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Density functional studies of the reactivity in the C–F bond activation of fluoromethane by bare lanthanum monocation

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Abstract

The potential energy surface and reaction mechanism corresponding to the reaction of lanthanum monocation with fluoromethane, which represents a prototype of the activation of C–F bond in fluorohydrocarbons by bare lanthanide cations, have been investigated for the first time by using density functional theory. A direct fluorine abstraction mechanism was revealed, namely after coordination of CH_3F to La^+, electron transfer from La^+ to the fluorine takes place, which favours the homolytic cleavage of the C–F bond to form LaF^+ species and methyl radical. The related thermochemistry data involved in reaction of $La^+ + CH_3F$ were determined, which can act as a guide for further experimental researches. The electron-transfer reactivity of the reaction was analyzed by using a state correlation diagram, in which a strongly avoided crossing behaviour on the transition state region was shown. The calculated state split energy between the ground and excited state on the transition state is 18.01 kcal mol^{-1}. The reaction of La^+ with CH_3F was concluded to process in the adiabatic potential surface. The present results support the reaction mechanism inferred early from experimental data. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electron transfer; C–F bond activation; Lanthanum monocation; Fluoromethane; DFT

1. Introduction

It is well known that C–F bond in organic compound is significantly stronger than the corresponding C–H and C–C bonds, and that C–F bond activation is a formidable task in organometallic chemistry [1]. In recent years, C–F bond activation by metal centers has attracted a great deal of interest [2–6] and many theoretical and experimental studies have shown that bare metal monocations are able to activate the C–F bond selectively [5–9]. In the gas phase, Ridge and co-workers reported the first case of C–F bond activation by Fe^+ in its reaction with fluorobenzene [7]. Recently, Schwarz and co-workers demonstrated the gas-phase reactions of bare lanthanide monocations Ln^+ (Ln = La to Lu) with various fluorinated hydrocarbons [6]. The main reaction pathway proposed in all cases was C–F bond activation to form LnF^+ and the corresponding neutral radical of various hydrocarbons. They proposed a 'harpoon'-like mechanism with a $[Ln\cdots F\cdots CH_3]^+$ type intermediate and a $[Ln^{2+}\cdots F\cdots CH_3]$ type transition state. As a supplement of the experimental studies reported by Schwarz and co-workers, we present here further theoretical study of the reaction of La^+, a representative lanthanide cation, with fluoromethane. Our focuses in this work are to learn more details about the reaction mechanism for $La^+ + CH_3F$ cationic system and to analyze the electron transfer reactivity of the reaction. And our main aim is to give a qualitative model that explains how the Ln^+ activates the C–F bond in fluorohydrocarbons. In addition, we also calculated related thermochemistry of the reaction process, which can act as a guide for future experimental researches. The theoretical predictions presented here for the reaction of La^+ with CH_3F can provide a template for further comprehension of the reactions of lanthanide cations with fluorohydrocarbons.

The theoretical research for the systems involving lanthanide is very difficult to deal with in ab initio Hartree–Fock theory since a relatively large number of electrons are present in these systems. As an alternative, density functional theory (DFT) [10,11] has recently

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attracted considerable attention, which has recently been widely applied to electronic structure calculations for systems that contain transition metals. The electron correlation effect in these systems is expected to play an important role in determining the system energetics as well as the electronic configurations. DFT method has been shown to be particularly useful and computationally efficient for system with a relatively large number of electrons that are difficult to deal with in ab initio Hartree–Fock theory [12,13]. In the present study, the structure optimizations and the energetics evaluation for the stationary points and saddle point on the potential energy surface (PES) of [La, C, H_3, F]$^+$ are carried out by using both local density approximation (LDA) and the gradient corrected DFT method under the generalized gradient approximation (GGA) [14].

2. Computational method

The present calculations employ all electrons in the system and the DFT method used in our calculations is provided by the Dmol^3 programs [15]. It is known that LDA calculation often overestimate the binding energy [16,17]. Several influential studies have shown that although gradient corrections normally do not significantly change the molecular structures or vibrational frequencies from those obtained at the LDA level, they can offer better energetics [16–18]. Furthermore, geometry optimization using GGA method is computationally intensive and the SCF convergence is very difficult for systems involving lanthanide. Therefore, we first optimized the structures of all the stationary points (reactants, products, intermediates and transition state) on the PES [La, C, H_3, F]$^+$ at LDA level. And then single point energy calculations are carried using GGA method for the geometries obtained at the LDA level. Finally, the vibrational frequencies are obtained at the LDA level to determine the nature of these stationary points and the zero-point vibrational energy (ZPE). All the stationary points on the PES have been identified for minima (number of imaginary frequencies NIMG = 0) or transition state (NIMG = 1). To ensure good accuracy, the Kohn–Sham equation is solved by using a double numerical basis set augmented polarization functions under fine numerical integration grid. The relativistic effects for all electrons have been taken into account. The PWC functional is used in the LDA calculations and PW91 exchange and correlation functionals are used in the GGA calculations. The spin-polarized computational scheme was utilized throughout this work to deal with the electronically open-shell systems. All processes designed here occur on both the singlet and triplet potential energy surfaces of [La, C, H_3, F]$^+$.

