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U⁺与CO₂气相反应的密度泛函理论研究

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摘要: 运用密度泛函理论(DFT)中的B3LYP方法, U原子用含相对论有效原子实势(ECP)校正的基组(SDD), C、O原子采用6-311+G(d)基组, 对气相中U⁺和CO₂的反应进行了理论研究. 通过研究二重和四重自旋态的反应势能面(PESs), 优化得到了两条反应路径的反应物、中间体、过渡态和产物的结构. 用“两态反应”(TSR)分析反应机理, 结果表明体系的优先选择路径为高自旋态进入和低自旋态离开反应, 发生在四重态和二重态的自旋多重度的改变使得整个反应系统能以一个低能反应途径进行.

关键词: 反应机理; 密度泛函理论; 相对论有效原子实势; 势能面; 自旋态
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Density Functional Theory Study of the Gas-Phase Reaction of U⁺ with CO₂

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Abstract: The gas-phase reaction of U⁺ with CO₂ was investigated with B3LYP density functional theory (DFT) in conjunction with the relativistic effective core potential (ECP) of the SDD basis sets for U and the 6-311 + G(d) basis set for C and O. The potential energy surfaces (PESs) of the reaction system were explored in detail for both doublet and quartet spin states. The geometries of reactants, intermediates, transition states, and products in the two reaction pathways were fully optimized. The reaction mechanism was analyzed using “two-state reactivity (TSR).” The calculations demonstrate that the reaction preferentially involves the high-spin state entrance channel and the low-spin state exit channel. The spin multiplicity transition from the quartet state to the doublet state enables the reaction system to find a lower energy pathway.

Key Words: Reaction mechanism; Density functional theory; Relativistic effective core potential; Potential energy surface; Spin state

1 Introduction

Actinides, as a group of strongly correlated and heavy fermion systems, especially have received notable increasing interests.^{1–3} Uranium is a very typical naturally occurring actinide metal and most generally used for nuclear fission in the field of aerospace and military industry.^{4,5} The uranium atom has six valence electrons with only three 5f electrons hybridizing with

the 6d and 7s electrons and can rapidly react with oxygen, carbon dioxide, and water when it is exposed at the air atmosphere.^{6–9} It has already been shown that the nuclear reaction ability of uranium declined obviously when environmental gases cause uranium surface to corrode. Moreover, the erosive consequences will distinctly reduce the performance of the given uranium compounds.^{10–12} Hence, theoretical studies on the

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uranium surface reaction in the presence of environmental gases have a potential interest. We can obtain a better understanding of the uranium surface corrosion mechanism and confirm the environmental consequences of nuclear materials.

The uranium surface corrosion process is one of the most complex metal oxidation reactions due to the high reactivity of uranium with CO_2 , CO , and O_2 . The study of O_2 , CO , and CO_2 adsorptions on thorium(111) crystal face and on polycrystalline-uranium has been performed using auger electron spectroscopy and second ion mass spectroscopy.¹³ Ultraviolet and X-ray photoelectron spectroscopy have been used to study CO_2/CO adsorption on polycrystalline U, UNi_3 , and UNi_5 .¹⁴ At 73 K, both dissociative adsorption and molecular chemisorption were observed at low exposure. The degree of molecular chemisorption was found to increase with the Ni content of the surface. On the other hand, only dissociative initial adsorption was observed on pure U. Some fundamental insight into such processes can be achieved by studying the reactions of uranium cation with CO_2 in the gas phase.

Koyanagi and Bohme¹⁵ carried out an experimental investigation on transition metal cations with carbon dioxide in the gas phase. It was found that carbon dioxide reacted in a bimolecular fashion by oxygen atom transfer only with early transition-metal cations. As expected, the complicated behavior was detected because the ground states of the reactants and products have different spin states. A non-adiabatic way may go along on two or more potential energy surfaces involving a change in the spin states, denoted as “two state reactivity” (TSR).^{16–19} Based on the above examinations, a deep understanding on the reactions of carbon dioxide with transition metal cations can be achieved.

