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STUDY OF ANALYTIC POTENTIAL ENERGY FUNCTION AND STABILITY FOR PuO^{n+} WITH DENSITY FUNCTIONAL THEORY*

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The theoretical study of PuO^{n+}(n=1,2,3) using a density functional method shows that PuO^+ ($X^6\Sigma^-$) and PuO^{2+} ($X^5\Sigma^-$, $^7\Sigma^-$, $^9\Sigma^-$) ions are stable, and the PuO^{3+} ($^4\Sigma^+$, $^6\Sigma^+$) ion is unstable. The analytic potential energy functions of $X^6\Sigma^-$ for PuO^+ and $X^5\Sigma^-$, $^7\Sigma^-$, $^9\Sigma^-$ for PuO^{2+} have been derived, and their force constants and spectroscopic data have been calculated.

Keywords: PuO^{n+}, molecular ions, potential energy function stability
PACC: 3120D, 3420

I. INTRODUCTION

For almost all neutral and singly charged diatomic molecules, the ground state has only one stationary point, namely that at the minimum. The Murrell-Sorbie function[1−7] is the most satisfactory theoretical method for accurately describing the behaviour of these neutral diatoms and singly charged diatomic ions.

However, doubly charged diatomic ions, e.g., molecule AB^{2+}, have more competitive dissociation channels, such as $A^{2+} + B$ or $A^+ + B^+$. The dissociation limits of molecule AB^{2+} are determined by the relation between single- and double-adiabatic ionization potentials, IP^+ and IP^{2+}, respectively.[8] For ground-state species, for which:

1. IP^{2+} (A or B) >IP^+ (A)+IP^+(B), thus AB^{2+} might show either a metastable or a repulsive character, the molecule constantly dissociates into A^++B^+; otherwise

2. IP^{2+} (A or B) <IP^+ (A)+IP^+(B), thus AB^{2+} can be stable and the dissociation limit must be A^{2+}+B.

The majority of the AB^{2+} ions reported so far belong to group (1), with A^++B^+ channel.[9−11] However, in this paper, study shows that the PuO^{2+} ions can be stable and their dissociation limit is Pu^{2+}+O. PuO^{3+} ions can be unstable and their dissociation limit is Pu^{2+}+O^+.

II. DETAILS OF CALCULATION

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. All calculations employed the Gaussian 94 program. The [3s3p2d2f] contracted basis sets and relativistic effective core potential (RECP) for Pu given in Ref.[12] and the 6-311G* basis set for O atom were used. Thus, for atom Pu, the three s orbital are expanded to five, six and one Gaussian functions, respectively; the three p orbital are expanded to four, five and one Gaussian functions, respectively; the two d orbital are expanded to one Gaussian functions, respectively; the two f orbital are expanded to two Gaussian functions, respectively. There are four s orbital for atom O and they are expanded to six, three, and one Gaussian functions, respectively; the three p orbital are expanded to three, one, and one Gaussian functions, respectively; the d orbital is expanded to one Gaussian function.

For PuO^{n+}, we use 54 symmetrical basis functions ($23A_1$ $5A_2$ $13B_1$ $13B_2$). The 54 symmetrical basis functions are expanded by 111 primitive Gaussian functions.

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Ⅲ. DISSOCIATION LIMIT AND ELECTRONIC STATES

The dissociation channels given by *ab initio* calculation of PuO^{n+} are

$PuO^+ \rightarrow Pu^+ + O$, $PuO^{2+} \rightarrow Pu^{2+} + O$

and $PuO^{3+} \rightarrow Pu^{2+} + O^+$.

The separated atomic group method[13,17] is used to derive the possible electronic states for PuO^{n+}. The ground states for Pu^+, Pu^{2+}, O and O^+ are ^8F_g, ^7F_g, ^3P_g and ^4S_u, respectively,[14−16] which are the components of irreducible representation of the $SU(n)$ group. PuO^{n+} belong to the $C_{\infty v}$ group. The irreducible representations of the $SU(n)$ group can be resolved into that of the $C_{\infty v}$ group, that is, the possible electronic states of PuO^{n+} are given. $Pu^+(^8F_g)$ and $O(^3P_g)$ are resolved into the direct sum of $C_{\infty v}$ as follows:

$$^8F_g = {}^8\Sigma^- \oplus {}^8\Pi \oplus {}^8\Delta \oplus \cdots,$$
$$^3P_g = {}^3\Sigma^- \oplus {}^3\Pi.$$