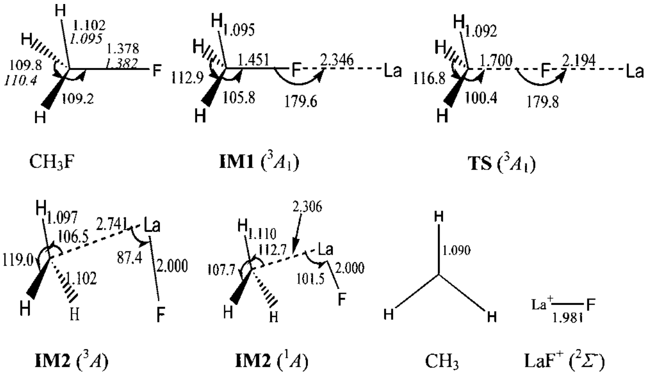


Fig. 1. Optimized geometrical parameters for the stationary points on the potential energy surface of [La, C, H_3, F]$^+$. The values in italic are experimental results. Distances are in Å and angles are in degrees.

Table 1
Total energies (in Hartree), relative energies (in kcal mol^{-1}) and zero-point energy (ZPE, in kcal mol^{-1}) of the species involved in reaction of La$^+$ + CH_3F

	E_{totle} [a]	ΔE [b]	ZPE
La$^+$ + CH_3F	−8678.769253	0.00	24.22
IM1($^3A_1$)	−8678.830678	−38.22	24.54
TS ($^3A_1$)	−8678.819276	−33.35	22.26
IM2 (^1A)	−8678.969188	−128.80	20.88
IM2 (^3A)	−8678.880395	−73.56	20.40
LaF$^+$ ($^2S^-$)+CH_3	−8678.861272	−62.91	19.05

[a] The energies do not include the ZPE.

[b] ZPE corrections have been taken into account.

3. Results and discussion

The optimized geometrical parameters are shown in Fig. 1 and relevant energies are given in Table 1. The theoretically vibrational frequencies and available experimental values are summarized in Table 2. The potential energy surface profile of the reaction of La$^+$ with CH_3F is shown in Fig. 2. And the state correlation diagram for the reaction is revealed in Fig. 3.

3.1. Geometries, energies and vibrational frequencies

Initially, a reactant-like intermediate, denoted as IM1, is formed as La$^+$ and CH_3F approach each other. This initially formed ion/molecule complex has C_{3v} symmetry, and its ground state (triplet) energy is computed to 38.22 kcal mol^{-1} more stable than La$^+$ + CH_3F entrance channel. The C–F bond length and H–C–H angle in the complex are calculated at 1.451 Å and 112.9°, respectively, and are slightly larger compared to 1.378 Å and 109.8° in free CH_3F. La–F distance in IM1 is calculated as 2.346 Å. Mulliken population analysis (MPA) shown that the charge distribution and spin density to be 0.893 and 2.003 for La,

Table 2
Vibrational frequencies (in cm^{-1}) of the species involved in the reaction of La$^+$ + CH$_3$F

No.	CH$_3$F [a]	IM1 ($^3A_1$)	TS ($^3A_1$) [b]	IM2 (^1A)	IM2 (^3A)	LaF$^+$ (^{2}S$^-$)	CH$_3$
1	1081 (1049)	36.2	638.7i	79.4	68.0	615.5	607.5
2	1151 (1182)	41.1	77.5	109.0	108.6		1336.7
3	1151 (1182)	219.1	77.6	270.7	268.8		1336.7
4	1424 (1464)	848.6	287.2	394.1	402.0		3059.2
5	1426 (1464)	1120.6	477.0	870.0	480.5		3252.6
6	1426 (1467)	1122.1	626.8	870.0	615.4		3252.6
7	2974 (2938)	1401.5	1119.4	1187.4	1132.4		
8	3068 (3006)	1411.6	1304.7	1373.4	1307.3		
9	3068 (3006)	1412.4	1321.1	1373.4	1317.9		
10		3042.2	2924.0	3065.1	2915.0		
11		3176.8	3020.6	3245.0	3002.7		
12		3180.7	3033.3	3245.0	3042.5		

[a] The experimental values are shown in parentheses.
[b] i represents imaginary frequency.

