Structural and spectroscopic properties of small Pu_n ($n = 2$–5) molecules

Jia Ting-Ting(贾婷婷)[a], Gao Tao(高 涛)[a]†, Zhang Yun-Guang(张云光)[b], Lei Qiang-Hua(雷强华)[c], and Luo De-Li(罗德礼)[c]

[a] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*

[b] *School of Sciences, Xi'an Institute of Posts and Telecommunications, Xi'an* 710100, *China*

[c] *National Key Laboratory of Surface Physics and Chemistry, Mianyang* 621907, *China*

(Received 19 November 2010; revised manuscript received 22 March 2011)

The equilibrium structures and the electronic, spectroscopic and thermodynamic properties of small Pu_n ($n = 2$–5) molecules are systematically investigated using the methods of general gradient approximation (GGA) of density functional theory (DFT). The results show that the bond length of the lowest-energy structure of Pu_2 is 2.578 Å. The ground state structure of Pu_3 is a triangle with D_{3h} symmetry, whereas for Pu_4, the ground state structure is a square (D_{4h}) and the spin polarization of 16 for molecule Pu_5 with square geometry (D_{4h}) is the most stable structure. For the ground state structures, the vibrational spectra as well as thermodynamic parameters are worked out. In addition, the values for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) along with the energy gap of all the Pu_{2-5} structures are presented. The relevant structural and chemical stabilities are predicted.

Keywords: Pu_n molecule, molecular geometry, vibrational spectrum

PACS: 36.40.Mr **DOI:** 10.1088/1674-1056/20/11/113601

1. Introduction

The physical and chemical properties of the actinide elements form the scientific basis for rational handling of nuclear materials.[1] Plutonium, an important element of the late actinides, has drawn much attention because of its nuclear property and wide application in energy generation.[2]

Over the last decade, the electronic structures of plutonium compound and correlated electrons in δ-plutonium have been paid much attention,[3–6], as a result of the anomalous properties of the plutonium stem from the competition between itinerancy and localization of its f-shell electrons.[7]. In 2001, the electronic structures of both the bulk and surfaces of plutonium dioxide were studied by Wu *et al.*[8] by using B3LYP. PuO_2 was found to be a semiconductor and the chemical bonding is found to be mostly ionic. Archibong and Ray[9] studied the structures, vibrational frequencies and energies of the low-lying electronic states of PuO_2 and PuN_2 molecules. They found the state $^5\sum_g^+$ was the preferred ground state for the dioxide. In 2008, Sun and Zhang[10] used all-electron projector-augmented-wave (PAW) method to study the electronic structures and properties of PuO_2 and Pu_2O_3, and the LDA+U and GGA+U formalisms had been used to account for the strong on-site Coulomb repulsion among the localized Pu 5f electrons.

In addition, Meng *et al.*[11] studied the small plutonium molecules. They used the DFT/B3LYP method and relativistic effective core potential (RECP) to study the Pu_2 molecule and they found there exists a strong spin-polarization in the plutonium diatomics. In addition, they obtained the structure and potential energy functions of Pu_2. In 2001, Meng *et al.*[12] extended the B3LYP method to calculate the structures of Pu_2 and Pu_3. They gave the spectral constants of Pu_2, the harmonic frequencies of Pu_3, as well as the potential energy functions of $Pu_2$and Pu_3. In 2002, Meng *et al.*[13] continued to conduct a systematic analysis of the geometrical configurations and the Jahn–Teller effect of Pu_4 molecule in the same *ab initio* level . They found that the ground state structure of Pu_4 is a parallelogram with C_{2h} symmetry instead of a square geometry with D_{4h}; furthermore, they concluded that no stable structure of Pu_4 with T_d symmetry can be found because of the

†Corresponding author. E-mail: gaotao2010@gmail.com

© 2011 Chinese Physical Society and IOP Publishing Ltd

Jahn–Teller effect.

The structures, properties and metallic bonds of the actinides elements have been the focus of numerous theoretical and experimental studies due to the interaction of the f orbital between Homonuclear diatomic molecules.[11] We present a theoretical study on Pu_n (n = 2–5) molecules. We focus our attention on the following four aspects: 1) to find out the ground state structure of Pu_5 molecule; 2) to judge whether the spin polarization effect in Pu_5 molecule exists or not; 3) to ascertain the chemical stability of different Pu_5 molecule isomers; and 4) to predict the structural stability of different Pu_n molecule sizes (n = 3–5).

