Vibrational Mode Analysis for the Multi-channel Reactions of $O(^3P)$ with CH_2F *

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Abstract All species involved in the multi-channel reaction of an oxygen atom with a fluorinated methyl radical have been investigated using density functional theory (DFT). The geometries of the reactants, intermediates, transition states and products are optimized at the B3LYP/6-311 + +G(2d,2p) level. The potential energy surface for this reaction is calculated at the same level of theory. Various possible production channels involved in the reaction of $O(^3P) + CH_2F$ are examined. The vibrational mode analysis is used to elucidate the relationship between the transition states, intermediates and the products. The extensive investigation shows that the reaction mechanism is reliable.

Keywords: Density functional theory(DFT), Multi-channel reaction, Vibrational modes

At typical fuel-lean combustion conditions, the reactions of halogenated alkyls with oxygen atoms are important in the oxidation process of polyhalogenated hydrocarbons. Incineration is an effective technique for the management of hazardous polyhalogenated hydrocarbon waste^[1]. Halogenated alkanes also can undergo photodecomposition to halogenated alkyl radicals. The reaction of halogenated alkyl radicals with $O(^3P)$ atoms is known to produce halogenated alkoxy radicals, which play an important role in stratospheric ozone depletion^[2]. How to control secondary pollution during the incineration becomes an important subject and has attracted great attention.

To date, there are only a few reports on the reactions of halogenated alkyl radicals with oxygen atoms^[3-4] and no direct experimental studies of the reaction of $O(^3P)$ with the simplest halogenated alkyl radical, CH_2F have been reported. Recently, Wang *et al.*^[5] studied the reaction of $O(^3P)$ with CH_2F and presented the mechanism using *ab initio* molecular orbital theory, but a DFT method has never been used to fully study the reaction mechanism. In this study, we shall use the vibrational mode analysis to elucidate the relationship between the transition states, intermediates and the products.

In the last twenty years, people have focused on analyzing the molecular energy, electron density and population in order to illustrate the existence and the relevant property of transition states and intermediates. Recently, analysis of the vibrational

modes and vibrational frequencies for transition states and intermediates has attracted the attention of Mann and McGrivern for the S_N2 reaction $Cl^- + CH_3Cl$ ^[6] and the calculation of the dissociation energy of $C-H$ and $C-X$ ^[7] respectively. However, the changes and the relationships of the vibrational modes and the frequencies between reactants, transition states, intermediates and products have not been noted. Elucidation of reaction mechanisms *via* vibrational mode analysis gets more attention^[8-10]. All multi-atom molecules can produce an infrared spectrum because of the rotation and vibration of atom groups. The characteristics of the normal mode vibrations are that all atoms reach their equilibrium points at the same time and come to the maximum simultaneously when vibrating, but the center of mass remains unchanged and the molecule as a whole does not rotate. If n is the atom number, for nonlinear molecules there are $(3n-6)$ normal vibration modes and for linear molecules there are $(3n-5)$. In a sense, the numerical values of the frequencies of a molecule can reflect the reaction potential barrier, namely the actual activation energy. If a bond is extended or weakened, the frequencies are red-shifted; on the contrary, if the bond is shortened and strengthened, the frequencies are blue-shifted. So changes of the vibrational frequencies and vibrational modes must be pertinent to the transformations of the structures.

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Fig. 1 The optimized structures for various species involved in the reactions of $O(^3P)$ with CH_2F at the B3LYP/6-311 + +G(2 d, 2 p) level (Bond distances are in nm and bond angles are in degrees)

1 Computation methods

The optimizations of the reactants, intermediates (IM) transition states (TS) and products are performed with the Gaussian 98 programs package^[11] at the B3LYP/6-311 + +G(2 d, 2 p) level. The popular hybrid density functional B3LYP method, namely Becke's^[12] three-parameter non-local exchange functional with the correlation functional of Lee *et al.*^[13], is used throughout the study. Subsequently, connections of the transition states and products are confirmed by intrinsic reaction coordinate (IRC) calculations^[14-16]. All relative energies discussed below are electronic and zero-point energy corrected. The number of imaginary frequencies (0 or 1) confirms a local minimum or a transition state.

