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Structure and stability of various states of the EuC and EuC_2 molecules*

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B3LYP level density functional theory (DFT) and multiconfiguration self-consistent-field (MCSCF) level *ab initio* method calculations have been performed on the basis of relativistic effective core potentials to investigate the nature of EuC and EuC_2 molecules. The computed results indicate that the ground states of EuC and EuC_2 are $^{12}\sum^{+}$ and $^{8}A_2$, respectively. Dissociation potential energy curves of the low-lying electronic states of EuC have been calculated using the MCSCF method, and the same level calculation on EuC_2 indicates that the dissociation energy of EuC_2 of ground state compares well with the available experimental data. The bond characteristic is also discussed using Mulliken populations.

Keywords: EuC, EuC_2, *ab initio* calculations, B3LYP method
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1. Introduction

Metal carbides have been extensively studied during the last four decades, both in experiment and in theory. Several *ab initio* calculations have been performed on metal carbides I_rC, R_uC, R_hC, YC_2, OsC, OsC_2 since 1982 to elucidate the electronic structure, nature of bonding and molecular parameters of their ground states and low-lying excited electronic states.[1−4] Among these metal carbides, rare earth (RE) metal carbides attract many attention due to the important roles they play in the synthesis of carbon nanotubes[5−7] and their interesting superconductivity.[8,9] Rare earth elements interact with carbon at high temperatures and can form different RE–carbides, such as REC and REC_2.[10] Among the rare earth elements, europium is an the element which differs slightly from its neighbours. For example, most of RE are trivalent, which Eu also has a valency of +2. Furthermore, some addition of rare earth elements into catalysts has been identified to greatly improve the yield of carbon nanotubes during the synthesis process by arc discharge.[5−7] However, when Eu was added into the catalyst to synthesize SWNTs, it did not improve the yield of SWNTs. It is suggested that europium has a valency of +2 and can hardly form Eu–carbide, which leads to very low yield of carbon nanotubes.[7] Therefore, some differences between europium carbide and other rare-earth carbides in the structure, nature of bonding and stability are expected. In high temperature arc discharge (above 3000 K) experiment, rare-earth metal and graphite are vaporized and can form metal–carbon clusters or RE–carbide clusters.[11] Therefore, it is interesting and of importance to study the nature of bonding, the stability and some other physical and chemical properties of EuC and EuC_2.

To our knowledge, there has been no report of theoretical investigation carried out on the EuC and EuC_2 molecules. In this study, the B3LYP of DFT theory and MCSCF method are used on EuC and EuC_2 molecules to investigate their molecular parameters and dissociation energy. Our MCSCF result about the dissociation energy of EuC_2 is consistent with that of experiment, which also indicates that our method is reliable and effective for computing ele-

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ments of large atomic numbers. We also calculate the amount of charge transfer from Eu to C atom.

2. Computation methods

The unrestricted B3LYP calculations were accomplished using the GAUSSIAN03 program package.[12] The MCSCF computations were made using the GAMESS program package.[13] For the UB3LYP method, because of large atomic number of europium atom, all the calculations were made using the relativistic effective core potentials (RECPs) with 35 ($4s^24p^64d^{10}5s^25p^64f^76s^2$) electrons in the valence space for the europium atom. In this work, the RECPs for Eu were generated by Cao and Michael.[14] For the carbon atom we used the basis set of 6-31G. The above basis sets lead to 70 and 79 atomic basis functions for the EuC and EuC_2 molecules, respectively. And for the MCSCF method, we also choose the RECP basis set.

3. Results and discussion

3.1. EuC theoretical results

The ground state of EuC is $^{12}A_1$, as was determined using both MCSCF and B3LYP method in our previous work.[15] The bond length between Eu and C of ground EuC has values 2.364 and 2.485 Å on the level of B3LYP and MCSCF, respectively. It was found that the $^{12}A_1$ electronic state is $^{12}\sum^+$ state when we chose C_{2v} point group to calculate the $C_{\infty v}$ point group of EuC molecule. Now, we have carried out MCSCF calculations for the ground state of EuC with Eu–C bond length varying from 0.5 to 8.0Å. The potential curve for the ground state $^{12}\sum^+$ dissociates to C^{2-} and Eu^{2+} ions and excited states $^{12}\prod$ and $^{12}\sum^-$ converge to different dissociation limits. That is to say, the $^{12}\prod$ converges to Eu (^8S) + C (^3P) and $^{12}\sum^-$ converges to C (^1D) + Eu (^8S) (see Fig.1).