The determination of the ground state structures is a challenge in molecule studies. In the present study, by relaxing the geometric structures, we start from a large number of initial candidate geometries to perform density functional theory (DFT) calculations for Pu_n molecules ($n \leq 5$) within the general gradient approximation (GGA) so as to find out the putative ground state structures, including the ones reported in the literature.[13−16] We present details of the computational scheme and a benchmark calculation in the following section. The computational methods are described in Section 2. The calculated results are presented in Section 3, including four parts concerning geometries, electronic properties, spectrum analysis and thermodynamics properties, followed by a conclusion given in Section 4.

2. Computational method

The calculations are carried out by using DFT implemented in the ADF package.[17−25] Zhang and Li[26] used ADF to study the molecular structures and the vibrational frequencies of uranium hexahalides UX_6 (X=F, Cl, Br and I). Moreover, DFT has been applied with great success to physical and chemical systems.[11] We used mainly the spin-polarized GGA with Becke Perdew (BP) functional[27,28] for the exchange and correlation (XC) interaction, and double zeta no polarized basis sets (DZ). When computing the total bonding energies of Pu_4 and Pu_5, GGA with modified density gradient corrections of Perdew and Wang (mPW) was used too.[29] Scalar relativistic (SR) zero order regular approximation (ZORA)[18,31] was adopted in our calculations, because the relativistic calculations are of importance to Pu_n molecules. Self-consistent field calculations were carried out with a convergence criterion of 10^{-4} Hartree (1 Hartree=4.35974417×10^{-18} J) on the total bonding energy. The direct inversion in an iterative subspace (DIIS) approach was used to speed up the self consistent field (SCF) convergence. A 0.005 Hartree electron smearing was applied to the molecular orbital occupation. In the geometry optimization, the converging threshold was set to be 10^{-3} Hartree for the energy, 10^{-2} Hartree/Å for the gradient and 10^{-2} Å for the radial. We started with the lowest spin multiplicity for the Pu_n molecules. Spin-unrestricted calculations were then performed for all possible spin multiplicities. Furthermore, large frozen core was used to accelerate the calculation.

3. Results and discussion

3.1. Pu_n molecules and their geometries

In order to evaluate the accuracy of our calculations, the parameter, such as the bond length r_0 used in the present work, was initially compared with the results of U_2 for which theoretical result is available. The equilibrium bond length of U_2 molecule we calculated is 2.407 Å, while is in good agreement with the previously theoretical result (2.43 Å) obtained by

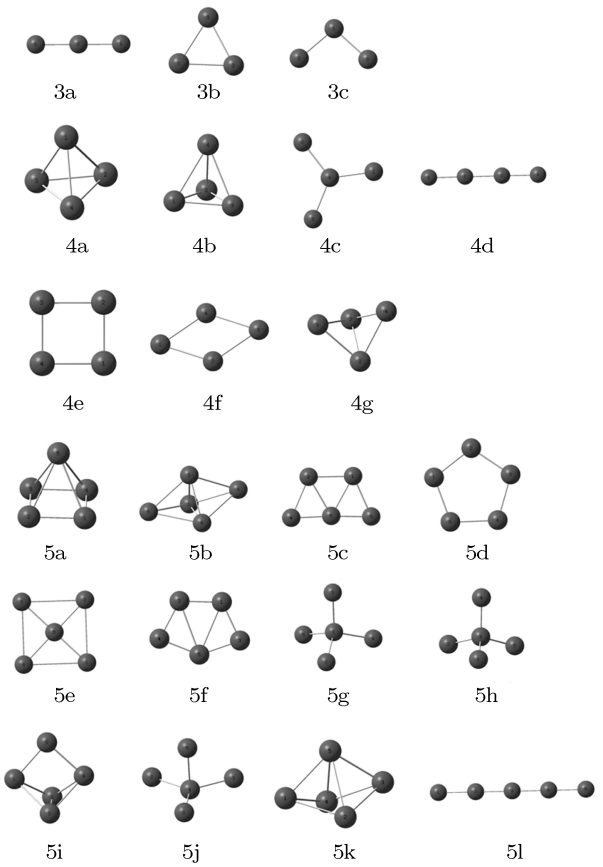


Fig. 1. Geometrical structures for the Pu_n (n = 3–5) molecules.