2 Results and discussion

The geometries of the reactants, intermediates, transition

states and products involved in the reaction $O(^3P) + CH_2F$ are shown in Fig. 1. The schematic potential energy profile is depicted in Fig. 2. The vibrational frequencies and the vibrational mode assignment of the reactants and products are listed in Table 1. The vibrational frequencies and the vibrational mode assignment of all the transition states and intermediates are listed in Table 2 and Table 3.

2.1 Vibrational mode analysis for the reactants and the products

The reactant of CH_2F belongs to the group point of C_s and the two hydrogen atoms are symmetrical with respect to the plane containing fluorine and carbon atoms. According to the fundamental vibrational modes of $(3n - 6)$, in nonlinear molecules, there are six vibrational modes. HCO and FCH have three frequencies, because the $C - H$ and $C - O$, $C - F$ and $C - H$ has an angle of 124.3° and 102.1° , respectively. The CH_2O should

Table 1 Vibrational frequencies and their vibrational mode assignment for the reactants and products involved in the reaction of $O(^3P)$ with CH_2F

Species	Frequency (cm^{-1})	Mode assignment	Species	Frequency (cm^{-1})	Mode assignment
CH_2F	490	CH_2 rock out of plane	CHF	1440	$C - H$ rock in plane
	1161	$C - F$ stretch		2785	$C - H$ stretch
	1166	CH_2 twist	CH_2O	1198	CH_2 rock out of plane
	1462	CH_2 scissors		1264	CH_2 rock in plane
	3138	CH_2 symmetric stretch		1530	CH_2 scissors
	3299	CH_2 asymmetric stretch		1809	$C - O$ stretch
$CHFO$	658	$F - C - O$ bend in plane	$HCOH$	2891	CH_2 symmetric stretch
	1029	$C - H$ rock out of plane		2950	CH_2 asymmetric stretch
	1044	$C - F$ stretch		1092	$H - C - O - H$ rock out of plane
	1362	$C - H$ rock in plane		1225	$H - C - O - H$ bend in plane
	1882	$C - O$ stretch		1317	$C - O$ stretch
	3090	$C - H$ stretch		1513	$H - C - O - H$ rock in plane
HCO	1104	$C - H$ rock in plane		2862	$C - H_2$ stretch
	1929	$C - O$ stretch		3717	$C - H_1$ stretchd
	2660	$H - O$ stretch	HF	4095	$H - F$ stretchd
CHF	1181	$C - F$ stretch	OH	3714	$O - H$ stretch

Fig. 2 The overall profile of the potential energy surface for the reactions of $O(^3P)$ with CH_2F (the energies were calculated at the B3LYP/6-311 + +G(2d, 2p) level)

be assigned to the C_{2v} group, and the two hydrogen atoms always vibrate simultaneously. The products of HF and HO are linear molecular and only have a stretch mode at 4095 cm^{-1} and 3714 cm^{-1} , respectively. HCOH and CHFO belong to the group point of C_s , and there are six vibrational modes.

2.2 Vibrational mode analysis for the reaction of $O(^3P)$ with CH_2F

When an $O(^3P)$ atom connects with the C atom of CH_2F to become OCH_2F (IM1), three modes of normal vibration are added. For IM1, the emergence of the O – C – F vibrational modes and the C – O stretch imply that a stable C – O bond forms. Because of the effect of oxygen atom, the symmetrical and asymmetrical stretching vibrational frequencies of CH_2 are red shifted from 3138 cm^{-1} to 2886 cm^{-1} and from 3299 cm^{-1} to 2903 cm^{-1} , respectively.

Once IM1 is formed, it can undergo various possible production channels immediately by isomerization or decompo-

sition. Four production channels of IM1 have been found, and they can be described as

The vibrational frequencies and their vibrational mode assignment of TS1, TS2, TS3, IM1 are listed in Table 2.

A hydrogen atom can cleave from IM1 via transition state TS1, forming $H + CHFO$, and it is the most favorable reaction channel, because the barrier height for this channel is $101.70\text{ kJ}\cdot\text{mol}^{-1}$ relative to IM1 at the B3LYP level. When one C – H bond is lengthened in the transition state TS1, there are great changes in all the vibrational modes of $H - C - H$. $H - C - H$ symmetric stretch and asymmetric stretch vanish, and two C – H stretching vibrational modes are formed, in which the stretching vibrational frequencies of the lengthened C – H1 bond become imaginary values ($903i\text{ cm}^{-1}$). The imaginary frequency means that the interaction between C and H is very weak and H atom is departing from the molecule. As it can be seen from Table 2, the vibrational frequencies of C – F bond stretch and C – O bond stretch are blue shifted from 968 cm^{-1} to 1005 cm^{-1} and from 1152 cm^{-1} to 1744 cm^{-1} , respectively. When the transition state (TS1) is contrasted with the product CHFO, it is evident that the imaginary frequency of C – H vanishes and the vibrational frequencies of other vibrational modes are increased.

