

Ab initio Quantum Chemical Calculation for Actinide Dimers *

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Abstract: Using the B3LYP method with the relativistic effective core potential and contract valence electron basis set $[5s4p3d4f]/[3s3p2d2f]$ for U and Pu atom, the present work optimized the structure of U_2 and Pu_2 dimers. Their long-bond-length and short-bond-length are found, which are 0.38965 nm, 0.29927 nm for U_2 and 0.45375 nm, 0.35202 nm for Pu_2 respectively, then the corresponding potential energy curves are calculated. For the ground states and the lowest energy excited states of U_2 and Pu_2 , their force constants, spectroscopic data and dissociation energies are obtained for the first time.

Key words: U_2 ; Pu_2 ; Potential energy function; Dissociation energy

1 Introduction

Metal-metal bonding in dimer actinide systems, which involves diatomic interactions between f orbital, has been the topic of several synthetic and computational studies, as well as considerable speculation. To date, no discrete molecules showing direct actinide-actinide bonding have been isolated, although bonding between two transition-metal atoms is commonly observed. Uranium and plutonium are the two most important elements in nuclear power generation, and their diatomic, such as U_2 and Pu_2 , are the simplest systems in which direct actinide-actinide bonds could be found. March *et al.* have predicted that such heavy-atom homonuclear diatomic are unlikely to exist^[1]. But U_2 has been detected in the gas phase^[2], and nonrelativistic MS-X α and relativistic core potentials (RCP) have addressed the question of the existence and molecular electronic structure of the naked actinide dimers U_2 and Np_2 ^[3]. MS-X α calculations demonstrate the significant $f\sigma$, $f\pi$, $f\delta$ and $f\phi$ diatomic interactions. RCP calculations indicate that the U_2 potential surface is quite complex, with two groups of states exhibiting energy minima at long-bond-length (0.30nm) and short-bond-length (0.22nm)^[4]. However, there was no empirical and theoretical work on Pu_2 .

Actinide elements are large with high nuclear charge so that they must be treated in a relativistic manner. Variety of relativistic effective core potentials (RECP) has been developed for calcula-

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Received date: 2000 - 12 - 19.

tions on molecules containing heavy atoms^[5]. Its application to actinide systems has been reviewed^[6]. Becke's published density function, which includes a nonlocal exchange correction, has yield accurate predictions of transition-metal-ligand and metal-metal bond energies^[7]. In the present paper, density functional method with RECP has been used to optimize the structures of U_2 and Pu_2 molecules. The calculations reported here employ relativistic effective core potentials (RECP) to replace the core electrons. The RECP for U and Pu have been published by Hay^[8-10], which based on the Cowan-Griffin approximate method for calculating relativistic atomic orbital. In the Cowan-Griffin method, the Hamiltonian includes the Darwin and mass-velocity terms from the Pauli approximation, but omits spin-orbit effects. The spin-orbit effects are treated by perturbation theory after the wave function has been determined.

2 Computational methods and electronic states

The relativistic effective core potentials of Hay replaces the core electrons of the actinide [xe] $4f^{14}5d^{10}$, in conjunction with a [$3s3p2d2f$] contracted Gaussian basis set to describe the valence electrons^[10]. Calculations were carried out using the popular density functional; the "hybrid" B3LYP functional, which is a three-parameter mixture of density functional and "exact" Hartree-Fock exchange. The use of HF-based relativistic ECPs with density functional based methods appears to be giving reasonable results for actinide species^[11], as has also been found to date for main group and transition metal. All calculations employed the Gaussian 98 program.

U_2 and Pu_2 belong to $D_{\infty h}$ group, whose irreducible representations can be resolved into those of D_{2h} . If the z axis of D_{2h} coincides with z axis of $D_{\infty h}$, the correspondent symmetry operations for $D_{\infty h}$ and D_{2h} are, as $\Sigma_g \rightarrow A_g$, $\Pi_g \rightarrow B_{2g} + B_{3g}$, $\Delta_g \rightarrow A_g + B_{1g}$, $\Phi_g \rightarrow B_{2g} + B_{3g}$, $\Sigma_u \rightarrow B_{1u}$, $\Pi_u \rightarrow B_{2u} + B_{3u}$, $\Delta_u \rightarrow A_u + B_{1u}$, $\Phi_u \rightarrow B_{2u} + B_{3u}$ ^[12]. Therefore, the symmetry basis function and their number for the contracted basis set of the dimers are $14A_g, 4B_{1g}, 9B_{2g}, 9B_{3g}, 4A_u, 14B_{1u}, 9B_{2u}, 9B_{3u}$, where there are 72 symmetric basis function, the number of expanding Gaussian function is 188.

