

Pu_4^+ 分子离子的几何构型与 Jahn-Teller

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摘 要: 在 Pu 原子的相对论有效原子实势近似下, 用密度泛函 B3LYP 方法对 Pu_4^+ 分子离子的几何构型及其电子状态进行理论计算, 得到了 6 种稳定的几何构型, 其中平面 C_{2v} 结构最稳定. T_d 构型不能稳定存在, 并详细讨论了 T_d 和 D_{4h} 构型的 Jahn-Teller 效应, 讨论结果显示它们的各种畸变方式都符合群的分解原理, 从而证明 Pu_4^+ 分子离子的 T_d 和 D_{4h} 构型存在 Jahn-Teller 效应.

关键词: 几何构型; Pu_4^+ ; Jahn-Teller 效应

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Geometrical Configuration of Pu_4^+ and the Jahn-Teller Effect

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Abstract It demonstrates six stable geometrical configurations of electronic states for Pu_4^+ using the density functional method B3LYP with relativistic effective core potentials. The most stable electronic state of Pu_4^+ is of the planar C_{2v} configuration. The Jahn-Teller distortions from the configurations $\text{Pu}_4^+(T_d)$ and $\text{Pu}_4^+(D_{4h})$ exist. The analysis of the relationships among these various geometrical configurations, based on the Jahn-Teller effect, vibronic interaction and the resolution of group representations, is in agreement with the calculated results.

Keywords Geometrical configuration, Pu_4^+ , Jahn-Teller effect

1 Introduction

One major current interest is the structure of plutonium compounds. The analytic potential energy function for $\text{PuO}^{[1]}$, $\text{PuO}_2^{[2]}$, $\text{PuH}^{[3]}$, $\text{PuH}_2^{[4]}$, $\text{PuO}^{n+ [5]}$, $\text{PuH}^{n+ [6]}$, $\text{PuN}^{n+ [7]}$, PuX^{2+} ($X = \text{O}, \text{H}, \text{N}, \text{F}^{[8]}$), PuX^+ ($X = \text{H}, \text{O}, \text{N}, \text{C}, \text{F}^{[9]}$) have been derived. The potential curves for the doubly charged diatomic cations are all stable with a potential minimum and without a potential maximum. The triply charged diatomic cations are all unstable. This is distinct from the doubly charged diatomic ions of light element. It is well known that^[10, 11] for almost all neutral diatomic, the potential curves of the ground state have only one mini-

mum, but doubly charged diatomic ions, for example, HCl^{2+} , HI^{2+} , BH^{2+} , CH^{2+} and NH^{2+} , always have a potential minimum due to the balance of nuclear repulsion and chemical bond forces and a potential maximum caused by the balance of chemical bond forces and ionic Coulomb repulsion. However, for the potential curves of doubly charged diatomic ions for the heavy element Pu, for example, PuO^{2+} , PuH^{2+} , PuN^{2+} and PuC^{2+} , this is not the case and they have only minimum. These ions have no maximum in their potential curves, because the positive charges are on the Pu atom and thus, and there will be no ionic Coulomb repulsion. This is because of the extremely low ionization potential of Pu, and the second ionization po-

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tential may be less than the first ionization potential of H, N, O and C.

The geometrical optimizations for the possible multiplicity of Pu_2 , i. e. $2S + 1 = 1, 3, 5, 7, 9, 11$ and 13 derived from the ground state 7F_g of Pu indicate that^[12] the energies of these states decrease gradually with the increase in multiplicity, and have a rather large energy difference $E(2S + 1 = 13) - E(2S + 1 = 1) = -16.435$ eV. Similarly, the geometrical optimizations for the possible multiplicities of Pu_3 , i. e. $2S = 1, 3, 5, 7, 9, 11, 13, 15, 17$ and 19, also show that^[13] the D_{3h} symmetry with $R = 0.42878$ nm and $2S + 1 = 19$ for Pu_3 is the lowest stable one. What are the implications of this situation? It means that if there are 6 valence electrons with parallel spin in atomic Pu, there will be 12 and 18 valence electrons of parallel spin in Pu_2 and Pu_3 , respectively. Therefore, spin-polarization is rather more important in the actinide molecules than in the light element molecules. It will be shown later that the multiplicity of $2S + 1 = 25$ and 26 for cluster Pu_4 and Pu_4^+ , respectively, is the most stable state regardless of geometry. This may be a

significant feature of actinide element molecules.

We are exploring this feature for other actinide element molecules. The present work is to examine a possible Jahn-Teller effect in Pu_4^+ . It is well known that there is a noticeable Jahn-Teller effect for C_4^{2+} ^[14] and H_4^{+} ^[15].