Their direct product and its reduction are

$$^3P_g \oplus {}^7F_g = ({}^3\Sigma^- \oplus {}^3\Pi) \oplus ({}^8\Sigma^- \oplus {}^8\Pi \oplus {}^8\Delta \oplus \cdots) = {}^{6,8,10}\Sigma^+ \oplus {}^{6,8,10}\Pi \oplus {}^{6,8,10}\Delta \oplus \cdots \oplus {}^{6,8,10}\Sigma^+ \oplus [{}^{6,8,10}\Sigma^-] \oplus \cdots,$$

where, $[^{6,8,10}\Sigma^-]$ are the antisymmetric direct product, all are the possible electronic states of PuO^+. Similarly, those of PuO^{2+} are $^{5,7,9}\Sigma^-$, $^{5,7,9}\Sigma^+$, $^{5,7,9}\Pi$, $^{5,7,9}\Delta, \cdots$, and those of PuO^{3+}, $^4\Sigma^+$, $^6\Sigma^+, \cdots$.

The electronic configuration of the ground state for PuO^+ is

α electrons $\sigma\ \sigma\ \sigma\ \pi\ \pi\ \sigma\ \pi\ \pi\ \sigma\ \delta\ \delta\ \pi\ \pi\ \sigma$,

β electrons $\sigma\ \sigma\ \sigma\ \pi\ \pi\ \sigma\ \pi\ \pi\ \sigma$,

The ground state is $^6\Sigma^-$.

The electronic configuration of the ground state for PuO^{2+} is

α electrons $\sigma\ \sigma\ \sigma\ \pi\ \pi\ \sigma\ \sigma\ \delta\ \delta\ \phi\ \phi\ \pi\ \pi$,

β electrons $\sigma\ \sigma\ \sigma\ \pi\ \pi\ \sigma\ \sigma\ \pi\ \pi$,

The ground state is $^5\Sigma^-$.

Ⅳ. POTENTIAL ENERGY FUNCTION AND STABILITY

The potential energy curves of *ab initio* calculation are shown in Figs.1, 2, 3 and 4, where the solid lines in Figs.2 and 3 are fitted by the Murrell-Sorbie (M-S) potential energy function[7]

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

where $\rho = R - R_e$, R is the interatomic distance, and R_e is its equilibrium distance.

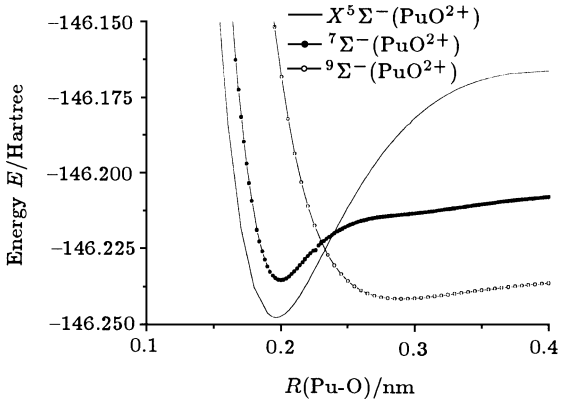


Fig.1. Potential energy curves of PuO^{2+}.

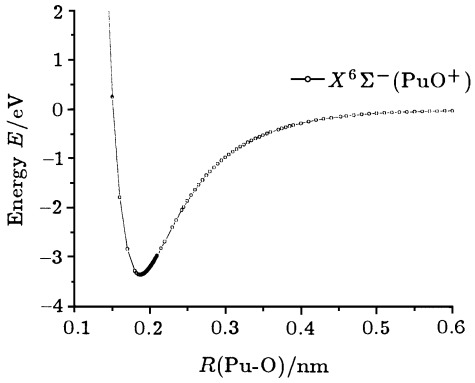


Fig.2. Potential energy curve of PuO^+.

