Theoretical calculations of lattice properties of secondary explosives

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A flexible potential including both intra- and inter-molecular potential was used to calculate the lattice properties of several secondary explosives such as nitramine crystals of HMX (1,3,5,7-tetranitro-1,3,5,7- tetraazacycrooctane), RDX (1,3,5- trinitro- 1,3,5-triazacycrohexane) and DMN (N,N-Dimethylnitramine), and non-nitramine crystals of PETN(Pentaerythritol tetranitrate), ANTA (3-Amino-5-nitro-1,2,4-triazole), NB (Nitrobenzene) and NM (Nitromethane). The intramolecular part of the potential contains bond stretching, angle bending, out-of-plane bending, torsional, and non-bonded motion terms. Parameters in these terms were taken from literatures and refitted to reproduce the experimental crystal structures and infrared spectra of these explosives. The Buckingham exp-6 function with Coulombic interactions was used for intermolecular potential of HMX, RDX, NB, DMN and NM, whereas the Lennard-Jones 6-12 potential with Coulombic interactions was applied for intermolecular interactions in PETN and ANTA(plus hydrogen bonding potential). It is confirmed that the flexible potentials could accurately predict lattice parameters and lattice energies of these explosives. In addition, the potentials could also predict the bulk modulus and its pressure derivatives. Calculated bulk modulus of NM had a deviation less than 4.5% compared with the experimental data at pressure region of P ≤ 3.0GPa. Calculated elastic constants, elastic stiffness, averaged Young's modulus and Poisson ratio of RDX were in agreement with the experimental data.

1. Introduction

Prediction of performance, sensitivity, chemical and physical properties of energetic materials are central problems for the development and the safe use of new energetic materials. In recent years, many efforts have been paid to understand and predict these properties based on theoretical [1)-10)] and experimental methods [11)-14)]. Computer simulation has been widely used and was proved to be a very effective mean for the prediction and understanding of various properties of high explosives.

In order to perform high quality simulation, accurate intermolecular and intramolecular potentials are required, and it is not an easy task to determine accurate potential parameters for the explosives, which are generally molecular solid composed of polyatomic organic molecules with complicated crystal structures. Thompson and his co-workers [1)-6)] have developed an intermolecular potential to predict the structural and thermochemical parameters for many explosives. The potential energy functions used in their studies are composed of pairwise atom-atom (exp-6) Buckingham or (6-m) Lennard-Jones functions together with the electrostatic interactions between different atoms in the molecules. As indicated by their results [1)-6)], their potentials have been very successful in their ability to describe the equilibrium structures of a variety of organic molecular crystals under ambient conditions and

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under moderately high pressure and temperature conditions. However, the physical and chemical processes of energetic materials are of most interest at extremely high pressures and temperatures, in which conformational molecular changes may become important. For example, analysis of the shock initiation of explosives requires understanding of crystal properties under extremely high pressure (~GPa) conditions. Consequently, further developments of the interaction potential are necessary to describe the intramolecular motion, molecular deformations, and the energy flow inside these crystals under such high pressures. Thompson et al. 7) improved their previous regid-molecule approximation and extended the potential to include a full intramolecular potential for the simulations of energetic materials. At their first attempt, they selected nitromethane as the prototype explosive to develop the fully flexible model of an energetic molecular crystal 7).

In the present paper, we applied the fully flexible model to the simulation of the lattice properties of secondary explosives such as PETN(Pentaerythritol tetranitrate), RDX (1,3,5-trinitro-1,3,5-triazacycrohexane), polymorphic forms of HMX (1,3,5,7- tetranitro-1,3,5,7- tetraazacycrooctane), ANTA (3-Amino-5-nitro-1,2,4-triazole), NB(nitrobenzene), DMN (N,N-Dimethylnitramine) and NM(nitromethane).

2. Potential energy functions

We assumed that the potential energy for N secondary explosive molecules can be described as the sum of inter and intramolecular interaction terms:

$$V^{total} = \sum_{i=1}^{N}(V^{\text{int ramolecular}} + \frac{1}{2}\sum_{j=1}^{N} V_{ij}^{\text{int ermolecule}}) \qquad (1)$$

Except for the PETN and ANTA, the intermolecular potential is the same as described in reference (1-7). It consists of the superposition of a pairwise sum of Buckingham potential, $V_{\alpha\beta}(r_{\alpha\beta})$, and coulombic potentials, $V_{\alpha\beta}{}^{C}(r_{\alpha\beta})$.

$$V_{\alpha\beta}(r_{\alpha\beta}) = A_{\alpha\beta}\exp(-B_{\alpha\beta}r_{\alpha\beta}) - \frac{C_{\alpha\beta}}{r_{\alpha\beta}^{6}}, \qquad (2)$$

and

$$V_{\alpha\beta}^{C}(r_{\alpha\beta}) = \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 r_{\alpha\beta}} \qquad (3)$$

