# Raman Study of structural change in 1,3,5-triamino-2,4,6trinitrobenzene under non-hydrostatic pressure

Xiaoyu Sun<sup>1</sup>, Chan Gao<sup>1</sup>, Zhilei sui<sup>1</sup>, Rucheng Dai<sup>2</sup>, Zhongping Wang<sup>2\*</sup>, Xianxu Zheng<sup>3</sup>, and Zengming Zhang<sup>1,2\*</sup>
<sup>1</sup>Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China
<sup>2</sup>The Centre for Physical Experiments, University of Science and Technology of China, Hefei, Anhui 230026, China
<sup>3</sup>Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang, Sichuan 621900, China
\*E-mail : zzm@ustc.edu.cn or zpwang@ustc.edu.cn

**Abstract:** Raman spectroscopy was applied to study the structure evolution of TATB powder under non-hydrostatic pressure. The variation of Raman vibrational modes of TATB is analyzed at low pressure. A new Raman peak that represents the NH<sub>2</sub> out-of-plane twist vibration mode occurs at 860 cm<sup>-1</sup>. The peak intensity increases gradually with increasing pressure and the adjacent NH<sub>2</sub> rocking vibration and NO<sub>2</sub> shear vibration mode gradually weakened and disappeared completely at 10.6 GPa. Raman peak shifts with increasing pressure show a clear discontinuity in the range of 5-8 GPa. The results reveal that there is a structural phase transformation in TATB around 5 GPa. During loading compression, the color of TATB undergoes a series of changes. After releasing pressure, the change of TATB is reversible, indicating that the molecular structure of TATB has not been destroyed and chemical stability is still maintained.

Keyword: Phase transition; Raman; Non-hydrostatic pressure; TATB

#### Xiaoyu Sun

## 1 Introduction

1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is a class of layered aromatic explosive. The molecular formula of TATB is  $C_6H_6N_6O_6$ . It displays an exceptional insensitivity to external stimuli such as light, shock wave, friction, mechanical impact and so on. So it was commonly known as "wood explosive". And it also exhibits powerful energy, is called the insensitive high energy explosive<sup>[1]</sup>. The high bonding rate of intermolecular and intramolecular hydrogen bondings in TATB results in its high volume energy density, high insensitivity and good heat resistance. Because of these outstanding properties it becomes a kind of widespread useful energetic material.

Pressure can modify crystal structure of energetic materials and influence their safety and storage. As for TATB, Sushil K. Satija et al.<sup>[2]</sup> Carried out a high pressure study using Raman scattering at a pressure of 16 GPa in 1991. This work didn't show any evidence for pressure-induced phase transition or chemical reactivity. In 2011, Davidson et al.<sup>[3]</sup> increased the pressure to 150 GPa, they observed the structural phase transitions at 28 GPa and 56 GPa by using Raman spectroscopy during the compression. The phase transformation is accompanied by significant color changes, from yellow below 28 GPa to orange to dark red upon 56 GPa. In 2012, Manaa et al.<sup>[4]</sup>employed pure spin polarized DFT to calculate the intermolecular and Intramolecular hydrogen bonding in TATB under the hydrostatic compression up to 250 GPa. An equation of state for unreacted TATB was obtained. And that was in good agreement with the experimental results. However, in these works researchers were more concerned about the nature of TATB in the ultrahigh pressure, resulting in many variations on the detail at low pressure were often overlooked. In this paper, the structure evolution of TATB powder crystal is studied by Raman spectroscopy under the non-hydrostatic pressure condition.

## 2 **Experiments**

A series of Raman experiments were performed on TATB under high pressure up to 50 GPa. Highpressure were generated by a diamond anvil cell (DAC) with 400  $\mu$ m diameter culets. The DAC device is shown in Fig.1 and the schematic of DAC is shown in Fig.2. A stainless steel gasket was preindented to a thickness of 60  $\mu$ m, and then, a hole was drilled by a spark eroder (BETSA, MH20M) to be used as the sample chamber. Sample chamber of 150  $\mu$ m diameter was utilized for this study. There is no transmitting medium in this high pressure experiment, so it was recognized as non-hydrostatic pressure condition. And the pressure was measured by the well-known ruby fluorescence technique. By monitoring the shifts of the ruby R<sub>1</sub> fluorescence line, we can calibrate the corresponding pressure. Raman spectra were recorded by an integrated laser Raman system (LABRAM HR, Jobin Yvon) with a confocal microscope, a stigmatic spectrometer, and a multichannel air-cooled CCD detector with resolution of 1 cm<sup>-1</sup>. The 632.8 nm line from a He-Ne laser was used as the excitation source at a power level of 7 mW to avoid any laser-induced damage. All spectra were recorded in the backscattering geometry at room temperature.

## **3** Results and discussion

TATB in this work is a yellow micrometer powder crystal. Figure 3 shows its XRD pattern. The figure shows that the sample is a pure TATB crystal with no impurities. IR and Raman spectra (not shown here) are consistent with the literature data<sup>[5]</sup>. The surface morphology of TATB is shown in Fig.4. These SEM images display the almost uniform grain size of about 10-50 µm.

