Calculations of the vibrational frequency and isotopic shift of UF_6 and U_2F_6*

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Molecular structure, vibrational frequency and infrared intensity of UF_6 are investigated by using the revised Perdew–Burke–Enzerhof function with the triple-zeta polarized basis set. The calculation results are in good agreement with the experimental values and indicate the existence of a stable U_2F_6 molecule with a multiple bonded U_2 unit. The calculation results also predict that the D_{3d} symmetry of U_2F_6 is more stable than D_{3h}. The optimized geometries, vibrational frequencies, and infrared intensities are also reported for U_2F_6 molecules in D_{3d} symmetry. In addition, the isotopic shift of vibrational frequencies of the two molecules under isotopic substitution of uranium atom are also investigated with the same method. The U_2F_6 molecule is predicted to be better than UF_6 for laser uranic isotope separation.

Keywords: molecular structure, vibrational frequency, infrared intensity, isotopic shift

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1. Introduction

Because uranium compounds play an important role in nuclear technology, there is a great interest in the physics and chemistry of actinides.[1,2] The radioactivity of uranium compounds is very difficult to study experimentally. Therefore, it is not surprising that the available experimental data on the physical and chemical properties of these compounds are rather scarce. However, the experimental infrared (IR) spectrum of UF_6 was analyzed by McDowell, Asprey, and Paine, who derived a vibrational force field.[3] A few diuranium compounds have been found experimentally. So far, only the OU_2O and $H_2U_2H_2$ molecules have been detected.[4,5] However, no real inorganic chemistry based on the U_2 unit has been observed. This chemistry could occur in solution, which is analogous to the widely studied transition metal dimmer chemistry.

It is very difficult to study uranium compounds in the laboratory, and thus quantum chemical calculations are very useful for investigating the physical and chemical properties of these compounds. Because of the importance in nuclear fuel enrichment and abundant experimental data of UF_6, the molecule has been used as a prototype to computationally test electronic structures for actinide complexes for a quarter of a century.[6,7] A large number of academic studies about the molecular structure and vibrational frequencies of UF_6 have been performed, which are in good agreement with experimental values.[8–20] For example, Hay and Martin[8] calculated the structure and harmonic vibrational frequency with their LC-RECPs, and found that B3LYP presented smaller deviations than HF and BLYP from the experimentally determined data. They also found that the average deviation for the best functional (B3LYP) was only 14 cm^{-1} for all vibrational frequencies. Satisfactory bond lengths and vibrational frequencies of UF_6 were also obtained by Batista *et al.*[20] using the Hartree–Fock method and three approximations of density functional theory, i.e., spin-density approximation, generalized gradient approximation, and hybrid density functionals. Gagliardi and Roos *et al.*[21,22] have explored how two uranium atoms bind to form a U_2 molecule with multiconfigurational quantum chemistry methods. They found that the U_2 chemical bond is more complex than any other known diatomic bond, with summation of the bonding electrons suggesting a quintuple bond. In other words, the uranium atom has the ground-state electronic configuration $(5f)^3(6d)^1(7s)^2$ (six valence electrons), and the U–U bond of U_2 molecule is composed of three normal two-electron bonds, four electrons in different bond-

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ing orbitals, and two nonbonded electrons, leading to a quintuple bond between the two uranium atoms. In addition, its multi-radical nature may support chemical bonds to the framework of diuranium chemistry, such as in $F_3U_2F_3$.

In the present work, we perform density functional calculations of optimized geometries, vibrational frequencies, and infrared intensities of UF_6 molecule. The same method has been used to show that diuranium compound U_2F_6 is stable with a multiple U–U bond and the D_{3d} symmetry of U_2F_6 is more stable than D_{3h} symmetry. The optimized geometries, vibrational frequencies, and infrared intensities are also obtained for the D_{3d} symmetry of U_2F_6 by using the revised Perdew–Burke–Enzerhof (RPBE) function with TZP basis set.[23] In addition, the isotopic shift of some frequencies of the two molecules under isotopic substitution of uranium atom is also investigated by using the same method.

This paper is organized as follows. The method of calculation is given in Section 2, and the results and discussion are presented in Section 3. The paper ends with the Conclusion in Section 4.