In order to determine the ground state configurations, all the possible states for U_2 and Pu_2 molecules have been optimized. The multiplicity of Pu_2 is 1, 3, 5, 7, 9, 11, 13, due to its ground electronic state 7F_g , and 1, 3, 5, 7, 9 for U_2 based on its 5L_u ground electronic state. The optimized results are listed in table 1. From table 1, we can see that the energy of the Pu_2 molecule decreased steadily from 1 multiplicity to 13 multiplicity, the lowest energy is $-143.42513a.u.$ When the multiplicity are 7, 9, 11, 13, two minims are existed for the same multiplicity, which are called short-bond-length (SBL) and long-bond-length (LBL). The same trend to U_2 molecule, but only at 9 multiplicity, there are two minims.

The electronic states for U_2 and Pu_2 molecule can be determined by the separated atom method^[12] based on the Wigner-Witmer rules from the ground electronic state 5L_u for U atom and the ground state 7F_g for Pu atom. It is well proved that the irreducible representations of $SU(2l+1)$ can be resolved into the irreducible representations of its subgroup $SO(2l+1)$ and then those of $SO(3)$, which include the 5L_u and 7F_g representing ground states of U and Pu, respectively.

Table 1 Optimized results for U₂ and Pu₂

Multiplicity	U ₂		Pu ₂	
	R/nm	E/a. u.	R/nm	E/a. u.
1	0.24454	-102.66251	0.35561	-142.82116
3	0.27592	-102.76384	0.34915	-143.10276
5	0.29927	-102.86394	0.32455	-143.16612
7	0.35701	-102.85545	0.31273	-143.20179
			0.32664	-143.26613
9	0.38965	-102.90702	0.34599	-143.27421
	0.44433	-102.85200	0.42714	-143.31418
11	0.32805	-102.836762	0.34665	-143.37511
			0.46395	-143.34106
13	0.33918	-102.72366	0.35202	-143.41986
			0.45375	-143.42513

The irreducible representations of SO(3) group, i. e. ⁵L_u and ⁷F_g, can be resolved into those of C_{∞v} as follows

$$\begin{aligned}
 {}^5L_u &\rightarrow {}^5\Sigma_u^- \oplus {}^5\Pi_u \oplus {}^5\Delta_u \oplus {}^5\Phi_u \oplus {}^5\Gamma_u \oplus \dots \\
 {}^7F_g &\rightarrow {}^7\Sigma_g^- \oplus {}^7\Pi_g \oplus {}^7\Delta_g \oplus {}^7\Phi_g \oplus {}^7\Gamma_g \oplus \dots
 \end{aligned}$$

Then the direct products by itself are $\Sigma \oplus \Pi \oplus \Delta \oplus \Phi \oplus \Gamma \oplus \dots$, which lists all possible electronic states for U₂ and Pu₂. It is necessary to consider the calculation results by ab initio method and f-f orbital interaction; the electronic states can be determined. Because the dimer of the actinide elements would likely involve diatomic interactions between f orbitals, which not only could generate bonds of α , π and δ symmetry, but also could lead to ϕ bonds as well. According to G98W program, for U₂, at 9 multiplicity, the molecular orbitals population are found to be

$$\begin{aligned}
 \alpha \text{ electron: } &\sigma_g \sigma_u \sigma_u \sigma_g \pi_g \pi_g \pi_u \pi_u \sigma_g \sigma_u \pi_u \pi_u \delta_g \delta_g \delta_u \pi_x \pi_x \\
 \beta \text{ electron: } &\sigma_g \sigma_u \sigma_u \sigma_g \pi_g \pi_g \pi_u \pi_u \sigma_g \sigma_u
 \end{aligned}$$

When the multiplicity is 5, the orbitals population for U₂ is

$$\begin{aligned}
 \alpha \text{ electron: } &\sigma_u \sigma_g \sigma_u \pi_u \pi_u \sigma_g \pi_g \pi_g \phi_g \pi_u \pi_u \delta_g \delta_g \delta_u \pi_x \pi_x \\
 \beta \text{ electron: } &\sigma_u \sigma_g \sigma_u \pi_u \pi_u \sigma_g \pi_g \pi_g \phi_g \pi_u \pi_u \delta_g
 \end{aligned}$$

Therefore, the ground state is ⁹Σ_g⁻ for U₂, which is LBL; the lowest excited state is ⁵Σ_g⁻, which is SBL. That results different from [4], in which ¹³Δ_g is the ground state, “so-called” LBL (0.30nm), ⁵Σ_g⁻ is excited state, so-called “SBL” (0.22nm).

In contrast to the U₂ molecule, a set of 22 high-spin MOs' states of Pu₂ can't be easily determined. Due to the configuration mixture, the MOs' symmetry in computation has changed with respected to different nuclear distance. So the G98W can not give their states. However, the potential curves of the ground state and the lowest excited state for Pu₂ are crossed each other, described following in the figure 2. In order to avoid crossing at the same multiplicity, their symmetry must be different; namely, their electronic states should be different.