By iterating a system of normal equations based on a least-squares fit, the parameters a_1, a_2 and a_3 of Eq.(1) have been calculated for PuO^+ and PuO^{2+} ions and listed in table 1. From these it is easy to derive f_2, f_3 and f_4, and then calculate spectroscopic data ω_e, $\omega_e X_e$, B_e, α_e using Eqs.(2)–(7) (see Table 2). The corresponding formulae are

$$f_2 = D_e({a_1}^2 - 2a_2), \quad (2)$$

$$f_3 = -6D_e(a_3 - a_1a_2 + {a_1}^3/3), \quad (3)$$

$$f_4 = D_e(3{a_1}^4 - 12{a_1}^2a_2 + 24a_1a_3), \quad (4)$$

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \quad (5)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(\frac{f_3R_e}{3f_2} + 1\right), \quad (6)$$

$$\omega_e\chi_e = \frac{B_e}{8}\left(-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right). \quad (7)$$

Table 1. Parameters of the analytical potential function (1).

Dissociation limits	R_e/nm	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}
$PuO^+(X^6\Sigma^-)\rightarrow Pu^+(^8F_g)+O(^3P_g)$	0.1875	23.091	–82.60	943.2
$PuO^{2+}(X^5\Sigma^-)\rightarrow Pu^{2+}(?)+O(?)$	0.196	40.955	494.94	2540.7
$PuO^{2+}(^9\Sigma^-)\rightarrow Pu^{2+}(^7F_g)+O(^3F_g)$	0.29	33.799	246.36	6009.9
$PuO^{2+}(^7\Sigma^-)\rightarrow Pu^{2+}(?)+O(?)$	0.2	60.159	917.21	4486.5

Table 2. Derived force constants and spectroscopic data.

Electronic state	f_2/fJ.nm^{-2}	f_3/fJ.nm^{-3}	f_4/fJ.nm^{-4}	ω_e/cm^{-1}	$\omega_e X_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
$PuO^+(X^6\Sigma^-)$	0.376	–22.4560	1024.714	652.311	4.530	0.3198	0.00253
$PuO^{2+}(X^5\Sigma^-)$	0.244	–11.0015	346.034	525.447	2.773	0.2927	0.00191
$PuO^{2+}(^9\Sigma^-)$	0.0198	–1.9266	164.692	149.5921	10.544	0.1337	0.00604
$PuO^{2+}(^7\Sigma^-)$	0.227	–16.7086	755.648	507.0829	8.0017	0.2811	0.00365

The potential energy curves in Figs.1, 2 and 3 show the minimum corresponding to the stable equilibrium structure of states for PuO^+ and PuO^{2+} ions, and Fig.4 shows that states $^4\Sigma^+$ and $^6\Sigma^+$ of PuO^{3+} ion are the repulsive states.

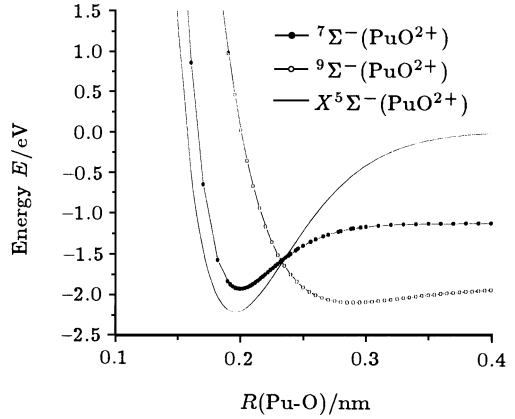


Fig.3. Potential energy curves of PuO^{2+}.

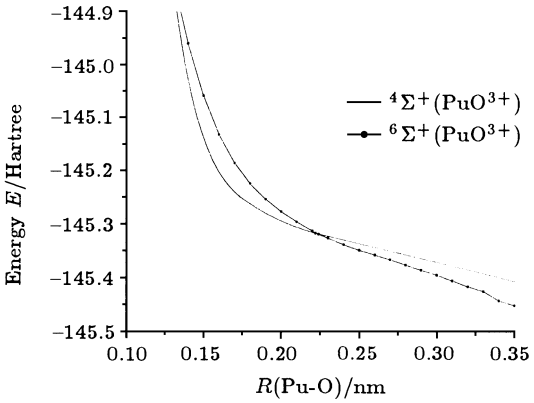


Fig.4. Potential energy curve of PuO^{3+}.