For PETN and ANTA, the potential function was constructed as a sum of pairwise additive Lennard-Jones, $V^{LJ}{}_{\alpha\beta}(r_{\alpha\beta})$, hydrogen bonding, $V^{HB}{}_{\alpha\beta}(r_{\alpha\beta})$, and coulomb, $V_{\alpha\beta}{}^{C}(r_{\alpha\beta})$, potentials;

$$V_{\alpha\beta}^{LJ}(r_{\alpha\beta}) = \varepsilon_{\alpha\beta}\left(\left(\frac{r_{\alpha\beta}^{0}}{r_{\alpha\beta}}\right)^{12} - 2\left(\frac{r_{\alpha\beta}^{0}}{r_{\alpha\beta}}\right)^{6}\right), \qquad (4)$$

$$V_{\alpha\beta}^{HB}(r_{\alpha\beta}) = \frac{A_{\alpha\beta}^{H}}{r_{\alpha\beta}^{12}} - \frac{B_{\alpha\beta}^{H}}{r_{\alpha\beta}^{10}}, \qquad (5)$$

where $r_{\alpha\beta}$ is the interatomic distance between the atoms α and β belonging to different molecules, q_α and q_β are the corresponding electrostatic charges on these atoms, and ε_0 is the dielectric permittivity constant for free space. The parameters $A_{\alpha\beta}$, $B_{\alpha\beta}$, $C_{\alpha\beta}$, $\varepsilon_{\alpha\beta}$, $r_{\alpha\beta}{}^{0}$, $A_{\alpha\beta}{}^{H}$ and $B_{\alpha\beta}{}^{H}$, for different types of atomic pairs have been previously published in references 1-7, 15, 16 and 17 and were used in the present study without change except for the pair of atoms O···H interaction and hydrogen bonding intermolecular potential. The pair of atoms O···H interaction and hydrogen bonding intermolecular potential were refitted to reproduce the experimental structure. The values of the intermolecular potential parameters are given in Tables 1~4.

A set of partial charges used in these calculations was determined by fitting to the electostatic

Table1. The Atom-Atom potential Parameters for RDX, HMX, NB, DMN and NM[a]

Pair (α - β)	$A_{\alpha\beta}$(kJ/mol)	$B_{\alpha\beta}$(Å^{-1})	$C_{\alpha\beta}$(kJ/mol)
H - H	9213.510	3.74	136.3800
C - C	369726.330	3.60	2439.3459
N - N	264795.246	3.78	1668.3316
O - O	290437.820	3.96	1453.3114

[a] With the exception for a pair of O - H, for pairs of unlike atoms, $A_{\alpha\beta}$, $B_{\alpha\beta}$ and $C_{\alpha\beta}$ were calculated from the formulate $A_{\alpha\beta} =(A_{\alpha\alpha} A_{\beta\beta})^{1/2}$, $B_{\alpha\beta} =(B_{\alpha\alpha} + B_{\beta\beta})/2$, $C_{\alpha\beta} =(C_{\alpha\alpha} C_{\beta\beta})^{1/2}$.

Table2. The Atom-Atom O · H potential parameters for RDX, HMX, NB, DMN and NM

Pair (α · β)	$A_{\alpha\beta}$(kJ/mol)	$B_{\alpha\beta}$($Å^{-1}$)	$C_{\alpha\beta}$(kJ/mol)
RDX	42079.341	3.85	445.2145
HMX	44012.177	3.85	445.2145
NB	61380.377	3.85	445.2145
DMN	51731.377	3.85	445.2145
NM	25661.516	3.85	0.0

Table3. The Atom-Atom potential parameters for ANTA[a]

Pair (α · β)	$\varepsilon_{\alpha\beta}$(kJ/mol)	$r_{\alpha\beta}^0$(Å)
H · H	0.213384	2.43
C · C	0.451746	3.912
N · N	0.218154	4.06
O · O	0.853452	2.97
	$A_{\alpha\beta}^{H}$ (kJ/mol)[b]	$B_{\alpha\beta}^{H}$(kJ/mol)[b]
O · H	16895.242	6830.6519
N · H	48401.827	5975.5324

[a] for pairs of unlike atoms, $r_{\alpha\beta}^0$ and $\varepsilon_{\alpha\beta}$ were calculated from the formulate $r_{\alpha\beta}^0 =(r_{\alpha\alpha}^0 + r_{\beta\beta}^0)/2$, $\varepsilon_{\alpha\beta} =(\varepsilon_{\alpha\alpha} \varepsilon_{\beta\beta})^{1/2}(r_{\alpha\alpha}^0 r_{\beta\beta}^0)^3/ (r_{\alpha\beta}^0)^6$. [b] Parameters of the hydrogen bond Lennard -Jones12 -10 potential.

Table4. The force constants of the intramolecular potential parameters for PETN.[a]

Bond stretching parameters			Angle bending parameters		
bond	k_r (kJ mol^{-1} $Å^{-2}$)	r^0(Å)	angle	k_θ(kJ mol^{-1} rad^{-2})	θ(deg)
N-O	3765.66	1.217	C-C-C	334.72	109.5
N-O_s	2510.44	1.389	C-C-H	418.41	110.4
C-C	2594.13	1.538	C-C-O_s	418.41	107.6
C-H	2941.65	1.03	H-C-O_s	418.41	108.7
C-O_s	2677.81	1.433	H-C-H	292.89	111.4
			O-N-O_s	585.77	115.98
			O-N-O	585.77	127.80
			C-O_s -N	585.77	117.7

Torsion potential parameters

Dihedral angle	V_Φ(kJ/mol)	δ(deg)	m	i
O-N-O_s-C	3.7658	0.0	2	-1
C-C-C-O_s	37.658	0.0	3	+1
N-O_s-C-C	-4.8117	0.0	3	-1
H-C-C-C	0.4824	0.0	2	+1

Intermolecular and nonbonded potential $V_{\alpha\beta}^{LJ}(r)= \varepsilon_{\alpha\beta} [(r_0/ r_{\alpha\beta})^{12} - 2(r/ r_{\alpha\beta})^6]$

