A full-dimensional analytical potential energy surface for the $F + CH_4 \rightarrow HF + CH_3$ reaction*

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A full-dimensional analytical potential energy surface (APES) for the $F + CH_4 \rightarrow HF + CH_3$ reaction is developed based on 7127 *ab initio* energy points at the unrestricted coupled-cluster with single, double, and perturbative triple excitations. The correlation-consistent polarized triple-split valence basis set is used. The APES is represented with a many-body expansion containing 239 parameters determined by the least square fitting method. The two-body terms of the APES are fitted by potential energy curves with multi-reference configuration interaction, which can describe the diatomic molecules (CH, H_2, HF, and CF) accurately. It is found that the APES can reproduce the geometry and vibrational frequencies of the saddle point better than those available in the literature. The rate constants based on the present APES support the experimental results of Moore *et al.* [*Int. J. Chem. Kin.* **26**, 813 (1994)]. The analytical first-order derivation of energy is also provided, making the present APES convenient and efficient for investigating the title reaction with quasiclassical trajectory calculations.

Keywords: analytical potential energy surface, least square fitting method, UCCSD(T), $F + CH_4 \rightarrow HF + CH_3$ reaction

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1. Introduction

Reactions involving the fluorine atom and methane have attracted much attention in experimental and theoretical studies because they play important roles in the atmosphere and the stratosphere. The state-resolved, pair-correlated differential cross sections for the reaction $F + CD_4 \rightarrow DF + CD_3$ have been reported.[1,2] CH stretching excitation in the early barrier $F + CHD_3$ reaction has also been investigated recently.[3] The construction of a potential energy surface (PES) for dynamic calculations in order to understand experimental results has continuously evolved in recent years. Several semiclassical analytical potential energy surfaces (APESs) have been calibrated[3–6] from the *ab initio* geometries of the stable points on the PES and the experimental reaction rate. Troya *et al.*[7] reported on a reduced dimensional APES fitted by *ab initio* energies at the PUMP4/UMP2/6-311 + G(2df, 2pd) level. Juse very recently, Czakó *et al.*[8] reported that a full-dimensional APES based on 19384 *ab initio* energies is believed to be at the theoretical level of the unrestricted coupled-cluster with single and double and perturbative triple excitations [UCCSD(T)][9,10] and aug-cc-PVTZ basis set quality. However, the energies are not truly calculated at the UCCSD(T)/aug-cc-PVTZ level but are obtained by an efficient composite method through employing explicit UCCSD(T)/aug-cc-PVDZ and UMP2/aug-cc-PV*XZ*[*X* = D, T] computations. Their APES is represented by a polynomial expansion on the Morse-like variables of internuclear distances through using basic invariant under-permutations of like atoms. No special treatment is employed for the diatomic product HF. Therefore, it cannot accurately represent the vibrational properties of the product HF, and the *ab initio* energies from the explicit calibrate formula are less accurate than those actually calculated at the UCCSD(T)/cc-PVTZ level.

In the present paper, we present a new full-dimensional APES represented with the many-body expansion that satisfies the permutation symmetry of H atoms. The two-body terms are constructed separately, which can describe the HF molecule accurately. The present APES contains 239 parameters fitted by 7127 *ab initio* energy points computed at the actual UCCSD(T)/cc-PVTZ level. No scale approximation is used.

2. *Ab initio* calculations

2.1. Choice of computational level

The computational levels used to calculate the single energy points are checked by performing calculations for the reactants, the saddle point, and the products at different theoretical levels, and by comparing the results with the theoretical and experimental data available in the literature. Two high levels of the *ab initio* method, namely, quadratic configuration interaction with single and double excitation (QCISD)[11] and UCCSD(T), are considered. The cc-PVTZ and augmented cc-PVTZ basis set (aug-cc-PVTZ) are checked.

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The considered levels as well as the experimental data[12] of the geometries and vibrational frequencies of the reactant CH_4 and product CH_3 are shown in Tables 1 and 2. Both QCISD and UCCSD(T) can give satisfactory results compared with the experimental values. Table 3 shows that the basis sets have some effect on the geometry and frequencies of the saddle point (the obvious change is the H–F bond length). However, no obvious improvement for the results of CH_3 and CH_4 are found in Tables 1 and 2. It should be noted that the aug-cc-PVTZ basis set increases CPU consumption, particularly for the CH_4F system, which results in an excessive need for computer resources in our laboratory for the calculations of the energy grid to build PES at this level. Therefore, UCCSD(T)/cc-PVTZ is chosen as the theoretical level for all single energies of the PES grid of CH_4F.