Gagliardi *et al.*[31] Hence, the method of the GGA/BP should be feasible to extend to the computation of Pu and other actinides molecules.

For Pu_2, Pu_3 and Pu_4, after exploring a large number of low-lying isomers of all the possible spin polarization, we find that the geometrical optimization for the possible spin polarization of Pu_n, i.e., $2S = 0, 2, 4, 6, 8, 10, \ldots$ and $6n$ derived from the ground state ^7F_g of Pu_n indicate that the energies of these states decrease gradually with the increase of spin polarization. This effect was defined as spin-polarization.[13] However, Pu_5 is very different from Pu_n (n = 2–4). There is no spin-polarization effect in the Pu_5 molecule. The lowest-energy structures for Pu_n molecules with n = 3–5 and some low-lying stable isomers are presented in Fig. 1. The point group, spin polarizations, total bonding energies and bond lengths are listed in Table 1.

Table 1. Point group (S), spin polarizations (spin), total bonding energies (E) and bond lengths (R) for the Pu_n (n = 2–5) molecules.

Mole	S	Spin	E/eV	R/Å
2	$D_{\infty h}$	12	–8.561	$R_{12} = 2.578$
3a	$D_{\infty h}$	18	–14.749	$R_{12} = R_{23} = 2.465$
3b	D_{3h}	**18**	**–14.756**	$\boldsymbol{R_{12} = R_{23} = R_{13} = 2.609}$
3c	C_{2v}	18	–14.334	$R_{12} = R_{13} = 2.531$
4a	T_d	24	–21.526 (–21.317)	$R_{12} = R_{23} = R_{13} = R_{14} = R_{24} = R_{34} = 2.730$ (2.732)
4b	C_{3v}	24	–21.542 (–21.353)	$R_{12} = R_{23} = R_{13} = 2.648$(2.647), $R_{14} = R_{24} = R3_4 = 2.832$ (2.823)
4c	D_{3h}	24	–20.556 (–20.378)	$R_{14} = R_{24} = R_{34} = 2.451$ (2.448)
4d	$D_{\infty h}$	24	–21.517 (–21.274)	$R_{12} = R_{34} = 2.486$(2.489), $R_{23} = 2.358$ (2.374)
4e	D_{4h}	**24**	**–22.383** (**–22.156**)	$\boldsymbol{R_{12} = R_{23} = R_{34} = R_{14} = 2.498}$ (2.500)
4f	D_{2h}	24	–21.416 (–21.213)	$R_{12} = R_{23} = R_{34} = R_{14} = 2.720$ (2.727)
4g	C_{2v}	24	–21.847 (–21.666)	$R_{12} = R_{13} = R_{34} = R_{24} = 2.670$ (2.668), $R_{23} = 2.552$ (2.526)
5a	C_{4v}	36	–29.716 (–29.461)	$R_{12} = R_{23} = R_{34} = R_{14} = 2.738$ (2.753),
				$R_{15} = R_{25} = R_{35} = R_{45} = 3.271$ (3.250)
5b	D_{3h}	38	–29.400 (–29.173)	$R_{12} = R_{24} = R_{14} = 3.316$ (3.313),
				$R_{13} = R_{23} = R_{43} = R_{15} = R_{25} = R_{45} = 3.070$ (3.107)
5c	C_{2v}	16	–29.80 (–29.464)	$R_{15} = R_{25} = 2.624$(2.639), $R_{13} = R_{24} = 2.572$ (2.599)
				$R_{35} = R_{45} = 2.322$(2.334), $R_{12} = 2.580$ (2.592)
5d	D_{5h}	36	–29.827 (–29.515)	$R_{12} = R_{23} = R_{34} = R_{45} = R_{15} = 2.617$ (2.617)
5e	D_{4h}	**16**	**–31.436** (–31.157)	$\boldsymbol{R_{12} = R_{23} = R_{34} = R_{14} = 3.307}$ (3.321),
				$\boldsymbol{R_{15} = R_{25} = R_{35} = R_{45} = 2.338}$ (2.349)
5f	C_{2v}	14	–29.293 (–28.856)	$R_{15} = R_{25} = 3.040$(3.063), $R_{13} = R_{24} = 2.267$ (2.283),
				$R_{35} = R_{45} = 2.279$ (2.298), $R_{12} = 2.244$ (2.255)
5g	T_d	14	–30.964 (–30.717)	$R_{12} = R_{13} = R_{14} = R_{15} = 2.276$ (2.291)
5h	D_{2d}	14	–30.922 (–30.653)	$R_{13} = R_{23} = R_{43} = R_{53} = 2.278$ (2.295)
5i	C_{2v}	28	–29.417 (–29.148)	$R_{12} = R_{13} = R_{34} = R_{24} = 2.584$ (2.584),
				$R_{23} = 2.673$(2.661), $R_{15} = R_{45} = 2.502$ (2.496)
5j	C_{3v}	14	–30.997 (–30.722)	$R_{14} = R_{24} = R_{34} = 2.287$ (2.305), $R_{45} = 2.299$ (2.317)
5k	C_{2v}	38	–29.402 (–29.141)	$R_{12} = R_{23} = R_{34} = R_{14} = 3.064$ (3.023),
				$R_{25} = R_{45} = 3.303$ (3.132), $R_{15} = R_{35} = 3.065$ (3.560)
5l	$D_{\infty h}$	38	–28.793 (–28.502)	$R_{12} = R_{45} = 2.684$ (2.685), $R_{23} = R_{34} = 2.653$ (2.669)