Raman spectra of TATB microcrystals under high pressure up to 12.8 GPa at room temperature are illustrated in Fig.5. Most of the Raman vibrational peaks move towards high wavenumbers with increasing

pressure. The significant change for Raman spectra is observed from ambient to 4.9 GPa under the nonhydrostatic pressure. At 4.9 GPa, a new Raman peak that represents the  $NH_2$  out-of-plane twist vibration mode occurs at 860 cm<sup>-1</sup>. The peak intensity increases gradually with increasing pressure continuously, indicating that the  $NH_2$  out-of-plane twist enhances, and finally,  $NH_2$  groups occupy more positions in the space. While the adjacent  $NH_2$  rocking vibration and  $NO_2$  shear vibration mode gradually weakened and disappeared completely at 10.6 GPa.

Figure 6 shows the Raman peak shifts with increasing pressure. The pressure shifts of the Raman peak position below 8 GPa are computed by linear fits, such as the torsional vibration, the deformational vibration, the stretching vibration, the rocking vibration and so on. It is clear from the pressure dependence of the shifts of Raman active modes that some vibrational modes shows a clear discontinuity in the range of 5-8 GPa. Specifically, just like ring twist, ring deformation, NH<sub>2</sub> rock and C-NO<sub>2</sub> stretching, ring stretching vibration modes etc., there are many discontinuous phenomena. The result indicates that a structural phase transformation occurs for TATB around 5 GPa. In 2016, Yuji Kohno et al.<sup>[6]</sup> verified spatial structure changes of TATB under high pressure by using molecular dynamics and first principles, and pointed out there is a unique structural change in the low pressure 2-4 GPa range. At ambient condition, TATB molecule's adjacent layer have two overlapping molecules, when the pressure reaches 5 GPa, the two molecules have the movement in the a-axis direction. Our results are in agreement with reported literature for structural changes and spatial rearrangements at 5 GPa<sup>[6]</sup>.

During compressing, we also found that the color has a significant change. Below 4 GPa, the sample remained light yellow. From 4 to 8 GPa, the color gradually deepened. Until about 12 GPa, the color becomes orange. As the pressure continues to increase, the color continues to deepen and becomes dark red. At 30 GPa, the middle region exhibits a partially opaque state. During the process of decompression down to ambient condition, it changed back to light once again, and the color is gradually restored. These are similar to the phenomena of color changes in the previous literature<sup>[3]</sup>, but the pressure points are earlier than in the literature.

After releasing pressure, TATB transforms back to the ambient phase, which reveals that the phase transition is reversible and the chemical properties of TATB under high pressure are not changed permanently.

## 4 Conclusion

The change of Raman vibrational modes of energetic materials TATB under non-hydrostatic pressure, especially at low pressure, is refined. From the Raman mode and the dependence of Raman shift on pressure and the changes in color, it can be concluded that there is a structural change in the range of about 5 to 10 GPa. This significant change is mainly reflected in the  $NH_2$  out-of-plane twist vibration mode. The reversible process of TATB shows that the molecular structure of TATB has not been destroyed, in other words, its chemical stability is maintained.

# **5** Figures



Figure 1. Pressure device (DAC)





Figure 3. XRD pattern of TATB powder crystals



Figure 4. SEM images of TATB powder crystals





Figure 5. Raman spectra of TATB microcrystals at various pressures



(increasing pressure on the left and decreasing pressure on the right)

Figure 6. Pressure dependence of the shift of Raman active modes of TATB

### Xiaoyu Sun



Figure 7. Color changes in TATB powder crystal under high pressure

## References

[1] Christine J. Wu, Lin H. Yang, and Laurence E. Fried. (2003). Electronic structure of solid 1,3,5-triamino-2,4,6-trinitrobenzene under uniaxial compression: Possible role of pressure-induced metallization in energetic materials. Physical Review B 67: 235101.

[2] Sushil K. Satija. (1991). High-Pressure Raman Scattering and Inelastic Neutron Scattering Studies of Triaminotrinitrobenzene. The Journal of Physical Chemistry. 95: 10103-10109.

[3] Davidson, A.J. (2011). "Stubborn" triaminotrinitrobenzene: Unusually high chemical stability of a molecular solid to 150 GPa. The Journal of Chemical Physics. 135 (17): 174507.

[4] Manaa, M.R., L.E. Fried. (2012). Nearly Equivalent Inter- and Intramolecular Hydrogen Bonding in 1,3,5-Triamino-2,4,6-trinitrobenzene at High Pressure. The Journal of Physical Chemistry C. 116 (3): 2116-2122.

[5] Liu, H. (2006). Vibrational properties of molecule and crystal of TATB: A comparative density functional study. Physics Letters A. 358 (1): 63-69.

[6] Kohno, Y. (2016). Molecular dynamics and first-principles studies of structural change in 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) in crystalline state under high pressure: Comparison of hydrogen bond systems of TATB versus 1,3-diamino-2,4,6-trinitrobenzene (DATB). Chemical Physics. 472: 163-172.