Pair (α · β)	ε(kJ)	r_0(Å)	Pair (α · β)	ε(kJ)	r_0(Å)
C_1-C_1	0.25104	3.60	C_2-C_2	0.37656	3.70
H-H	0.04184	3.08	O_s-O_s	0.62760	3.30
O-O	0.8368	3.20	N-N	0.66944	3.50

[a] Except N-H, for pairs of unlike atoms, $r_{\alpha\beta}^0$ and $\varepsilon_{\alpha\beta}$ were calculated from the formulate $r_{\alpha\beta}^0 =(r_{\alpha\alpha}^0 + r_{\beta\beta}^0)/2$, $\varepsilon_{\alpha\beta} =(\varepsilon_{\alpha\alpha} \varepsilon_{\beta\beta})^{1/2}(r_{\alpha\alpha}^0 r_{\beta\beta}^0)^3/ (r_{\alpha\beta}^0)^6$. The intermolecular potential parameter for the pair of N-H is $A_{\alpha\beta}$=47789.6612 eV, $B_{\alpha\beta}$=5.39953eV, in $V_{\alpha\beta}^{LJ}(r)=A_{\alpha\beta}/r_{\alpha\beta}^{12} - B_{\alpha\beta}/ r_{\alpha\beta}^6$.

interaction potential derived from the quantum mechanical calculations for an isolated molecule whose atoms are arranged in the experimental crystallographic arrangement. These calculations have been done using the CHELPG (electrostatic-potential-derived atom charges) procedure as implemented in the Gaussian 98 series of program [18] at the MP2/6-31G** level of theory.

The intramolecular potentials were assumed the form as follows:

$$V^{intramolecular} = \sum V_{bond} + \sum V_{angle} + \sum V_{outofplane} + \sum V_{torsion} + \sum V_{nonbond} \tag{6}$$

Terms in the right hand side of equation (6) represent the bond stretching, angle bending, out-of-plane bending, torsional and non-bonded motions in an isolated molecule. The covalent bond stretches can be approximated as a harmonic oscillator

$$V_{bond} = \frac{1}{2} k_r (r_i - r_i^0)^2 , \tag{7}$$

where r_i is the bond distance, r_i^0 is the equilibrium bond length and k_r is the force constant describing the stiffness of the bond. The angle-bending potential is represented by the form,

$$V_{angle} = \frac{1}{2} k_\theta (\theta_i - \theta_i^0)^2 , \tag{8}$$

where k_θ is the force constant and θ^0 is the equilibrium value of the angle. The out-of-plane bending potential is represented by the form,

$$V_{outofplane} = k_d d^2 , \tag{9}$$

where k_d is the force constant and d is the perpendicular distance of atom i from the plane of j, k and l to which it is boned. The torsion potential are represented by the form,

$$V_{torsion} = V_\Phi (1 + i \cos(m\Phi_i - \Phi_0)) , \tag{10}$$

where V_Φ is half of the intramolecular torsion barrier, Φ is the torsion angle, m is the phase of periodicity and m=1, 2, 3, or 4, and i is +1 or −1 according to the sign of m phase. We also considered intramolecular nonbonded interactions of PETN, RDX, NB and HMX molecules. The intramolecular nonbonded interactions are referred to the interactions between these atoms separated by three or more bonds in an isolated molecule. The potential is represented by the Buckingham or Lennard-Jones form in expression (2) or (4).

All force-field parameters in expression (7)~(10) are taken directly from literatures for NM [7], HMX [19], RDX [20),21], ANTA [22], NB [23], DMN [24] and PETN[17], and refitted to produce the experimental observed structure and infrared spectra. The values of these parameters are given in Tables 4 ~10. The phonon and vibron densities of states calculated with these potential parameters are compared with the experimental spectra in Fig.1. Although the intensity is different between calculation and experiment, the positions of phonon and vibron modes in density of states are in good agreement with the experimental spectra.

3. Computational details

The calculations in this study were performed using the software package of the general utility lattice program (GULP)[25),26]. For a crystal with *Z* molecules per unit cell (*N* atoms per molecule) at arbitrary positions, these degrees of freedom are determined by the 3*NZ* positions of the atoms in the unit cell as well as the dimensions and angles of the unit cell. Considering symmetry constraints on either lattice parameters or on different subsets of atomic coordinates decreases this number of the degrees of freedom. The symmetry-adapted energy minimization can attain significant reduction of the computational time necessary to minimize the lattice energy starting with a trial configuration. The GULP program tries to use the crystal symmetry both to make it easier to generate structures and to speed up the calculations by considering the asymmetric unit. The flexible potential presented in GULP not only contains many kinds of intermolecular potential functions such as Buckingham and Lennard-Jones potentials, but also contains a variety of two-, three-, and four-body potentials for intramolecular potential. Thus it is suitable for the treatment of both inorganic and organic systems with fully flexible molecules[25),26]. It was used to optimize the crystal structure and calculate the elastic constants for Ammonium nitrate [27),28] and other molecules[29].

In the present calculations, we locate molecules based on covalent radii and retain all coulomb interaction within the molecule, and then exclude the intramolecular coulomb potential. The cut-off

Table5. The force constants of the intramolecular potential parameters for NM.