2. Computational details

Our calculations were performed by using the Amsterdam density functional (ADF) program. The underlying theory of the program is the Kohn–Sham approach to the density-functional theory (DFT). The Kohn–Sham DFT is an important computational method to predict chemical properties accurately and to analyse and interpret them in convenient and simple chemical terms.[24] The DFT is superior to the Hartree–Fock theory and semi-empirical approaches in accuracy, and is well suited for molecules containing heavy metal atoms.[25,26]

This method allows for scalar relativistic effect by introducing the zeroth-order regular approximation (ZORA) approach into the Dirac equation, and the spin–orbit coupling is not included in the present study.[27–29] It will have only a minor effect on the computed structure for singlet electronic state. Certainly, the spin–orbit coupling effect will further lower the energy but has a negligible effect on the geometry. For the close-shell systems, the spin restricted DFT scheme is used. In this paper, a triple-ζ slater type basis set augmented with one set of polarization functions, i.e. the triple-zeta polarized (TZP) basis set is employed for all atoms (F and U). A frozen core approximation is used. Core electrons (F.1s and U.5d) are frozen for fluorine and uranium, respectively. Moreover, the calculations are performed by using the GGA level to DFT: RPBE function.[30,31]

3. Results and discussion

In this section, we present the calculation results of molecular structures, vibrational frequencies, infrared intensities, and isotopic shifts of UF_6 and U_2F_6 molecules. In addition, in view of high computational cost and the lack of analytic forces for our relativistic all-electron calculations, all computations are performed by using the frozen core approximation.

3.1. Structures of UF_6 and U_2F_6

The equilibrium bond length of UF_6 has been obtained by using the electron diffraction techniques initiated by Seip (1.996 Å)[32] and Kimura *et al.* (1.999 Å).[33] In this paper, the geometric parameter of UF_6 is studied by using the RPBE function with the triple-zeta polarized basis set, and it is calculated to be 2.027 Å. It is encouraging that the calculated bond length is in reasonably good agreement with experimental data. The errors are only 1.553% and 1.401%, respectively.

For an octahedral UF_6 (see Fig. 1), the electronic configuration is

$$\cdots \quad (3A_{1g})^2(1T_{2u})^6(1T_{1g})^6(4T_{1u})^6 \\ (1A_{2u})^2(2T_{2u})^6(5T_{1u})^6,$$

where the highest occupied molecular orbits of each molecule are indicated. The part of molecular orbitals (MOs) in order of energy, with the most significant SFO gross populations are reported in Table 1.

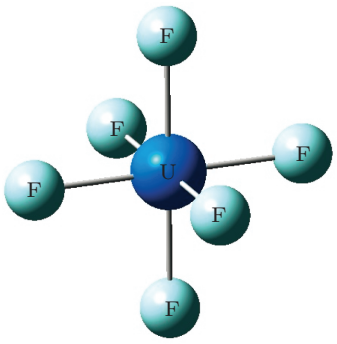


Fig. 1. (colour online) Octahedral conformation of UF_6.

Table 1. Part of MOs in order of energy, and the most significant SFO gross population of UF_6 molecule.

E/eV	Occ	MOs	%	SFO	Fragment
–11.767	2	$3A_{1g}$	92.71	1P:x	2F
			1.69	2s	1U
			1.61	4s	1U
–11.490	6	$1T_{2u}$	69.68	1P: z	2F
			9.643	1P: y	4F
			7.357	1P: x	2F
			6.52	1F:z2x	1U
			4.48	1F:z2y	1U
			2.50	1F:z	1U
–10.692	6	$1T_{1g}$	99.46	1P:yz	4F
			0.48	2P:yz	2F
–10.312	6	$4T_{1u}$	64.73	1P:z	2F
			13.32	1P:x	2F
			11.68	1P:y	4F
			5.82	1F:z2x	1U
			3.83	2F:z2y	1U
			1.17	2F:z3	1U
–7.335	2	$1A_{2u}$	98.92	1F:xyz	1U
			0.73	2F:xyz	1U
–6.659	6	$2T_{2u}$	62.73	1F:z2x	1U
			11.31	1F:z2y	1U
			8.81	1P:x	2F
			6.87	1P:y	4F
			5.82	1P:z	2F
			4.12	2F:z	1U
–5.460	6	$5T_{1u}$	69.83	1F:z2y	1U
			16.54	2F:z3	1U
			4.97	1P:x	2F
			3.14	1P:y	4F
			2.62	1P:y	2F

