

Vibrational and thermodynamic properties of β -HMX: A first-principles investigation

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Thermodynamic properties of β -HMX crystal are investigated using the quasi-harmonic approximation and density functional theory within the local density approximation (LDA), generalized gradient approximation (GGA), and GGA + empirical van der Waals (vdW) correction. It is found that GGA well describes the thermal expansion coefficient and heat capacity but fails to produce correct bulk modulus and equilibrium volume. The vdW correction improves the bulk modulus and volume, but worsens the thermal expansion coefficient and heat capacity. In contrast, LDA describes all thermodynamic properties with reasonable accuracy, and overall is a good exchange-correlation functional for β -HMX molecular crystal. The results also demonstrate significant contributions of phonons to the equation of state. The static calculation of equilibrium volume for β -HMX differs from the room-temperature value incorporating lattice vibrations by over 5%. Therefore, for molecular crystals, it is essential to include phonon contributions when calculated equation of state is compared with experimental data at ambient condition. © 2011 American Institute of Physics. [doi:10.1063/1.3587135]

I. INTRODUCTION

The knowledge of thermodynamic properties of energetic materials at high temperature and pressure is critical to fundamental understanding of their explosion and other processes.¹⁻³ Due to the experimental challenge in measuring these properties of energetic molecular crystals; however, our knowledge about their properties at high pressure and temperature is still very limited. It is thus highly desirable to establish a reliable theoretical scheme⁴ to calculate the thermodynamic properties of energetic molecular crystals.

Density functional theory (DFT) (Refs. 5 and 6) has widely been applied to the study of condensed-phase materials because of its reasonable accuracy and high computational efficiency. In contrast to its success in electronic structure of metals and covalently bonded semiconductors, however, DFT calculations have not demonstrated a similar success in predicting basic properties such as the lattice constants and equilibrium volume of molecular crystals. For example, DFT calculations with generalized gradient approximation (GGA) or local density approximation (LDA) for the exchange-correlation functional usually overestimate or underestimate the equilibrium volume of energetic materials by more than 10%.⁷⁻¹² The failure of DFT with GGA in molecular crystals is often ascribed to its inadequacy in describing the disperse interaction. As a result, there is great interest in improving GGA calculations by incorporating van der Waals (vdW) corrections.¹³⁻¹⁶

Although DFT calculations fail to predict the lattice constants of energetic molecular crystals, they are able to describe their vibrational properties reasonably well.^{7,17-22} These results suggest that DFT may be able to describe well the thermodynamic properties of these energetic materials.

The predictive power of DFT calculations combined with the quasi-harmonic approximation (QHA) for thermodynamic properties has been proven widely for crystals with metallic, covalent, or ionic bonds.²³⁻²⁵ However, it is still not established how well the DFT + QHA approach predicts the thermodynamic properties of energetic molecular crystals. Since the equilibrium volume of molecular crystals depends critically on the exchange-correlation functional, it is of urgent importance to establish which exchange-correlation functional between LDA or GGA is better for calculating the thermodynamic properties of the energetic materials. It has been shown that an empirical vdW correction works well in predicting the volume of energetic molecular crystals. What is then the effect of the empirical vdW correction on the thermodynamic properties of the energetic materials?

To answer these questions, here we investigate the thermodynamic properties of a representative energetic molecular crystal, β -HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), with DFT combined with QHA. HMX is an important energetic material used in many propellant and explosive applications. HMX crystal exists in several polymorphs, with β -HMX stable at ambient condition.^{26,27} HMX crystals have been extensively investigated by a variety of experimental methods²⁸⁻⁵¹ and first-principles calculations.^{8,9,19,20,22,52-63} To our surprise, although LDA and GGA calculations have predicted a totally different equilibrium volume of β -HMX,^{9,61} with difference of nearly 30%, both LDA and GGA describe the thermal expansion coefficient and heat capacity quite well. Furthermore, LDA also predicts the bulk modulus well. Although the empirical vdW correction used here significantly improves the equilibrium volume and bulk modulus estimated by GGA for β -HMX,

it substantially deteriorates the estimates of other thermodynamic properties such as thermal expansion and heat capacity. In the following, we systematically compare the thermodynamics properties of β -HMX calculated by the DFT + QHA approach using LDA, GGA, and GGA with van der Waals correction (GGA + vdW).

II. CALCULATION DETAILS

The calculations are performed using the Quantum Espresso software for DFT calculations based on the plane-wave basis and pseudopotentials.⁶⁴ The plane-wave cutoff energy (E_{cut}) of 30 Ry is found sufficient to obtain the converged results. Brillouin-zone summations over electronic states are performed over $2 \times 2 \times 2$ (2 points) k mesh with (1/2, 1/2, 1/2) shift from the origin. The Vanderbilt ultrasoft pseudopotentials are generated for C, N, H, and O.⁶⁵ For the exchange-correlation functional, we use LDA (Refs. 66 and 67) and GGA by Perdew, Burke, and Ernzerhof (PBE).⁶⁸

vdW correction is included using an empirical method proposed by Grimme.^{13,69} The empirical dispersion correction for the energy is given by

$$E_{\text{disp}} = -s_6 \sum_{i < j} \frac{C_{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij}), \quad (1)$$

where C_{ij} and R_{ij} denote the dispersion coefficient and the interatomic distance between the i th and j th atoms, s_6 is a global scaling factor that only depends on the density functional used. A damping function, $f_{\text{damp}}(R_{ij}) = 1/[1 + e^{-a(R_{ij}/R_0-1)}]$, is introduced to ensure that the dispersion correction is negligible for small R_{ij} . For the parameters in Eq. (1) above, see Eq. (11) and Table I in Ref. 69, where the parameters for most of the elements can be found.⁶⁹ Structural optimizations, with and without vdW correction, are achieved using the damped variable cell shape molecular dynamics method.⁷⁰ For each fully optimized structure, dynamical matrices are computed on $2 \times 2 \times 2$ q (wave vector) mesh based on the density functional perturbation theory (DFPT),²³ which are modified by incorporating the vdW contribution, if the structure has been optimized with the vdW correction. The results are then interpolated in a regular $8 \times 8 \times 8$ q mesh to obtain the vibrational density of states. The Helmholtz free energy in the quasi-harmonic approximation is given by

$$F(V, T) = U_0(V) + \frac{1}{2} \sum_{q,j} \hbar \varpi_j(q, V) + k_B T \sum_{q,j} \ln \left\{ 1 - \exp \left[\frac{-\hbar \varpi_j(q, V)}{k_B T} \right] \right\}, \quad (2)$$

where q is a wave vector in the first Brillouin zone, j is an index of phonon mode with frequency $\varpi_j(q, V)$, V and T are the volume and temperature of the system, and k_B and \hbar are the Boltzmann and Planck constants. The first, second, and third terms in Eq. (2) are the static internal, zero-point, and vibrational energy contributions, respectively. The calculated Helmholtz free energy versus volume is fitted by the third-order Birch-Murnaghan finite strain equation of states,⁷¹ which in turn is used to derive all thermodynamic properties.