Bond Stretching Parameters			angle bending parameters		
bond	k_r (kJ mol^{-1} $Å^{-2}$)	r^0(Å)	angle	k_θ(kJ mol^{-1} rad^{-2})	θ(deg)
C-N	2019.32	1.499574	C-N-O	294.52	117.04
O-N	4724.32	1.226747	O-N-O	657.85	125.89
C-H	3050.85	1.0900	N-C-H	224.81	107.56
			H-C-H	149.94	111.31

Torsion potential parameters

Dihedral angle	V_Φ(kJ/mol)	δ(deg)	m	i
$H-C-N-O_1$	0.27	90.0	3	-1
$H-C-N-O_2$	0.27	90.0	3	+1
$N-O_2-O_1-C$	240.37	0.0	2	-1

Table6. The force constants of the intramolecular potential parameters for RDX.

Bond Stretching Parameters

bond	k_r (kJ mol^{-1} $Å^{-2}$)	r^0(Å)	bond	k_r (kJ mol^{-1} $Å^{-2}$)	r^0(Å)
C-N	2717.12	1.454	C-H	2998.23	1.081
O-N	3123.92	1.210	N-N	2812.60	1.380

angle bending parameters

angle	k_θ(kJ mol^{-1} rad^{-2})	θ(deg)	angle	k_θ(kJ mol^{-1} rad^{-2})	θ(deg)
O-N-O	859.75	125.596	C-N-C	793.26	109.500
N-C-N	608.08	109.500	C-N-N	969.23	125.250
N-N-O	1008.82	117.200	N-C-H	243.82	109.500
H-C-H	235.06	109.328			

Torsion potential $V_{torsions} = V_\Phi\,(1+i\cos(m\,\Phi_i - \Phi_0))$, V_Φ in kJ mol^{-1}

Dihedral angle	V_Φ(kJ/mol)	δ(deg)	m	i
C-N-N-O	8.6835	0.0	2	-1
C-N-C-N	0.96483	0	0	+1
C-N-C-N	11.5780	60.0	1	-1
C-N-C-N	-5.7890	60.0	2	-1

Out-of-Plane parameters $V_{outofplane} = k_d d^2$, k_d in kJ mol^{-1} $Å^{-2}$

$N-N-(C)_2$	14.472

Nonbonded potential $V_{\alpha\beta}^{LJ}(r) = A_{\alpha\beta}/r_{\alpha\beta}^{12} - B_{\alpha\beta}/r_{\alpha\beta}^{6}$

Pair (α – β)	$A_{\alpha\beta}$/eV	$B_{\alpha\beta}$/eV	Pair (α – β)	$A_{\alpha\beta}$/eV	$B_{\alpha\beta}$/eV
C-N(cross ring)	20542.7448	12.39675	N-N(ring exocyclic)	1392.376	12.4412
O-O	144.676718	0.2240343			

distance R_{cut} = 40.0Å (for hydrogen bonding potential, R_{cut} =3.0 Å) were used in order to obtain accurate summation of the intermolecular potential.

Some parameters in expressions (2) ~ (10) were determined to reproduce the experimental crystal structure and infrared spectra. In minimized configuration, we didn't fix lattice parameters and the atom positions. The intra- and intermolecular potential parameters used here are presented in Tables 1-10. The minimized configurations have been verified by phonon calculations that the first three vibrational frequencies are equal to zero and all of other frequencies have positive values, indicating the existence of a local minimum. The experimental crystal structure of these molecules are taken from literatures30)-38). And the numerical designations of the atoms are arranged in the experimental crystallographic arrangement30)-38).

Table7. The force constants of the intramolecular potential parameters for HMX,DMN.[a]

β-HMX	α-HMX	δ-HMX	DMN	
Bond	Bond Stretches $V_{bonds} = 1/2\, k_r (r_i - r_i^0)^2$, k_r in kJ mol^{-1} Å^{-2}			
O - N	3888.64	3888.64	8327.18	5348.24
N - N	4149.55	4149.55	4149.55	3417.24
N - C	3005.25	3005.25	3005.25	3055.66
C - H	2954.81	2954.81	2954.81	3362.85
Bond angle	$V_{angles} = 1/2\, k_\theta (\theta_i - \theta_i^0)^2$, k_θ in kJ mol^{-1} rad^{-2}			
O-N-O	426.54	426.54	426.54	1616.78
O-N-N	523.03	523.03	523.03	2240.62
N-N-C	543.96	543.96	543.96	1041.90
C-N-C	292.91	292.91	292.91	1484.48
N-C-H	361.52	361.52	361.52	694.71
H-C-H	322.19	322.19	322.19	610.70
N-C-N	292.91	292.91	292.91	—
Dihedral angle	[b] $V_{torsions} = V_\Phi (1+i\cos(m\, \Phi_i - \Phi_0))$, V_Φ in kJ mol^{-1}			
O-N-N-C	17.6787(-2)	17.6787(-2)	17.6787(-2)	90.25(-2)
O-N-N-C	1.6529(-4)	1.6529(-4)	1.6529(-4)	—
O-N-N-C	0.0084(-8)	0.0084(-8)	0.0084(-8)	—
H-C-N-N	-0.3348(-3)	-4.535(+3)	-4.535(+3)	9.20(+3)
C-N-C-N	4.728(-2)	9.649(-2)	8.684(-2)	—
H-C-N-C	-0.3348(-3)	-0.3348(-3)	-0.3348(-3)	—
H- C-H-H	—	—	—	-0.1930(-2)
Out of plane	Out-of-plane bending potential $V_{outofplane} = k_d d^2$, k_d in kJ mol^{-1} Å^{-2}			
N-N-(C)$_2$	0.0051	0.0051	0.0051	—
N-N-(O)$_2$	0.0569	0.0569	0.0569	—

[a] the equilibrium value of r^0 and θ^0 is equal to the averaged value of experiment, $\Phi_0 = 0$.