In a previous study of the U_2 molecule, it is shown that the ground-state configuration is $(7s\sigma_g)^2$ $(6d\pi_u)^4(6d\sigma_g)^1$ $(6d\delta_g)^1$ $(5f\delta_g)^1$ $(5f\pi_u)^1$ $(5f\phi_u)^1$ $(5f\phi_g)^1$, and thus the chemical bond is thus more complex than any other known diatomic bond, with summation of the bonding electrons suggesting a quintuple bond.[21,22] Its multi-radical nature (six electrons are available for binding) may support chemical bonds to $F_3U_2F_3$ molecule. Here we consider the diuranium compound of U_2F_6. It can have either an eclipsed or a staggered conformation (see Figs. 2 and 3). Previous calculations have indicated that the staggered conformation is lower in energy than the eclipsed form, and the calculations are carried out for the case of limiting symmetry. Moreover, when the molecular structures of U_2F_6 are optimized under D_{3d} symmetry and D_{3h} symmetry, respectively (unlimiting symmetry), the final optimum structure is found to be staggered. Thus, the stability of D_{3d} symmetry is better than that of D_{3h}. Hence, we will focus our analysis on the staggered structure.

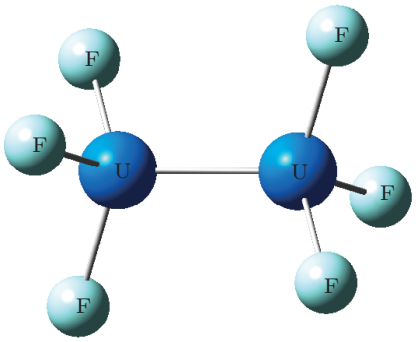


Fig. 2. (colour online) Staggered conformation of U_2F_6.

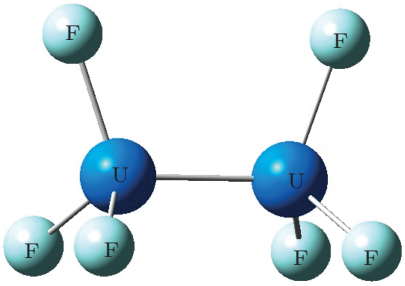


Fig. 3. (colour online) Eclipsed conformation of U_2F_6.

Optimization of the geometry is performed at the RPBE level of theory by using the TZP basis set. The most stable spin-free electronic state is found to be a singlet state. The U–U bond distance is 2.470 Å, the U–F bond distance is 2.068 Å, and the U–U–F angle is 120°.

In the U_2F_6, the formal charge of uranium atom is +3. Thus, 6 of 12 valence electrons remain there, and a triple bond can be formed. The electronic configuration for this molecule including all the electrons on U and F atoms is

$$\cdots\ (2A_{1u})^2(2A_{2g})^2(18E_{1u})^4(18E_{1g})^4(20A_{2u})^2 (19E_{1u})^4(21A_{1g})^2,$$

where the highest occupied molecular orbitals of each symmetry are indicated. Part of molecular orbitals in order of energy, and the most significant SFO gross populations are reported in Table 2.

Table 2. Part of MOs in order of energy, and the most significant SFO gross population of U_2F_6 molecule.

E/eV	Occ	MOs	%	SFO	Fragment
–10.260	2	$2A_{1u}$	93.85	1P:x	3F
			6.05	2F:x	1U
–10.249	2	$2A_{2g}$	94.02	1P:x	3F
			5.67	2F:x	1U
–10.147	4	$18E_{1u}$	61.21	1P:z	3F
			16.48	1P:x	3F
			15.86	1P:y	3F
			3.66	2F:z2x	1U
–9.974	4	$18E_{1g}$	62.07	1P:z	3F
			19.60	1P:y	3F
			14.54	1P:x	3F
			2.14	5P:y	1U
–9.830	2	$20A_{2u}$	90.51	1P:x	3F
			4.99	5P:z	1U
			1.55	6P:z	1U
			1.48	7s	1U
			1.11	2F:y	1U
–5.875	4	$19E_{1u}$	74.93	2F:z2y	1U
			16.01	4D:yz	1U
			3.32	1P:z	3F
			1.71	1P:x	3F
			1.07	2F:z	1U
–5.860	2	$21A_{1g}$	64.24	2F:z3	1U
			19.10	7s	1U
			6.05	6P:z	1U
			3.25	4D:z2	1U
			2.77	3s	3F
			1.36	2F:y	1U
			1.35	1P:x	3F
			1.16	6D:z2	1U