3 Potential energy function and spectroscopic parameter of U_2 and Pu_2

Using Gaussian 98 program with the external RECP and contracted basis set for U and Pu, the potential curves for the ground states and the lowest energy states of U_2 and Pu_2 have been calculated by B3LYP method. By least-square fitting a series of calculated single points, their potential energy curves are derived as the extended Rydberg function form developed by Murrell and Sorbie^[13]:

$$V = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho) \quad (1)$$

Where $\rho = r - r_e$, r is the interatomic distance, r_e is its equilibrium value. D_e , a_1 , a_2 and a_3 are parameters which are determined by a least-square fitting to a series of single point calculations data, table 2. The fitting potential curves are plotted as Fig. 1 and Fig. 2. The calculated points are good agreed with them.

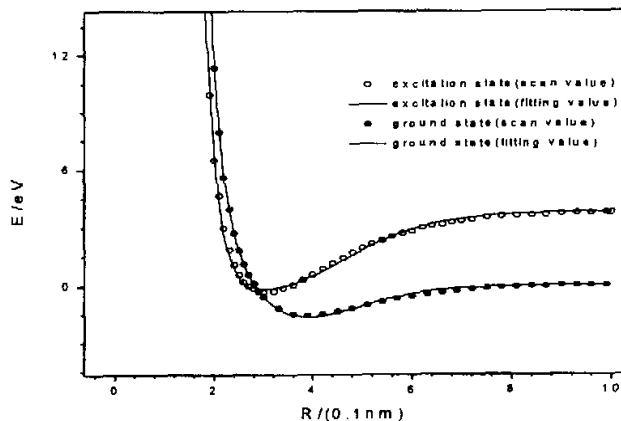


Fig. 1 The potential curve of U_2

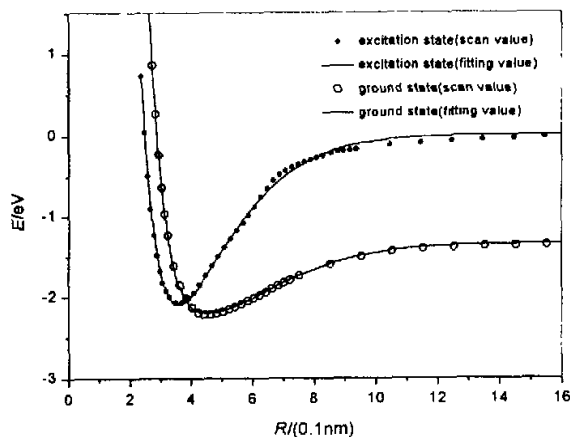


Fig. 2 The potential curve of Pu_2

Table 2 Murrell-Sorbie potential function parameters for U_2 and Pu_2

State	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	D_e/eV
$U_2(X^9\Sigma_g)$	18.226	110.29	252.66	1.6498
$U_2(^5\Sigma_g)$	16.512	108.40	569.23	3.9763
$Pu_2(X^{13}\Sigma_g)$	10.008	28.511	93.210	0.85438
$Pu_2(^{13}\Sigma_g)$	10.780	21.921	64.704	2.0938

The force constants and spectroscopic constants of U_2 and Pu_2 can be calculated by BWK method^[13], which are listed in table 3 and table 4.

Table 3 Spectroscopic parameters of U_2 and Pu_2

State	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	B_e/cm^{-1}	α_e/cm^{-1}	D_e/eV
$U_2(X^9\Sigma_g)$	0.38965	64.860	0.05481	0.0093135	0.00001	1.6498
$U_2(^5\Sigma_g)$	0.29927	71.228	-0.03074	0.015788	0.00004	3.9763
$Pu_2(X^{13}\Sigma_g)$	0.45375	28.658	0.03929	0.0066987	0.00002	0.85438
$Pu_2(^{13}\Sigma_g)$	0.35202	58.1072	0.05593	0.011129	0.00002	2.0938

Table 4 Force constants of U_2 and Pu_2

State	$f_2/(\text{a J/nm}^2)$	$f_3/(\text{a J/nm}^3)$	$f_4/(\text{a J/nm}^4)$
$U_2(X^9\Sigma_g)$	29.501	-413.40	507.9
$U_2(^5\Sigma_g)$	35.578	-1070.18	59839.6
$Pu_2(X^{13}\Sigma_g)$	5.905	-116.63	2493.6
$Pu_2(^{13}\Sigma_g)$	24.276	-495.09	8951.7