The stability of PuO^+, PuO^{2+} and PuO^{3+} is related to the dissociation channels. The dissociation channel for PuO^+ and PuO^{2+} are Pu^+ + O and Pu^{2+} + O, respectively. There are chemical bond and nuclear repulsive forces between the two atoms, and there exist, as usual, one minimum corresponding to the stable state on the potential energy curves. However, the dissociation channel for PuO^{3+} is Pu^{2+} + O^+, hence, there will be considerable Coulomb repulsive force between positive Pu^{2+} and O^+, besides the chemical bond and nuclear repulsive forces. If Coulomb repulsive and nuclear repulsive forces dominate over the others, the potential energy curve is repulsive completely without minimum, such as the cases of HF^{2+}, HCl^{3+}, HCl^{2-} ions[9] and PuH^{3+},[17] PuO^{3+} ions. [14] Equilibrium between the chemical bond force and the nuclear repulsive force will cause an energy minimum and equilibrium between the chemical bond force and Coulomb repulsive force will result in an energy maximum, such as the cases of HCl^{2+}, HBr^{2+}, HI^{2+} ions[9] and BH^{2+}, CH^{2+}, NH^{2+} ions.[11]

It is well known that there are three different types of potential energy maximum for diatomic molecules or ions, i.e. the potential energy maximum resulting from predissociation, or van der Waals interaction, or the non-crossing of potential curves of two electronic states with the same irreducible representation for a given molecular group. A fourth is due to Coulomb repulsion between the ionic pair of diatom. The Coulomb repulsive potential is closely related to interionic distance and proportional to the product of ionic charges, therefore, highly charged molecular ions would always be unstable.

The present work further confirms the maximum caused by Coulomb repulsion. The energy maximum does not appear in the ground state $X^5\Sigma^-$ and two exited states $^7\Sigma^-$, $^9\Sigma^-$, although PuO^{2+} belongs to

the doubly charged ion. The first ionization potentials of lanthanides are considerably low and not much at variance in this series. The first, second and third ionization potentials for U are 4.96, 11.07 and 17.74 eV, respectively, and those for O are 13.58, 35.15 and 55.13 eV, respectively. So, the positive charge distribution for PuO^{2+} will not be possible as Pu^{+} and O^{+}, but Pu^{2+} and O. Therefore, the potential energy maximum does not appear. Similarly, there is no potential energy maximum in PuO^{+} ion. Thus, the PuO^{3+} ion cannot exist stably because of the strong Coulomb repulsion between positive charged ions Pu^{2+} and O^{+}.

References

[1] Murrell J N and Sorbie K S 1974 *J. Chem. Soc. Faraday Trans.* **2** (70) 1552

[2] Murrell J N, Carter S, Farantos S C, Huxley P and Varandas A J C 1984 *Molecular Potential Energy Functions* (New York: Wiley)

[3] Zhu Z H, Shen S Y and Mou W M 1984 *J. Mol. Sci.* **2** 79

[4] Huxley P and Murrell J N 1983 *J. Chem. Soc. Faraday Trans.* **2** (79) 323

[5] Zhu Z H and Xu Z R 1985 *J. Chengdu Univ. Sci. Technol.* **4** 31 (in Chinese)

[6] Wang F H, Jang D L and Zhu Z H 1997 *J. Sichuan Univ.* **2** 198 (in Chinese)

[7] Zhu Z H and Yu H G 1997 *Molecular Structure and Molecular Potential Energy Function* (Beijing: Science Press)

[8] Bruna P J and Wrigh J S 1990 *J. Chem. Phys.* **93** 2617

[9] Zhu Z H, Wang F H, Chen B, Tan M L and Wang H Y 1997 *Mol. Phys.* **92** 1061

[10] Wang F H, Zhu Z H, Yang C L and Jing F Q 1998 *Chin. Phys. Lett.* **15** 715

[11] Wang F H, Zhu Z H and Jing F Q 1998 *J. Mol. Struct.* **453** 71

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

[13] Zhu Z H 1996 *Atomic and Molecular Reaction Statics* (Beijing: Science Press)

[14] Li Q, Liu X Y, Zhu Z H, Gao T, Fu Y B and Wang X L 2000 *Acta Physico-Chem. Sin.* **16**(11) 978 (in Chinese)

[15] Koga T and Watanabe S 1995 *Int. J. Quant. Chem.* **54**(4) 261

[16] Martin W C, Hagan L and Reader J 1974 *J. Phys. Chem. Ref. Data* **3**(3) 771

[17] Li Q, Liu X Y, Zhu Z H, Wang H Y, Fu Y B and Wang X L 2000 *Acta Phys. Sin.* **49** 2347 (in Chinese)