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Properties and phase transitions of the solid β-HMX: different force fields

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Abstract. The structure, cell volume and lattice constants of β-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (β-HMX) crystal are studied by using the classical molecular dynamics method. The variations of cell volume and lattice constants are presented and discussed under different pressures and temperatures. The main purpose of the present work is to understand effect of different force fields, the CVFF and PCFF force fields were used instead of usual COMPASS. It is found that the cell volume is less satisfactory, and there was an abrupt change at 370 K and 440 K for the lattice constants and cell volume with CVFF force field. However, for PCFF force field, an abrupt change occurred at 360 K and 430 K, respectively. It means that β-HMX may have phase transitions at these temperatures in accordance with experimental observation. It is suggested that selection of suitable force field play an important role in achieving desired accuracy of simulation results.

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Key words: β-HMX crystal, molecular dynamics, force fields, phase transitions

1 Introduction

The high explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) which also referred to as high melting explosive is a typical energetic material and one of the most potent chem-

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ical explosives manufactured. It have been widely used in the polymer bonded explosives (PBXs) and propellant formulation [1]. HMX is an achromatous crystal and exhibits four pure crystal polymorphs at ambient pressure, namely α-HMX, β-HMX, γ-HMX and δ-HMX [2]. The stabilities of these polymorphs are known to be $\beta<\alpha<\gamma<\delta$ at ambient conditions [3]. Although the stability field of these phases at high pressures and temperatures are not very clear, the β phase is considered the most stable phase at high pressures at least to 10 GPa [4, 5]. Also, it crystallizes into the monoclinic space group $P2_{1/c}$ according to x-ray [6] and neutron experiments, with the crystal lattice $a=6.54$ Å, $b=11.05$ Å, $c=8.70$ Å, $\beta=124.3°$. The β phase has a monoclinic $P2_{1/c}$ structure with two $C_4H_8N_8O_8$ molecules per unit cell at ambient conditions [7] and transforms to the δ phase at 165–210 $°C$ at ambient pressure [8]. The unit cell and single molecular structure of β-HMX in the crystal phase obtained from geometry optimization was shown in Fig. 1. It can be seen that each $C_4H_8N_8O_8$ molecule involves two NO_2 groups above and two below the ring plane, and there is a central ring having eight atoms for N or C across. The α-phase crystal structure was reported to be stable in the temperature range 376–435 K [2] with the orthorhombic symmetry (space group Fdd2) and has eight molecules in the unit cell. The δ-polymorph belongs to the hexagonal symmetry with space group $P6_1$ and $Z=6$ molecules per unit cell, and stable above 433 K up to the melting point 553 K. Each $C_4H_8N_8O_8$ molecule in α-and δ-phase is in so called "boat" conformation, having all four NO_2 groups on the same side of the ring plane.

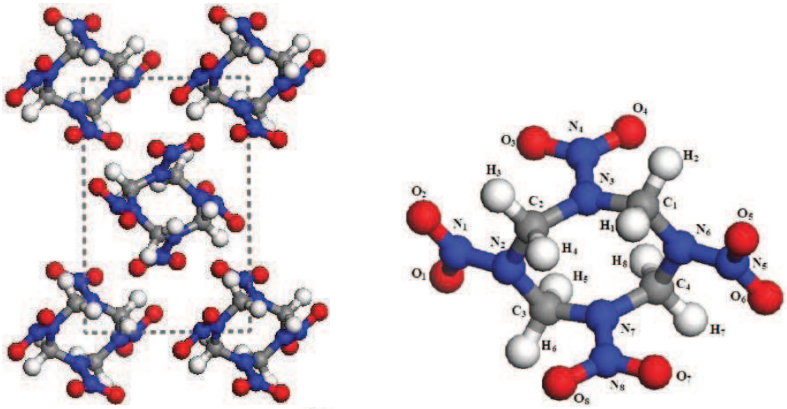

Figure 1: Unit cell of the β-HMX crystal (left) and the molecular structure (right), where C: Gray, N: blue, O: red, H: white.

Dan *et al.* [9] performed the isothermal-isobaric molecular dynamics (NPT-MD) simulations of the β, α, and δ phases of HMX over the temperature range 4.2–553 K and 1 atm. The predicted space group symmetries and structural parameters for the three phases of HMX are in close agreement with experimental values. Choong-Shik *et al.* [10] investigated β-HMX at high pressures and temperatures by using a DAC coupled with micro-Raman spectroscopy and angle-resolved x-ray diffraction using an intense monochromatic synchrotron beam and