2 The geometrical configurations of Pu_4^+

A full electron calculation for Pu_4^+ is rather time consuming, so it is better to consider only 16 valence electrons $5f^6 6s^2 6p^6 7s^2$. The relativistic effective core potential (RECP) of Martin and Hay including mass-velocity^[16], Darwin and spin-orbit coupling corrections was used to replace 78 of core electrons. The corresponding valence electron basis^[16] was used in the present work. Based on the density functional method B3LYP, the geometry optimizations of Pu_4^+ have been carried on using the program Gaussian 98^[17]. It is found that there are at least six stable configurations. All of these configurations with their point group, electronic state, geometrical structure and energy are listed in Table 1.

Table 1 The geometry, symmetry and energy of Pu_4^+

No.	Geometry	Symmetry and state	Bond length (nm) and bond angle/ $(^\circ)$	- Energy/a. u.
1		C_{2v} (${}^{26}B_2$)	$R_{23} = R_{24} = 0.46454$ $R_{12} = 0.44925$ $\angle 324 = 50.9324$ $\angle 123 = \angle 124 = 154.5338$	286.9364247
2		D_{2h} (${}^{26}B_{1u}$)	$R_{12} = R_{34} = 0.40078$ $R_{23} = R_{14} = 0.55713$	286.8980752
3		$C_{\infty v}$ (${}^{26}\gamma$)	$R_{12} = 0.41308$ $R_{23} = 0.41684$ $R_{34} = 0.43038$	286.8845431
4		$D_{\infty h}$ (${}^{26}\gamma$)	$R_{12} = R_{34} = 0.40552$ $R_{23} = 0.46789$	286.8780015
5		C_{2v} (${}^{26}A_1$)	$R_{12} = R_{13} = 0.42938$ $R_{14} = 0.40493$ $\angle 213 = 56.0451$ $\angle 214 = \angle 314 = 61.8666$	286.8726445
6		D_{4h} (${}^{26}\gamma$)	$R_{12} = R_{23} = R_{34} = R_{14} = 0.35256$	286.7860201

Because of the Jahn-Teller effect, no stable configuration of Pu_4^+ (T_d) can be found by geometry optimization. However, there is a less stable one for D_{4h} (No. 6) symmetry with multiplicity $2S + 1 = 26$, which must be a nondegenerate electronic state. Similarly,

the electronic state of $D_{\infty h}$ (No. 4) may also be nondegenerate, otherwise it will be distorted owing to the Renner-Teller effect.

The most stable configuration is ${}^{26}B_2$ (plane C_{2v}), No. 1. The next stable configuration is No. 2 with the

electronic state ${}^{26}\text{B}_{1u}$ of D_{2h} symmetry. The energy difference between ${}^{26}\text{B}_2$ and ${}^{26}\text{B}_{1u}$ is 1.044 eV. The energy difference between No. 1 (plane C_{2v} symmetry) and No. 6 (square D_{4h} symmetry) is 4.093 eV. One of the reasons for the variety of geometrical configurations of Pu_4^+ is the Jahn-Teller effect.

3 Square geometry Pu_4^+ (D_{4h}) and Jahn-Teller effect

The Jahn-Teller theorem states that a symmetric nonlinear molecule in a degenerate electronic state (other than Kramers degeneracy) distorts in such a way as to reduce the symmetry and therefore remove the degeneracy. Thus , orbitally nondegenerate ground states are the rules rather than the exception. The Jahn-Teller theorem is rather than general , however , and does not tell us why there is such a distortion and what distortion will occur. It is known that there are usually some other mechanisms for relieving the degeneracy of these orbitals , for example , spin-orbit coupling or crystal forces etc.

Jahn-Teller distortions can be classified by vibronic interaction analysis ^[18,19]. Based on the normal vibration analysis ^[20] , there are five fundamental vibration modes for Pu_4^+ (D_{4h}) , i. e. ν_1 (A_{1g}) , ν_2 (B_{1g}) , ν_3 (B_{2u}) , ν_4 (B_{2g}) and ν_5 (E_u) , where , ν_1 (A_{1g}) is the totally symmetric normal vibration and ν_2 (B_{1g}) and ν_4 (B_{2g}) are the nontotally symmetric normal vibration modes , which cause Jahn-Teller instability in the degenerate states E_g or E_u of Pu_4^+ (D_{4h}). When the nuclei move into the displaced positions , the symmetry will be lower. Therefore , ν_2 (B_{1g}) and ν_4 (B_{2g}) will distort the square geometry D_{4h} towards a rectangle geometry D_{2h} and a rhomboid geometry D_{2h} or C_{2h} , respectively. It is obvious that the configuration D_{2h} (No. 2) is indeed rather stable from the present calculations.