III. RESULTS AND DISCUSSION

A. Lattice structure

β -HMX crystal has monoclinic structure with space group $P2_1/c$, where each unit cell has two molecules as shown in Fig. 1. This crystal has been investigated using DFT with various exchange-correlation functional.^{9,20,52,58,72} The calculated lattice parameters are listed in Table I along with experimental values. GGA calculation overestimates the equilibrium volume by 17%, while LDA underestimates it by 11%. The lattice constants along the three crystal axes are overestimated by GGA by a similar amount of about 5%, while the underestimation of the lattice constants by LDA is prominent along the b axis. Similar to what was reported for another energetic molecular crystal, cyclotrimethylene trinitramine (RDX), the empirical vdW correction proposed by Grimme^{13,69} works well in reducing the overestimation by GGA in lattice parameters of β -HMX. Namely, the volume difference from the experimental value reduces to less than 0.5% when the vdW correction is included.

Here, it should be noted that the lattice parameters of β -HMX at 0 GPa deviates widely among various GGA calculations. Our GGA calculation is consistent with a previous GGA calculation by Bryd *et al.*,⁹ which shows similar overestimation of lattice parameters. In contrast, other GGA calculations by Conroy *et al.*,⁷² and Zhu *et al.*²⁰ exhibit a much smaller overestimation in lattice parameters. In fact, the GGA result by Zhu *et al.*²⁰ is very close to the experimental value. This divergence is likely due to a numerical convergence issue among different ways of calculating the lattice parameters, as shown below. In this work, we first obtain V_0 (the volume at zero pressure) based on the energy–volume (E – V) curve, and then obtain the lattice parameters corresponding to V_0 by interpolation. Conroy *et al.*⁷² and Zhu *et al.*²⁰ on the other hand, directly obtained lattice parameters by relaxing the structure as well as the unit-cell shape at zero pressure. In principle, both approaches should give the same result, but actual

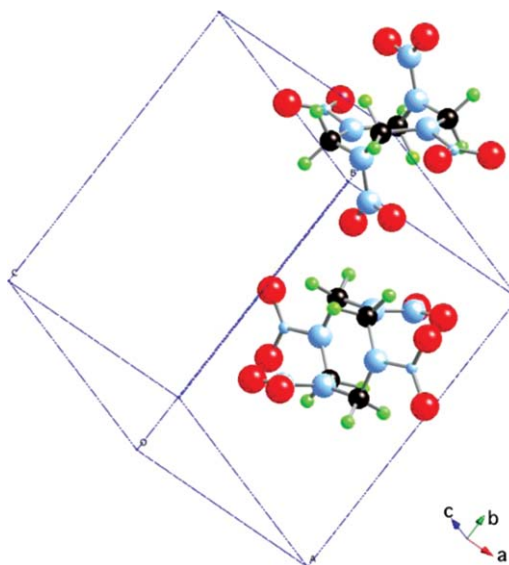


FIG. 1. Crystal structure of β -HMX. Carbon, nitrogen, oxygen, and hydrogen atoms are shown in black, blue, red, and green, respectively.

TABLE I. The lattice parameters, unit cell volume V , and bulk modulus of β -HMX from calculation at 0 GPa and experiment at ambient condition. The number in parenthesis shows the deviation from the experimental value.

a (Å)	b (Å)	c (Å)	β (°)	V (Å ³ /cell)	Bulk modulus (GPa)	
6.38	10.41	8.43	123.0	463.6	21.5	LDA static
(−2.5%)	(−5.8%)	(−3.1%)	(−1.0%)	(−10.7%)		
6.48	10.59	8.57	123.5	486.7	14.4	LDA 300 K ^a
(−0.9%)	(−4.1%)	(−1.6%)	(−0.6%)	(−6.2%)		
6.90	11.65	9.15	124.5	608.1	4.60	GGA static
(5.5%)	(5.4%)	(5.1%)	(0.2%)	(17%)		
7.07	11.93	9.34	124.6	653.6	1.8	GGA 300 K ^a
(8.1%)	(8.0%)	(7.4%)	(0.2%)	(25.8%)		
6.56	10.97	8.70	124.4	517.4	17.7	GGA + VDW static
(0.3%)	(−0.7%)	(0.0%)	(0.1%)	(−0.4%)		
6.63	11.08	8.80	124.5	534.05	13.2	GGA + VDW 300 K ^a
(1.4%)	(0.3%)	(1.1%)	(0.2%)	(2.8%)		
6.54	11.05	8.70	124.3	519.4 ^{b,c}	8.4 ^d , 16.7 ^e , 21 ^f	Experiment
					9.9–12.5 ^g	

^aThe lattice parameters at room temperature is obtained by using static lattice parameters at corresponding volume, which has been shown to be a good approximation (Ref. 83).

^bReference 27.

^cReference 81.

^dReference 82.

^eReference 50.

^fReference 30.

^gReference 49.

results using a finite energy cutoff can be significantly different, especially for materials with a small bulk modulus such as molecular crystals. For example, the lattice parameters relaxed at zero pressure with $E_{\text{cut}} = 30$ Ry in this study also agree very well with the experimental data, with the volume difference between calculation and experimental result less than 2%. However, the equilibrium volume from E - V curve is 17% larger than the experimental value (see GGA static in Table I). Namely, the two different approaches produce a volume difference of more than 10%. We have also observed similar effects in other energetic molecular crystals: RDX, pentaerythritol tetranitrate (PETN), and triaminotrinitrobenzene (TATB).

We have identified the cause of the divergence between the two lattice-parameter calculation methods: through E - V curve fitting and direct unit-cell relaxation. Namely, the stress calculation involved in the latter method requires much larger E_{cut} than that required for convergent total-energy calculation used in the former. Specifically, E_{cut} of 30 Ry in this calculation is sufficient to obtain the converged E - V curve, and increasing E_{cut} from 30 to 50 Ry does not produce any noticeable change in the estimated V_0 . On the other hand, the same increase of E_{cut} significantly modifies the lattice parameters relaxed at zero pressure.^{8,9,55} Note that the volume difference due to stress error is given by $\Delta V/V = -\Delta P/K$, where K is the bulk modulus. For crystals with the bulk modulus larger than 100 GPa, failure in converging the stress within ~ 1 GPa does not cause a serious problem, and the lattice parameters obtained by the two ways are the same to within 1%. However, the bulk modulus of an energetic molecular crystal is usually around 10 GPa, and stress error of ~ 1 GPa causes a volume difference of about 10% in the lattice relaxation method. Thus, it is preferred to use the E - V curve to obtain V_0 for molecular crystals.

It is remarkable that, despite the lack of convergence in the lattice relaxation method using $E_{\text{cut}} = 30$ Ry, its zero-pressure structure agrees well with experimental data, including the lattice parameters, bond length, and bond angles. The calculated vibrational properties are also consistent with experimental data. This is true not only for β -HMX but also for RDX, PETN, and TATB. Therefore, these calculations can still provide useful information in spite of their non-convergent stress.²⁰ This might be because the stress error and inadequacy of the functional in describing vdW interaction cancel each other out, as we will see in the subsequent section.

B. Vibrational and thermodynamic properties

The vibrational properties of β -HMX at zero pressure are listed in Tables II and III. The point group of β -HMX, C_{2h} , has four irreducible representations, A_g , B_g , A_u , and B_u . A_g and B_g modes have inversion symmetry and hence are Raman active. A_u and B_u change the sign under inversion and hence are infrared active. Although the volume difference between LDA and GGA is almost 30%, the corresponding frequency difference is insignificant (smaller than 3%) for modes with frequency > 1000 cm^{-1} . Both LDA and GGA results agree well with the experimental data for these modes. However, for low-frequency modes, the LDA frequency is far larger than the GGA frequency, especially for modes with frequency < 300 cm^{-1} . The experimental results are located between LDA and GGA results. The difference between GGA and GGA + vdW arises from two causes. One is the vdW effect on the volume at 0 GPa, and the other is the vdW correction on force constants. These effects are negligible for the high-frequency modes but are significant at low frequencies. GGA + vdW results are more consistent with experimental

TABLE II. Raman modes of β -HMX calculated at 0 GPa along with the experimental data at ambient condition. γ is the mode Grüneisen parameter [see Eq. (3)] at gamma point, and $\bar{\gamma}$ is the average of the mode Grüneisen parameters in the first Brillouin zone [see Eq. (4)].