Notes: The values in parentheses are from present calculation with GGA/mPW. The most stable geometries are marked by bold typefaced letters.

For Pu_2, the spin polarization is 12 and the bond length of Pu_2 is 2.578 Å, which is different from the previous theoretical result of Meng *et al.*[11] They gave a bond length of 3.520 Å obtained by using Becke's three-parameter hybrid functional [20–24] with the LYP correlation functional (B3LYP). We use Becke's exchange functional with Perdew's correlation functional (BP).[32] We have a good reason to believe the

rationality of our result, since the equilibrium bond length of U_2 is consistent with the theoretical result.

Three isomers are found for Pu_3 and all of them have been reported previously. The spin polarization of 18 for molecule Pu_3 with equilateral triangle geometry (D_{3h}) is the lowest-energy structure (3b). Our structure is the same as that obtain by using the GGA/B3LYP method.[12] The total bonding energy and the bond length of 3b are −14.756 eV and 2.609 Å, respectively. The second lowest-energy structure of Pu_3 is the linear configuration (3a), its total bonding energy is −14.750 eV, which lies only 0.007 eV above the lowest-energy structure (3b). The isomer 3c with an isosceles triangle form (C_{2v}) comes first in energy and the total bonding energy of 3c is 0.422 eV higher than the ground state structure (3b). In addition, the apex angle of 3c is 97.38° and the minimum bond length is 2.531 Å.

For Pu_4, we obtain 7 isomers and four of them have not been reported before. Meng *et al.*[13] obtained that the ground state configuration was a parallelogram (C_{2h}), but our results differ from the previous studies. From Table 1, we see that the total bonding energies of the D_{4h} symmetry are the lowest among the seven symmetries. The overall BP approach gives the lowest energy, although GGA/BP and GGA/mPW methods give similar results. All the computations before were carried out under symmetry limitation. When the molecular structure of the Pu_4 was optimized under different symmetries, the final optimum structure was found to be D_{4h} symmetry. Therefore, we can draw a conclusion that the stability of the D_{4h} symmetry (4e) is the best among the seven symmetries. The second lowest-energy structure (4g) is a new isomer with C_{2v} symmetry and its total bonding energy is −21.847 eV, which is higher than the lowest-energy structure (4e) by 0.536 eV. To the structures of the third and the fourth lowest-energy structures (4b) and (4a) we should pay much attention; they can be built by adding one atom on top of the isomer (3b). According to our calculation, it can be seen that the total bonding energies of 4a is only 0.016 eV higher than that of (4b), indicating that the two structures can coexist in the same reaction conditions. Specifically, Meng *et al.*[13] did not find the stable configuration of Pu_4 with T_d symmetry by using GAUSSIAN 98 package. However, in the present research, Pu_4 molecule with T_d symmetry is predicted as a metastable structure. After comparing our results with the previous ones, we can find some differences. The disagreements between our results and the previous results may be related to the different precision of ADF package and GAUSSIAN 98 package.