Table 1. The C–H bonds and vibrational frequencies of CH_4.

	QCISD cc-pVTZ	UCCSD(T) cc-pVTZ	Present APES	UCCSD(T) aug-cc-pVTZ	CSBB[7] APES	EBR[5] model	RNE[4] model	Expt.[11]
R_e/Å	1.088	1.089	1.082	1.090	1.091	1.094	1.094	1.091
Freqencies/cm^{-1}	1356	1343	1163	1350	1329	1344	1286	1306
	1356	1344	1376	1350	1329	1344	1286	1306
	1356	1344	1414	1350	1329	1344	1286	1306
	1581	1570	1477	1573	1569	1538	1468	1534
	1581	1570	1538	1573	1569	1538	1468	1534
	3046	3034	3188	3027	3032	2984	2978	2916
	3163	3153	3218	3146	3145	3145	3138	3018
	3163	3153	3381	3146	3145	3145	3138	3018
	3163	3153	3808	3146	3145	3145	3138	3018

Table 2. The C–H bonds and vibrational frequencies of CH_3.

	QCISD cc-pVTZ	UCCSD(T) cc-pVTZ	Present APES	UCCSD(T) aug-cc-pVTZ	CSBB[7] APES	EBR[5] model	RNE[4] model	Expt.[11]
R_e/Å	1.078	1.079	1.117	1.080	1.081	1.094	1.094	1.079
Frequencies/cm^{-1}	492	496	528	496	508	580	580	580
	1434	1426	1377	1419	1407	1383	1380	1383
	1436	1426	1383	1419	1407	1383	1380	1383
	3132	3119	2684	3114	3090	3002	3072	3002
	3312	3300	2645	3294	3280	3184	3182	3184
	3312	3300	2638	3294	3280	3184	3182	3184

Table 3. Geometries and frequencies of the saddle point.

	QCISD cc-pVTZ	CCSD(T) cc-pVTZ	Present APES	CCSD(T) aug-cc-pVTZ	CSBB[7] APES	EBR[5] model	RNE[4] model
R (C–H)	1.086	1.088	1.088	1.089	1.091	1.094	1.094
R (C–H′)	1.124	1.117	1.117	1.109	1.105	1.100	1.107
R (F–H′)	1.483	1.537	1.536	1.641	1.656	1.777	1.550
				Frequencies			
	373i	421i	302i	765i	357i	122i	106i
	85	244	253	265	40	120	119
	85	437	257	388	117	120	119
	1278	1242	1278	1222	1255	1265	1201
	1278	1274	1371	1222	1335	1265	1201
	1280	1300	1381	1345	1361	1283	1221
	1501	1490	1455	1478	1520	1485	1416
	1501	1573	1557	1499	1539	1485	1416
	2121	2339	2329	2608	2604	2880	2711
	3087	3092	3110	3096	3070	3058	3032
	3196	3191	3144	3177	3185	3133	3127
	3196	3196	3217	3208	3203	3133	3127

2.2. Choice of grid

The section near the minimum energy path (MEP) is the most important part on the PES. We first optimize the MEP of $CH_4 + F \rightarrow CH_3 + HF$ reaction. Then we choose the grid according to the MEP. It should be pointed out that the saddle point optimization at UCCSD(T)/cc-PVTZ is difficult because the PES of CH_4F is smooth near the saddle point. We first perform optimization with Gaussian03 codes,[13] in which the calculation can be limited by the structures of the reactant and the product, which is made successful and easier.

However, the highest computational level for this method supported by Gaussian03 is QCISD; therefore, we first obtain the geometry of the saddle point at QCISD/cc-PVTZ. Then we perform calculations at UCCSD(T)/cc-PVTZ in MOLPRO[14] using the geometry given by Gaussian03 as the initial structure. Figure 1 shows that the saddle points at both calculation levels are the same as those obtained from the C_{3v} symmetry reported in Refs. [15]–[17] although other symmetries are also reported.[3,8] Based on the saddle point at UCCSD(T)/cc-PVTZ, we calculate the MEPs at the same level. Figure 2 shows that there are 40 points obtained for MEP. They are used as the basic reference to construct the PES grid. The entire grid is divided into several parts as follows.