Calculation													
LDA			GGA			GGA + VDW			Experiment (cm ⁻¹)				
ω (cm ⁻¹)	γ	$\bar{\gamma}$	ω (cm ⁻¹)	γ	$\bar{\gamma}$	ω (cm ⁻¹)	γ	$\bar{\gamma}$	Reference 84	Reference 85	Reference 46	Reference 86	
2985	Bg	0.07	0.07	3056	0.01	0.01	3059	0.06	0.06	3037	3038	3042	
2983	Ag	0.07	0.07	3055	0.01	0.01	3058	0.06	0.06			3042	
2976	Bg	0.00	0.00	3044	0.02	0.02	3054	0.06	0.06			3033	
2975	Ag	0.01	0.01	3043	0.02	0.02	3054	0.06	0.06	3028	3028	3032	
2932	Bg	0.07	0.07	2996	0.01	0.01	2997	0.07	0.07	2992	2994	2998	
2931	Ag	0.07	0.07	2995	0.01	0.01	2996	0.07	0.07			2998	
2916	Bg	0.01	0.01	2984	0.03	0.02	2986	0.06	0.06				
2916	Ag	0.01	0.01	2983	0.03	0.03	2986	0.06	0.06				
1572	Bg	0.00	0.00	1543	-0.01	-0.01	1538	0.00	0.00			1571	
1564	Ag	-0.01	-0.01	1535	-0.02	-0.02	1529	0.00	0.00	1558	1560	1571	
1531	Bg	0.01	0.03	1507	-0.03	-0.00	1500	0.01	0.02	1532	1535	1561	
1522	Ag	-0.01	0.00	1502	-0.02	-0.02	1494	0.00	0.00			1538	
1410	Bg	0.09	0.08	1422	0.01	0.01	1435	0.06	0.05	1460	1461		
1392	Ag	0.06	0.07	1417	0.00	0.01	1430	0.04	0.05	1438	1438		1437
1377	Bg	0.02	0.05	1406	0.00	0.00	1404	0.03	0.03	1418	1420	1421	1418
1374	Ag	0.04	0.04	1406	0.00	0.00	1403	0.01	0.03			1421	
1368	Ag	0.05	0.03	1383	0.00	0.00	1388	0.05	0.04	1368	1369		1369
1359	Bg	0.01	0.02	1382	0.00	0.01	1387	0.04	0.04				
1345	Ag	0.02	0.05	1334	0.01	0.01	1344	0.06	0.06	1350	1351	1353	1354
1344	Bg	0.04	0.05	1334	0.01	0.01	1344	0.06	0.06			1353	
1323	Bg	0.08	0.07	1311	0.01	0.01	1318	0.10	0.11		1318	1320	
1318	Ag	0.05	0.05	1308	0.00	0.01	1314	0.09	0.10			1319	
1302	Bg	0.10	0.09	1287	0.02	0.03	1299	0.08	0.09	1312	1310	1313	
1299	Ag	0.03	0.05	1286	0.02	0.03	1299	0.09	0.09			1313	
1292	Bg	0.07	0.05	1276	0.04	0.03	1286	0.11	0.09	1268	1270		
1288	Ag	0.05	0.05	1270	0.02	0.03	1274	0.09	0.09				
1267	Bg	0.05	0.05	1229	0.02	0.02	1235	0.08	0.09			1253	
1254	Ag	0.08	0.06	1219	0.02	0.02	1223	0.09	0.08	1248	1251	1252	
1229	Ag	0.07	0.08	1214	0.02	0.02	1220	0.08	0.08				
1227	Bg	0.07	0.09	1210	0.02	0.02	1216	0.10	0.09				
1214	Bg	0.05	0.05	1167	0.02	0.02	1173	0.12	0.12	1190	1192		
1214	Ag	0.05	0.05	1166	0.02	0.02	1172	0.11	0.11				
1157	Bg	0.07	0.07	1137	0.02	0.02	1140	0.11	0.10	1168	1170	1172	1171
1150	Ag	0.07	0.07	1134	0.02	0.02	1136	0.09	0.09			1171	
1099	Bg	0.14	0.15	1044	0.06	0.07	1058	0.18	0.17	1090	1088		
1087	Ag	0.14	0.13	1032	0.06	0.07	1044	0.17	0.17				
946	Bg	0.12	0.10	920	0.08	0.06	938	0.14	0.12			974	
944	Ag	0.11	0.09	920	0.06	0.06	935	0.10	0.13	965	966		972
939	Ag	0.11	0.12	910	0.09	0.07	924	0.17	0.16			955	
937	Bg	0.07	0.10	906	0.08	0.07	918	0.17	0.16	950	953	955	
892	Bg	0.11	0.12	854	0.04	0.04	864	0.14	0.13			885	
888	Ag	0.12	0.12	852	0.04	0.04	861	0.15	0.13	881	884	885	885
851	Bg	0.14	0.15	809	0.04	0.04	817	0.15	0.15			838	
851	Ag	0.15	0.15	808	0.04	0.04	816	0.15	0.15	834	834	837	
756	Bg	-0.01	-0.01	730	0.01	0.01	734	0.02	0.00			764	
752	Ag	-0.02	-0.00	728	0.01	0.01	731	0.01	0.00	759	762	763	
744	Bg	-0.03	-0.03	726	0.01	0.01	726	0.02	0.01				
744	Ag	-0.03	-0.03	726	0.01	0.01	726	0.02	0.00				
712	Ag	0.02	0.02	697	0.00	0.01	696	0.06	0.05	721	721		
711	Bg	0.02	0.02	697	0.00	0.01	696	0.05	0.05				
662	Ag	0.14	0.13	629	0.05	0.06	638	0.13	0.13				
660	Bg	0.12	0.13	628	0.05	0.06	638	0.13	0.13	662	663		
646	Bg	0.15	0.15	609	0.08	0.07	624	0.22	0.20				
642	Ag	0.14	0.15	608	0.07	0.07	622	0.21	0.20	638	640		
603	Ag	0.22	0.18	571	0.06	0.06	580	0.23	0.17			600	

TABLE II. (Continued)