The total energies of the 12 isomers of Pu_5 molecule are predicted by using BP and mPW functions. The spin polarization of 16 for 2D planar molecule Pu_5 with square geometry (D_{4h}) is the preferential structure (5e). Its bonding energy is −31.436 eV and its minimum bond length is 2.338 Å. Furthermore, (5e) can be obtained by adding one atom in the middle of the isomer (4e). The spin polarization of 14 for configuration (5j) with C_{3v} symmetry is found to be the second lowest-energy structure. The total bonding energy of (5j) is −30.997 eV, which is higher than the ground state configuration (5e) by 0.439 eV. The third lowest-energy isomer 5g with the spin polarization of 14 is higher in energy than the ground state configuration (5e) by 0.472 eV. When comparing the configurations and the total bonding energies of isomers (5j), (5g) and (5h), it is particularly noteworthy that these three structures have the similar configurations and energies. The structure of (5b) with D_{3h} symmetry is obtained from (3b) by adding two atoms and (5b) is higher in energy than (5e) by 2.036 eV. In addition, (5j) can be obtained by adding one atom on top of the isomer (4g). Other isomers of Pu_5 along with their relative symmetries, spin polarizations, total bonding energies and bond lengths are given in Fig. 1 and Table 1, respectively.

Table 1 lists the size dependence of the minimum bond length of Pu_n (n = 3–5) molecules. We can see from Table 1 that the nearest bond lengths of ground state structures decrease with n. It demonstrates that the interactions among plutonium atoms enhance and the stability of Pu_n (n = 3–5) increase as molecule size increases. The increase of the stability could be attributed to the metallic interaction in Pu_n (n = 3–5) molecule; this metallic interaction may be due to the use of geometrical close packing model and electronic shell model.

3.2. Electronic properties

Let LUMO be the abbreviation of the lowest unoccupied molecular orbital and HOMO that of as the highest occupied molecular orbital.[33] The energy gap between LUMO and HOMO has been considered as a characteristic quantity of electronic structure of molecules and also a measure of the ability for molecules to undergo activated chemical re-

actions with small molecules.[34] The HOMO–LUMO gap for each stable and metastable structure has been calculated. The HOMO and LUMO along with the HOMO–LUMO gap for all the 19 structures are given in Table 2.

As seen from the list, the different structures with the same size have different HOMO–LUMO gaps. For Pu_3, the HOMO–LUMO gaps for the 3 structures are nearly the same; this indicates that they have the similar chemical stability. For Pu_4, the HOMO–LUMO gap of 4b reaches a maximum (17.281 eV), corresponding to the strongest chemical stability of the Pu_4 molecules. Moreover, as shown in Table 2, the ground state configuration (4e) has the smallest HOMO–LUMO gap (3.102 eV); this indicates the chemical instability of (4e).

Table 2. The HOMO, LUMO eigenvalues and gap energies (GAP) for the Pu_n ($n = 2$–5) molecules.

Mole	HOMO/eV	LUMO/eV	GAP/eV
2	–18.564	–1.110	17.455
3a	–17.334	–0.986	16.349
3b	–18.543	–1.242	17.300
3c	–18.143	–1.320	16.823
4a	–4.542	–1.400	3.142
4b	–18.665	–1.385	17.281
4c	–17.495	–0.923	16.572
4d	–16.578	–1.666	14.912
4e	–4.899	–1.797	3.102
4f	–18.077	–1.291	16.786
4g	–18.420	–1.671	16.750
5a	–18.243	–1.761	16.482
5b	–18.782	–1.921	16.861
5c	–5.305	–1.617	3.687
5d	–17.854	–1.948	15.906
5e	–4.281	–0.638	3.643
5f	–4.798	–1.736	3.062
5g	–5.030	–0.446	4.584
5h	–4.191	–1.437	2.755
5i	–5.215	–1.837	3.378
5j	–4.235	–1.046	3.188
5k	–18.782	–1.918	16.864
5l	–17.557	–1.669	15.889

For Pu_5, the energy gap of (5k) is 16.864 eV, larger than those of the other Pu_5 structures. This fact shows the strongest chemical stability of (5k). The energy gap of (5h) reaches a minimum (2.755 eV), corresponding to the high chemical instability. The HOMO–LUMO gap of the ground state configuration (5e) is 3.643 eV, which is larger than the lowest gap (5h) by 0.888 eV. This means that it is not easy for (5e) to have chemical reaction with small molecules. The structures and electronic properties of Pu_n ($n \leq 5$) calculated may be beneficial for further study of Pu_nY_m compound molecule.