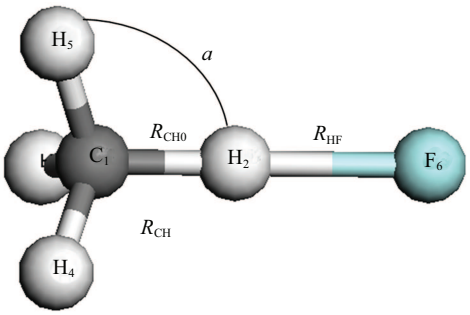


Fig. 1. (color online) Optimized saddle point geometry of CH_4F at UCCSD(T)/cc-pVTZ level.

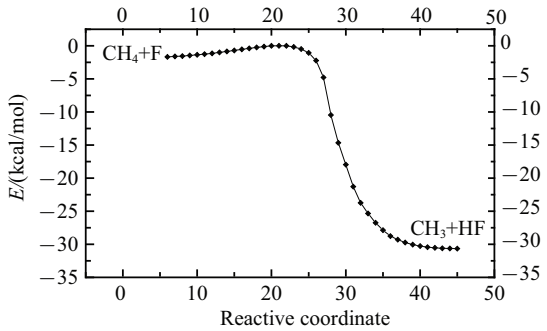


Fig. 2. MEP of $CH_4 + F \rightarrow CH_3 + HF$ at UCCSD(T)/cc-pVTZ level.

1) Structures in C_{3v} symmetry. Based on the points of MEP, we change the values of R_{CH_0}, R_{CH}, α, and R_{HF} in Fig. 1, respectively, but keep the structures in C_{3v} symmetry. There are 3640 structures calculated.

2) Construct geometries by varying the Cartesian coordinates regardless of the symmetry of CH_4F. MEP is still used as the basis of choosing geometries. The 18 Cartesian coordinates of the six atoms increase or reduce two steps based on the values of the points on MEP, which result in 2880 geometries. The points on MEP are re-calculated to make the geometries vary smoothly and converge more easily.

3) Construct geometries by varying the internal coordinates regardless of the symmetry of the molecule. There are 12 internal coordinates for the six-atom system. We choose four values for each coordinate, resulting in a total of 1920 geometries.

4) Geometries in the section near the saddle point. To describe the section more accurately, we choose about 1000 geometries using the aforementioned policy, but using smaller steps.

The computed geometries more than 9000 in total, and the geometries whose energies are five times higher than that of the saddle point and the same geometries in different calculations are discarded. A total of 7127 geometries are retained in the fitting process.

3. Construction of the analytical expressions for fitting

Using the symmetry function to represent PES, the effect of the energy points in the fitting process, particularly on the system containing several equal atoms is evaluated. We use the many-body expansion to construct the function for fitting. For the six-atom system, the expression can be written as

$$V = V^{(2)} + V^{(3)} + V^{(4)} + V^{(5)} + V^{(6)}, \quad (1)$$

where $V^{(n)}$ represents the n-body interactions among the atoms. The general policy of the fitting is to construct the isolated n-body terms one by one. There will be 15 two-body terms, 20 three-body terms, 15 four-body terms, six five-body terms, and one six-body term. Some terms can be reduced because they contain the same atoms as the other terms. However, the energy grid calculations of all the terms are still too large to be undertaken using the present computational resource if the terms are constructed one by one. Therefore, we construct a function including two- to four-body terms in order to fit the present *ab initio* energies. These two-body terms are constructed solely for each dimer and are fitted by energies computed with multi-reference configuration interaction (MRCI) and large basis sets. The most important product, HF, can be described accurately. However, the three- and four-body terms are not solely fitted for each trimer or tetramer, but though the whole expression including all the two- to four-body terms. There are 239 parameters to be fitted in the whole APES for all interactions among the six atoms. All parameters are determined at the same time using the *ab initio* energies of the six-atom molecule. This implies that the effect of five- and six-body terms is represented by the effect of the parameters deviating from their value for the separate trimer or tetramer. This will in turn affect the accuracy of the PES for the separated three-body (CH_3) or four-body (CH_4) radicals. Fortunately, they are less important in the reaction section.