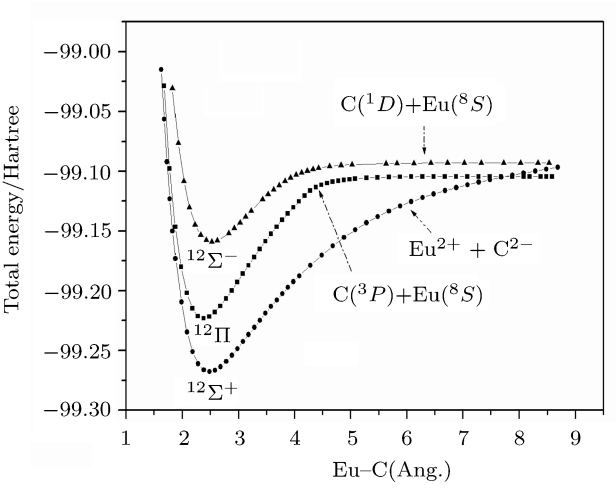


Fig.1. Potential surfaces for the 12 states of Eu–C.

3.2. EuC_2 theoretical results

The geometry of the gaseous EuC_2 is not yet determined experimentally. In our initial studies, in order to obtain an overview of the low-lying electronic states of EuC_2, several states of different symmetries and multiplicities have been investigated. Of the C_{2v} point group symmetry CEuC, linear EuCC, and linear CEuC structures studied using B3LYP and MCSCF method, at variance with the geometry of C_{2v} point group symmetry structure, the last two structures exhibit imaginary frequencies. With four different multiplicities ($2s+1 = 4, 6, 8, 10$) of C_{2v} point group symmetry, CEuC structures are investigated using both the B3LYP and MCSCF method.

Table 1. The optimized molecular parameters, vibrational frequencies and relative energies of different electronic states of EuC_2 molecule (bond distance in Å, angles in degree and energy in eV).

State	R_{Eu-C}	R_{C-C}	∠CEuC	ν			ΔE
$^4A_1$	2.308	1.284	32.3	343	456	1792	6.317
$^6A_1$	2.314	1.282	32.2	370	458	1797	4.470
$^8A_2$	2.330	1.282	31.9	368	459	1802	0
$^{10}A_2$	2.628	1.279	28.2	168	315	1824	1.076

From Tables 1 and 2 we can obviously see that the ground state of EuC_2 is $^8A_2$; the optimized molecular parameters are $R_{Eu-C} = 2.330$ Å, $R_{C-C} = 1.282$ Å, and the ∠CEuC = 31.9°; the vibrational frequencies are 368 cm^{-1}, 459 cm^{-1} and 1802 cm^{-1} at the B3LYP level. When we choose the (13e, 13o) active space on the level of MCSCF, the corresponding parameters are $R_{Eu-C} = 2.393$ Å, $R_{C-C} = 1.311$ Å, the ∠CEuC = 31.8° and the energy is −104.684 Hartree and the configuration spin functions (CSFs) are 18912. The results using B3LYP are consistent with that using MCSCF method. Our calculation results confirm that

the formation of EuC_2 weakens the C–C bond, which is demonstrated by the C–C bond length increasing from 1.260 Å (C_2 molecule) to 1.282 Å (B3LYP) and 1.311 Å (MCSCF). It has been reported that the C–C bond of HoC_2 molecule is 1.31 Å,[16] which is also longer than that of C_2 molecule.

Table 2. The optimized molecular parameters, energies and CSF of different electronic states of EuC_2 molecule. (bond distance in Å, angle in degree and energy in Hartree).

