

The Unexpected Stability of Hydrazine Molecules in Hydrous Environment under Pressure *

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The incomplete decomposition product of metastable hydrazine (N_2H_4) instead of the energetically favorable ammonia (NH_3) upon decompression is one drawback in applications of energetic material oligomeric hydronitrogens. We explore the stability of hydrazine molecules in hydrazine hydrate ($N_2H_4 \cdot H_2O$) under pressure in diamond anvil cells (DACs) combined with *in situ* Raman spectroscopy and synchrotron x-ray diffraction (XRD) measurements. The results show that one NH_2 branch forms NH_3 group by hydrogen bonds between hydrazine and water molecules after the sample crystallizes at 3.2 GPa. The strengthening hydrogen bonds cause the torsion of hydrazine molecules and further dominate a phase transition at 7.2 GPa. Surprisingly, the NN single bonds are strengthened with increasing pressure, which keeps the hydrazine molecules stable up to the ultimate pressure of 36 GPa. Furthermore, the main diffraction patterns show continuous shift to higher degrees in the whole pressure range while some weak lines disappear above 8.2 GPa. The present peak-indexing results of the diffraction patterns with Materials Studio show that the phase transition occurs in the same monoclinic crystal system. Upon decompression, all of the hydrazine molecules extract from hydrazine hydrate crystal at 2.3 GPa, which may provide a new way to purify hydrazine from hydrate.

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Nitrogen and hydrogen are similar simple molecules that are constructed by strong covalent bonds. These elements are abundant on the earth and on the giant planets, such as Uranus and Neptune. Rupturing the covalent bonds in nitrogen and hydrogen molecules needs very extreme conditions, such as high pressure and high temperature.^[1–8] However, breakup of the covalent bonds could lead to polymerization of nitrogen and metallization of hydrogen, attracting considerable attention as a way to generate high-energy density materials (HEDMs).^[4,9–11] The large energy difference between single-bonded polymeric nitrogen (~ 160 kJ/mol) and the triple-bonded molecule (~ 954 kJ/mol) means that a large amount of energy can be released under the transformation from the polymer to diatomic nitrogen. Similarly, the released energy from atomic metallic hydrogen to molecular hydrogen is as high as 436 kJ/mol. The energy capacities of the polymeric nitrogen and atomic hydrogen are about one order of magnitude higher than any other known energetic explosives.

Surprisingly, synthesis of energetic hydronitrogen polymers with nitrogen and hydrogen molecules can be realized at relatively modest conditions. As revealed in previous studies,^[12–18] the complex firstly forms N_2-H_2 van der Waals solids at pressures of a few GPa and further transforms to oligomeric materials at higher pressures, which even come to about 10 GPa through photochemistry.^[13] Characteristic NN

and NH single bonds of the oligomers were identified with various spectroscopy measurements, and the absence of torsion and wagging modes further indicated that molecules longer than hydrazine may be synthesized.^[14] However, the reaction byproduct of the oligomeric hydronitrogen upon decompression was metastable hydrazine instead of the energetically favorable ammonia, which was one drawback in applications of the energetic hydronitrogens.^[14,17] Hydrazine is well known as a major fuel in the aerospace field,^[19–21] which is relatively environment friendly because of its quick degradation. The catalytic decompositions are NH_3 , N_2 and H_2 while the combustion products are N_2 and H_2O with heat release of 534 kJ/mol. In the previous study,^[22] hydrazine molecules exhibit persistent stability up to 46 GPa because of the stable 3D network structure formed by abundant $-N-H-N-$ chains between hydrazine molecules in their solid state. Under ambient conditions, hydrazine is hygroscopic and contains certain proportions of water. At low temperatures, different eutectics of hydrazine and water molecules exist at various ratios as summarized in the phase-equilibria diagram.^[23] In particular, solid hydrazine monohydrate formed in 50 mol% hydrazine complex below 222 K, later the structure was confirmed to be either *Fcc* or trigonal ($P3_121$).^[24,25] So far, the stability of hydrazine in the hydrous environment has not been conducted at high pressures that the hydro-

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gen bonds would dominate the behavior of hydrazine molecules and even promote its dissociation. The NH_2 branch of hydrazine molecules can attract hydrogen atoms from water molecules, thus further forms NH_3 group, which may decompose into NH_3 molecules with rupture of the NN covalent bond under pressure.

In this Letter, the *in situ* Raman spectroscopy and synchrotron x-ray diffraction (XRD) measurements are employed to explore the stability of hydrazine molecules in the hydrous environment (hydrazine hydrate) under pressure in Diamond anvil cells. The results show that hydrazine is unusually stable in hydrazine hydrate up to the ultimate pressure of 36 GPa because of the strengthened NN covalent bonds. Pure hydrazine can be extracted from the hydrate at 2.3 GPa upon decompression, which may provide a new way to purify hydrazine from hydrate. These results may have special significance for storage and applications of hydrazine under extreme conditions.