− 0.440 and − 0.008 for F, and 0.543 and − 0.006 for CH$_3$ group (Table 3). The results indicated that the interaction between La$^+$ and CH$_3$F is electrostatic interaction in nature, as evidenced by the long bond distance and charge distribution. The calculated bond dissociation energy of La$^+$–FCH$_3$ is 38.22 kcal mol^{-1}, which indicated that the electrostatic interaction is weak. The early experimental findings [6] proposed that the initial ion/molecule complexes of lanthanide monocation and fluorohydrocarbons could be the rate-determining step of the C–F bond activation. This suggestion is in good agreement with the weak electrostatic interaction between La$^+$ and CH$_3$F. We also calculated the energy of the corresponding singlet of IM1, and found that it is be only less stable than the triglet by 2.05 kcal mol^{-1}. The finding indicated that the singlet PES for the system is very close to that of the triplet, and that two PESs could across in the reaction process.

Along the reaction coordinate, a transition state (TS) was found, which was characterized by the presence of one imaginary frequency (638.7i) and one negative eigenvalue in the corresponding hessian matrix. The transition structure has also C_{3v} symmetry and its ground state (triplet) energy is 4.87 kcal mol^{-1} above the **IM1** and 33.35 kcal mol^{-1} below the entrance channel. The corresponding singlet TS is less stable by 2.50 kcal mol^{-1}. In the ground state TS, the C–F bond is elongated to 1.700 Å and the La–F bond is shorted to 2.194 Å. The corresponding transition vector indicated by the vibration analysis corresponds to the breaking of the C–F bond and the forming of the La–F bond. MPA given the charge distribution and spin density as follows: 1.030 and 1.765 for La, − 0.492 and − 0.006 for F, and 0.463 and 0.243 for CH$_3$ group. The transition state is a tightly bonded structure, and in which the electron transfer has been occurred from La to F compared to the MPA of IM1. The electron transfer from the 6s orbital of La$^+$ to the σ* orbital of CH$_3$F favours the homolytic cleavage of the C–F bond to form the LaF$^+$ species and CH$_3$ radical.

The other minim on the PES is a product-like complex, denoted as IM2. Our computational data shown that the ground state (singlet) of IM2 (^1A) is a global

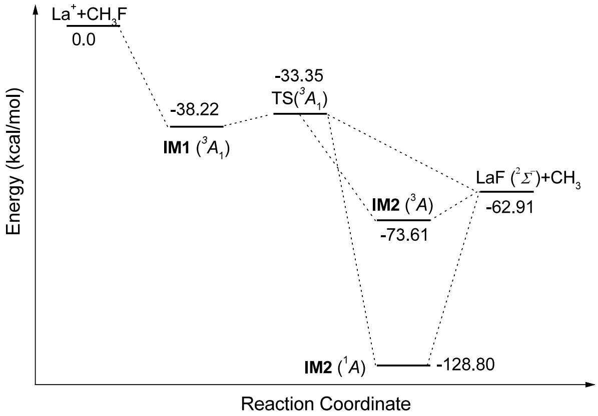


Fig. 2. Potential energy surface profile of the reaction of La$^+$ with CH$_3$F.

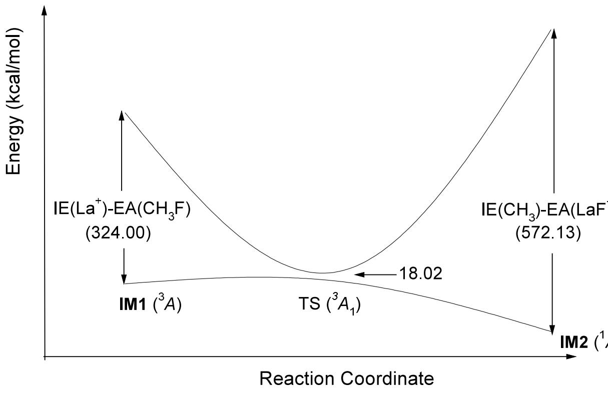
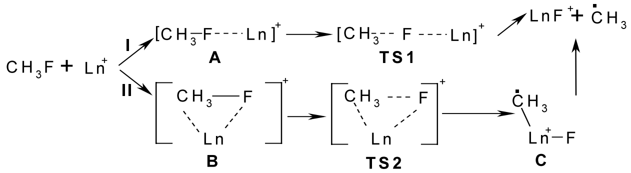


Fig. 3. State correlation diagram for the reaction of La$^+$ with CH$_3$F.

