dependency up to 20 GPa.

| INS$^a$ [20]$^b$ | 1.4 (GPa) | 2.4 (GPa) | $dν/dP^c$ (cm$^{-1}$/GPa) | INS$^a$ [20]$^b$ | 1.4 (GPa) | 2.4 (GPa) | $dν/dP^c$ (cm$^{-1}$/GPa) |
|------------------|-----------|-----------|---------------------------|------------------|-----------|-----------|---------------------------|
|                  | I         | II        |                           |                  | I         | II        |                           |
| Lattice          |           |           |                           |                  |           |           |                           |
| 434              | 1114s     | 1117s     | 1138s                    | 4.9              | 4.7       |
| 61,68            | 1133m     | 1135m     |                           |                  |           |           |                           |
| 78,96 99 T       | 101m      | 113m      | 5.6                      | 2.9              |
| 103,112 111 L    | 108w      | 134m      | 7.1                      | 5.9              |
| 126 122 L        | 134m      | 131m      | 10.5                     | 6.3              |
| 133 131 L        | 144w      | 184w      | (<14)                    | (>8.2)$^d$       |
| 150 172 T        | 203m$^d$  | 9.0       | 9.0                      |
| 178,197          |           |           |                           |                  |           |           |                           |
| 247,270 199 L    | 232m      | 225m      | 12.7                     | 5.9              |
| 304,335 226 L    |           |           |                           |                  |           |           |                           |
| 368,386 288 L    | 301m      | 299w      | 12.4                     | 10.1             |
| 385,418          |           |           |                           | (<14)            |
| 434              | 322m$^d$  | 9.0       | 9.0                      |
| 520              | 3205      | 3188w     | 4.7                      | 0.4              |
| 529              | 3188w     | 3196w     |                           |                  |           |           |                           |
| 608,652 619vw    |           |           |                           |                  |           |           |                           |
| 715,757          | 664m      | 9.1       | 9.4                      |
|                  |           |           |                           |                  |           |           |                           |
| ν(NH$_2$)        |           |           |                           |                  |           |           |                           |
| 818vw            | 3194m     | 33169s    | 3167s                    | 3165s$^e$        | -4.7      | -2.5      |
| 884s             | 3483      | 3301vs    | 3305s                    | 3305m            | 1.8       | 5.1       |
| 892s             | 3305s     | 3305m     |                           |                  |           |           |                           |
| 904s             | 3316m$^e$ | 3.5       |                           |
| 994w             |           |           |                           |
| 1077w            |           |           |                           |
| 1122$^d$         | 3.6       | (>4.8)$^e$|

$^a$ 10 K (this work); $^b$~130 K; $^c$ν(dP)/dP is divided into two regions, I (<5 GPa) and II (>5 GPa); $^d$New modes, dν/dP, and pressures at which they appear (in parenthesis). $^e$Redshifting modes (-dν/dP).

3.3.3. Discussion. The presence N-H 'N hydrogen bonding in hydrazine has a major influence on its physical and chemical properties in the liquid phase including high boiling point, solvation chemistry, and self-association, similar to water (H$_2$O). It is of interest to determine if the strength of this intermolecular interaction drives multiple structural transitions at high-$P$, similar to ice phases. The vibrational spectra of the low-$T$ solid phase shows familiar redshifts ($Δν$ ~160-200 cm$^{-1}$) in ν(NH$_2$) stretching frequencies (gas to solid), and as seen in table 1, the high-$P$ solid exhibits the same. Based on the available atomic coordinates information (a full determination is not available) for the low-$T$ solid (figure 1a), it is evident that the hydrogen bonding network is extensive with multiple N-H contacts (< 2.6 Å) that are asymmetrical and bifurcated. Given the spectral likeness and similar unit cell, the high-$P$ phase will likely possess similar hydrogen bonding characteristics. Increasing pressure is expected to strengthen hydrogen bonding resulting in a redshift of the ν(X-H) frequencies [21]. It is noted that a blueshift is observed in some rare cases with symmetrical, strong H-bonding or compounds undergoing orientational distortion (NH$_4^+$ moieties in NH$_2$N$_3$) [22]. The strengthening
effects of pressure on N-H·N contacts are manifested in the redshifting behavior of the \( \delta(NH_2) \) bending mode \((-1.7 \text{ cm}^{-1}/\text{GPa}) \) and \( \nu_s(NH_2) \) stretching mode \((-4.7 \text{ cm}^{-1}/\text{GPa}) \). However, the \( \nu_s(NH_2) \) antisymmetric \( \nu_s(NH_2) \) stretching mode \((1.8 <5 \text{ GPa}) \) and \( 5.1 (>5 \text{ GPa}) \) \text{ cm}^{-1}/\text{GPa} \) exhibits the opposite behavior, indicating anti-cooperative nature of certain hydrogen bonding contacts.

At pressures beyond 5 GPa, the emergence of new \( \nu_s(NH_2) \) stretching mode is an indication of formation of new hydrogen bonding contacts. Corresponding to this, changes in the lattice mode region are seen by the appearance of new librational modes beyond 6 GPa. These changes indicate a possible phase transition however it is unlikely that this is associated with any major structural change and likely associated with simple distortions of hydrogen bonding contacts. Also, the changes in slope from region I \((<5 \text{ GPa}) \) and region II \((>5 \text{ GPa}) \) are not dramatic enough. Similar changes to Raman spectra as a function pressure (small changes in slope and the appearance of a new \( \nu \) \( (NH_2) \) mode) reported in a recent study \[10\] that inferred two phase transitions at \(-5 \) and \( 8 \text{ GPa} \). Further XRD studies are necessary to confirm and identify the nature of these phase transitions.

4. Conclusions

We have investigated the effects of compression on hydrogen bonding (N-H·N) in hydrazine (N2H4) up to 20 GPa to explore the possibility for formation of “hydronitrogen” solids with 3D N...H-N-H...N frameworks. Analysis of Raman spectra as a function of pressure reveals a sluggish phase in the 5-7 GPa driven by modifications to the hydrogen bonding network. The as-crystallized high pressure phase is isostructural with low-\( T \) solid phase and further structural studies are desired to establish structural details of both these phases.

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