The pressure-induced behavior of hydrazine in hydrazine hydrate is traced by *in situ* Raman spectroscopy. As shown in Fig. 1, hydrazine monohydrate is in liquid state at 1.6 GPa and further solidifies into phase I above 3.2 GPa. There are 15 peaks that are collected in the frequency region below 700 cm^{-1} , indicating that complicated interactions appear between the hydrazine and water molecules. The assignments of internal vibrations of hydrazine hydrate are listed in Table 1 with comparisons of hydrazine, hydrazine hydrochloride and ammonia samples. In detail, the sharp peak at 968 cm^{-1} is assigned to the NN stretching vibrons while a few weak peaks at around 900 cm^{-1} coming from its splits. At higher frequencies, four peaks at 1073, 1114, 1153 and 1185 cm^{-1} are related to the components of NH_2 rocking mode. As shown in Fig. 1(b), two intense peaks at 1609 and 1659 cm^{-1} with a weak shoulder at 1649 cm^{-1} are contributed to NH_2 deformation mode. It is noted that two sharp peaks at 3367 and 3390 cm^{-1} are from NH_2 group, which are the same as pure hydrazine sample.^[22] However, the three broad peaks at 3194, 3237 and 3272 cm^{-1} are similar to the NH_3 configuration of ammonia. Therefore, it is deduced that one NH_2 branch forms NH_3 group by the $\text{N}\cdots\text{H}-\text{O}$ hydrogen bond between the N atom and the H atom of

neighboring water molecules. In addition, three broad NH_3 stretching peaks red-shift to low frequency with increasing pressure, which are attributed to another form of the $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond between the H atom of NH_3 group and the O atom of water. The H atoms are attracted by O atoms and further cause the softening behavior of NH_3 group. Therefore, these two forms of hydrogen bonds in hydrazine hydrate give rise to diverse behaviors of NH_3 and NH_2 groups compared to pure hydrazine. In this case, both hydrazine and water molecules would be pulled by the hydrogen bonds, which usually causes dramatic structural transition in this system. This characteristic configuration is supposed to induce the instability of hydrazine molecules and even molecular dissociation at higher pressures.

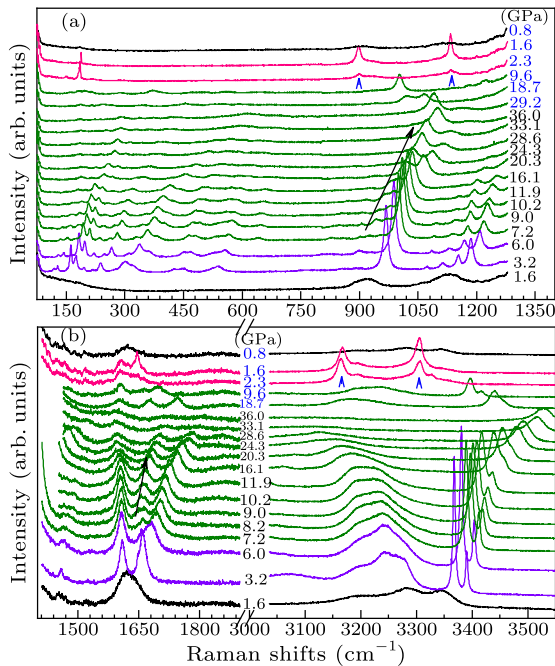


Fig. 1. The evolution of Raman spectra and phase transitions of hydrazine hydrate at selected pressures to 36 GPa upon compression and decompression. (a) The black arrow guides the abnormal enhancement of new NN stretching peaks in phase II, two blue arrows mark the characteristic peaks of solid pure hydrazine. (b) The black arrow guides the new deformation peak in phase II, two blue arrows indicate the characteristic vibrons of pure hydrazine.

Table 1. Assignments of the internal vibrons of hydrazine hydrate (3.6 GPa) in comparisons of referred samples of hydrazine (0.5 GPa),^[22] hydrazine hydrochloride (1.8 GPa)^[26] and ammonia (6.3 GPa).^[27]

Sample assignments	Hydrazine hydrate					Hydrazine			Hydrazine hydrochloride					Ammonia					
NH stretching (cm ⁻¹)	3390	3367	3272	3237	3194	3304	3226	3168	3248	3238	3145	3048	3018	2994	3391	3381	3367	3345	3199
NH deformation (cm ⁻¹)	1659 1649 1609					1662 1637			1637 1560 1493 1486					1663 1643 1621					
NH rocking (cm ⁻¹)	1185 1153 1114 1073					911 891			1275 1247 1123 1107 1096					1163 1151 1111					
NN stretching (cm ⁻¹)	968					1118			975 969										