3.3. Spectrum analysis

Since vibrational frequency is often one of the main observable data for many experiments, we present the irreducible representations corresponding to the vibrations, frequencies and absorption intensity for the ground state of Pu_3, Pu_4 and Pu_5 molecules in Table 3. Moreover, the vibrational spectra of the three lowest-energy structure are all shown in Fig. 2. Figure 3 shows the vibrational modes corresponding to the maximal infrared (IR) peaks, in which the vibrational direction is shown by the black arrowhead.

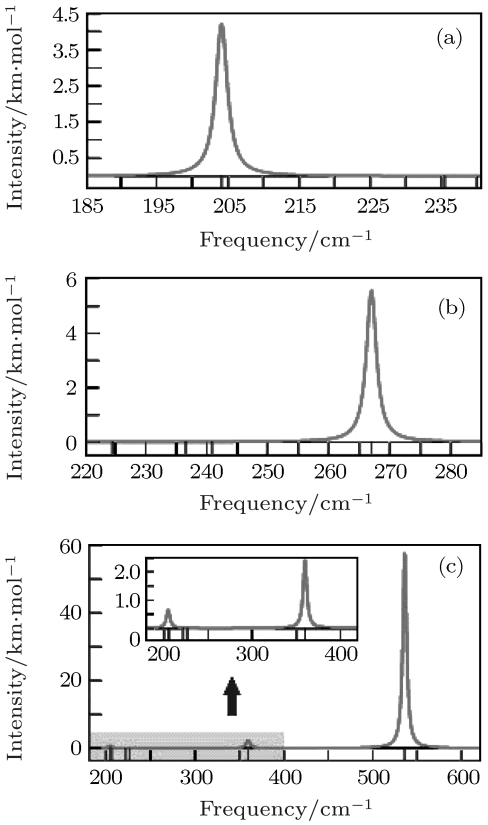


Fig. 2. The vibrational spectra of the ground states of Pu_n) molecules: (a) $n = 3$, (b) $n = 4$, (c) $n = 5$.

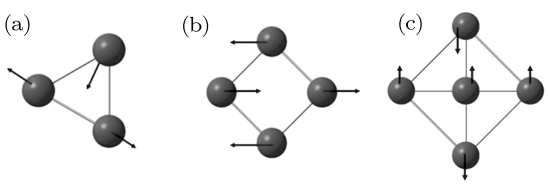


Fig. 3. The vibrational modes corresponding to the maximal IR peaks of Pu_n molecules: (a) $n = 3$, (b) $n = 4$, (c) $n = 5$.

Table 3. The irreducible representations corresponding to the vibrations (Irr), frequencies and absorption intensity (IR.int) for the most stable Pu_n ($n = 3$–5) molecules.

Mole	Vibration	Irr	Frequencies/cm^{-1}	IR.int/km·mol^{-1}
Pu_2	ν_1	$\sum_g^+$	201.776	0.00
3b	ν_1	E'_1	204.121	2.108
	ν_2	E'_1	204.121	2.108
	ν_3	A'_1	235.502	0.00
4e	ν_1	B_{1g}	182.728	0.00
	ν_2	A_{1g}	224.560	0.00
	ν_3	B_{2g}	236.591	0.00
	ν_4	B_{2u}	240.851	0.00
	ν_5	E_{1u}	266.969	2.787
	ν_6	E_{1u}	266.969	2.787
5e	ν_1	E_{1u}	204.927	0.323
	ν_2	B_{2u}	205.189	0.00
	ν_3	B_{1g}	206.036	0.00
	ν_4	A_{1g}	221.949	0.00
	ν_5	B_{2g}	226.585	0.00
	ν_6	A_{2u}	359.821	2.391
	ν_7	E_{1u}	536.024	29.907
	ν_8	E_{1u}	536.024	29.907

The maximal IR peak of the ground state structure of Pu_3 molecule is at 204.1 cm^{-1} with the infrared intensity of 2.108 km/mol, as shown in Fig. 2(a). From Fig. 3(a), it can be seen that the vibrational mode is symmetry stretching. For Pu_3, we find that the vibrational frequencies are different from those reported before ($\nu_2 = 56.9007$ cm^{-1}, $\nu_2 = 57.1816$ cm^{-1}, $\nu_3 = 64.0785$ cm^{-1}),[12] which perhaps are due to the different bond lengths.