The 15 distances between atoms are used as the variables of APES. R_1–R_3 are the three CH bonds, and R_4–R_6 are the three H–H bonds of the CH_3 radical. R_7–R_9 are the distances

between H_3–H_5 and H_2. R_{10}–R_{12} are the distances between H_3–H_5 and F_6. R_{14} is the bond of C_1–H_2, and R_{15} is the bond of H_2–F_6.

3.1. Two-body terms

There are 15 two-body terms divided into four types: C–H, H–F, C–F, and H–H. Therefore, we use four different sets of parameters for two-body terms.

All the two-body terms are as follows:

$$\begin{aligned} V^{(2)} &= V^{(2)}(R_1)+V^{(2)}(R_2)+V^{(2)}(R_3)+V^{(2)}(R_4)V^{(2)}(R_5) \\ &\quad + V^{(2)}(R_6)+V^{(2)}(R_7)+V^{(2)}(R_8)+V^{(2)}(R_9) \\ &\quad + V^{(2)}(R_{10})+V^{(2)}(R_{11})+V^{(2)}(R_{12})+V^{(2)}(R_{13}) \\ &\quad + V^{(2)}(R_{14})+V^{(2)}(R_{15}). \end{aligned} \tag{2}$$

The function used to fit the two-body terms is the Murrell Sorbie (MS)[16] function, which has been used to construct many diatomic analytical potential energy functions (APEFs)[18–23] in our group and others.[24,25] The MS function is as follows:

$$V(\rho) = -D_e\left(1+\sum_{i=1}^{n} a_i\rho^i\right)\exp(-a_1\rho), \tag{3}$$

where n will be truncated according to the different dimers. The fitting results are collected in Table 4. The very small root-mean-square (RMS) errors show that the present fitting results are accurate. To test the accuracy of the APEF, we calculate the spectroscopic constants using the APEFs and compare the results with the experimental data presently available.[26–28] Both the experimental and calculational values are collected in Table 5. The table shows that the present spectroscopic constants for all the two-body terms are in good agreement with the corresponding experimental values, indicating that the present APEFs are highly accurate and can be used to credibly construct APES.

Table 4. Fitting parameters of MS functions for two-body terms.

	H_2	CH	HF	CF
R_e/Å	0.7415	1.12051	0.9176	1.28512
D_e/eV	4.7444	3.59261	6.1131	5.8536
a_1/Å^{-1}	5.62775	4.91354	6.15323	4.66408
a_2/Å^{-2}	12.05447	8.18948	13.97448	6.93435
a_3/Å^{-3}	16.60972	8.39213	20.36331	7.69136
a_4/Å^{-4}	14.97177	5.69278	20.17076	5.63957
a_5/Å^{-5}	10.12269	2.76801	15.76236	0.76064
a_6/Å^{-6}	4.67868	–1.24578	8.18966	–1.74004
a_7/Å^{-7}	2.09014	–2.31058	–2.69549	2.24348
a_8/Å^{-8}	–2.99408	1.72857	–5.47295	–1.43164
a_9/Å^{-9}	1.40101	–0.18574	3.3377	0.36724
RMS/eV	2.7×10^{-4}	4.3×10^{-4}	5.5×10^{-4}	7.7×10^{-3}

3.2. Three-body terms

There are 20 three-body terms; however, only four different molecules (CH_2, FH_2, CHF, H_3) are contained. Generally, the APES and parameters should be the same for the terms are comprised of the same atoms. However, we allow different parameters when the geometries are obviously different although they contain the same atoms. We expect that this policy will bring more satisfactory fitting results for the present energy grid. The six CH_2 terms cannot be neglected because they join the rupture or building of bonds, or strong interactions exist among the atoms in the radicals. For the six FH_2 terms, we use two sets of parameters, one is for F–H_2–H_3 (H_4, H_5) and the other for F–H_3–H_4, F–H_4–H_5, and F–H_3–H_5. The C–H_2–F and C–H_3 (H_4, H_5)–F are treated by two sets of parameters. The three-body terms used are as follows:

$$\begin{aligned} V^{(3)}_{CH_2} &= V^{(3)}_1(R_4,R_1,R_2) \\ &\quad + V^{(3)}_1(R_5,R_2,R_3)+V^{(3)}_1(R_6,R_1,R_3) \\ &\quad + V^{(3)}_1(R_7,R_1,R_{10}) \\ &\quad + V^{(3)}_1(R_8,R_2,R_{10})+V^{(3)}_1(R_9,R_3,R_{10}), \end{aligned} \tag{4}$$

