



Hydrazine at high pressure

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ABSTRACT

We report the first high pressure study of the important rocket fuel, hydrazine in a diamond anvil cell up to 19 GPa. Using Raman spectroscopy, two phase transitions were observed between 5.5 and 8 GPa. Above 8 GPa, a new peak emerged near 3000 cm^{-1} . The pressure-induced changes appear to be reversible as pressure was cycled down to 3.5 GPa. We then performed a second experiment at this pressure examining X-ray induced decomposition of the material using an unfocused synchrotron white beam. After some 2.4 h of irradiation (estimated to be a dose of $1.6 \times 10^5\text{ Gy}$), molecular nitrogen was produced as confirmed with Raman spectroscopy.

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1. Introduction

Hydrazine (also known as diazene) is a toxic inorganic compound that has many industrial uses but is primarily known as a liquid monopropellant/rocket fuel that burns in the absence of oxygen [1,2]. It is also used in a number of applications for chemical synthesis due to the reactive nature of singly-bonded nitrogen, in particular the synthesis of BN at high pressure [3]. High pressure would thus be expected to an important variable determining the reaction rate [4]. Yet, to the best of our knowledge, no high pressure study has ever been conducted of this flammable, and important compound to the best of our knowledge. Beyond this, we have recently demonstrated that novel and useful chemistry can be achieved using hard X-rays that initiate decomposition reactions *in situ* without conventional catalysts [5–7]. Our desire was to initiate the decomposition of hydrazine into nitrogen and hydrogen or nitrogen and ammonia using hard X-rays without the need for catalysts or heat input. If successful, this would add yet one more potentially useful reaction to our arsenal to demonstrate very controllable and useful chemistry for creating novel materials under extreme conditions. It would also aid in introducing combinations of simple molecules (N_2 , H_2 , O_2 , etc.) to study oxidation/reduction and detonation products to better understand intermolecular interactions under extreme conditions.

2. Experimental

Two experiments were performed. The first experiment sought to study the effect of pressure on hydrazine confined with a diamond anvil cell (DAC) using Raman spectroscopy. The second

experiment investigated the effects of X-ray irradiation when the sample was set at a fixed pressure.

A symmetric-style Diamond Anvil Cell (DAC) with 250 μm thick stainless steel gaskets was employed to pressurize hydrazine for our experiments. The diamonds used each had a culet diameter of $\sim 300\text{ }\mu\text{m}$ and were low fluorescence type II quality. The sample-confining gasket was preindented to $\sim 50\text{ }\mu\text{m}$ thickness and a sample hole of diameter 140 μm was drilled via electric discharge machining. Liquid hydrazine (Sigma–Aldrich 98%) was loaded via a syringe into the gasket hole along with one ruby (for pressure measurement purposes) and then the assembly was closed to seal the sample. No pressure transmitting medium was used in our experiments.

The first experiment was performed within the Raman facility at Sector 16 of the High Pressure Collaborative Access Team (HP-CAT) at the Advanced Photon Source. The laser power source consisted of a Coherent[®] 532 nm laser set at 50 mW. An HR 460 spectrometer dispersed the scattered light which was then stored via an Andor MCD detector. The Raman spectrometer instrumental resolution was $\sim 4\text{ cm}^{-1}$.

The second experiment was performed at the 16 BM-B beamline at the Advanced Photon Source. ‘White’ X-ray radiation (mostly within the 10 keV \leftrightarrow 100 keV energy range) served as the energy source. The sample was placed in the path of an unfocused $200 \times 200\text{ }\mu\text{m}$ X-ray beam. Both experiments were conducted at ambient temperature.

3. Results

3.1. Raman study

We first present the results of our Raman experiment in Figure 1 along with Table 1 which explains the modes and compares our measurements at 5.2 GPa with modal frequencies of hydrazine in