600	B _g	0.17	0.16	571	0.05	0.06	578	0.22	0.16	597	600	600	
430	B _g	0.24	0.29	410	0.08	0.08	431	0.23	0.23			440	
428	A _g	0.24	0.28	408	0.07	0.09	427	0.20	0.23	432	437	438	
422	A _g	0.20	0.23	390	0.14	0.13	408	0.30	0.29			416	
422	B _g	0.22	0.21	388	0.13	0.13	405	0.23	0.24	412	417	416	
378	B _g	0.40	0.33	341	0.12	0.15	358	0.37	0.29			365	365
371	A _g	0.39	0.33	340	0.18	0.16	357	0.38	0.30			365	
320	B _g	0.42	0.44	292	0.20	0.20	306	0.55	0.39				
320	A _g	0.37	0.45	290	0.20	0.21	304	0.47	0.38				
281	A _g	0.38	0.41	261	0.05	0.07	271	0.38	0.34				281
280	B _g	0.32	0.37	261	0.04	0.07	270	0.40	0.32				
232	B _g	0.54	0.58	214	0.22	0.13	224	0.58	0.38			233	234
228	A _g	0.44	0.48	212	0.20	0.29	222	0.48	0.36			233	232
206	A _g	0.72	0.93	170	0.20	0.29	185	0.72	0.48			181	
204	B _g	0.82	0.92	168	0.24	0.32	185	0.70	0.48			179	
179	B _g	1.47	1.28	141	0.74	0.36	162	1.13	0.48			157	
177	A _g	1.47	1.23	138	0.56	0.43	158	0.84	0.51			157	
170	A _g	1.86	1.67	118	0.90	0.49	149	1.44	0.55			147	
158	B _g	1.46	1.57	116	0.99	0.47	139	1.37	0.55			147	
150	A _g	2.31	1.92	96	1.37	0.66	133	2.11	0.78			138	
142	B _g	2.37	2.00	87	1.92	0.61	128	2.28	0.74			138	
116	B _g	1.91	1.97	79	1.33	0.57	103	2.17	0.52			130	
109	A _g	2.50	1.96	74	1.02	0.59	98	2.80	0.56			128	
100	B _g	3.33	2.28	66	2.20	0.68	97	2.64	0.79			80	
94	A _g	2.12	2.29	61	2.84	0.66	90	3.03	0.87			79	
88	B _g	2.39	2.58	48	4.91	0.71	75	3.63	0.83			65	
74	A _g	2.65	2.97	44	4.59	0.68	73	4.16	0.77			65	
71	B _g	2.18	2.81	35	13.54	0.72	53	4.99	0.90			36	
46	A _g	0.74	2.59	17	9.36	1.01	36	9.98	0.93			36	

data than GGA results. Raman experiment⁴⁶ indicates that frequency split between A_g and B_g modes is less than 1 cm⁻¹ for all the modes measured. Our calculated results show similar insignificant split for most of modes. But for some low-frequency modes, the split is larger than 5 cm⁻¹.

The mode Grüneisen parameter, $\gamma_{i,q}$, describes how the phonon frequency depends on the volume, is critical to computation of the thermodynamic properties. It is defined as

$$\gamma_{i,q} = -\frac{\partial \ln \omega_{i,q}}{\partial \ln V}, \quad (3)$$

where i is the mode index and q is the wave vector in the reciprocal space. (Note that there is no thermal expansion within the harmonic approximation, because $\gamma_{i,q} = 0$.) γ_i in Tables II and III are for $q = 0$ (gamma point), where γ_i evidently depends on the mode frequency. For high-frequency modes, γ_i is close to 0 because the length of strong molecular bonds in the molecular crystal is not sensitive to the volume change. On the contrary, low-frequency modes usually have a γ_i far larger than 1. Tables II and III also list the integration of γ_i over the first Brillouin zone:

$$\bar{\gamma}_i = \frac{\int \gamma_{i,q} dq}{\int dq}. \quad (4)$$

High-frequency modes in some way are like Einstein modes, and their γ_i and $\bar{\gamma}_i$ are the same since their frequencies are almost independent of wave vector q . For low-frequency modes, LDA and GGA calculations exhibit vastly different

behaviors. γ_i and $\bar{\gamma}_i$ are not much different with LDA, which means that the gamma point ($q = 0$) value γ_i is a good representation of the integration of $\gamma_{i,q}$ over the first Brillouin zone. In contrast, in GGA calculations, $\bar{\gamma}_i$ is only about 1/4–1/2 γ_i . Therefore, thermodynamic properties derived from GGA calculations using only the gamma point are not converged. vdW correction only slightly increases $\bar{\gamma}_i$, and does not change the major feature that $\bar{\gamma}_i$ is far smaller than γ_i .

Thermal expansion coefficient (α) of β -HMX at 0 GPa is shown in Fig. 2. In both LDA and GGA calculations, α

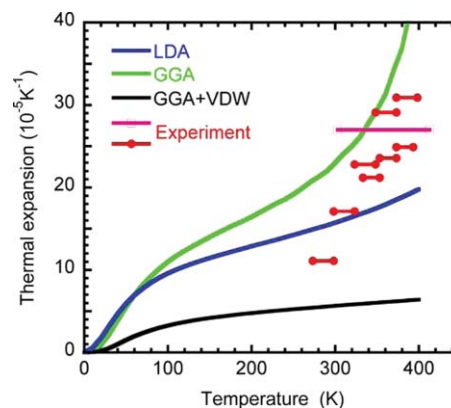


FIG. 2. Volumetric thermal expansion coefficient (α) of β -HMX at 0 GPa calculated using LDA, GGA, and GGA + vdW. The experimental data at ambient pressure are from Ref. 47 (lines with solid circles) and Ref. 30 (line with open squares).

TABLE III. Infrared modes of β -HMX calculated at 0 GPa along with the experimental data at ambient condition. γ is mode Grüneisen parameter [see Eq. (3)] at gamma point, and $\bar{\gamma}$ is the average of the mode Grüneisen parameters in the first Brillouin zone [see Eq. (4)].