For the ground state structure of Pu_4 molecule, Fig. 2(b) shows that the maximal IR peak is at 266.97 cm^{-1} with the infrared intensity of 2.787 km/mol, which corresponds to the symmetry stretching vibration (shown in Fig. 3(b)).

For the ground state structure of Pu pentamer, Figs. 2(c) and 3(c) show the vibrational spectrum and vibrational mode respectively. The maximal IR peak of Pu_5 appears at 536.024 cm^{-1} with IR intensity of 29.907 km/mol. Its vibrational mode is symmetry stretching too. Our frequencies and other results presented are capable of being compared with future IR experiments. From Fig. 2, it can be seen that the frequency of the IR peak generally increases with the molecule size, indicating that the interaction force between Pu atoms enhances as the molecule size increases. These results are in good agreement with the stability of different molecule size.

3.4. Thermodynamic properties

On the basis of vibrational and spectrum analysis, some thermodynamic parameters such as the entropy (S) and the internal energy (E) are obtained. Table 4 lists the entropy and internal energy of the lowest energy structures of Pu_n ($n = 2$–5) molecules at temperatures from 400 to 1200 K. Table 4 shows that the entropies and internal energies increase with the increase in temperature and molecule size. The results indicate that the higher the temperature of a body, the quicker the motion of its molecules, so the internal energy of plutonium molecule is increased. Since entropy is a measure of disorder, it increases when the temperature rises. However, as the molecule size increases, the entropies of Pu_n ($n = 2$–5) molecule change less and less, but the internal energies increase more and more.

Table 4. The entropy S (cal·mol^{-1}·K^{-1}) and internal energy E (kcal·mol^{-1}) of Pu_n ($n = 2$–5) molecules.

T/K	2		3b		4e		5e	
	S	E	S	E	S	E	S	E
400	68.057	2.817	84.414	4.887	93.145	7.442	100.182	10.341
450	69.101	3.161	86.022	5.470	95.412	8.305	103.028	11.450
500	70.037	3.505	87.466	6.056	97.453	9.174	105.606	12.575
550	70.885	3.851	88.775	6.644	99.307	10.047	107.961	13.710
600	71.659	4.196	89.973	7.233	101.006	10.924	110.125	14.855
650	72.372	4.542	91.077	7.823	102.573	11.804	112.128	16.007
700	73.032	4.889	92.100	8.414	104.027	12.685	113.990	17.164
750	73.647	5.235	93.054	9.006	105.383	13.569	115.730	18.325
800	74.223	5.582	93.946	9.598	106.653	14.453	117.363	19.491
850	74.764	5.928	94.786	10.191	107.847	15.339	118.900	20.659
900	75.274	6.275	95.577	10.784	108.974	16.226	120.352	21.830
950	75.757	6.622	96.326	11.377	110.041	17.113	121.728	23.004
1000	76.215	6.969	97.037	11.971	111.054	18.001	123.036	24.179
1050	76.65	7.316	97.714	12.565	112.019	18.89	124.281	25.355
1100	77.066	7.663	98.359	13.159	112.938	19.779	125.469	26.533
1150	77.463	8.011	98.976	13.753	113.818	20.669	126.606	27.713
1200	77.843	8.358	99.566	14.347	114.66	21.559	127.695	28.893

4. Conclusions

In summary, the stable structures, electronic, spectroscopic and thermodynamic properties of small Pu_n ($n = 2$–5) molecules have been systematically investigated using DFT–GGA calculations. At this theoretical level, we obtain that the ground state configuration of Pu_3 is an equilateral triangle (C_{3v}). For Pu tetramer, the ground state configuration is a square with D_{4h} symmetry. Moreover, we obtain the new Pu_4 structure with T_d symmetry. For Pu pentamer, the ground state configuration is also a square with D_{4h} symmetry. Different from Pu_n ($n = 2$–4) molecules, there is no spin polarization effect in Pu_5 molecule. According to the HOMO–LUMO gap difference, the structures of (3b), (4b) and (5k) possess excellent chemical stability. On the contrary, the structure of (3a), (4e), and (5h) show extreme chemical instability. For all the ground state configurations of Pu_n ($n = 3$–5), the vibrational modes corresponding to the maximal IR peaks have been listed. In addition, the vibrational spectra and minimum bond length of Pu_n ($n = 3$–5) molecules in their ground-state structures are analysed. We find that the stability of Pu_n ($n = 3$–5) molecules generally increases with the increase in molecule size. Finally, the thermodynamic properties are also worked out for the corresponding stable isomers.