3.2. Vibrational frequency

The octahedral UF_6 molecule has six normal modes of vibration: $T_{mol}=A_{1g}+E_g+2T_{1u}+T_{2g}+T_{2u}$, where only the T_{1u} vibrations (ν_3 and ν_4) are infrared active. The two modes ν_3 and ν_4 correspond to the asymmetric strethching and bending modes, respectively. The vibrational frequencies of the UF_6 have been studied extensively in the gas phase and matrix spectroscopy. McDowell *et al.*,[34] analysed the infrared spectrum of UF_6 and derived a vibrational force field. Paine *et al.*[35] reported the matrix-isolated UF_6 vibrational spectra. In the present paper, the vibrational frequencies of UF_6 calculated in optimized geometries by using the RPBE functions with the TZP basis set are listed in Table 3. As shown in this table, we find that the frequencies predicted via the RPBE approach are in good agreement with experimental values for UF_6 molecule. Fox example, the RPBE frequencies for the ν_3 and ν_4 bands are 623.642 and 181.472 cm^{-1}, which are comparable with the experimental frequencies of 626 and 186 cm^{-1}. The errors are only 2.358 and 4.528 cm^{-1}, respectively. In addition, the calculated dipole strengths and intensities for the IR-allowed modes in the molecule are also given in Table 3. For example, the calculated intensities for the ν_3 and ν_4 modes are 191.027 and 10.326 kM/mol, respectively.

Table 3. Calculated vibrational frequency, dipole strength, and absorption intensity of UF_6 molecule.

Vibration	Symmetry	Frequency/cm^{-1}	Exp.[34]	Dipole strength	IR intensity/kM·mol^{-1}
ν_1	A_{1g}	669.279	667	0	0
ν_2	E_g	533.887	534	0	0
ν_3	T_{1u}	623.642	626	1196.889	191.027
ν_4	T_{1u}	181.472	186	202.442	10.326
ν_5	T_{2g}	191.462	200	0	0
ν_6	T_{2u}	139.744	143	0	0

The fundamental vibrational frequencies of U_2F_6 are obtained by using the RPBE method with TZP basis set, and are reported in Table 4. There are no experimental results available to compare with the computational values up to now. This Table also gives the values of the infrared intensity and dipole strength. In the D_{3d} symmetry, 12 fundamental vibrational modes of U_2F_6 are classified into various symmetry species: $3A_{1g}+A_{1u}+2A_{2u}+3E_{1g}+3E_{1u}$. We also give a detailed description of the assignment of all vibrational modes of U_2F_6 molecule in Table 4. Two A_{2u} modes (ν_6 and ν_7) and three E_{1u} modes (ν_1, ν_{11}, and ν_{12}) are only infrared active under D_{3d} symmetry. The five modes ν_1, ν_6, ν_7, ν_{11}, and ν_{12} correspond to the symmetric stretching, deformation symmetric stretching, antisymmetric stretching, deformation antisymmetric stretching, and rocking modes, respectively. In addition, the E_{1u} mode ν_1 and A_{2u} mode ν_7 are assigned to the strong infrared bands at 230.683 and 373.885 cm^{-1}, respectively.

Table 4. Calculated vibrational frequency, dipole strength, and absorption intensity of U_2F_6 molecule.

Vibration	Symmetry	Frequency/cm^{-1}	Dipole strength	IR intensity/kM·mol^{-1}
ν_1	E_{1u}	544.953	1688.799	230.683
ν_2	A_{1g}	247.541	0.000	0.000
ν_3	E_{1g}	125.366	0.000	0.000
ν_4	A_{1u}	19.906	0.000	0.000
ν_5	E_{1g}	542.022	0.000	0.000
ν_6	A_{2u}	151.024	218.977	8.289
ν_7	A_{2u}	587.019	2541.022	373.885
ν_8	A_{1g}	140.613	0.000	0.000
ν_9	E_{1g}	47.508	0.000	0.000
ν_{10}	A_{1g}	611.816	0.000	0.000
ν_{11}	E_{1u}	127.863	247.926	7.946
ν_{12}	E_{1u}	25.121	1586.907	9.992

3.3. Isotopic shifts of UF_6 and U_2F_6

Uranium has three stable isotopes with a natural composition of 99.275% (^{238}U), 0.720% (^{235}U), and 0.0057% (^{234}U), respectively. The isotope selective infrared multiphoton dissociation is one of the most promising methods of separating uranium isotope. One of the important factors that influence successful utilization of this method is an appropriate vibrational isotopic shift. The experimental vibrational isotopic shift of uranium isotope may be found in literatures only for UF_6 molecule. In the present paper, we present the results of the analytical calculations of the isotopic shift of some frequencies of UF_6 and U_2F_6 molecules under the isotopic substitution of uranium atom.