$$\begin{aligned} V^{(3)}_{H_3} &= V^{(3)}_2(R_4,R_5,R_6)+V^{(3)}_2(R_4,R_7,R_8) \\ &\quad + V^{(3)}_2(R_5,R_8,R_9)+V^{(3)}_2(R_6,R_7,R_9), \end{aligned} \tag{5}$$

$$\begin{aligned} V^{(3)}_{FH_2} &= V^{(3)}_3(R_{12},R_7,R_{11})+V^{(3)}_3(R_{13},R_8,R_{11}) \\ &\quad + V^{(3)}_3(R_{14},R_9,R_{11}), \end{aligned} \tag{6}$$

$$V^{(3)}_{CHF} = V^{(3)}_4(R_{15},R_{10},R_{11}). \tag{7}$$

3.2.1. Function for $CH_2/FH_2(XYY)$

The symmetry coordinates are used to construct the permutable terms. Based on the reference D_{3h} structure, R_{YY}, R_{XY1}, and R_{XY2} are used to represent the distances of Y_1–Y_2, X–Y_1, and X–Y_2, while $Re_{Y_1Y_2}$, Re_{XY_1}, and Re_{XY_2} represent the bond lengths of the stable reference. The symmetry coordinates can be built as follows:

$$\rho_1 = R_{Y_1Y_2} - Re_{Y_1Y_2},\ \ \rho_2 = R_{XY_1} - Re_{XY_1},\ \ \rho_3 = R_{XY_2} - Re_{XY_2},$$

then S_1, S_2, S_3 are determined by

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix} = \begin{bmatrix} \sqrt{1/3} & \sqrt{1/3} & \sqrt{1/3} \\ 0 & \sqrt{1/2} & -\sqrt{1/2} \\ \sqrt{2/3} & -\sqrt{1/6} & -\sqrt{1/6} \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{bmatrix} \tag{8}$$

and

$$Q_1 = S_1,\ \ Q_2 = S_2^2+S_3^2,\ \ Q_3 = S_3^3 - 3S_3S_2^2.$$

Here, Q_1, Q_2, and Q_3 are symmetry internal coordinates, and they satisfy the invariance of the permutation of the two H atoms. They can be used to construct the APES as follows:

$$V^{XYY}(Q_1,Q_2,Q_3) = P^{XYY}(Q_1,Q_2,Q_3)\cdot T^{XYY}(S_1,S_3),$$

where P is a polynomial consisting of Q_1, Q_2, Q_3,

$$\begin{aligned} &P^{XYY}(Q_1,Q_2,Q_3) \\ &= C_0 + C_1Q_1 + C_2Q_1^2 + C_3Q_2 + C_4Q_1^3 + C_5Q_1Q_2 \\ &\quad + C_6Q_3 + C_7Q_1^4 + C_8Q_1^2Q_2 + C_9Q_1^2Q_3 + C_{10}Q_2^2 \\ &\quad + C_{11}Q_1^5 + C_{12}Q_1^3Q_2 + C_{13}Q_1^2Q_3 + C_{14}Q_1Q_2^2 \end{aligned}$$

$$+C_{15}Q_2Q_3+C_{16}Q_1^6+C_{17}Q_1^4Q_2+C_{18}Q_1^2Q_2^2$$
$$+C_{19}Q_2^3+C_{20}Q_1^3Q_3+C_{21}Q_3^2+C_{22}Q_1Q_2Q_3, \quad (9)$$

T is a range function of the form

$$T^{XYY}(S_1,S_3)=[1-\tanh(C_{23}\cdot S_1)]\cdot[1-\tanh(C_{24}\cdot S_3)]. \quad (10)$$

Here S_2 disappears from the expression because it does not satisfy the invariance of permutation of the two H atoms. C_0–C_{24} are parameters determined by fitting. Usually, $Re_{Y_1Y_2}$, Re_{XY_1}, and Re_{XY_2} are fixed at the equilibrium positions of the reference geometries. However, they are also fitted in the present work to obtain more satisfactory fitting results. We chose the values of the saddle point geometry as the initial values in the fitting.

