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A comparative study of 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX) and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) under high pressures using Raman spectroscopy and DFT calculations

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ABSTRACT

High pressure Raman experiment was performed to compare RDX and HMX crystals. Ab initio calculations using B3LYP Density Functional Theory method with Sadlej's medium-sized polarized basis set (SadlejpVTZ) were carried out for Caae RDX and 1,5-diaxial-3,7-diequatorial chair HMX molecules. Our calculations and measured Raman vibrational spectra reveal both molecules have similarities on bonding and vibrational properties at ambient pressure. However, high pressure responses for both molecules aren't the same. For RDX, at pressure near 4 GPa, a number of changes become apparent in the Raman spectra, such as modes splitting, intensity modification, and discontinuity of pressure-dependence of frequency shifts, which are consistent with previous experiment and believed to associate with α-γ phase transition. For HMX, only slight conformational deformation involving NO_2 group was observed, and was considered as an onset of β-ε phase transition. It is proposed that the markedly different behavior under high pressure for these two molecules results from different molecular packing in unit cell.

1. Introduction

A thorough knowledge of physical and chemical properties of high explosives under extreme conditions (e.g. shock waves) is important for desirable sensitivity, performance and safety in explosives manufacturing. Typically, static compression experiments can provide the ability to investigate fundamental changes over the range of pressures and temperatures relevant to those under shock compression [1]. High explosives are molecular solids in nature, which are highly compressible under pressure. Therefore, changing of various intra- and inter-molecular interactions by high pressure leads to modifications of molecular conformation, crystal packing, and even new polymorphic phases with totally different properties and functionality.

RDX ($C_3H_6N_6O_6$, molar mass: 222.1163, formally known as 1,3,5-Trinitroperhydro-1,3,5-triazine, informally as **R**oyal **D**emolition **E**xplosive) and HMX ($C_4H_8N_8O_8$, molar mass: 296.1551, formally known as Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, informally as **H**er **M**ajesty's **E**xplosive), as shown in Fig. 1, are widely used explosives. They have similar molecular structures and belong to same chemical group: their basic chemical properties are closely related to cyclohexane and cyclooctane with nitro group as fundamental explosive properties. Properties of molecular solids are determined by chemical and crystalline structures. As molecular solids, their crystal structures both show polymorphs. At ambient conditions, α-RDX is the most stable form. It is a white crystalline solid. Its density is 1.82 g/cm^3 at 20 °C and melting point 205.5 °C. RDX is known to exist in other four polymorphs at different temperatures and pressures: β, γ, ε and δ [2]. The β-polymorph is highly unstable; the γ-polymorph is a high pressure phase, which can be transformed from α-RDX at 4 GPa; The ε-RDX is a high-pressure high-temperature polymorph; The δ-polymorph is a high pressure phase. It is generally known that HMX exists in four different crystal structures, designated as α, β, γ and δ phases of HMX [3]. At ambient conditions, β phase is the most stable form. It is a white solid. Its density is 1.91 g/cm^3 at 20 °C and melting point 276–286 °C. The α-polymorph is not thermodynamically stable at

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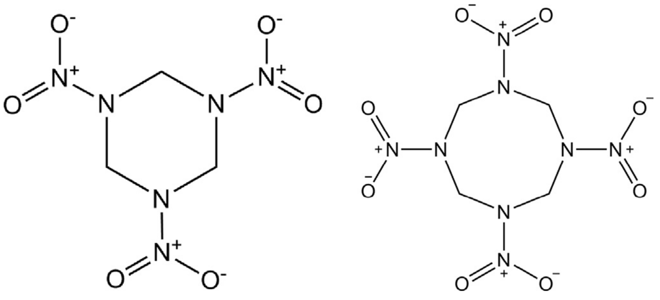

Fig. 1. RDX (left) and HMX (right) molecules.

room temperature; the β-α transformation occurs when β-HMX is heated between 170 °C and 190 °C; The γ-polymorph is a hydrate, $2C_4H_8N_8O_8$ $0.5H_2O$; The δ-polymorph can also be transformed from β-HMX about 160 °C. Besides general physical and chemical properties, the detonation velocity of HMX (density at 1.91 g/cm^3) is 9100 m/s, higher than 8750 m/s for RDX (density at 1.76 g/cm^3). With such abundant polymorphs of different properties, responses of RDX and HMX under high pressure are expected to exhibit important changes.

At high pressure, it has been confirmed by experiments that α-RDX undergoes a phase transition to the γ-polymorphic form [4–8]. Raman spectra at high pressure have been performed by Dreger and Gupta [9] (see Ref. [10] for review). The α-γ phase transitions associated with structural modifications were observed and analyzed. Vibrational spectroscopy (Raman and far-infrared) have also been used to study α-γ and γ-δ phase transitions by Ciezak et al. [11]. The full crystal structures of the high-pressure γ-RDX have been determined later by using X-ray and neutron diffraction techniques [12]. It is found that after phase transition, conformation and packing arrangement of molecules differs in γ-form from those in α-form with volume reduction.