For UF_6 molecule, only the asymmetric strethching mode ν_3 and bending mode ν_4 of T_{1u} vibration are infrared active. In our study, the ν_3 and ν_4 for $^{235,238}UF_6$ are calculated by employing scaled DFT force field. The value of the shift $\Delta\nu_3$ between the frequencies for $^{235}UF_6$ and $^{238}UF_6$ is 0.746 cm^{-1} which is in excellent agreement with observed result of 0.7 cm^{-1}.[36] The predicted values of the shift $\Delta\nu_4$ between the fundamental vibrational frequencies for $^{235}UF_6$ and $^{238}UF_6$ are 0.049 cm^{-1}. For U_2F_6 molecule, two A_{2u} modes (ν_6 and ν_7) and three E_{1u} modes (ν_1, ν_{11}, and ν_{12}) are infrared active in D_{3d} symmetry. The values of isotopic shift for the five vibrational modes are fairly well reproduced by quantum chemical calculations, which are listed in Table 5. For ν_1 mode we obtain $\Delta\nu_1(^{235}U^{235}UF_6$–$^{238}U^{238}UF_6)$=1.245 cm^{-1} and $\Delta\nu_1(^{235}U^{238}UF_6$–$^{238}U^{238}UF_6)$=0.673 cm^{-1}. For ν_7 mode, the predicted values of shift $\Delta\nu_7$ between frequencies for $^{235}U^{235/238}UF_6$ and $^{238}U^{238}UF_6$ are 2.672 and 1.417 cm^{-1}, respectively. From Table 5, we find that the maximal isotopic shift of U_2F_6 is $\Delta\nu_7(^{235}U^{235}UF_6$–$^{238}U^{238}UF_6)$= 2.672 cm^{-1}. The most noticeable isotopic shift of UF_6 molecule is found to be 0.746 cm^{-1}. Thus, it is clear that the isotopic shift of $\Delta\nu_7(^{235}U^{235}UF_6$–$^{238}U^{238}UF_6)$ is larger than that of $\Delta\nu_3(^{235}UF_6$–$^{238}UF_6)$. Thus, we predict that the U_2F_6 molecule is a better material for the laser isotope separation than UF_6.

Table 5. Calculated isotopic shift (in cm^{-1}) of U_2F_6 molecule.

Vibration	$\nu(^{238}U^{238}UF_6)$	$\Delta\nu(^{235}U^{235}UF_6$–$^{238}U^{238}UF_6)$	$\Delta\nu(^{235}U^{238}UF_6$–$^{238}U^{238}UF_6)$
ν_1	544.953	1.245	0.673
ν_6	151.024	0.215	0.103
ν_7	587.019	2.672	1.417
ν_{11}	127.863	0.174	0.098
ν_{12}	25.121	0.083	0.034

4. Conclusion

The molecular properties of UF_6 and U_2F_6 are investigated by using the RPBE function with TZP basis set. The molecular structure, vibrational frequency, and infrared intensity of UF_6 are obtained, which are in excellent agreement with experimental results. For example, the calculated asymmetric stretching and bending modes (ν_3 and ν_4) of UF_6 are in good agreement with the experimental data with errors of 2.358 and 4.528 cm^{-1}, respectively. The calculation results predict the existence of U_2F_6molecule, which is found to be stable with a multiply bonded U_2 unit. The calculation results also predict that the D_{3d} symmetry of U_2F_6 is more stable than D_{3h} symmetry. The predicted infrared bands of D_{3d} symmetry at 230.683, 8.289, 373.885, 7.947, and 9.992 cm^{-1} are assigned to the symmetric stretching mode ν_1, deformation symmetric stretching mode ν_6, antisymmetric stretching mode ν_7, deformation antisymmetric stretching mode ν_{11}, and rocking mode ν_{12}, respectively. After the molecular vibrational frequencies of UF_6 and U_2F_6 are obtained, the isotopic shifts of some frequencies of the two molecules under isotopic substitution of uranium atom are also investigated by using the same method. For example, the value of the shift $\Delta\nu_3$ between the frequencies of $^{235}UF_6$ and $^{238}UF_6$ is 0.746 cm^{-1} which is in excellent agreement with the observed result of 0.7 cm^{-1}. In addition, we find that the isotopic shift of $\Delta\nu_7(^{235}U^{235}UF_6{-}^{238}U^{238}UF_6)$=2.672 cm^{-1} is larger than the isotopic shift of $\Delta\nu_3(^{235}UF_6{-}^{238}UF_6)$=0.746 cm^{-1}. Thus, we predict that the U_2F_6 molecule is better than UF_6 for laser uranic isotope separation.