[b] The values in parenthesis are the sign of m phase and m.

Table8. The non-bonded intramolecular potential parameters for HMX.

Pair (α - β)	$A_{\alpha\beta}$(kJ/mol)	$B_{\alpha\beta}$(Å^{-1})	$C_{\alpha\beta}$(kJ/mol)
H - H(α,β,δ-HMX)	11087.145	3.74	114.6494
C - C(α,β,δ-HMX)	62664.080	3.09	2681.3027
N - N(α,β,δ-HMX)	254547.403	3.78	2092.1541
O - O(α,β,δ-HMX)	317357.530	4.063	1669.1226
H-C(δ-HMX)	43723.412	3.415	554.4460
H-C(α-HMX)	29253.105	3.415	554.4460

Table9. The force constants of the intramolecular potential parameters for ANTA.[a]

Bond stretching parameters, k_r (kJ mol^{-1} Å^{-2})

bond	k_r	bond	k_r	Bond	k_r	bond	k_r
N1-N2	2616.76	N1-C2	1034.03	C2-N3	1837.95	N3-C1	2870.56
C1-N2	2332.16	C1-N4	2482.62	N4-O1	2035.10	N4-O2	2364.67
C2-N5	2539.35	N5-H2	3909.11	N5-H3	4032.54	N1-H1	4011.62

Angle bending parameters, k_θ(kJ mol^{-1} rad^{-2})

angle	k_θ	angle	K_θ	Angle	k_θ	angle	k_θ
N2-N1-C2	1945.43	N1-N2-C1	1446.45	C2-N3-C1	863.62	N2-C1-N3	871.95
N2-C1-N4	943.78	N3-C1-N4	1344.95	C1-N4-O2	1227.54	C1-N4-O1	1464.65
O2-N4-O1	1202.48	N1-C2-N5	930.73	N3-C2-N5	2032.29	C2-N5-H2	285.35
C2-N5-H3	197.15	H2-N5-H3	176.61	N2-N1-H1	414.93	C2-N1-H1	116.23

Torsion potential [b] $V_{torsions} = V_\Phi\ (1+i\cos(m\ \Phi_i - \Phi_0))$, V_Φ in kJ mol^{-1}

Dihedral angle	V_Φ	Dihedral angle	V_Φ
O2-N4-C1-N3	-33.81(+2)	O2-N4-C1-N3	13.09(+4)
O1-N4-C1-N2	-35.07(+2)	O1-N4-C1-N2	13.31(+4)
H3-N5-C2-N3	100.44(-2)	H3-N5-C2-N3	25.21(+4)
H2-N5-C2-N1	16.26(+2)	H2-N5-C2-N1	20.42(+4)
N3-C2-N1-N2	8.829(-2)	C2-N1-N2-C1	7.532(-2)
N5-C2-N1-H1	9.205(-2)	N3-C2-N1-H1	7.532(+2)
N4-C1-N2-N1	7.364(+2)		

Out-of-plane bending potential $V_{outofplane} = k_d\, d^2$, k_d in kJ mol^{-1} Å^{-2}

Out-of-plane bending	k_d	Out-of-plane bending	k_d
N4-C1(N2N3)	0.0135	N5-C2(N1N3)	0.00695
H1-N1(C2N2)	0.066		

[a] the equilibrium value of r^0 and θ^0 is equal to the averaged value of experiment, Φ_0=0. [b] The values in parenthesis are the sign of m phase and m.

4. Results and discussion

A. Molecular packing calculations

A general procedure for testing empirical or semiempirical inter- and intramolecular potential energy functions for organic crystals is the use of molecular packing calculations[39]. The results of the molecular packing calculation by using the GULP program are given in Tables 11-13. The differences between lattice and molecular parameters obtained by energy minimization and the experimental structures are given in Table 11. The maximum deviation of the lattice dimensions is -3.77% for NM and DMN, and the maximum deviation of unit cell volume is –3.77%. On the other hand, the deviation of lattice dimensions and unit cell volume of NB, RDX, PETN and HMX are less than 2.0%. For NM, RDX, PETN, α-HMX and δ-HMX, there are no changes caused by the optimization in the values of the unit cell angles, which remain 90° or 120° consistent with the space group symmetry.

For the minimized configuration, the total lattice energies together with the corresponding electrostatic energy contribution are also given in the Table 11. It is worthy mentioning that the calculated lattice energies are also in excellent agreement with the available experiment data with a maximum deviation of only 2.4%.