One finds naturally to deduce that RDX and HMX may have similar high pressure response from the fact that their molecular conformations are basically analogous. However, pressure-induced phase transition of HMX takes place at a much higher pressure at 12 GPa compared with that for RDX [13]. There is no apparent abrupt volume change found in phase transition. Recently, the crystal structure for ε-HMX has been determined [14]. It has been found that molecules in this phase adopt the same conformation as those in β-HMX; only the packing of molecules has been changed. The far- and mid-infrared studies of HMX suggest the possibility of two phase changes near 6 GPa and near 12 GPa [15]. Hence, the different results of RDX and HMX show that one cannot easily deduce that their properties, especially under high pressure are alike.

Computational studies on RDX and HMX have offered us conformers and their full vibrational modes [16,17]. Ab initio studies with high accuracy on conformers of RDX and HMX molecules have gave us information on energetics, decomposition of gas-phase molecules and possible new crystalline forms [18,19]. First-principles investigations on solid-state α-RDX and β-HMX have revealed the importance of taking weak van der Waals interactions into consideration when calculating structure, thermal and vibrational properties [20,21]. Polarized Raman scattering experiment has afforded a consistent interpretation of the Raman spectra by assignment of fundamental modes, overtones, and combination bands [22,23]. Although experimental and computational works have provided insight into bonding and structures, there have been no experiments focused on comparison of RDX and HMX under high pressure. How structures evolve behind the different responses of RDX and HMX under high pressure? Is there a phase transition for HMX under 10 GPa? To answer these questions, one needs to compare directly properties of RDX and HMX.

Raman spectroscopy has been used as one of the most powerful and sensitive tool for high-pressure research [24]. The vibrational selection rules permit analysis of materials phase by probing lattice and molecular vibrations, and monitoring the evolution of crystal structures during pressure-induced subtle structure deformation, complex phase transition and even chemical reactivity. The fingerprinting analysis of RDX and HMX under high pressure, in particular, can be performed through the observations of band shifts, splitting or softening of modes in Raman spectra. In this work, we performed high pressure Raman spectroscopy experiment on RDX and HMX up to about 12 GPa at room temperature. Ab initio density functional theory methods were also used to investigate gas phase RDX and HMX molecules. We expected that some distinct behaviors related to their chemical structures could be compared and analyzed.

2. Experimental and computational methods

RDX and HMX single crystals of 99.9% purity were obtained from Institute of Chemical Materials at China Academy of Engineering Physics. The samples were in the form of small grains and used in high pressure experiment without further purification.

In the high pressure Raman experiments, a diamond anvil cell (DAC) with a 400 μm culet was used. A stainless-steel gasket, pre-indented to 0.09 mm with a hole drilled manually in diameter of 120 μm was used as a sample compartment. The 4:1 methanol/ethanol mixture was used as pressure-transmitting medium. The pressure calibration was achieved by applying the pressure shift of Ruby luminescence R1 line. The precision of our pressure measurements was estimated to be 0.05 GPa. The maximum pressure for RDX and HMX achieved in the experiments was 13.2 and 12.3 GPa respectively. A 532 nm, 100 mW laser beam from a diode laser (Spectra-Physics, Millennia type) was used for Raman excitation. A lens ($f = 100$ mm) was used to collect Raman signal, and a holographic notch filters (Semrock Co., Inc., OD >6) was used to filter out Rayleigh scattering. A thermoelectric (TE) cooled CCD detector (Andor Technology) was used as detector which was equipped on a spectrometer (Bruker Spec). The scattering signal was dispersed using 0.5 m spectrograph with a 1200 grooves/mm grating with a spectral resolution of about 1 cm^{-1}. The wavelength calibration was performed using a mercury-arc lamp. All the experiments were carried out at room temperature. Pressure-induced shifts of overlapping bands were analyzed by fitting Raman spectra to a Voigt function using a nonlinear least-squares algorithm.

The geometries of gas phase RDX and HMX for specific conformation were optimized with SadlejpVTZ basis sets and B3LYP density functional method. Calculations were performed with Gaussian 03 computation package [25]. Normal mode analysis in Cartesian coordinates is used for identify Raman modes assignment. Raman spectra and deformation electron density were generated by Multiwfn [26].

3. Results and disscussions

3.1. Raman spectra at ambient pressure

Fig. 2 shows the molecular structures of RDX and HMX, crystal structures of α-RDX and β-HMX. The RDX molecule consists of three NO_2 groups connected to the nitrogen atoms of triazine ring. The ring can be present as a chair (C), twist or boat conformer in terms of the nomenclature associated with cyclo-hexane chemistry. The three nitro groups can be distinguished by the so-called wag angle between the N—N bond and the plane created by the C—N—C triple.