Table 3
Mulliken charge and spin density of the species involved in the reaction of La^+ with CH_3F [a]

	CH_3F	IM1 ($^3A_1$)	TS ($^3A_1$)	IM2 (^1A)	IM2 (^3A)	LaF^+ ($^2S^-$)	CH_3
La		0.896, 2.003	1.030, 1.765	1.668, 0.000	1.260, 1.134	1.439, 1.015	
F	−0.332, 0.000	−0.440, 0.008	−0.492, −0.006	−0.4326, 0.000	−0.438, −0.009	−0.439, −0.015	
C	−0.013, 0.000	−0.027, 0.000	−0.128, 0.258	−0.870, 0.000	−0.516, 0.914		−0.428, 1.096
H	0.115, 0.000	0.190, 0.002	0.197, −0.005	0.204, 0.000	0.231, −0.023		0.143, −0.032
H	0.115, 0.000	0.190, 0.002	0.197, −0.005	0.208, 0.000	0.231, −0.008		0.143, −0.032
H	0.115, 0.000	0.190, 0.002	0.197, −0.005	0.225, 0.000	0.233, −0.008		0.143, −0.032

[a] For each species, the first number corresponds to the atomic Mulliken charge and the second number corresponds to atomic spin density.



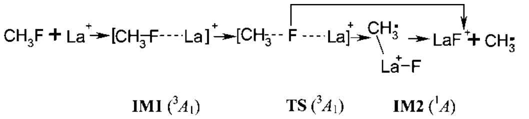
Scheme 1. Experimentally inferred reaction mechanism for $Ln^+ + CH_3F$.

minim on the PES, and its energy is 128.80 kcal mol^{-1} more stable than the entrance channel. The corresponding triplet (^3A) of IM2 is 55.19 kcal mol^{-1} less stable compared to its singlet. Thus, we concluded that a cross between singlet and triplet occurs on the PES of $[La, C, H_3, F]^+$ along the reaction coordinate to form more stable IM2 (^1A). The intermediate looks like an inserted species of La^+ into the C–F bond very. Both the ground state (singlet) and the corresponding triplet have C_1 symmetry. La–F distances and H–C–H angles in IM2 (^1A) and IM2 (^3A) are respectively 2.306 Å and 107.7°, and 2.741 Å and 119.0°. The geometry parameters of IM2 (^3A) have already been very similar to those of the free LaF^+ (^2S) and CH_3 group. Obviously, its exit channel is forming LaF^+ and CH_3 like that of IM2 (^1A). In Table 2, we compared the theoretical vibrational frequencies of CH_3F with the available experimental values and the good agreement is found. The fact indicates that the calculation method used in this work is reliable.

3.2. Reaction mechanism

Now we consider the reaction mechanism of La^+ with fluoromethane. Recently in the reactions of several lanthanide cations with fluoromethane, one observed that Ln^+ can selectively activate the C–F bond to yield LnF^+ and methyl radical. In light of the experimental fact, the following two alternative reaction mechanisms could be inferred from the electronic structure of La^+, which has two non-f electrons.

In mechanism I CH_3–F could first coordinate to Ln^+ through the electronegative fluorine atom to form a initial ion/molecule complex (A), then this complex undergoes a transition state to form the LnF^+ species and methyl radical. Mechanism II is an insertion–elimination process, in which a three-number-cycle initial complex (B) and a three-center transition state (TS2) were postulated to insert Ln^+ into C–F bond. In our calculations, however, these cyclic structures for the reaction of La^+ with CH_3F are not found on the PES of $[La, C, H_3, F]^+$ in spite of careful searching. But in present calculation, we really located an inserted species-like, IM2, which is denoted as C in Scheme 1. The intermediate is an overall manimum on the PES, and it connects the transition state and products. Thus, according to our calculations, the reaction mechanism for $La^+ + CH_3F$ system is proposed as follows: (Scheme 2)



Scheme 2. Proposed reaction mechanism for the of La^+ with CH_3F from the present calculations.

If the mechanism is constant along the 4f row elements, we conclude that the ability of Ln^+ to abstract an F atom from CH_3–F should be related to the second ionization energy of the lanthanide monocation. Schwarz and co-workers observed the different reactivities of six lanthanides with CH_3F, and found that the lower the second ionization energy of the lanthanide's is, the higher its abstraction reactivity on the fluorine atom in CH_3F is. Hence, they also proposed that these reactions are direct abstract reactions of F atom by La^+. The conclusion is in line with our suggestion.