We also calculate lattice parameters at high pressure below 4.0 GPa. For different explosives, a, b and c axis have different compressible property. The volume of unit cell as a function of pressure is given in Table12. Thompson et al.[3),6),7)] have calculated the crystal structure of NM, PETN, RDX and β-HMX under hydrostatic compression using constant pressure and temperature molecular

Table 10. The force constants of the intramolecular potential parameters for NB.[a]

Bond stretching parameters, k_r (kJ mol^{-1} Å^{-2})

bond	k_r	bond	k_r	Bond	k_r	bond	k_r
C-N	2659.42	N-O	5717.56	C1-C2	3823.80	C1-C6	3823.80
C2-C3	3846.61	C5-C6	3846.61	C3-C4	3788.15	C4-C5	3788.15
C2-H	3186.93	C6-H	3186.93	C3-H	3096.99	C5-H	3096.99
C4-H	3085.72						

Angle bending parameters, k_θ(kJ mol^{-1} rad^{-2})

angle	k_θ	angle	k_θ	Angle	K_θ	angle	k_θ
O-N-O	1142.99	C1-N-O2	1100.47	C1-N-O1	1100.47	C2-C1-N	1013.09
C6-C1-N	1013.09	C-C-H	234.35	C-C-C	527.22		

Torsion potential [b] $V_{torsions} = V_\Phi\,(1+i\cos(m\,\Phi_i - \Phi_0))$, V_Φ in kJ mol^{-1}

Dihedral angle	V_Φ	Dihedral angle	V_Φ
C6-C1-N-O1	18.11(-2)	C2-C1-N-O2	18.11(-2)
C1-C2-C3-C4	-4.313(-2)	C2-C3-C4-C5	-4.313 (-2)
C3-C4-C5-C6	-4.313 (-2)	C4-C5-C6-C1	-4.313 (-2)
C5-C6-C1-C2	-4.313 (-2)	C6-C1-C2-C3	-4.313 (-2)

Out-of-plane bending potential $V_{outofplane} = k_d\, d^2$, k_d in kJ mol^{-1} Å^{-2}

Out-of-plane bending	k_d	Out-of-plane bending	k_d
C1-N(O)$_2$	7.756	H-C(C)$_2$	4.928
N-C(C)$_2$	3.811		

Nonbonded potential $V_{\alpha\beta}^{LJ}(r) = A_{\alpha\beta}/ r_{\alpha\beta}^{12} - B_{\alpha\beta}/ r_{\alpha\beta}^{6}$

Pair ($\alpha - \beta$)	$A_{\alpha\beta}$/eV	$B_{\alpha\beta}$/eV
O-C4	24908.65	24.097
O-H	2072.455	4.4918
N-C4	38274.895	28.333

[a] the equilibrium value of r^0 and θ^0 is equal to the averaged value of experiment, $\Phi_0 = 0$.

[b] The values in parenthesis are the sign of m phase and m.

dynamics simulations (NPT-MD). They also performed molecular packing (MP) calculations3),6),7). Present flexible potential model can produce better agreement with the experimental data than the potential used by Thompson et al1),6). The explosives in the present study have the compressibility of NM>NB>DMN, RDX>α-HMX > δ-HMX > PETN >β-HMX > ANTA.

We didn't fix lattice parameters and the atom positions in energy minimization. However, the lattice parameters and molecular geometrical parameters obtained by minimized equilibrium are very close to the corresponding experimental values, which suggest that the present flexible potential can accurately predict the equilibrium properties such as lattice parameters, molecular geometrical parameters and lattice energies in these explosive crystals.

B. Elastic constants and bulk modulus

The elastic constant matrix is a 6×6 matrix which contains the second derivatives of the energy density with respect to external strain24).

$$E = \frac{1}{V(W_{ss} - W_{sc}W_{cc}^{-1}W_{cs})}, \qquad (11)$$

where W_{ss} is the strain-strain second derivative matrix, W_{cc} is the Cartesian-space coordinate second derivative matrix, W_{cs} is the mixed Cartesian-strain second derivative matrix, and V is the volume of the unit cell.

It is important to note that the elastic constant matrix, in general, depends on the orientation of the unit cell relative to the Cartesian axes. Because GULP program aligns the *a* vector along the x axis, *b* in the xy plane, then the elastic constants can be calculated accordingly.

Except for the calculations of elastic constants,

Table 11. Comparison of the calculated and experimental lattice parameters and total energies[a]

		Lattice energy		Lattice parameter						
Explosive		E_{total}	E_{elect}	V	a	b	C	α	β	γ
NM	exp	-52.3[b]	—	289.3304	5.244	6.320	8.730	90.0	90.0	90.0
	calc	-52.31	-35.79	278.4161	5.047	6.405	8.613	90.0	90.0	90.0
change	%	0.0		-3.77	-3.76	1.34	-1.34	0.0	0.0	0.0
DMN	exp	-74.83[c]	—	219.4374	6.129	6.501	6.060	90.0	114.66	90.0
	calc	-74.14	-26.20	213.9499	6.231	6.256	6.053	90.0	114.93	90.0
change	%	0.92		-2.50	1.66	-3.77	-0.12	0.0	0.24	0.0
ANTA	exp	—	—	942.7696	14.199	4.844	14.258	90.0	105.98	90.0
	calc	-124.60	-71.57	951.6173	14.256	4.930	13.929	90.0	103.54	90.0
change	%			0.94	0.40	1.78	-2.31	0.0	-2.30	0.0
NB	exp	—	—	571.1463	3.8014	11.6153	12.9843	90.0	94.984	90.0
	calc	-83.57	-13.52	564.4706	3.7523	11.5037	13.0951	90.0	93.025	90.0
change	%			-1.17	-1.29	-0.96	0.85	0.0	-2.06	0.0
β-HMX	exp	-180.16[d]	—	519.3869	6.540	11.050	8.700	90.0	124.3	90.0
	calc	-180.29	-60.27	516.4701	6.409	11.026	8.797	90.0	123.82	90.0
change	%	-0.07		-0.56	-2.00	-0.22	1.11	0.0	-0.39	0.0
α-HMX	exp	—	—	2138.7002	15.14	23.89	5.913	90.0	90.0	90.0
	calc	-179.35	-72.48	2138.3476	15.191	23.826	5.908	90.0	90.0	90.0
change	%			-0.016	0.34	-0.27	-0.85	0.0	0.0	0.0
δ-HMX	exp	-166.86[e]	—	1676.2665	7.711	7.711	32.553	90.0	90.0	120.0
	calc	-169.15	-68.31	1662.3923	7.684	7.684	32.514	90.0	90.0	120.0
change	%	-1.37		-0.83	-0.35	-0.35	-0.12	0.0	0.0	0.0
RDX	exp	-135.06[d]	—	1633.8557	13.181	11.574	10.709	90.0	90.0	90.0
	calc	-134.91	-52.34	1658.1047	13.366	11.694	10.609	90.0	90.0	90.0
change	%	0.11		1.48	1.40	1.04	-0.93	0.0	0.0	0.0
PETN(II)	exp	-156.9[f]	—	1224.4967	13.29	13.49	6.83	90.0	90.0	90.0
	calc	-153.14	-43.86	1241.4611	13.237	13.588	6.902	90.0	90.0	90.0
change	%	2.4		1.39	-0.40	0.73	1.05	0.0	0.0	0.0