Calculation										Experiment (cm ⁻¹)			
LDA			GGA			GGA+VDW							
ω (cm ⁻¹)		γ	$\bar{\gamma}$	ω (cm ⁻¹)	γ	$\bar{\gamma}$	ω (cm ⁻¹)	γ	$\bar{\gamma}$	Reference 87	Reference 84	Reference 85	Reference 35
2982	Au	0.07	0.07	3056	0.01	0.01	3058	0.05	0.05	3037			3037
2982	Bu	0.07	0.07	3056	0.01	0.01	3058	0.05	0.05	3027			3027
2976	Au	0.01	0.01	3043	0.02	0.02	3054	0.06	0.06				
2975	Bu	0.00	0.01	3043	0.02	0.02	3054	0.06	0.06				
2932	Bu	0.07	0.07	2996	0.01	0.01	2996	0.07	0.07	2992			2983
2930	Au	0.07	0.07	2995	0.01	0.01	2995	0.07	0.07				
2915	Bu	0.01	0.01	2984	0.03	0.03	2986	0.06	0.06	2985			2978
2915	Au	0.01	0.01	2983	0.03	0.03	2986	0.06	0.06				
1574	Au	0.00	-0.00	1545	-0.00	-0.01	1556	0.02	0.01	1563	1570		1565
1562	Bu	-0.01	-0.01	1535	-0.01	-0.02	1539	0.01	0.01				
1541	Bu	0.04	0.03	1509	-0.00	-0.00	1511	0.03	0.02	1534	1540		1538
1530	Au	0.03	0.00	1499	-0.00	-0.02	1498	0.03	0.01				
1412	Au	0.08	0.08	1430	0.02	0.01	1444	0.07	0.06	1462	1465		1463
1397	Bu	0.07	0.07	1426	0.01	0.01	1439	0.06	0.06				
1382	Bu	0.05	0.06	1401	0.00	0.00	1401	0.03	0.03	1433	1433		1434
1382	Au	0.04	0.05	1401	-0.00	0.00	1395	0.00	0.02				
1356	Bu	0.05	0.05	1369	0.01	0.01	1380	0.05	0.04	1395	1397		1401
1349	Au	0.05	0.05	1368	0.00	0.01	1376	0.03	0.04	1385			1395
1341	Au	0.04	0.02	1356	0.02	0.01	1366	0.07	0.06				
1340	Bu	0.01	0.01	1355	0.01	0.01	1364	0.06	0.06	1349	1348		1348
1324	Bu	0.07	0.07	1313	0.01	0.01	1317	0.10	0.10	1325	1320		1325
1312	Au	0.04	0.04	1311	0.01	0.01	1314	0.10	0.10				
1304	Au	0.11	0.09	1294	0.01	0.01	1306	0.07	0.08				
1300	Bu	0.05	0.07	1293	0.01	0.02	1306	0.07	0.08	1296			1298
1298	Au	0.05	0.06	1253	0.02	0.03	1262	0.10	0.09	1279	1280		1281
1280	Bu	0.04	0.05	1244	0.03	0.02	1261	0.10	0.09				
1274	Au	0.08	0.06	1228	0.02	0.03	1239	0.09	0.09				
1273	Bu	0.08	0.06	1227	0.03	0.02	1234	0.10	0.08	1239	1240		
1224	Bu	0.10	0.07	1208	0.03	0.02	1213	0.09	0.08				
1218	Au	0.06	0.06	1206	0.02	0.02	1210	0.09	0.08				
1211	Bu	0.04	0.04	1180	0.01	0.01	1187	0.09	0.09	1204	1205		1203
1210	Au	0.04	0.04	1178	0.01	0.01	1182	0.10	0.09				
1134	Au	0.09	0.10	1104	0.04	0.04	1112	0.13	0.13	1146	1146		1145
1130	Bu	0.10	0.10	1104	0.05	0.04	1111	0.14	0.13				
1092	Au	0.14	0.14	1043	0.07	0.06	1056	0.14	0.15	1088	1090		1089
1090	Bu	0.13	0.13	1042	0.06	0.06	1055	0.15	0.16				
947	Bu	0.08	0.09	917	0.06	0.06	945	0.14	0.13	967	965		966
945	Au	0.12	0.09	914	0.07	0.07	930	0.14	0.13				
930	Bu	0.14	0.11	899	0.08	0.08	912	0.19	0.19	947	945		948
928	Au	0.09	0.10	899	0.08	0.09	912	0.19	0.19				
880	Au	0.10	0.10	845	0.03	0.03	852	0.13	0.11	872	871		872
879	Bu	0.10	0.10	844	0.03	0.04	852	0.13	0.11				
842	Au	0.15	0.13	806	0.02	0.03	810	0.14	0.13	832	827		833
839	Bu	0.13	0.13	805	0.02	0.03	809	0.14	0.13				
765	Bu	0.02	0.04	747	0.01	0.02	749	0.04	0.04	772	769		773
764	Au	0.04	0.04	745	0.01	0.02	746	0.05	0.05	760	758		762
752	Au	-0.00	-0.01	729	0.01	0.01	731	0.01	0.00				
750	Bu	-0.00	-0.00	728	0.01	0.01	729	0.01	0.00	754	752		755
743	Bu	-0.03	-0.03	724	0.01	0.01	724	0.02	0.01				
743	Au	-0.03	-0.03	723	0.01	0.01	724	0.02	0.01				
657	Au	0.14	0.14	627	0.06	0.06	642	0.21	0.19		660		658
654	Bu	0.12	0.13	626	0.05	0.06	640	0.17	0.18				
628	Bu	0.12	0.12	601	0.05	0.05	610	0.17	0.14				
627	Au	0.11	0.12	601	0.05	0.05	607	0.14	0.14	627			630
606	Bu	0.16	0.16	575	0.05	0.05	583	0.22	0.18				
605	Au	0.17	0.17	573	0.05	0.06	581	0.21	0.18	600			605

TABLE III. (Continued)

445	Bu	0.30	0.32	412	0.12	0.11	434	0.33	0.28		
440	Au	0.32	0.31	410	0.12	0.10	433	0.33	0.27	438	441
428	Au	0.25	0.25	397	0.10	0.11	409	0.32	0.30		
425	Bu	0.25	0.25	396	0.11	0.12	408	0.30	0.27	419	420
387	Bu	0.18	0.19	367	0.06	0.07	375	0.28	0.21		380
385	Au	0.07	0.20	366	0.06	0.08	372	0.25	0.21		
355	Au	0.29	0.26	335	0.10	0.12	348	0.26	0.20		355
355	Bu	0.23	0.24	334	0.10	0.11	346	0.20	0.18		
251	Bu	0.62	0.64	213	0.29	0.18	237	0.69	0.53		224
249	Au	0.71	0.65	209	0.23	0.35	232	0.53	0.52		
198	Bu	1.10	1.20	168	0.28	0.29	183	0.69	0.44		177
192	Au	1.62	1.25	163	0.08	0.28	175	0.66	0.45		
184	Bu	1.21	1.28	140	0.63	0.38	165	1.09	0.48		
184	Au	1.23	1.32	133	0.59	0.45	161	0.97	0.48		
158	Bu	1.51	1.77	119	0.90	0.48	138	1.30	0.48		137
152	Au	1.84	1.69	116	1.04	0.42	138	1.35	0.43		
150	Au	1.76	1.96	90	1.58	0.68	131	2.60	0.77		
141	Bu	1.81	1.83	84	1.66	0.63	123	2.27	0.66		
112	Au	2.07	1.97	70	1.58	0.61	106	2.18	0.61		114
112	Bu	1.94	1.95	68	1.57	0.67	103	2.13	0.60		
103	Bu	2.45	2.38	66	1.82	0.61	96	2.14	0.86		96
102	Au	2.63	2.29	60	2.98	0.67	90	2.35	0.76		
88	Bu	2.49	2.73	49	5.08	0.69	89	2.00	0.77		83
78	Au	2.86	2.87	35	5.14	0.74	63	5.60	0.73		
57	Au	2.38	2.66	27	7.89	0.76	43	8.72	0.99		59

increases linearly with temperature from 150 to 300 K. Above 300 K, it increases superlinearly with temperature. The superlinear behavior in α has been seen in DFT + QHA (Ref. 21) calculations in other materials such as MgO (Ref. 25) and Pt. These materials usually have a temperature T_{su} , at which the superlinear behavior begins, which is far larger than 300 K. For MgO and Pt, the superlinear behavior has been identified as an artifact of QHA: it ignores the intrinsic anharmonicity, which causes α to deviate from the experimental value at T_{su} .^{25,73} This is likely the cause of the superlinear behavior in α of β -HMX. The LDA and GGA results on α agree with experimental data.^{30,47} In contrast, α with vdW correction is far smaller than experimental data. Although vdW correction dramatically reduces the overestimation of the volume, it thus significantly deteriorates α .

Pressure has dramatic effects on α of β -HMX at low pressures. At 0 GPa, β -HMX has α far larger than most non-molecular crystals. However, with increasing pressure, it becomes close to the general value of non-molecular crystals. As shown in Fig. 3, α value from GGA is very sensitive to the pressure below 1 GPa and decreases rapidly to 5.4 at 1 GPa. The vibrational contribution to volume decreases from 7.5% at 0 GPa to 2.7% at 1 GPa, where 1.1% is from temperature contribution and the remaining 1.6% is from the zero-point motion contribution. α from LDA also decreases rapidly with the pressure. Both LDA and GGA results are consistent with a high-pressure measurement, which shows unnoticeable volume expansion at 3 GPa between temperature 30 and 140 °C.³⁰ The deterioration of α estimation by vdW correction occurs only at low pressure, and α with vdW correction is close to the GGA result above 1 GPa. The GGA and GGA + vdW results are almost identical above 4 GPa. The vdW

correction not only deteriorates α but also other thermodynamic properties such as heat capacity at constant pressure (C_P) as shown in Fig. 4 and listed in Table IV. C_P calculated using GGA and LDA agrees well with the experimental data,^{74,75} whereas vdW correction decreases C_P by 6 J/(mol K⁻¹) at 300 K, worsening the agreement.