The second reaction channel of IM1 is the HF elimination process via a three-centered transition state (TS2), forming $HF + HCO$. The only imaginary frequency ($613i\text{ cm}^{-1}$) of TS2 is assigned to the F – H2 stretch, and it implies the emergence of

Table 2 Vibrational frequencies and vibrational mode assignment for TS1, TS2, TS3 and IM1

Species	Frequency (cm^{-1})	Frequency assignment	Species	Frequency (cm^{-1})	Frequency assignment
TS1	903 <i>i</i>	C – H1 stretch	TS2	613 <i>i</i>	F – H2 stretch
	467	C – H1 rock in plane		347	O – C – F bend in plane
	504	C – H1 rock out of plane		640	C – H2 rock in plane
	643	O – C – F bend in plane		897	C – H1 rock in plane
	1005	F – C stretch		1022	CH_2 twist
	1059	C – H2 rock out of plane		1285	CH_2 scissors
	1059	C – H2 rock in plane		1728	C – O stretch
	1744	C – O stretch		2428	C – H2 stretch
	3050	C – H2 stretch		3026	C – H1 stretch
			IM1	546	O – C – F bend in plane
TS3	2016 <i>i</i>	C – H2 rock out of plane		786	CH_2 rock in plane
	545	O – C – F bend in plane		968	C – F stretch
	642	C – H2 rock in plane		1139	CH_2 twist
	993	C – H1 rock out of plane		1152	O – C stretch
	1077	C – F stretch		1315	CH_2 rock out of plane
	1224	C – O stretch		1339	CH_2 scissors
	1322	C – H1 rock in plane		2886	CH_2 symmetric stretch
	2353	C – H2 stretch		2903	CH_2 asymmetric stretch
	3091	C – H1 stretch			

Table 3 Vibrational frequencies and vibrational mode assignment for TS4, TS5, and IM2

Species	Frequency (cm^{-1})	Frequency assignment
IM2	348	H2 – O rock out of plane
	546	F – C – O – H2 twist
	935	C – H1 rock out of plane
	1029	C – F stretch
	1175	C – O stretch
	1295	H2 – O – C – H1 bend in plane
	1379	H2 – O – C – H1 rock out of plane
	3159	H1 – C stretch
	3798	H2 – O stretch
TS5	1747 <i>i</i>	H2 – F stretch
	567	C – F stretch
	682	O – C – F bend in plane
	805	C – H1 rock in plane
	986	O – H2 rock out of plane
	1089	C – H1 rock out of plane
	1534	C – O stretch
	1983	O – C – H1 stretch
	2979	C – H1 stretch
TS4	1352 <i>i</i>	H2 – O stretch
	261	H2 – O rock out of plane
	596	H2 – O rock in plane
	669	O – C – F bend in plane
	911	H1 – C rock out of plane
	1071	F – C stretch
	1347	H1 – C rock in plane
	1672	C – H1 stretch
	3134	C – H1 stretch

the H2 – F bond. Because the C – F bond and the C – H2 bond are increased from 0.1391 nm to 0.1886 nm and from 0.1106 nm to 0.1159 nm, respectively, the vibrational frequencies of C – O stretch and C – H1 stretch are strengthened, but the CH_2 twist and scissors are weakened. In TS2, the forming H2 – F bond is 0.1531 nm, which is longer than that of the HF molecule (0.0923 nm).

IM1 can isomerize to another intermediate CHFOH (IM2) *via* a three-atom ring TS3. For TS3, the imaginary frequency is assigned to the C – H2 rock out of plane, which means the C – H2 bond is weakened, and the H2 atom will migrate to the O atom. The C – H2 rock in plane and the C – H2 stretch show that C – H2 bond has not broken completely. When the vibrational modes and vibrational frequencies of TS3 are compared with those of IM2, it can be found that the imaginary frequency of C – H2 vanished and the vibrational modes of O – H2 were produced. These results show that the C – H2 has been ruptured in IM2. The H2 – O rock out of plane, the F – C – O – H2 twist, the H2 – O – C – H1 bend in plane and the H2 – O – C – H1 rock out of plane show that the O – H2 bond has formed. The energy of IM2 is $16.06 \text{ kJ} \cdot \text{mol}^{-1}$ lower than IM1. Therefore, IM2 has higher internal energy and can further decom-

pose.

