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To cite this article: X R Liu et al 2010 J. Phys.: Conf. Ser. 215 012045

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Raman Spectroscopy of Melamine at High Pressures

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Abstract. In this work, the Raman scattering of melamine was studied under high pressure up to 25 GPa. Behavior of the most intensive peaks of the Raman spectrum of melamine, 677 cm⁻¹ and 985 cm⁻¹ modes, and their line widths do not show any phase transition or indication of formation of sp³ bonds. Comparing behavior of the line width of the Raman peaks of graphite under pressure and that of melamine leads us to conclude that the s-triazine ring is more rigid than the C-C graphite ring.

1. Introduction
Prediction of a dense C₃N₄ phase [1] stimulated a search for novel C₃N₄ phases of dense nitrides of the groups 4 and 14 elements [2]. A cubic phase of silicon nitride with a spinel structure, γ-Si₃N₄ cubic zirconium, and hafnium nitrides with Th₃P₄ structure have been synthesized at high pressures (HP) and high temperatures (HT) in a diamond anvil cell (DAC) [3]. Despite the progress in the synthesis of novel nitrides of groups 4 and 14 elements, dense C₃N₄ has not yet been synthesized. Recent attempts to transform the graphitic C₃N₄ (g-C₃N₄) phase to a novel phase under HP and HT led to the synthesis of a new cubic C₃N₄ (c-C₃N₄) phase that appears to be only slightly denser than g-C₃N₄ phase [4]. Discovering what type of transformation the graphitic C₃N₄ phase undergoes under HP and HT conditions should assist in finding a way to synthesize the theoretically predicted numerous C₃N₄ phases [5, 6]. The conventional method to study a phase transformation under HP is by x-ray diffraction (XRD). Unfortunately, the HP study of the g-C₃N₄ phase by XRD showed that it is difficult to detect the x-ray spectrum above 16 GPa [4]. The study of the Raman spectra of g-C₃N₄ leads us to conclude that the strong and distinguishing features of the UV and NIR Raman spectra of g-C₃N₄ phases should provide a valuable fingerprint for Raman spectroscopy studies of a phase transition of these phases under HP and HT [7]. Unfortunately, UV Raman is difficult to use for studying materials behavior under HP inside a DAC because UV radiation attenuates strongly by diamond. Alternatively, comparative studies of the Raman scattering of g-C₃N₄ and melamine C₆N₃(NH₂)₃ have revealed a strong similarity in the Raman spectra of these components. This similarity is determined by the resemblance between the structure of g-C₃N₄ and that of C₆N₃(NH₂)₃. Melamine is a simple molecule containing a s-triazine ring, which is the building element of the g-C₃N₄ phase, and has, therefore, been used as a suitable molecular precursor for synthesis of the g-C₃N₄ under HPHT conditions [8, 10]. Raman scattering of melamine can be excited by a green laser, which is not absorbed by diamond. Crystal structures of melamine under HP have already been investigated up to 14 GPa [9]. The
purpose of this report is to study the Raman active mode behavior in the \textit{s}-triazine ring in melamine under HP up to 25 GPa.

2. Experimental methods

The HP Raman spectroscopic study was carried out using a symmetric type DAC, which contained a pair of type-I anvils with a culet of 500 µm. Without the use of a pressure-transmitting medium, melamine powder (Alfa Aesar # A11295, 99.99% purity) was loaded together with several ruby chips into a hole of 135 µm in diameter, drilled on a stainless steel gasket. Pressure was calibrated using the ruby fluorescence method. The Raman spectra were excited at 514.5 nm using an argon laser (Lexel Laser Inc., Fremont, CA, USA). The spectra were collected on a × 20, long working-distance objective using Renishaw confocal Raman microscope “\textit{inVia}” (Renishaw, Gloucestershire GL12 7DW, United Kingdom). To avoid sample heating, the power of the incident laser beam was kept at around 3 mW. Spectral resolution was 2 cm\(^{-1}\) and peak fitting analysis was conducted using GRAMS Software (version 7.02, Thermo Fisher Scientific Inc.).

3. Results and Discussion

Raman active modes of the \textit{s}-triazine rings in different molecules have been studied theoretically [11] and experimentally [12, 13]. Figure 1 shows the main Raman spectrum of melamine powder placed on a glass slice. The Raman peaks are assigned to different vibrations of the triazine ring [7, 13]. The most intense feature in the melamine Raman spectrum appears at 677 cm\(^{-1}\) (Fig. 1a) is assigned to the ring breathing 2 mode and involves an in-plane deformation of the triazine ring [13]. The other strong Raman band with an experimental frequency of 985 cm\(^{-1}\) is the ring breathing mode 1 of the triazine ring [13].