[a] Lattice dimensions a,b,c are given in angstroms and the angles α, β, γ indegrees. Total(E_{total}) and Electrostatic (E_{elec}) lattice energies are in $kJmol^{-1}$. The lattice energies are calculated using the relationship: $E \approx -\Delta H_{subl} - 2RT$, ΔH_{subl} is the experimental sublimation enthalpy, T=298K. [b] data from ref.7 and 40, [c] data from ref.41, [d] data from ref.42, [e] data from ref.43, [f] data from ref.40.

in the minimized configuration, bulk modulus can be calculated by the equation $B=(1/V)(d^2E/dV^2)$. We calculate the bulk modulus as a function of pressure. The results are given in Table 12. Except for NM, PETN, β-HMX and RDX, there are no experimental data for comparison. However, the bulk modulus B and its pressure derivatives $B'=dB/dP$ of NM, PETN, β-HMX and RDX at zero pressure are in good agreement with the experimental value. The calculated bulk modulus of NM, PETN, β-HMX and RDX are 10.110, 13.389, 15.975 and 11.978 GPa, whereas the corresponding experimental values are 10.1, 9.9, 13.5 and 13.0 GPa[12),13),44)]. The values of their pressure derivatives $B'=dB/dP$ are 5.695, 12.030, 8.377 and 6.618 while the experimental data are 5.966, 11.0, 9.3 and 6.6[12),13),44)].

The elastic constants for the optimized structure of NM are given in Table 13. Since the matrix is symmetric, only the upper half is given. Unfortunately, no experimental data were available for elastic constant. However, the bulk modulus of B=10.11 GPa in Table 12 is in excellent agreement with the experimental value B_{exp} =10.1 GPa reported by Yarger and Olinger[12)]. We calculate the bulk modulus and Young's Modulus as a function of hydrostatic pressure. As shown in Fig.2, in the pressure range of P ≤ 3.0GPa, the bulk modulus has a deviation less than 4.5% compared with the

Table 12. Coefficients of the quadratic fits of the form $A_0(1+A_1P+A_2P^2)$ of the unit cell volume and bulk modulus as function of pressure (GPa).

System		A_0(exp)	A_0	A_1	A_2
NM	V(Å^3)	289.3304	277.06657	-7.3193×10^{-2}	7.6006×10^{-3}
	B(GPa)	10.1[a]	10.11046	0.56324	-9.97877×10^{-3}
DMN	V(Å^3)	219.4374	213.1150	$-6{:}3729\times10^{-2}$	6.4473×10^{-3}
	B(GPa)	—	11.33071	0.63436	-2.38564×10^{-2}
ANTA	V(Å^3)	942.7696	949.8063	-4.4589×10^{-2}	3.8904×10^{-3}
	B(GPa)	—	18.3242	0.39880	-8.73817×10^{-3}
NB	V(Å^3)	571.1463	562.6989	-6.7556×10^{-2}	7.0390×10^{-3}
	B(GPa)	—	9.18662	0.82419	-2.82541×10^{-2}
β-HMX	V(Å^3)	519.3869	515.2163	-4.8111×10^{-2}	4.0141×10^{-3}
	B(GPa)	13.5[b]	15.975	0.52436	-5.54644×10^{-2}
α-HMX	V(Å^3)	2138.7002	2133.1262	-6.0448×10^{-2}	6.2816×10^{-3}
	B(GPa)	—	12.53829	0.67039	-4.36543×10^{-2}
δ-HMX	V(Å^3)	1676.2665	1656.1678	-5.7584×10^{-2}	5.5259×10^{-3}
	B(GPa)	—	12.48942	0.67004	-5.20553×10^{-2}
RDX	V(Å^3)	1633.8557	1658.2127	-6.4119×10^{-2}	6.08818×10^{-3}
	B(GPa)	13.0[b]	11.97804	0.55250	-3.03080×10^{-2}
PETN	V(Å^3)	1224.4967	1237.1661	-5.0119×10^{-2}	4.7681×10^{-3}
	B(GPa)	9.9[c]	13.38934	0.89847	-0.1061

[a] data from ref. 12, [b] data from ref. 13, [c] data from ref. 44.