The fourth production channel of IM1 is the formation of $F + CH_2O$. This production channel is a simple C – F bond fission without a pronounced barrier at the B3LYP/6-311++G(2*d*, 2*p*) level. The disappearance of the vibrational frequencies of O – C – F bend in plane and C – F stretch confirm the fission of the C – F bond. It has been noted that the extrusion of a fluorine atom from an OCH_2F radical was studied by Rayez *et al.*^[17] using MNDO/CI and SCF/CI methods. It is confirmed that the electron correlation effect is important in this bond fission process. The product channel $F + CH_2O$ is the most unfavorable because of its endothermicity of $71.93 \text{ kJ} \cdot \text{mol}^{-1}$.

2.3 Vibrational mode analysis for reaction channels of IM2

The four reaction channels of IM2 are

The frequencies and vibrational mode assignment of TS4, TS5 and IM2 are shown in Table 3. Two simple bond cleavage pathways of IM2 are C – F bond scission leading to $F + HCOH$ and C – O bond scission leading to $OH + FCH$. No transition states were found for both paths. The disappearances of the vibrational frequencies of C – F stretch and F – C – O – H2 twist show the fission of C – F bond. Similarly, the disappearances of the vibrational frequencies of C – O stretch, H1 – C – O – H2 bend in plane, H1 – C – O – H2 rock out of plane, F – C – O – H2 twist also confirm the fission of the C – O bond.

The cleavage of the O – H2 bond can form $H + CHFO$ *via* transition state TS4. It is the most favorable decomposition channel of IM2. As H2 atom is apart from O atom in TS4, the stretching vibrational modes of O – H2 are momentarily decreased from 3798 cm^{-1} to 1352 cm^{-1} . The imaginary frequency is always relative to the bond that is forming or rupturing, in this case the imaginary frequency means that the H2 – O is unstable. As Fig. 1 also shows that the H2 – O bond has been elongated to about 0.1485 nm, which is longer than the normal length of the H – O bond. Compare to the product, CHFO, the imaginary frequency of O – H2 vanishes, which confirms the fission of O – H2 bond.

The last reaction channel of IM2 is the 1, 2-HF elimination forming $HF + HCO$ *via* a four-atom ring transition state TS5. In TS5, the imaginary frequency belongs to the H2 – F stretch, which confirms the formation of H2 – F bond. Because the O – H2 bond and C – F bond are elongated from 0.0965 to 0.1215

nm and from 0.1363 to 0.1744 nm, respectively, the vibrational frequencies of C – O stretch, C – H1 rock out of plane are blue shifted. Because the vibrational frequencies of the C – F stretch, O – H2 rock out of plane still exist, the C – F bond and the O – H2 bond have not cleaved completely. The length of the forming H – F bond (0.1224 nm) is larger than the equilibrium bond length of HF molecule.

In conclusion, on the grounds of computed results from the GAUSSIAN 98 programs package at the B3LYP/6-311 + + G (2d, 2p) level, the reaction mechanism of O(³P) with CH₂F has been investigated thoroughly *via* the vibrational model analysis. From Fig. 2 it can be seen that H + CHFO is the main product because of its lowest internal energy (–329.65 kJ·mol^{–1}), so the main reaction channel involving this system should be O(³P) + CH₂F → IM1 → TS1 → H + CHFO

And the relationships among the reactants, five transition states, two intermediates and various products involved this multi-channel reaction are elucidated. The vibrational mode analysis shows that the reaction mechanism is reliable.

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多通道反应 O(³P) + CH₂F 的理论研究*

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摘要 用密度泛函理论研究了氧原子与氟代甲基自由基的反应. 反应中出现的所有物种的平衡构型用 B3LYP 方法在 6-311 + + G (2d, 2p) 基组水平上进行了优化, 同时对各物种进行了频率分析; 在同一理论水平上计算了各反应通道的势能面变化, 分析了反应物、中间体、过渡态、产物的振动模式随反应途径的变化关系, 阐明了该多通道反应的反应机理.

关键词: 密度泛函理论, 多通道反应, 振动模式
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