References

[1] Katz J J, Seaborg G T and Morss L R 1986 *The Chemistry of the Actinide Elements* (London: Chapman and Hall)

[2] Fuger J and Brown D 1975 *J. Chem. Soc. Dalton Trans.* 2256

[3] Aldridge J P, Brock E G, Filip H, Flicker H, Fox K, Galbraith H W, Holland R F, Kim K C, Krohn B J, Magnuson D J, Maier II W B, McDowell R S, Patterson C W, Person W B, Smith D F and Werner G K 1985 *J. Chem. Phys.* **83** 34

[4] Gorokhov L N, Khodeev A M and Teplofiz Y S 1974 *Vys. Temp.* **12** 1307

[5] Souter P F, Kushto G P, Andrews L and Neurock M J 1997 *Am. Chem. Soc.* **119** 1682

[6] Hay P J, Wadt W R, Kahn L R and Phillips D H 1979 *J. Chem. Phys.* **71** 1767

[7] Case D A and Yang C Y 1979 *J. Phys. Chem.* **72** 3443

[8] Hay P J and Martin R L 1998 *J. Chem. Phys.* **109** 3875

[9] Schreckenbach G, Hay P J and Martin R L 1999 *J. Comput. Chem.* **20** 70

[10] Kaltsoyannis N and Bursten B E 1995 *Inorg. Chem.* **34** 2735

[11] Schrechkenbach G 2000 *Inorg. Chem.* **39** 1265

[12] Privalov T, Schimmelpfennig B, Wahlgren U and Grenthe I 2002 *J. Phys. Chem.* A **106** 11277

[13] Jong W A de and Nieuwpoort W C 1996 *Int. J. Quantum Chem.* **58** 203

[14] Gagliardi L, Willetts A, Skylaris C K, Handy N C, Spencer S, Ioannou A G and Simper A M 1998 *J. Am. Chem. Soc.* **120** 11727

[15] Han Y K and Hirao K 2000 *J. Chem. Phys.* **113** 7345

[16] Han Y K 2001 *J. Comput. Chem.* **22** 2010

[17] García-Hernández M, Lauterbach C, Krüger S, Matveev A and Rösch N 2002 *J. Comput. Chem.* **23** 834

[18] Straka M, Patzschke M and Pyykkö P 2003 *Theor. Chem. Acc.* **109** 332

[19] Kovacs A and Konings R J M 2004 *J. Mol. Struct* (Theochem) **684** 35

[20] Batista E R, Martin R L, Hay P J, Peralta J E and Scuseria G E 2004 *J. Chem. Phys.* **121** 2144

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

[22] Roos B O, Malmqvist P and Gagliardi L J 2006 *Am. Chem. Soc.* **128** 17000

[23] Lee L, Yang W and Parr R G 1988 *Phys. Rev.* B **37** 785

[24] te Velde G, Bickelhaupt F M, Baerends E J, Fonseca Guerra C, van Gisbergen S J A, Snijders J G and Ziegler T 2001 *J. Comput. Chem.* **22** 931

[25] Chen J, Meng D Q, Du J G, Jiang G, Gao T and Zhu Z H 2010 *Acta. Phys. Sin.* **59** 1658 (in Chinese)

[26] Li Y C, Yang C L, Sun M Y, Li X X, An Y P and Wang M S 2010 *Chin. Phys.* B **19** 083602

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

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

[29] van Lenthe E, Ehlers A and Baerends E J 1999 *J. Chem. Phys.* **110** 8943

[30] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

[31] Hammer B, Hansen L B and Norskov J K 1999 *Phys. Rev.* B **59** 7413

[32] Seip H M 1965 *Acta Chem. Scand.* **19** 1955

[33] Kimura M, Schomaker V, Smith D W and Weinstock B 1967 *J. Chem. Phys.* **48** 4001

[34] McDowell R S, Asprey L B and Paine R T 1974 *J. Chem. Phys.* **61** 3571

[35] Paine R T, McDowell R S, Asprey L B and Jones L H 1976 *J. Chem. Phys.* **64** 3081

[36] Song W Z and Gu D 1990 *J. Nucl. Radiochem.* **12** 175