References

[1] Korzhavyi P A, Vitos L, Andersson D A and Johansson B 2004 *Nature Mater.* **3** 225

[2] Shim J H, Haule K and Kotliar G 2007 *Nature* **446** 513

[3] Wu X Y and Ray A K 2001 *Phys.* B **293** 362

[4] Savrasov S Y, Kotllar G and Abrahams E 2001 *Nature* **410** 793

[5] Silver G L 2003 *Appl. Radi. Isot.* **59** 217

[6] Huda M N and Ray A K 2005 *Phys. Rev.* B **72** 085101

[7] Sarrao J L, Morales L A, Thompson J D, Scott B L, Stewart G R, Wastin F, Rebizant J, Boulet P, Colineau E and Lander G H 2002 *Nature* **420** 297

[8] Wu X Y and Ray A K 2001 *Phys.* B **301** 359

[9] Archibong E F and Ray A K 2000 *J. Mol. Struct.* (Theochem) **530** 165

[10] Sun B and Zhang P 2008 *Chin. Phys.* B **17** 1364

[11] Meng D Q, Liu X Y, Zhang W X, Wang H Y, Li Q and Zhu Z H 2000 *Journal of Atomic and Molecular Physics* **17** 411 (in Chinese)

[12] Meng D Q, Jiang G, Liu X Y, Luo D L, Zhang W X and Zhu Z H 2001 *Acta Phys. Sin.* **50** 1268 (in Chinese)

[13] Meng D Q, Zhu Z H and Jiang G 2002 *J. Mol. Struct.* **610** 241

[14] Zhang X R, Ding X L, Fu Q and Yang J L 2008 *J. Mol. Struct.* (Theochem) **867** 17

[15] Villanueva M S, Tejeda P H H, Pal U, Silva J F R, Mora J I R and Ascencio J A 2006 *J. Phys. Chem.* A **110** 10274

[16] Sebetci A 2008 *Chem. Phys.* **354** 196

[17] van Lenthe E, Baerends E J and Snijders J G 1993 *J. Chem. Phys.* **99** 4597

[18] van Lenthe E, Baerends E J and Snijders J G 1994 *J. Chem. Phys.* **101** 9783

[19] van Lenthe E, Baerends E J and Snijders J G 1999 *J. Chem. Phys.* **110** 8943

[20] Perdew J P 1986 *Phys. Rev.* B **33** 8822

[21] Perdew J P 1986 *Phys. Rev.* B **34** 7406

[22] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13244

[23] Becke A D 1986 *J. Chem. Phys.* **84** 4524

[24] Becke A D 1993 *J. Chem. Phys.* **98** 5648

[25] Shannon R D 1976 *Acta Crys. Sect.* A **32** 751

[26] Zhang Y G and Li Y D 2010 *Chin. Phys.* B **19** 033302

[27] Kaltsoyannis N 2000 *Inorg. Chem.* **39** 6009

[28] Bowmaker G A, Görling A, Häbberlen O, Rösch N, Goodman G L and Ellis D E 1992 *Inorg. Chem.* **31** 577

[29] Adamo C and Barone V 1998 *J. Chem. Phys.* **108** 664

[30] van Lenthe E, Snijders J G and Baerends E J 1996 *J. Chem. Phys.* **105** 6505

[31] Gagliardi L and Roos B O 2005 *Nature* **433** 848

[32] Becke A D 1988 *Phys. Rev.* A **38** 3098

[33] Mao H P, Wang H Y, Ni Y, Xu G L, Ma M Z, Zhu Z Z and Tang Y J 2004 *Acta Phys. Sin.* **53** 1766 (in Chinese)

[34] Wang M, Huang X W, Du Z L and Li Y C 2009 *Chem. Phys. Lett.* **480** 258