The rapid growth of theoretical achievements has drastically changed the research way and quantum chemistry is now able to explore the properties and reactions of the uranium associated reactions. Our research group recently reported theoretical investigations of interatomic potential energy surface of diatomic uranium and UO .^{20,21} Meanwhile, the three-dimensional potential energy surfaces (PESs) of the $\text{U}-\text{O}_2$ interaction were explored to investigate reaction mechanism of uranium with oxygen.²² In this paper, DFT-B3LYP calculations are adopted to survey the reaction pathways of carbon dioxide with U^+ . The structures of the reactants, products, intermediates, and transition states (TSs) as well as their accurate energies are obtained. The crossing point (CP) between the two potential energy surfaces (PESs) of different spin states is discussed.

2 Computational details

All molecular geometries including reactants, intermediates, transition states, and products were fully optimized. The spin-unrestricted Becke's three parameter hybrid functional combined with the Lee, Yang, and Parr (LYP) correlation functional known as UB3LYP was used in our calculations. The UB3LYP^{23,24} functional has been successfully employed to

study on transition metal cations reaction with carbon dioxide.^{25,26} It is worth noting that UB3LYP functional can accurately describe PESs of the reaction system containing a relatively large number of electrons. The 6-311+G* basis set was used for O and C. For U the Stuttgart/Dresden relativistic effective core potential (RECP) basis set SDD²⁷ was applied, with a [8s7p6d/6s5p3d] basis set for 5s5p5d6s valence electrons. All stationary points are characterized by vibrational analysis and the zero-point energy (ZPE) corrections are included. The transition states characterized by only one negative eigenvalue of the Hessian matrix all represent saddlepoints. The intrinsic reaction coordinate (IRC) calculation was employed to survey the minimum energy path from transition states to the corresponding minima. The reaction path was found and the correct transition state was located. Computations were carried out with the Gaussian 03 program package.²⁸

3 Results and discussion

The optimized geometry for the reactants, intermediates, transition states, and products in doublet and quartet states are collected in Fig.1. The potential energy diagrams connecting the reaction intermediates and the transition states in two different spin surfaces are displayed in Fig.2. The single-point energy profiles in two spin states along the IRC of the quartet state in the crossing region are depicted in Fig.3, the structure of CP is also included. Table 1 shows the relative energies for the above optimized species and activation energies which are calculated at UB3LYP level.

3.1 Reaction process in two different spin surfaces

According to the previous study proposed by Sodupe *et al.*,²⁹ when the first-row transition metal cations are bound to CO_2 electrostatically, the linear $\eta^1\text{-O}$ (end-on) coordination is the most favorable because the leading term is charge-quadrupole and CO_2 has a negative quadrupole moment. As shown in Fig.1, along the reaction pathway, there are IM1, TS₁₂, IM2, TS₂₃, and IM3 species in turn. As expected, the reaction is initiated rapidly by U^+ and CO_2 colliding end-on with each other. There are two possible intermediates $^3\text{IM1}$ and $^4\text{IM1}$ in doublet and quartet spin states. $^3\text{IM1}$ and $^4\text{IM1}$ are encounter complexes for the interaction of U^+ and CO_2 due to the different multiplicity of U^+ . Both IM1 structures are planar and have C_s symmetry. There is only a small asymmetry in the two CO bond lengths because the attraction of U^+ and CO_2 is mainly electrostatic. The CO bond length which is conjunct to uranium ion increases about 0.002 nm, while the other CO bond length decreases about 0.002 nm. It is very similar to the first transition-metal cation reaction with CO_2 .²⁹ From the data in Fig.2 and Table 1, it is noted that $^3\text{IM1}$ and $^4\text{IM1}$ locate below the corresponding reactants by 151.30 and 121.29 $\text{kJ}\cdot\text{mol}^{-1}$, while $^4\text{IM1}$ is more stable than $^3\text{IM1}$ by 69.03 $\text{kJ}\cdot\text{mol}^{-1}$.

In doublet and quartet PESs, the next step is associated with rearranging to form the IM2 intermediate *via* the transition structure TS₁₂. In the intermediate structure IM2, the CO_2 mole-

Fig.1 Geometries of the critical points on the potential energy surface

bond length in nm, bond angle in degree

Fig.2 Diagram for the reaction of $\text{U}^+ + \text{CO}_2$ on two spin state PESs E_R : relative energy

cule has remarkably changed its symmetrical structure, in which CO bond length adjacent to uranium ion is elongated to 0.1426 nm in doublet and 0.1483 nm in quartet spin states. After IM2, the reaction proceeds to form the IM3 *via* transition state TS_{23} , in which the stretched CO bond continues to elongate. Notably, in the IM3 structure, the C—O bond becomes nearly broken since it is elongated to over 0.32 nm, while the concerted $\text{U}^+\text{—O}$ bond is formed since the bond length is about 0.18 nm. The last step is rupture of C—O bond in the IM3 resulting in the products UO^+ and CO.