Table 13. The elastic constants for the optimized structure of NM and RDX(10GPa)

Species	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
NM	1.64873	1.49782	1.92516	0.63213	0.41066	0.78144	0.64893	0.45362	0.68050
RDX	2.89100	2.50470	1.42922	0.51448	0.38449	0.42370	1.02984	0.65250	0.75896
Exp.[a]	1.958	2.498	1.789	0.406	0.515	0.690	0.819	0.590	0.580

[a] data from ref. 14

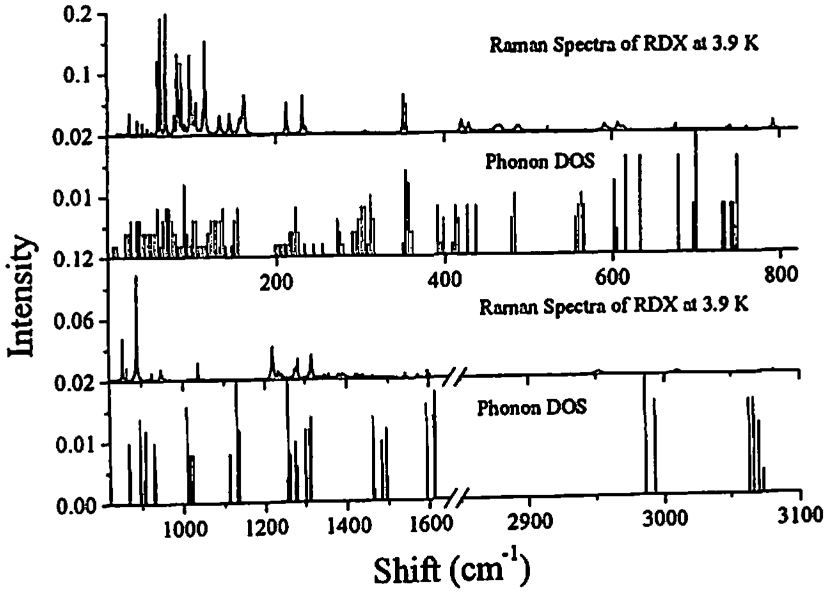

Fig.1 The Raman spectra of RDX at 3.9 K and the calculated phonon/vibron density of states.

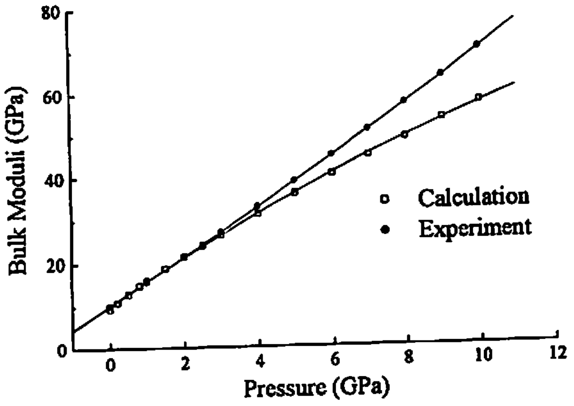

Fig.2 The bulk moduli of NM as a function of the pressure at 298 K.

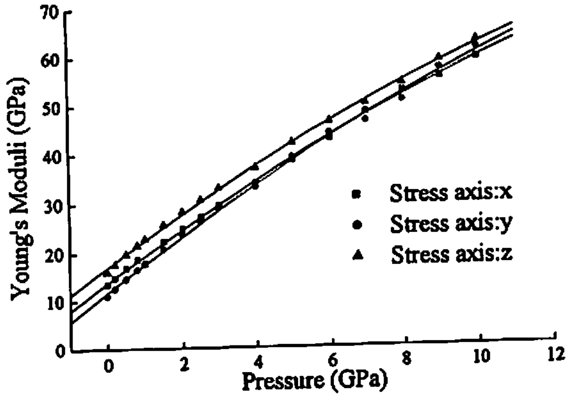

Fig.3 The Young's moduli of NM as a function of the pressure at 298 K.

experimental data[12]. Figure 3 shows a plot of the Young's modulus against pressures. The Young's modulus increases dramatically with increasing pressure. The Young's modulus for x axis becomes the most compressible direction above 9.0 GPa, while the young's modulus for *z* axis is least compressible direction at any pressure.

Recently, the entire set of elastic constants for RDX has been measured by Haussül[14]. Comparison between experimental results and calculation in Table 13, accepts that the value of C_{11} has large deviation, other elastic constants are consistent with the experimental data. The elastic stiffness $C=(C_{11}+C_{22}+C_{33}+C_{44}+C_{55}+C_{66}+C_{12}+C_{13}+C_{23})/9$ of RDX was also calculated. The calculation value of C= 1.177 is almost the same as the experimental value of C=1.105. The averaged Young's modulus (18.149GPa) has a deviation of only 2.93% compared with the experimental value (17.633 GPa). The averaged Poisson ratio of 0.278 is comparable to the experimental value of 0.238.

5. Conclusions

A flexible potential including both intra- and inter-molecular potential terms was used to calculate the lattice properties of secondary explosives such as nitramine crystals of HMX, RDX and DMN and non-nitramine crystals of PETN, ANTA, NB, and NM. Not only the calculated lattice parameters and lattice energies, but also bulk modulus and its pressure derivative are in excellent agreement with the available experiment data. In addition, the calculated elastic constants, elastic stiffness, the averaged Young's modulus and Poisson ratio of RDX are in agreement with the experimental data. These indicate that the flexible potentials are appropriate for these explosives with different structures. The flexible potentials are very useful to describe the intramolecular motion, molecular deformations and the energy flow inside these crystals with different impact sensitivity.

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