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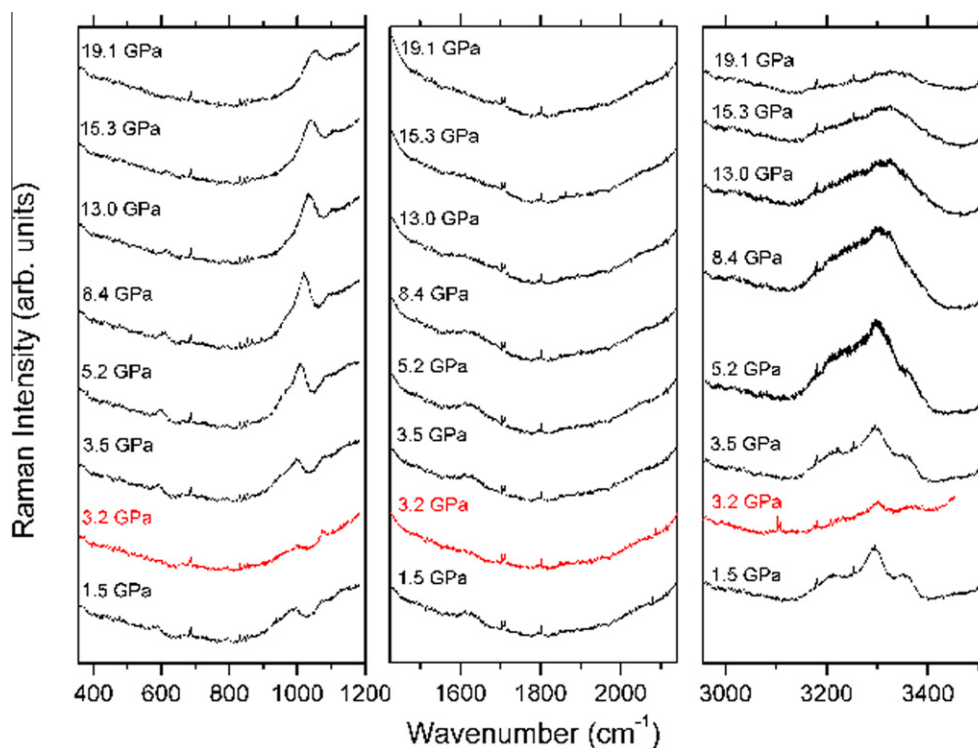


Figure 1. Stacked Raman spectra of hydrazine at various pressures in three different regions. The spectrum in red (3.2 GPa) was taken in decompression. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the low temperature solid phase at ambient pressure [8]. One-to-one comparison is somewhat difficult as hydrazine has a melting point of 2 °C at ambient pressure and we report, to the best of our knowledge the first study of hydrazine at high pressure. Though the Raman signal was relatively weak in this solid, various modal trends with pressure are apparent which can be better observed in Figure 2. The background-removed fits were performed using PeakFit®. The errors of the fits are within the size of the dots used to make the plots. Further glancing at Figure 2, slight slope discontinuities appear to exist in many of the modes near 5 GPa suggesting a phase transition. We note that as the sample was pressurized, a slight darkening of the sample was observed near this pressure. With pressure increase, all of the observable modes move toward higher frequencies and broaden with the exception of the mode commencing near 1620 cm⁻¹, which has been assigned to NH₂ deformation [8–11]. This trend is frequently

observed in strongly hydrogen bonded systems subjected to high pressure [12,13]. Above 8 GPa, a new peak emerged near 3000 cm⁻¹ (see Figure 3) which also decreases in energy with increase in pressure suggesting strong hydrogen bonding interactions in this new phase.

After reaching the terminal pressure (19 GPa), the sample pressure was reduced to 3.2 GPa, and the spectral frequencies appeared to return to the earlier values near this pressure and the peak near 3000 cm⁻¹ disappeared. We found no evidence of laser-induced damage of our sample.

3.2. X-ray Irradiation

Shortly after reducing the pressure to 3.5 GPa, the DAC was irradiated for approximately 2.4 h with white X-rays at the 16 BM-B beamline at the APS. We estimated the dose received at the sample

Table 1
Raman (R) and infrared (IR) frequencies observed at ambient pressure (solid) conditions and in this Letter at 5.2 GPa. Data are taken from references 8, 9 and 11.

Vibrational modes					Observed shifts		
Classification	Species	No.	Approximate description	This Letter R, 5.2 GPa	Giguere and Liu [11] IR, -70° C	Durig et al. [8] IR, -193° C	Durig et al. [9] R, -196° C
N-H stretching	A	1	NH ₂ antisymmetric stretching	3312		3310	3301
		2	NH ₂ symmetric stretching	3232		3200	3169
	B	8	NH ₂ antisymmetric stretching	3374	3315	3310	3194
		9	NH ₂ symmetric stretching		3204	3310	3188
N-H bending	A	3	NH ₂ deformation			1603	1609
		4	NH ₂ wagging		1124	1304	1335
		6	NH ₂ rocking		795	884	884
	B	10	NH ₂ deformation	1621		1655	1662
		11	NH ₂ wagging		1320	1350	1318
		12	NH ₂ rocking	967, 1009	1072, 1078	1066	994
N-N stretching	A	5	N-N stretching	1085	885	1126	1114
N-N torsional	B	7	N-N torsional	599		627	534/510

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