As can be seen from Fig.2 and Table 1, at the initial step of the reaction, $^4\text{U}^+ + \text{CO}_2$ is predicted to be more stable than the

$^2\text{U}^+ + \text{CO}_2$ entrance channel by $99.04 \text{ kJ} \cdot \text{mol}^{-1}$ at the B3LYP/6-311+G(d)USDD level. Simultaneously, $^4\text{IM1}$ lies below $^2\text{IM1}$ by $69.03 \text{ kJ} \cdot \text{mol}^{-1}$. These all suggest that the initial reaction favors pathway of high spin state. After IM1, it is apparent that the quartet PES is always higher than the doublet PES. Since energies of the species on quartet PES are significantly higher than those on doublet PES, the following reaction is more likely to proceed through the doublet pathway. Based on the above discussions, we know that the reaction of ground-state $^4\text{U}^+$ with CO_2 leads to excited-state products, $^2\text{UO}^+$ and CO.

3.2 Crossing between the two PESs

The fundamental insight into the potential energy surface

Fig.3 Potential energy curve-crossing point diagram between two spin state PESs

Table 1 Energies of various species in the reaction of $\text{U}^+ + \text{CO}_2$

Species	$E_R/(\text{kJ} \cdot \text{mol}^{-1})$		$E^\ddagger/(\text{kJ} \cdot \text{mol}^{-1})$	
	double spin state	quartet spin state	double spin state	quartet spin state
$\text{U}^+ + \text{CO}_2$	99.04	0.00	—	—
IM1	-52.26	-121.29	—	—
TS ₁₂	-0.68	83.34	51.58	204.63
IM2	-299.36	71.62	—	—
TS ₂₃	-224.75	151.69	54.61	80.07
IM3	-256.24	139.83	—	—
$\text{UO}^+ + \text{CO}$	-76.67	202.19	—	—

$E^\ddagger$: activation energy

(PES) crossing behavior found in the thermal chemical reaction of transition-metal compounds was firstly reported by Armentrout¹⁸ and experimentally confirmed by Schroder *et al.*¹⁶ Those reactions show that PES-crossing behavior may involve a change in the spin states and thus proceed *via* a non-adiabatic way on two or more potential energy surfaces, denoted as “two state reactivity (TSR)”. As a matter of fact, the thermal chemical reactions of transition-metal compounds are often spin-forbidden in that the reactants and products involved have different overall electronic spin states. “Two state reactivity” reactions which involve spin-inversion (SI) and intersystem-crossing (ISC) may enable the system to find and follow low-energy reaction pathways that would not be accessible otherwise.

Crossing seams and spin inversion processes are important to understand the mechanism of “two state reactivity” reaction such as the reaction of U^+ with CO_2 . The potential energy surface (PES) of the system that consists of four atoms is a function of internal degree of freedom of dimension 6. As a result, the crossing seam between the two PESs is a ‘line’ of dimension 5, and it is difficult to perform a detailed inspection of the crossing seam as a practical example. According to the “two-state reactivity” postulate, the reaction entrance channel prefers to the quartet surface and exit channel prefers to the doublet surface. So the crossing region is approximately located between IM1 and IM2. As it is clearly seen in Fig.2, the energy of saddlepoint TS₁₂ on quartet PES is more than that of saddlepoint TS₁₂ on doublet PES. It would appear, therefore, that the

crossing point (CP) should be located in the region from IM1 to TS₁₂.