3.2.2. Function for H_3 (*XXX*)

The geometry in D_{3h} symmetry is used as reference structure. The construction of the functions is as follows:

$$\rho_1=R_{X_1X_2}-Re_{X_1X_2},\ \rho_2=R_{X_2X_3}-Re_{X_2X_3},\ \rho_3=R_{X_1X_3}-Re_{X_1X_3},$$

S_1, S_2, and S_3 are related to ρ_1, ρ_2, and ρ_3 by Eq. (8).

$$V^{XXX}(Q_1,Q_2,Q_3)=P^{XXX}(Q_1,Q_2,Q_3)\cdot T^{XXX}(S_1,S_3), \quad (11)$$

where P is the same polynomial as $P^{XYY}(Q_1,\ Q_2,\ Q_3)$ in Eq. (9), but only S_1 can satisfy the invariance of permutation of the three H atoms. Therefore, T^{XXX} is

$$T^{XXX}(S_1)=1-\tanh(C_{23}\cdot S_1). \quad (12)$$

The fitting parameter C_{24} in the function XYY is unnecessary here.

3.2.3. Function for CHF (*XYZ*)

In this case, there is no restriction on symmetry, and it is unnecessary to perform symmetry transformation. However, more polynomials are needed. S_1, S_2, and S_3 are still used as the variables of the expression

$$S_1=\rho_1=R_{XY}-R_{eXY},$$
$$S_2=\rho_2=R_{XZ}-R_{eXZ},$$
$$S_3=\rho_3=R_{YZ}-R_{eYZ},$$

P^{XYZ} truncated at the sixth-order polynomial is

$$\begin{aligned}P^{XYZ}=\ & C_1+C_2S_3+C_3S_3^2+C_4S_3^3+C_5S_3^4+C_6S_3^5+C_7S_3^6\\ &+C_8S_2+C_9S_2S_3+C_{10}S_2S_3^2+C_{11}S_2S_3^3+C_{12}S_2S_3^4\\ &+C_{13}S_2S_3^5+C_{14}S_2^2+C_{15}S_2^2S_3+C_{16}S_2^2S_3^2\\ &+C_{17}S_2^2S_3^3+C_{18}S_2^2S_3^4+C_{19}S_2^3+C_{20}S_2^3S_3\\ &+C_{21}S_2^3S_3^2+C_{22}S_2^3S_3^3+C_{23}S_2^4+C_{24}S_2^4S_3\\ &+C_{25}S_2^4S_3^2+C_{26}S_2^5+C_{27}S_2^5S_3+C_{28}S_2^6\\ &+C_{29}S_1+C_{30}S_1S_3+C_{31}S_1S_3^2+C_{32}S_1S_3^3\\ &+C_{33}S_1S_3^4+C_{34}S_1S_3^5+C_{35}S_1S_2+C_{36}S_1S_2S_3\\ &+C_{37}S_1S_2S_3^2+C_{38}S_1S_2S_3^3+C_{39}S_1S_2S_3^4\\ &+C_{40}S_1S_2^2+C_{41}S_1S_2^2S_3+C_{42}S_1S_2^2S_3^2+C_{43}S_1S_2^2S_3^3\\ &+C_{44}S_1S_2^3+C_{45}S_1S_2^3S_3+C_{46}S_1S_2^3S_3^2+C_{47}S_1S_2^4\\ &+C_{48}S_1S_2^4S_3+C_{49}S_1S_2^5+C_{50}S_1^2+C_{51}S_1^2S_3\\ &+C_{52}S_1^2S_3^2+C_{53}S_1^2S_3^3+C_{54}S_1^2S_3^4+C_{55}S_1^2S_2\\ &+C_{56}S_1^2S_2S_3+C_{57}S_1^2S_2S_3^2+C_{58}S_1^2S_2S_3^3+C_{59}S_1^2S_2^2\\ &+C_{60}S_1^2S_2^2S_3+C_{61}S_1^2S_2^2S_3^2+C_{62}S_1^2S_2^3+C_{63}S_1^2S_2^3S_3\\ &+C_{64}S_1^2S_2^4+C_{65}S_1^3+C_{66}S_1^3S_3+C_{67}S_1^3S_3^2\\ &+C_{68}S_1^3S_3^3+C_{69}S_1^3S_2+C_{70}S_1^3S_2S_3+C_{71}S_1^3S_2S_3^2\\ &+C_{72}S_1^3S_2^2+C_{73}S_1^3S_2^2S_3+C_{74}S_1^3S_2^3+C_{75}S_1^4\\ &+C_{76}S_1^4S_3+C_{77}S_1^4S_3^2+C_{78}S_1^4S_2+C_{79}S_1^4S_2S_3\\ &+C_{80}S_1^4S_2^2+C_{81}S_1^5+C_{82}S_1^5S_3\\ &+C_{83}S_1^5S_2+C_{84}S_1^6. \quad (13)\end{aligned}$$