State	R_{Eu-C}	R_{C-C}	∠CEuC	E	CSF
$^4A_1$	2.384	1.312	32.0	−104.403	286096
$^4A_2$	2.384	1.312	32.0	−104.403	286476
$^4B_1$	2.387	1.311	31.8	−104.418	286096
$^4B_2$	2.387	1.311	31.8	−104.417	286476
$^6A_1$	2.720	1.310	27.8	−104.526	107637
$^6A_2$	2.387	1.311	31.8	−104.509	107172
$^6B_1$	2.387	1.312	31.8	−104.510	107448
$^6B_2$	2.388	1.312	31.8	−104.523	107172
$^8A_1$	2.778	1.307	27.2	−104.578	18944
$^8A_2$	2.393	1.311	31.8	−104.684	18912
$^8B_1$	2.330	1.313	32.8	−104.669	18944
$^8B_2$	2.319	1.312	32.8	−104.654	18912
$^{10}A_1$	2.771	1.305	27.2	−104.594	1499
$^{10}A_2$	2.601	1.324	29.4	−104.578	1476
$^{10}B_1$	2.758	1.262	26.4	−104.462	1464
$^{10}B_2$	2.380	1.414	34.6	−104.572	1476

3.3. The charge transfer and dissociation energy of EuC and EuC_2

Bonding energy depends primarily on the average number of unpaired electrons per atom available for bonding. Increasing or decreasing of Mulliken electronic charge changes the intensity of chemical bond(s). In this work, the Mulliken population analysis of the two molecules suggests charge transfer from europium to carbon resulting in Eu^+C^- polar bonds. We calculated the charge transfer from europium to carbon using both B3LYP and MCSCF methods and the results are listed in Table 3. From Table 3 we can see that, for either EuC or EuC_2 molecule, the amount of the charge transfer from one europium atom to carbon using B3LYP method is very close to that obtained using the MCSCF method.

Table 3. The charge transfer from metal to carbon of the ground state of EuC and EuC_2 molecule using B3LYP and MCSCF method.

Method	atom	EuC ($^{12}\sum^+$)	EuC_2 ($^8A_2$)
	M	0.574	0.704
B3LYP	C	−0.574	−0.352
	C		−0.352
	M	0.593	0.772
MCSCF	C	−0.593	−0.386
	C		−0.386

Further, we calculated the dissociation energy of EuC and EuC_2. For molecules having heavy atoms, their structures are often optimized using DFT method.[17] It can be argued that nonrelativistic DFT might be unreliable for the calculation of dissociation energy.[3] Therefore, we calculated the dissociation energy of EuC and EuC_2 using MCSCF method on the basis of relativistic effective core potentials and the results are listed in Table 4.

Table 4. Comparison of the theoretical and experiment metal-carbon bond dissociation energy for the EuC and EuC_2 molecules at the level of MCSCF, energy in kJ/mol.

Metal carbides	MCSCF	experiment
D_0 °(EuC)	435.3	
D_0 °(EuC_2)	1139.5	1142.74(+/−)20.92[10]

The dissociation energy of ground state for EuC is 435.3 kJ/mol, while the dissociation energy of EuO is 469.98±10.08 kJ/mol.[18] Therefore, it is possible that EuO is frequently present after arc discharge during the synthesis of carbon nanotubes because the Eu–O bond is stronger than Eu–C bond.[7] When the metal atom is dissociated along the perpendicular bisector of two carbon atoms, the europium–dicarbon bond dissociation energy D_0(Eu–C_2) of EuC_2 is 1139.5 kJ/mol, which is in excellent agreement with the experimental

data of 1142.74 ± 20.92 kJ/mol reported in handbook [10]. This also indicates that our method and selected active space is advisable.

4. Conclusions

In summary, we applied the density functional theory and quantum chemistry *ab initio* method on the basis of relativistic effective core potentials (RECPs) to various electronic states of EuC and EuC_2 to investigate the nature of EuC and EuC_2 molecules. The ground state of EuC and EuC_2 molecules were found to be $^{12}\sum^{+}$ and $^{8}A_2$, respectively. We employed MCSCF method to calculate the dissociation potential energy curves of the low-lying electronic states of EuC and the dissociation energy of the ground state EuC_2. The obtained dissociation energy of EuC_2 compares well with the available experimental data. Our results also indicate that the EuO is more stable than EuC.

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