![Figure 1](image1.png)

\textbf{Figure 1.} Raman spectrum (100 \textasciitilde 3500 cm\(^{-1}\)) of melamine powder placed on a glass slice at ambient conditions in the (a) low frequency region of the spectrum and the (b) high frequency region of the spectrum.

Another prominent mode at 1444 cm\(^{-1}\) is assigned to the A\(_1\) vibration of the triazine ring [14]. The peak is considered an envelope for the three triazine ring vibrations [15]. The second ring-valence vibration of species E\(_1\) is observed near 1560 cm\(^{-1}\); also, in the low-frequency region, the band at 585 cm\(^{-1}\) belongs to species E\(_1\) [14]. Figure 2 shows the Raman spectrum of melamine at 25 GPa. The noise to signal ration is high in Figure 2, however, breathing modes 1 and 2 can be easily identified. The energy-dispersive X-ray diffraction (EDX) measurements of melamine show that melamine undergoes two pressure-induced structure phase transitions at pressures up to 14.7 GPa— from monoclinic to a triclinic structure at about 1.3 GPa and from a triclinic to an orthorhombic structure at
about 8.2 GPa [9]. Figure 3 illustrates the effect of the pressure on the behaviour of the strongest Raman peaks of melamine. Frequencies of the Raman peaks increase with pressure monotonically and show no indication of the phase transition, including the area around 1.3 or 8 GPa. The possible explanation is related to the fact that triazine breathing modes are not sensitive to the structural transitions (presumably orientational ordering of molecules) observed in Ref. [9]. It is obvious that the _s_-triazine ring is not deformed. One possible indication of approaching a phase transition in graphitic phases is a sharp variation in the peak line widths with pressure. The behavior of the Raman peaks of graphite under pressure showed that above 10 GPa the line width (the full width at a half maximum) of the _G_ mode shows a drastic increase [16]. It was suggested that the increase in line width arose from the formation of _sp^3_ bonds upon approaching a phase transition [16]. Figure 4 shows the effect of pressure on the line width of the 677 cm\(^{-1}\) mode associated with ring breathing mode 2. The line width of the 677 cm\(^{-1}\) peak increases with pressure monotonically. Absence of an increase in line width was associated with the formation of _sp^3_ bonds observed in graphite at 10 GPa, which may indicate that the _s_-triazine ring is more rigid than the _C-C_ ring in graphite.

**Figure 2.** Raman spectrum (200-1200cm\(^{-1}\)) of melamine powder placed in DAC at 25 GPa.  

**Figure 3.** Behavior of 583, 677, 985, 1444, and 1559 cm\(^{-1}\) Raman modes as a function of pressure in melamine.

Raman spectra of melamine exhibit strong peaks due to NH stretching vibrations (figure 1b) — sharp peaks form at 3420 and 3471 cm\(^{-1}\) in melamine [7]. Four peaks in the frequency region from 3100 to 3500 cm\(^{-1}\) are linked to the C–NH\(_2\) group and assigned to the N-H stretching vibration. Their softening and disappearing indicates that the N-H bond is weakening becoming highly disordered. Soft modes were observed in 3100–3500 cm\(^{-1}\), which shifted to a lower frequency and declining intensity with increasing pressure until 15.87 GPa, and finally disappeared at 21.26 GPa. In figure 5, it shows the behavior of 3128 cm\(^{-1}\) Raman mode as a function of pressure in melamine. The cause of the anomalous behavior of C–NH\(_2\) stretching vibration is not fully understood.
4. Conclusions
In this work, Raman scattering of melamine was studied under HP up to 25 GPa. The behavior of the most intensive peaks of the Raman spectrum of melamine, 677 cm$^{-1}$ and 985 cm$^{-1}$ modes, and their line widths do not show any phase transition or any indication of the formation of $sp^3$ bonds. Comparing the behaviour of the Raman peaks line width of graphite under pressure and that of melamine leads us to conclude that C$_3$N$_3$ or the s-triazine ring is more rigid than the C-C graphite ring. The modes at 3100–3500 cm$^{-1}$ were observed to soften and their peak intensity faded under high pressure. This seems to indicate that under pressure, the N-H$_2$ bonds weaken and the structure of melamine becomes unstable.

5. Acknowledgements
This work was supported by U.S. Department of Energy Grant NO. DE-FG02-07ER46408. The authors (SM Hong and XR Liu) are also grateful for the financial support of National Natural Science Foundation of China (Grant No. 10774123) and Youthful Teacher Foundation of Southwest Jiaotong University.

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