Although LDA and GGA calculations produce consistent α and heat capacity, they have totally different bulk modulus as shown in Table IV. The table also lists experimental bulk modulus. There are two different ways to determine bulk modulus in experiments. One is by fitting the isotherm P - V curve. Isothermal bulk modulus (K_T) determined this way is sensitive to the equation-of-states used and can vary by as much as 5 GPa using the same data.⁷⁶ The other way is

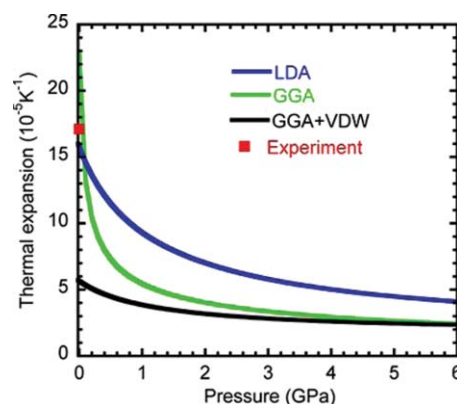


FIG. 3. The pressure dependence of the volumetric thermal expansion coefficient (α) of β -HMX at 300 K calculated using LDA, GGA, and GGA + vdW. The experimental data are from Ref. 47 (solid square).

TABLE IV. Thermodynamic properties of β -HMX at ambient condition.

α ($10^{-5}/\text{K}$)	C_P ($\text{J}/(\text{mol K}^{-1})$)	C_V ($\text{J}/(\text{mol K}^{-1})$)	γ_{th}	K_T (GPa)	K_S (GPa)	
15.7	303.72	288.08	1.14	14.36	15.1	LDA
22.97	298.85	293.31	0.27	1.78	1.81	GGA
5.57	283.24	281.33	0.42	13.17	13.26	GGA + VDW
13–27 ^a	304.58 ^b			8.4–21 ^c	10–12.5 ^d	Experiment

^aReferences 30 and 47.^bReference 75.^cReferences 30 and 50, and 82.^dReference 49.

directly measuring the sound velocity and hence the adiabatic bulk modulus (K_S) at ambient condition. K_T can be derived further through the relation $K_S - K_T = \alpha K_T T (\frac{\alpha K_S V}{C_P})$. The difference between K_S and K_T is not big because of small K_T and K_S . Our calculation shows the difference is smaller than 1 GPa at ambient condition. The bulk modulus using the latter method agrees better with each other than the first method, and K_S values range from 10 to 12.5 GPa.⁴⁹ The bulk modulus from LDA agrees well with these experimental data. In contrast, β -HMX described by GGA is too soft, which is largely improved by vdW correction.

As shown above, GGA is good at describing α and heat capacity, but fails to describe K_T and V correctly. In comparison to GGA, LDA overall describes all the four properties reasonably. Since the thermal Grüneisen parameter, γ_{th} , is determined by these properties through the relation,

$$\gamma_{th} = \frac{\alpha V K_T}{C_V}, \quad (5)$$

where C_V is the heat capacity at constant volume, γ_{th} estimated by LDA should be reasonable as well. As shown in Fig. 5, GGA gives γ_{th} far smaller than the LDA value. Although the vdW correction increases γ_{th} , it is still not enough to obtain an accurate γ_{th} . γ_{th} is a weighted average of the mode Grüneisen parameter, $\bar{\gamma}_i$. At low temperature, low-frequency modes contribute more to γ_{th} than high-frequency modes. As listed in Tables II and III, for low frequency modes, $\bar{\gamma}_i$ from GGA is significantly smaller than that from LDA.

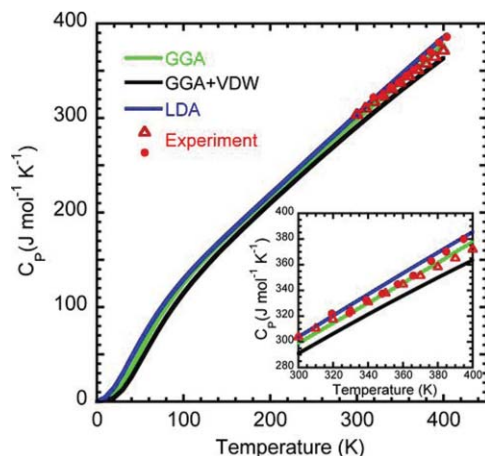


FIG. 4. Specific heat at constant pressure (C_P) of β -HMX at 0 GPa calculated using LDA, GGA, and GGA + vdW. The experimental data at ambient pressure are from Ref. 74 (solid circles) and Ref. 75 (crosses).

This explains why γ_{th} from GGA is smaller than LDA. It is evident that GGA considerably underestimates $\bar{\gamma}_i$. Interestingly, because GGA also underestimates $V K_T$ (K_T is smaller than 1/3 of the experimental value, see GGA 300 K in Table I) at the same time to cancel out this error, GGA can still describe α well. In contrast, vdW correction improves $V K_T$ dramatically but increases $\bar{\gamma}_i$ only slightly. As a result, vdW correction worsens α from GGA. Therefore, in order to describe correct thermodynamic properties, vdW correction must significantly increase $\bar{\gamma}_i$ from GGA calculation. Note that all dispersion coefficients in the empirical vdW method adopted here are fixed independent of the electron density distribution. In reality, the local electron density varies from atom to atom, and this should have effects on dispersion coefficients. Although this effect may change the phonon frequency itself only slightly, it may cause a dramatic change in $\bar{\gamma}_i$, i.e., the volume dependence of phonon frequency. Some vdW methods^{14,15} incorporating this effect are being developed, which could in future provide better estimates of all thermodynamic properties.

It should be noted that lattice vibration has significant effects on the volume of β -HMX at zero pressure, much more than in most crystals with ionic, metallic, covalent bonding.^{73,77} The volume expansion from 0 to 300 K is about 4% and 3% with GGA and LDA, respectively. The zero-point motion further contributes 3.5% and 1.8% volume expansion with GGA and LDA, respectively. In all, the

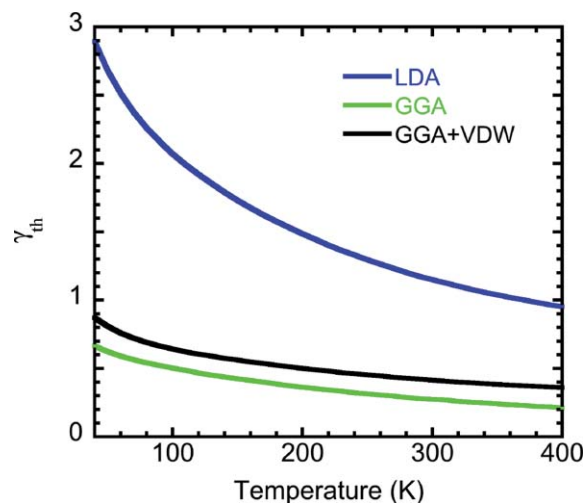


FIG. 5. Thermal Grüneisen parameter (γ_{th}) of β -HMX at 0 GPa calculated using LDA, GGA, and GGA + vdW.

vibrational effects increase the volume at 0 GPa by 7.5% and 4.8% with GGA and LDA, respectively. Since experimental data show that other energetic materials such as RDX,⁷⁸ TATB,⁷⁹ PETN,⁷⁸ and nitrotriazolone (NTO)⁸⁰ also have similarly large α as β -HMX, we expect that the large vibrational contribution to volume may be common for all these energetic molecular crystals. This is in contrast to most other crystals like MgO, where the vibration contribution to volume is only 1%–2%. Consequently, for molecular crystals such as β -HMX, common practice of evaluating the exchange-correlation functional by comparing static DFT calculation result with room-temperature experimental data is problematic. LDA is usually not preferred because it significantly underestimates the volume of most of molecular crystals with static calculation. However, after the vibrational effects are considered, the discrepancy between the volume predicted by LDA and experimental value is reduced considerably. For β -HMX, the volume discrepancy between LDA and experiment decreases from -11% to -6% when vibrational effects are included (see Table I). Therefore, in contrast to common belief, LDA is a rather good exchange-correlation functional for predicting thermodynamic properties of molecular crystals.