The peak positions in the frequency region of $0-1900\text{ cm}^{-1}$ are plotted as a function of pressure as shown in Fig. 2. All the lattice peaks below 700 cm^{-1}

shift to higher frequency rapidly, indicating that crystal can be easily compressed. At 7.2 GPa , one NN vibron split at 927 cm^{-1} becomes intense with increasing

pressure and dominates above 20 GPa as marked by black arrows, suggesting a structural transition from phase I to II. Particularly, the intensity of the new NN stretching peak in phase II increases abnormally up to the ultimate pressure 36 GPa. This means that the NN single bond strengthens by the increasing pressure, which can keep the hydrazine molecule stable in the hydrate. The phase transition is attributed to torsion of hydrazine molecules rather than polymerization of hydrazine molecules, because no byproducts such as extra H_2 are observed. Moreover, this transition is also verified by the new torsion peak at 642 cm^{-1} and deformation peak at 1650 cm^{-1} . As described above, the strengthening of hydrogen bonds is closely related to the softening behavior of NH_3 stretching mode. Hence, the detailed behaviors of the NH_3 group with comparison of hydrazine, ammonia and ammonia hydrate samples are shown in Fig. 3. The NH_3 group shows similar behaviors to the referred samples, which all lose intensities at around 30 GPa. It is reported that the $\text{N-H}\cdots\text{N}$ hydrogen bond symmetrization occurs at around 60 GPa in hydrazine and ammonia as predicted by the double Morse potential (DMP) model.^[22,28,29] Similarly, the symmetric pressure of $\text{O-H}\cdots\text{O}$ bond in ice is also around 60 GPa according to parabolic function of soft-mode.^[30,31] Therefore, it is deduced that the $\text{N-H}\cdots\text{O}$ hydrogen bond in hydrazine hydrate may symmetrized at around 60 GPa. The combined actions of the strengthening NN and hydrogen bonds stabilize hydrazine hydrate in phase II, thus no further phase transition occurs up to 36 GPa.

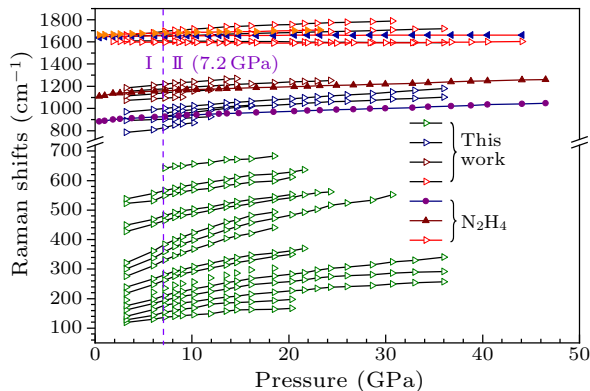


Fig. 2. Pressure dependence of frequencies of Raman peaks from hydrazine hydrate in $0\text{--}1900\text{ cm}^{-1}$ in comparison with pure hydrazine (lines). The phase transitions from I to II are marked by vertical dashed line at 7.2 GPa.

As revealed in previous studies, the long NN single bonds in oligomeric hydronitrogen can decompose to hydrazine as pressure decreases to a few GPa. It is expected that this dissociation would be further enhanced at lower pressures in the hydrate. Surprisingly, the phase transition can only recover down to 9.6 GPa upon decompression. At 2.3 GPa, four new peaks appear at 899 , 1134 , 3164 and 3305 cm^{-1} as marked by blue arrows, which are obviously different from phase I of hydrazine hydrate. Further analysis indicates that these internal modes match well with pure hydrazine, indicating that pure hydrazine molecules

extract from the solid hydrate. Generally, the phase transitions are reversible in the hydrogen-bonded crystals even from higher pressures than hydrogen-bond symmetrization.^[30] Moreover, the extraction process usually occurs in the gas-liquid mixtures such as $\text{H}_2\text{--H}_2\text{O}$ system. Because the hydrogen molecule is stored in the voids of water framework,^[32] the H_2 is small enough to be squeezed out from the framework with increasing pressure. However, the hydrazine and water molecules are similar in size and they are staggered with hydrogen bonds in solid hydrazine hydrate. Therefore, it is deduced that this transition must follow the sudden rupture of hydrogen bonds between the molecules at 2.3 GPa although it is still unclear how this process happens in this case. At 0.8 GPa, the mixed samples transform back to liquid hydrazine hydrate. The separation of hydrogen-bonded molecules upon decompression is firstly observed in the hydrate system, which may provide a new way to purify hydrazine from hydrate.