3.3. Heat of reaction and bond dissociation energy

As far as we know, no precise thermochemical information is available for the reactions, $Ln^+ + CH_3F \rightarrow LnF^+ + CH_3$. In the present work, the calculated heat of reaction for the reaction is exothermic by 62.91 kcal mol^{-1}. If the theoretical values is used, together with a value of 112 ± 0.3 kcal mol^{-1} for the bond dissociation energy (BDE) of the C–F bond in fluoromethane, the BDE for diatomic species La^+–F is determined to be 174.91 ± 0.3 kcal mol^{-1}. The early experimental research [6] estimated a lower bound of 123 kcal mol^{-1} for the BDE from their experimental data. No available experimental data, however, allow for an estimation of the upper bound of the BDE. The theoretical data given in this work can provide a guide for further experimental researches.

3.4. Potential energy surface crossing behaviour on the transition state area

To study the electron transfer reactivity in the reaction of La$^+$ with CH_3F, we now analyze the potential energy surface crossing behaviour on the transition state area by building a state correlation diagram for the reaction. Since both the wavefunctions of the reactant-like and product-like states on the transition region, which clearly differ by a single electron transfer from the 6s orbital of La$^+$ to the σ* orbital of CH_3F, belong to the A_1 irreducible representation of C_{3v} point group, they should in principle mix and avoid the crossing. IM1 is an electrostatic complex between La$^+$ and CH_3F and a 6s electron is basically located on the metal ion. Proceeding along the reaction coordinate the electron transfer occurs from La$^+$ to F, which favours the homolytic cleavage of the C–F bond to form IM2. Consequently, IM1 correlates with an excited states of IM2 and the corresponding excited energy approximately equals to the difference between the second ionization energy (IE) of lanthanum and the electron affinity (EA) of CH_3F. Similarly, IM2 correlates with an excited state of IM1, the excited energy can be approximate by the difference between the IE of CH_3 radical and the EA of LaF$^+$ species. In present calculations, vertical excited energies of the reactant-like and products-like species are respectively 324.00 and 572.13 kcal mol^{-1}.

The electron transfer reactivity of the crossing region on the PES can be analyzed according to the two-state model of the electronic structure. We denote the electronic state energies of the reactant-like and product-like species by E_r and E_p, respectively, when $H_{rp} = 0$. The two-state electronic secular equation at any geometry can be expressed as

$$\begin{vmatrix} E_r - E & H_{rp} - ES_{rp} \\ H_{rp} - ES_{rp} & E_p - E \end{vmatrix} = 0 \tag{1}$$

where S_{rp} is the overlaps between the two states. The difference between the two eigenvalues at the avoided crossing point is

$$\Delta = E_1 - E_2 = 2H_{rp} \tag{2}$$

Δ can be approximated using the simple Koopmans' theorem (KT) in the Hartree–Fock method. The Hartree–Fock orbital energies correspond to the negative of IE for occupied orbitals and to the negative of the electron affinities for unoccupied orbitals. KT applied to the orbital energy difference between HOMO + 1 and HOMO of the neutral system [La–F–CH_3], which has the geometrical parameters of the TS, and then gives the energy difference between the first excited state and the ground state. Our calculated the state split energy is 18.02 kcal mol^{-1} for the La$^+$ + CH_3F system. The result indicates that the mixing between the two states is significant on the transition state region, which leads to strongly avoided crossing behaviour. So the reaction of La$^+$ with CH_3F processes on an adiabatic potential energy surface and does not involve nonadiabatic surface-hopping behaviour. The state correlation diagram is given in Fig. 3.

4. Conclusions

In this work we present a theoretical study of the mechanistic details of the La$^+$-mediate C–F bond activation in fluoromethane, which is a representative prototype of the reaction mechanism of bare Ln$^+$ cations with fluorocarbons. The theoretical results given in this work for the reaction of La$^+$ with CH_3F support a direct fluorine abstraction mechanism. After coordination of CH_3F to La$^+$, the electron transfer from La$^+$ to the fluorine takes place, and then the C–F bond homolyticlly rupture to form the inserted species-like, which exits by forming LaF$^+$ and methyl radical. The reaction is substantially adiabatic, and the state split energy between the ground and excited states was calculated to be 18.01 kcal mol^{-1}. The calculated heat of reaction for $La^+ + CH_3F \rightarrow LaF^+ + CH_3$ is exothermic by 62.91 kcal mol^{-1}, and the BDEs are 38.22 and 174.91 kcal mol^{-1} for La$^+$–FCH_3 ion/molecule complex and La$^+$–F diatomic species, respectively. These theoretical results can provide a guide for further experimental researches.

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