IV. CONCLUSION

In conclusion, GGA well describes the thermal expansion coefficient (α) of β -HMX. This is remarkable given the fact that GGA dramatically underestimates the bulk modulus (K_T). Phonon calculation indicates that this is because the GGA also underestimates the mode Grüneisen parameter $\bar{\gamma}_i$, resulting in a small thermal Grüneisen parameter (γ_{th}). The underestimation in γ_{th} and K_T cancels each other, and accordingly GGA predicts α quite well. The empirical vdW correction resolves the underestimation of K_T by GGA but only slightly increases γ_{th} , making α from GGA + vdW too small. When compared with GGA and GGA + vdW, LDA satisfactorily describes all thermodynamic properties including α , K_T , C_P , and γ_{th} .

Because molecular crystals like HMX have similar γ_{th} and much smaller K_T compared with other types of crystals, α s of molecular crystals are usually several times larger than α s of non-molecular crystals. Accordingly, the volume of molecular crystal changes significantly with temperature. Therefore, for molecular crystals like HMX, it is essential to consider phonon contributions to volume in evaluating the exchange-correlation functional. GGA calculations, which already overestimate the volume of β -HMX by 17% in static calculation, become worse after including phonon contributions. In contrast, LDA results become much better after including phonon contributions with volume difference at room temperature of only 6%. Given the fact that LDA can also describe the thermodynamic properties of β -HMX well, LDA turns out to be a considerably good exchange-correlation functional for β -HMX molecular crystal.

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- ¹K. L. McNesby, A. W. Miziolek, T. Nguyen, F. C. Delucia, R. R. Skaggs, and T. A. Litzinger, *Combust. Flame* **142**, 413 (2005).
- ²R. A. Yetter, F. L. Dryer, M. T. Allen, and J. L. Gatto, *J. Propul. Power* **11**, 683 (1995).
- ³K. K. Kuo, *Principles of Combustion* (Wiley, New York, 1986).
- ⁴S. P. Karna, *J. Phys. Chem. A* **104**, 4671 (2000).
- ⁵P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ⁶W. Kohn and P. Vashishta, *Inhomogeneous Electron Gas Vol. 79*, edited by N. H. March and S. Lundqvist (Plenum, New York, 1983).
- ⁷M. S. Miao, Z. A. Dreger, J. M. Winey, and Y. M. Gupta, *J. Phys. Chem. A* **112**, 12228 (2008).
- ⁸E. F. C. Byrd, G. E. Scuseria, and C. F. Chabalowski, *J. Phys. Chem. B* **108**, 13100 (2004).
- ⁹E. F. C. Byrd and B. M. Rice, *J. Phys. Chem. C* **111**, 2787 (2007).
- ¹⁰L. Qiu, H. M. Xiao, W. H. Zhu, J. J. Xiao, and W. Zhu, *J. Phys. Chem. B* **110**, 10651 (2006).
- ¹¹H. Liu, J. J. Zhao, J. G. Du, Z. Z. Gong, G. F. Ji, and D. Q. Wei, *Phys. Lett. A* **367**, 383 (2007).
- ¹²J. J. Zhao and H. Liu, *Comput. Mater. Sci.* **42**, 698 (2008).
- ¹³S. Grimme, *J. Comput. Chem.* **25**, 1463 (2004).
- ¹⁴M. Dion, H. Rydberg, E. Schroder, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Lett.* **92**, 246401 (2004).
- ¹⁵A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009).
- ¹⁶F. Shimojo, Z. Q. Wu, A. Nakano, R. K. Kalia, and P. Vashishta, *J. Chem. Phys.* **132**, 094106 (2010).
- ¹⁷J. A. Ciezak and S. F. Trevino, *J. Mol. Struct.: THEOCHEM* **732**, 211 (2005).
- ¹⁸W. F. Perger, J. J. Zhao, J. M. Winey, and Y. M. Gupta, *Chem. Phys. Lett.* **428**, 394 (2006).
- ¹⁹L. Y. Lu, D. Q. Wei, X. R. Chen, D. Lian, G. F. Ji, Q. M. Zhang, and Z. Z. Gong, *Mol. Phys.* **106**, 2569 (2008).
- ²⁰W. H. Zhu, J. J. Xiao, G. F. Ji, F. Zhao, and H. M. Xiao, *J. Phys. Chem. B* **111**, 12715 (2007).
- ²¹D. G. Allis and T. M. Korter, *ChemPhysChem* **7**, 2398 (2006).
- ²²W. H. Zhu, X. W. Zhang, T. Wei, and H. M. Xiao, *Theor. Chem. Acc.* **124**, 179 (2009).
- ²³S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- ²⁴Z. Wu and R. M. Wentzcovitch, *J. Geophys. Res.* **112**, B12202 (2007).
- ²⁵Z. Q. Wu and R. M. Wentzcovitch, *Phys. Rev. B* **79**, 104304 (2009).
- ²⁶W. C. McCrone, *Anal. Chem.* **22**, 1225 (1950).
- ²⁷H. H. Cady, D. T. Cromer, and A. C. Larson, *Acta Crystallogr.* **16**, 617 (1963).
- ²⁸E. A. Glascoe, J. M. Zaug, and A. K. Burnham, *J. Phys. Chem. A* **113**, 13548 (2009).
- ²⁹M. W. Beckstead, K. Puduppakkam, P. Thakre, and V. Yang, *Progr. Energy Combust. Sci.* **33**, 497 (2007).
- ³⁰J. C. Gump and S. M. Peiris, *J. Appl. Phys.* **97** (2005).
- ³¹J. L. Lyman, Y. C. Liau, and H. V. Brand, *Combust. Flame* **130**, 185 (2002).
- ³²B. F. Henson, L. Smilowitz, B. W. Asay, and P. M. Dickson, *J. Chem. Phys.* **117**, 3780 (2002).
- ³³K. S. Vandersall, C. M. Tarver, F. Garcia, and S. K. Chidester, *J. Appl. Phys.* **107** (2010).
- ³⁴D. D. Tuschel, A. V. Mikhonin, B. E. Lemoff, and S. A. Asher, *Appl. Spectrosc.* **64**, 425 (2010).
- ³⁵C. T. Konek, B. P. Mason, J. P. Hooper, C. A. Stoltz, and J. Wilkinson, *Chem. Phys. Lett.* **489**, 48 (2010).
- ³⁶E. B. Washburn, T. P. Parr, and D. M. Hanson-Parr, *Propellants, Explos., Pyrotech.* **35**, 46 (2010).
- ³⁷B. Sun, J. M. Winey, Y. M. Gupta, and D. E. Hooks, *J. Appl. Phys.* **106** (2009).
- ³⁸P. A. Urtiew, J. W. Forbes, C. M. Tarver, F. Garcia, D. W. Greenwood, and K. S. Vandersall, *Russ. J. Phys. Chem. B* **1**, 46 (2007).
- ³⁹D. S. Moore, K. Y. Lee, and S. I. Hagelberg, *J. Energ. Mater.* **26**, 70 (2008).