4 Summary and discussion

Using B3LYP with RECP for U and Pu, their potential energy curves of ground state and the lowest excited state are calculated, which show that their LBL are 0.38965nm and 0.45375nm for $U_2(X^9\Sigma_g)$ and $Pu_2(X^{13}\Sigma_g)$, and their SBL are 0.29927nm($U_2(^5\Sigma_g)$) and 0.35202nm($Pu_2(^{13}\Sigma_g)$). Due to the f-f coupling, there probably exist more than one minim point at the same multiplicity, which indicate the existence of bound metastable species. The SBL states show steep potential curves, and may indicate the existence of bound metastable species. While LBL states exhibit flat potential curves, the diffuse 6d and 7s orbitals of the actinide atom should have optimal overlap at long bond lengths. Using the same method, the energy of single atom is calculated. U atom is -51.503198a. u., and Pu atom is -71.761117a. u.. Regardless of U_2 or Pu_2 , their ground states lie below the separated atoms, one is 2.704eV, the other is 2.642eV. This shows the stability of actinide dimers is less than atomic.

The dissociation energy are 1.6498eV for $U_2(X^9\Sigma_g)$ and 0.85438eV for $Pu_2(X^{13}\Sigma_g)$, by the

least-square fitting. The results are agreement with the literature [14], where the valence bond model has been applied to calculate the dissociation energies, those of U_2 and Pu_2 are (1.7234 ± 0.6032) eV and (0.2585 ± 0.2585) eV, respectively. The available dissociation energy for Pu_2 is less than that of U_2 , its cohesion of the atoms must be due primarily to van der Waals interactions. Because of the ground state configuration $5f^3 6d^1 7s^2$ for U, the unpaired electron per U atom contributes towards bonding. In contrast, Pu_2 falls into the van der Waals class. Though the ground state configuration for Pu atom is $5f^6 7s^2$, which have unpaired 5f electrons, the 5f electrons are so localized, particularly for the second half of the series that they contribute insignificantly to the bonding. It should be van der Waals molecule, analogous to the rare gas diatomics, with very small dissociation energy.

The analytical potential energy function of ground states and the lowest energy excited states for U_2 and Pu_2 molecules are derived for the first time, and their equilibrium geometry force constants and spectroscopic data are also given out. Using the present potential energy functions of dimmers as the two-body terms, it has been derived the potential energy function of U_3 and Pu_3 , based on which the global potential for small polyatomic systems can usually be derived which is not outrageously complicated. They are accurate in the interaction region and should reproduce structural and spectroscopic data on stable species or transition states on the surface. A globally accurate potential function can always be written as a many-body expansion, in which the two-body potential is the base. The potential functions for U_3 and Pu_3 are in progress. The many-body expansion expressions will be arrived for clusters and the condensed phases of U and Pu.

References

- [1] Pucci R, March N H. *Phys. Rev. A*, 1986, **33**: 3511
- [2] Gingerich K A. *Symp. Faraday Soc.*, 1980, **14**: 109
- [3] Bursten B E, Ozin G A. *Inorg. Chem.*, 1984, **23**: 2910
- [4] Pepper M, Bursten B E. *J. Am. Chem. Soc.*, 1990, **111**: 7803
- [5] Ran M, Giang C, Gao T. *Chin. J. Chem. Phys.*, 2000, **4**: 430
- [6] Pepper M, Bursten B E. *Chem. Rev.*, 1991, **91**: 719
- [7] Becke A. *J. Chem. Phys.*, 1986, **84**: 4524
- [8] Hay P J, Wadt W R. *J. Chem. Phys.*, 1979, **71**: 1767
- [9] Hay P J. *J. Chem. Phys.*, 1983, **79**: 5469
- [10] Hay P J, Martin R L. *J. Chem. Phys.*, 1998, **109**: 3875
- [11] Shuai M B, Hu H R, Zhao P J. *Chin. J. Chem. Phys.*, 2000, **13**: 165
- [12] Zhu Z H. *Atomic and Molecular Reaction Statics*, Science Press, Beijing, 1996: 38
- [13] Zhu Z H, Yu H G. *Molecular Structure and Molecular Potential Energy Function*, Science Press, Beijing, Chap. 4, 1997
- [14] Brewer B, Winn J S. *Faraday Symp. R. Soc. Chem.*, 1980, **14**: 126

铜系双原子分子的从头算研究*

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摘要: 用相对论有效原子实势(RECP)和密度泛函方法(B3LYP), 采用 U 和 Pu 原子的紧缩价基集合[5s4p3d4f]/[3s3p2d2f], 优化了 U_2 和 Pu_2 分子的平衡结构, 得到它们的长键长(LBL)和短键长(SBL)分别为: U_2 分子是0.38965和0.29927 nm, Pu_2 分子是0.45375和0.35202 nm; 导出了基态和最低激发态的势能函数, 计算出它们的力常数、光谱数据和离解能。

关键词: U_2 ; Pu_2 ; 势能函数; 离解能

中图分类号: O561.1 **文献标识码:** A

* 国家工程物理研究院科学基金资助项目。

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收稿日期: 2000-12-19; 修回日期: 2001-04-12。