As for what electronic state , i. e. the irreducible representations , for these configurations , i. e. D_{2h} , which should be formed , this can be described by neither the Jahn-Teller theorem nor vibronic interaction analysis. On the other hand , it is completely determined by the resolution of group representations ^[21,22]. For ex-

ample , the irreducible representations E_g and E_u of D_{4h} can be resolved into the direct sum of the representations of D_{2h} as

$$\begin{array}{cccccc} \text{D}_{4h} & \text{D}_{2h}(\text{Z} \rightarrow \text{Z}) & \text{D}_{2h}(\text{Z} \rightarrow \text{X}) & \text{C}_{2h}(\text{Z} \rightarrow \text{Z}) & \text{C}_{2h}(\text{Z} \rightarrow \text{X}) & \\ \text{E}_g & \text{B}_{2g} + \text{B}_{3g} & \text{B}_{1g} + \text{B}_{2g} & \text{B}_g & \text{A}_g + \text{B}_g & \\ \text{E}_u & \text{B}_{2u} + \text{B}_{3u} & \text{B}_{1u} + \text{B}_{2u} & \text{B}_u & \text{A}_u + \text{B}_u & \end{array}$$

Where the notations $\text{Z} \rightarrow \text{Z}$ and $\text{Z} \rightarrow \text{X}$ represent the case that the Z -axis of D_{4h} coincides with Z -axis or X -axis of D_{2h} .

It is shown that the orbitally nondegenerate electronic ground states caused by distortion , i. e. ${}^{26}\text{B}_{1u}$ of No. 2 is indeed the irreducible components of the resolution of group representations. Therefore , the calculations are in good agreement with the analysis given earlier.

4 Tetrahedral geometry Pu_4^+ (T_d) and Jahn-Teller effect

From the normal vibration analysis of Pu_4^+ (T_d) ^[20] , there are three fundamental vibration modes , i. e. ν_1 (A_1) , ν_2 (E) and ν_3 (T_2) , where A_1 , and E and T_2 are one , two and three-fold degenerate vibrational modes , respectively. A_1 is a totally symmetric vibration , E and T_2 are nontotally symmetric vibrations which will lead to the geometric distortion.

Similarly , what orbitally nondegenerate electronic state will be formed the distortion of orbitally degenerate electronic states ? It can be determined by the resolution of group representation as follows :

$$\begin{array}{cccc} \text{T}_d & \text{C}_{2v} & \text{C}_{3v} & \text{D}_{2d} \\ \text{A}_1 & \text{A}_1 & \text{A}_1 & \text{A}_1 \\ \text{A}_2 & \text{A}_2 & \text{A}_2 & \text{B}_1 \\ \text{E} & \text{A}_1 + \text{A}_2 & \text{E} & \text{A}_1 + \text{B}_1 \\ \text{T}_1 & \text{A}_2 + \text{B}_1 + \text{B}_2 & \text{A}_2 + \text{E} & \text{A}_2 + \text{E} \\ \text{T}_2 & \text{A}_1 + \text{B}_1 + \text{B}_2 & \text{A}_1 + \text{E} & \text{B}_2 + \text{E} \end{array}$$

where we have had the irreducible components of B_2 and A_1 for C_{2v} , which are in agreement with the present calculations , i. e. ${}^{26}\text{B}_2$ and ${}^{26}\text{A}_1$ for C_{2v} . It is noticed that no stable T_d configuration could be found. Therefore , the Jahn-Teller distortion for Pu_4^+ (T_d)

may be rather more important than that for Pu_4^+ (D_{4h}).

5 Spin-polarization effect

As mentioned earlier, for Pu , Pu_2 , Pu_3 , Pu_4 and Pu_4^+ , there are 6, 12, 18, 24 and 25 unpaired electron spins, respectively, that is, all these electrons are placed into different spatial orbitals. The unbalanced spin can be called spin polarization. The exchange integrals for parallel electrons are positive, and can low the total energy of systems. However, the electron correlation energy may be mainly associated with the consequences of electron pairing, and this can also lower the total energy of a system. If there is not enough electron pairing, the total energy of system will be raised. It is known that the electron correlation energy is remarkably constant for two-electron systems^[23, 24].

Zhu Zhenghe proposed that the electron correlation energy does not change much with the atomic number^[24]. However, the spin polarization effect increases for actinide element molecules. Therefore, the actinide element molecules will have many parallel spin electrons and high multiplicity states will have the lowest energy. The Pu cluster is one of the typical examples.

We do agree with the comments that the lanthanide dimmer can have a high multiplicity because of the compact nature of the unpaired electrons in the 4f sub-shell. A similar effect occurs indeed for the actinides.

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