- ⁴⁰E. A. Zhurova, V. V. Zhurov, and A. A. Pinkerton, *J. Am. Chem. Soc.* **129**, 13887 (2007).
- ⁴¹M. J. Fitch, M. R. Leahy-Hoppa, E. W. Ott, and R. Osiander, *Chem. Phys. Lett.* **443**, 284 (2007).
- ⁴²E. Surber, A. Lozano, A. Lagutchev, H. Kim, and D. D. Dlott, *J. Phys. Chem. C* **111**, 2235 (2007).
- ⁴³D. E. Hooks, D. B. Hayes, D. E. Hare, D. B. Reisman, K. S. Vandersall, J. W. Forbes, and C. A. Hall, *J. Appl. Phys.* **99** (2006).
- ⁴⁴R. E. Winter, S. S. Sorber, D. A. Salisbury, P. Taylor, R. Gustavsen, S. Sheffield, and R. Alcon, *Shock Waves* **15**, 89 (2006).
- ⁴⁵V. I. Levitas, B. F. Henson, L. B. Smilowitz, and B. W. Asay, *J. Phys. Chem. B* **110**, 10105 (2006).
- ⁴⁶L. L. Stevens, J. J. Haycraft, and C. J. Eckhardt, *Cryst. Growth Des.* **5**, 2060 (2005).
- ⁴⁷R. K. Weese and A. K. Burnham, *Propellants, Explos., Pyrotech.* **30**, 344 (2005).
- ⁴⁸Y. Q. Guo, M. Greenfield, and E. R. Bernstein, *J. Chem. Phys.* **122** (2005).
- ⁴⁹L. L. Stevens and C. J. Eckhardt, *J. Chem. Phys.* **122**, 174701 (2005).
- ⁵⁰C. S. Yoo and H. Cynn, *J. Chem. Phys.* **111**, 10229 (1999).
- ⁵¹B. F. Henson, B. W. Asay, R. K. Sander, S. F. Son, J. M. Robinson, and P. M. Dickson, *Phys. Rev. Lett.* **82**, 1213 (1999).
- ⁵²J. P. Lewis, T. D. Sewell, R. B. Evans, and G. A. Voth, *J. Phys. Chem. B* **104**, 1009 (2000).
- ⁵³F. Chen, H. Zhang, F. Zhao, C. M. Meng, and X. L. Cheng, *Sci. China Ser. G* **53**, 1080 (2010).
- ⁵⁴F. J. Zerilli and M. M. Kuklja, *J. Phys. Chem. A* **114**, 5372 (2010).
- ⁵⁵D. C. Sorescu and B. M. Rice, *J. Phys. Chem. C* **114**, 6734 (2010).
- ⁵⁶F. L. Jiang, G. H. Zhai, L. Ding, K. F. Yue, N. Liu, Q. Z. Shi, and Z. Y. Wen, *Acta Phys. -Chim Sin.* **26**, 409 (2010).
- ⁵⁷J. Hooper, E. Mitchell, C. Konek, and J. Wilkinson, *Chem. Phys. Lett.* **467**, 309 (2009).
- ⁵⁸H. L. Cui, G. F. Ji, X. R. Chen, W. H. Zhu, F. Zhao, Y. Wen, and D. Q. Wei, *J. Phys. Chem. A* **114**, 1082 (2010).
- ⁵⁹L. Z. Zhang, S. V. Zybin, A. C. T. van Duin, S. Dasgupta, W. A. Goddard, and E. M. Kober, *J. Phys. Chem. A* **113**, 10619 (2009).
- ⁶⁰M. W. Conroy, Oleynik, II, S. V. Zybin, and C. T. White, *Phys. Rev. B* **77**, 094107 (2008).
- ⁶¹D. Lian, L. Y. Lu, D. Q. Wei, Q. M. Zhang, Z. Z. Gong, and Y. X. Guo, *Chin. Phys. Lett.* **25**, 899 (2008).
- ⁶²F. J. Zerilli and M. M. Kuklja, *J. Phys. Chem. A* **110**, 5173 (2006).
- ⁶³D. G. Allis, D. A. Prokhorova, and T. M. Korter, *J. Phys. Chem. A* **110**, 1951 (2006).
- ⁶⁴P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougousis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- ⁶⁵D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ⁶⁶J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ⁶⁷D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ⁶⁸J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁶⁹S. Grimme, *J. Comput. Chem.* **27**, 1787 (2006).
- ⁷⁰R. M. Wentzcovitch, *Phys. Rev. B* **44**, 2358 (1991).
- ⁷¹F. Birch, *Phys. Rev.* **71**, 809 (1947).
- ⁷²M. W. Conroy, I. I. Oleynik, S. V. Zybin, and C. T. White, *J. Appl. Phys.* **104**, 053506 (2008).
- ⁷³T. Sun, K. Umamoto, Z. Q. Wu, J. C. Zheng, and R. M. Wentzcovitch, *Phys. Rev. B* **78**, 024304 (2008).
- ⁷⁴J. Rylance and D. Stubley, *Thermochim. Acta* **13**, 253 (1975).
- ⁷⁵J. F. Baytos, Report LA-8034-MS, Los Alamos Scientific Laboratory (1979).
- ⁷⁶T. D. Sewell, R. Menikoff, D. Bedrov, and G. D. Smith, *J. Chem. Phys.* **119**, 7417 (2003).
- ⁷⁷B. B. Karki, R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni, *Phys. Rev. B* **61**, 8793 (2000).
- ⁷⁸H. H. Cady, *J. Chem. Eng. Data* **17**, 369 (1972).
- ⁷⁹J. R. Kolb and H. F. Rizzo, *Propellants, Explos., Pyrotech.* **4**, 10 (1979).
- ⁸⁰N. B. Bolotina, E. A. Zhurova, and A. A. Pinkerton, *J. Appl. Crystallogr.* **36**, 280 (2003).
- ⁸¹C. S. Choi and H. P. Boutin, *Acta Crystallogr.* **B26**, 1235 (1970).
- ⁸²B. R. B. Olinger, and H. Cady, *Proceedings of the International Symposium on High Dynamic Pressures* (C.E.A., Paris, 1978), pp 3–8.
- ⁸³P. Carrier, R. Wentzcovitch, and J. Tsuchiya, *Phys. Rev. B* **76**, 064116 (2007).
- ⁸⁴F. Goetz and T. B. Brill, *J. Phys. Chem.* **83**, 340 (1979).
- ⁸⁵Z. Iqbal, S. Bulusu, and J. R. Autera, *J. Chem. Phys.* **60**, 221 (1974).
- ⁸⁶S. Ye, K. Tonokura, and M. Koshi, *Chem. Phys.* **293**, 1 (2003).
- ⁸⁷H. V. Brand, R. L. Rabie, D. J. Funk, I. Diaz-Acosta, P. Pulay, and T. K. Lippert, *J. Phys. Chem. B* **106**, 10594 (2002).