An effective approach suggested by Yoshizawa³⁰ is taken to approximately locating the crossing point of two PESs with different multiplicities. At present, we performed single-point computations of the doublet state as a function of the structural change along the IRC of the quartet state, and *vice versa*.^{31,32} In Fig.3, the solid and the dotted lines indicate computed potential energy profiles of each optimized point along IRC paths in doublet and quartet states, respectively. Fig.3 points out the crossing point (CP) in that the complex in the doublet and quartet states have the same energy and geometry at this point. The complex at CP point has C_s geometry, in which the dissociating C—O bond distance is 0.1201 nm and the forming U—O bond distance is 0.2399 nm. The quartet and doublet PESs can begin to touch at this point. Evidently, the reaction path of the quartet state lies below that of the doublet state in this region before the CP point. After passing CP, the doublet PES can provide an energetically favored reaction pathway toward the products. For brevity, a feasible path which starts from the separated reactants in the quartet state $^4\text{U}^+ + \text{CO}_2$ along the reaction pathway would continue through $^4\text{IM1}$ on the quartet state PES. Before reaching $^4\text{TS}_{12}$, CP is found. At CP point, ISC occurs between two PESs and the reaction system may transform its spin multiplicity from the quartet to doublet state in the crossing region. After this point, the reaction can proceed on the doublet PES as a low-cost reaction pathway toward the product complex. Therefore, the minimum energy pathways can be described as: $^4\text{U}^+ \text{CO}_2 \rightarrow ^4\text{IM1} \rightarrow ^2\text{TS}_{12} \rightarrow ^2\text{IM2} \rightarrow ^2\text{TS}_{23} \rightarrow ^2\text{IM3} \rightarrow ^2\text{UO}^+ + \text{CO}$.

3.3 O-atom affinities in different spin states

During the reaction of unimolecular $\text{CO}_2 \rightarrow \text{CO} + \text{O}$ (^3P) decomposition, the cleavage of C—O bond is very difficult and the reaction barrier height is 131 $\text{kJ} \cdot \text{mol}^{-1}$ at least. The relevant experimental and theoretical studies report that the reaction of some gas-phase transition-metal cations M^+ ($\text{M}^+ = \text{Sc}^+, \text{Y}^+, \text{La}^+, \text{Ti}^+, \text{Zr}^+, \text{Hf}^+, \text{Nb}^+, \text{Ta}^+, \text{W}^+$) with CO_2 can enhance the ability of unimolecular CO_2 decomposition. To our knowledge, the reacting system should change its spin multiplicities from the high state to the low state in the crossing region and then move on the low-spin potential energy surface as the reaction proceeds. This crossing seam plays the most important role in the reaction pathway so that the energetically favorable reaction pathway is entrance on high-spin surface and exit on the low-spin surface. So the reaction of M^+ with CO_2 leads to a significant decrease in the activation barrier and makes it into weak endothermic.

It is worth noting that the ability of O capture would likely impact on the dissociating CO_2 to CO. The O-atom affinity(OA) is a measure of the propensity for a substance to capture O when exposed to ambi-oxygen condition. According to the method of depicting M^+ OA presented by Koyanagi *et al.*,¹⁵ the OAs of M^+ and CO are defined as following:

$$\text{OA}(\text{M}^+) = E(\text{M}^+) + E(^1\text{O}) - E(\text{MO}^+)$$

$$OA(CO)=E(CO)+E(^1O)-E(CO_2)$$

The predicting OA of U^+ in two spin states and CO from DFT-B3LYP calculations with 6-311+G(d)USDD basis set are $OA(^2U^+)=986.88 \text{ kJ} \cdot \text{mol}^{-1}$, $OA(^4U^+)=608.98 \text{ kJ} \cdot \text{mol}^{-1}$, and $OA(CO)=811.17 \text{ kJ} \cdot \text{mol}^{-1}$ respectively. Among the three compounds, $^2U^+$ has the highest, followed by CO and then $^4U^+$. The comparison of OA suggests that $^2U^+$ can capture O from CO_2 in doublet spin states, but $^4U^+$ cannot. The conclusions discussed above are in good consistent with the corresponding experimental findings.

4 Conclusions

The DFT-B3LYP calculations with SDD basis set for U and 6-311+G(d) basis set for C and O were performed to investigate the U^+ reaction with CO_2 in gas phase. The reaction system can transform its spin multiplicity from quartet to doublet state in the crossing region. The spin inversion and the intersystem crossing (ISC) take place between two PESs, which are efficient to decrease reaction activation height. The minimum energy pathway has also been described. Compared with the strong endothermic process of the CO_2 decomposition, the reaction of U^+ with CO_2 is weak endothermic for the participation of U^+ cation. The reaction system initially takes place on the quartet surface; the products U^+ and CO exit the channel on the doublet surface. The ability of capture O from CO_2 is in the order $^2U^+ > CO > ^4U^+$, which is also in agreement with the above conclusion.

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