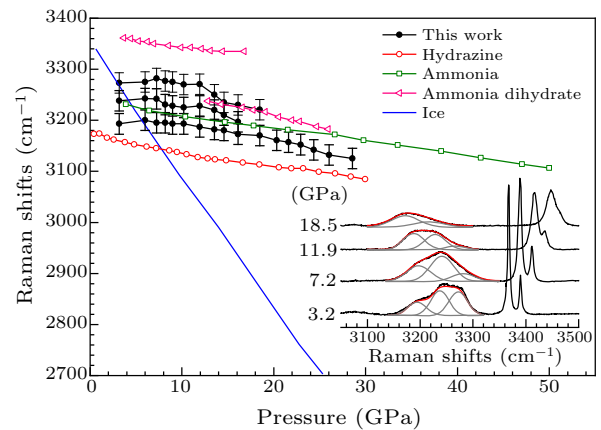


Fig. 3. The frequency shifts of the NH_3 stretching vibrons in comparison of pure hydrazine, ammonia, and ammonia hydrate. The blue line is the extrapolation of the soft OH mode in ice. The inset illustrates detailed peaks' fit of the NH_3 group at selected pressures.

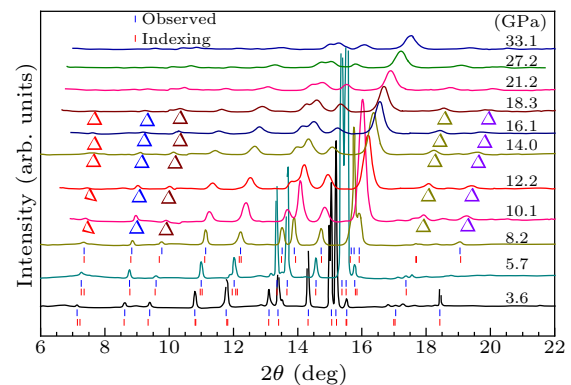


Fig. 4. Synchrotron x-ray diffraction measurement of hydrazine hydrate up to 33.1 GPa (incident wavelength $\lambda = 0.6199\text{ Å}$). The blue short lines mark the peak positions observed at 3.6, 5.7 and 8.2 GPa, the red short lines are indexing diffraction patterns of simulated monoclinic structure. The hollow triangles guide their evolutions at higher pressures.

To further explore the behavior of hydrazine hydrate at extremes, the *in situ* synchrotron x-ray diffraction measurement was performed to 33.1 GPa.

Representative XRD patterns with increasing pressure are shown in Fig. 4. Because the liquid sample crystallizes into polycrystals at 3.6 GPa, many diffraction spots appear on the rings and affect the actual intensities in phase I. The main 13 diffraction patterns in the range 6° – 20° are recognized at 3.6 GPa as the blue lines marked and the indexing peak positions with the Materials Studio program are marked by red lines. It is seen that the simulated results fit the experimental peaks well and many weak shoulders have also been indexed. The indexing result suggests a monoclinic structure with lattice parameters of $a = 7.56 \text{ \AA}$, $b = 7.61 \text{ \AA}$, $c = 5.66 \text{ \AA}$ and $\beta = 119.65^{\circ}$ with unit cell volume $V = 283.08 \text{ \AA}^3$ at 3.6 GPa. These lattice parameters become $a = 6.76 \text{ \AA}$, $b = 7.44 \text{ \AA}$, $c = 5.55 \text{ \AA}$ and $\beta = 106.15^{\circ}$ with unit cell volume $V = 267.90 \text{ \AA}^3$ at 5.7 GPa. Because of the distortion of the structure during phase transition at 8.2 GPa, many weak shoulders disappear in phase II above 8.2 GPa. Based on the main diffraction lines in the range 5° – 20° , the indexing result gives a suggested monoclinic structure with parameters $a = 4.83 \text{ \AA}$, $b = 7.34 \text{ \AA}$, $c = 3.56 \text{ \AA}$ and $\beta = 91.68^{\circ}$ for unit cell volume $V = 126.20 \text{ \AA}^3$. Any other attempts to fit all the observed lines will lead to an unreasonable unit cell volume of more than 300 \AA^3 and overmuch unnecessary indexing lines. Although the unit cell volumes change a lot during the phase transition, it is deduced that the transition occurs in the monoclinic crystal system, which is consistent with the Raman spectroscopy result.

In summary, the behaviors of hydrazine hydrate under pressure are investigated with *in situ* optical measurements in diamond anvil cell under pressure. The hydrazine molecules exhibit unusual stability in hydrous environment owing to the strengthening NN bond with increasing pressure up to 36 GPa. Upon decompression, hydrazine molecules can be extracted from the solid hydrazine hydrate because of abrupt breakup of hydrogen bonds between hydrazine and water molecules. The unexpected stability of hydrazine molecules may have special significance for its storage and applications under extreme conditions. Furthermore, these results would also extend our understanding of N–H–O systems in the Jovian planets' atmospheres, where ammonia is considered as the only stable hydronitrogen.

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