S_1, S_2, and S_3 can all appear in T^{XYZ}, which is written as follows:

$$\begin{aligned}T^{XYZ}=\ & [1-\tanh(C_{85}\cdot S_1)]\cdot[1-\tanh(C_{86}\cdot S_2))]\\ &\times[1-\tanh(C_{87}\cdot S_3)], \quad (14)\end{aligned}$$

C_1–C_{87}, R_{eXY}, R_{eXZ}, and R_{eYZ} are determined by fitting.

3.3. Four-body term

In the present expression, one H_4 and four CH_3 terms are included, while six CH_2F and four H_3F terms are neglected because the F is at a large distance from the other atoms in the reaction. This makes the four-body interactions among CH_2–F and H_3–F small. The considered four-body terms are as follows:

$$V_{H_4}^{(4)}=V_1^{(4)}(R_7,R_8,R_9,R_5,R_6,R_4), \quad (15)$$
$$\begin{aligned}V_{CH_3}^{(4)}=\ & V_2^{(4)}(R_1,R_2,R_3,R_5,R_6,R_4)\\ &\times V_2^{(4)}(R_1,R_2,R_{10},R_8,R_7,R_4)\\ &+V_2^{(4)}(R_1,R_3,R_{10},R_9,R_7,R_6)\\ &\times V_2^{(4)}(R_2,R_3,R_{10},R_9,R_8,R_5). \quad (16)\end{aligned}$$

3.3.1. Function for H_4 (*XXXX*)

The policy for constructing the expression of the $XXXX$ molecule is similar to that for constructing three-body terms. The six internuclear distances in the four-atom molecule (R_1–R_6) are used to build the function. The ρ_1–ρ_6 are the differences between R and the corresponding equilibrium positions of the reference structure. The S_1–S_6 are related to ρ_1–ρ_6 as follows:

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} = \begin{bmatrix} \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} & \sqrt{1/6} \\ \sqrt{1/2} & 0 & 0 & -\sqrt{1/2} & 0 & 0 \\ 0 & \sqrt{1/2} & 0 & 0 & -\sqrt{1/2} & 0 \\ 0 & 0 & \sqrt{1/2} & 0 & 0 & -\sqrt{1/2} \\ 0 & 1/2 & -1/2 & 0 & 1/2 & -1/2 \\ \sqrt{1/3} & -\sqrt{1/12} & -\sqrt{1/12} & \sqrt{1/3} & -\sqrt{1/12} & -\sqrt{1/12} \end{bmatrix} \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \\ \rho_4 \\ \rho_5 \\ \rho_6 \end{bmatrix}. \quad (17)$$

The symmetry coordinates are written as follows:

$$Q_1 = S_1,\ \ Q_2 = S_2^2 + S_3^2 + S_4^2,\ \ Q_3 = S_5^2 + S_6^2,\ \ Q_4 = S_2 S_3 S_4,$$
$$Q_5 = S_6^3 - 3S_6 S_5^2,\ \ Q_6 = S_6(2S_2^2 - S_3^2 - S_4^2) + \sqrt{3}S_5(S_3^2 - S_4^2).$$

The polynomial P^{XXXX} is

$$\begin{aligned} P^{XXXX} &= C_1Q_1 + C_2Q_2 + C_3Q_3 + C_4Q_4 + C_5Q_5 + C_6Q_6 \\ &\quad + C_7Q_1^2 + C_8Q_1Q_2 + C_9Q_1Q_3 \\ &\quad + C_{10}Q_3^2 + C_{11}Q_1^2Q_2. \end{aligned} \quad (18)$$

Among S_1–S_6, only S_1 can satisfy the required D_{4h} and be included in T^{XXXX}:

$$T^{XXXX}(S_1) = 1 - \tanh(C_{12} \cdot S_1). \quad (19)$$

3.3.2. Function for CH_3 (*XYYY*)

The symmetry coordinates and polynomial P^{XYYY} are the same as those in the case of H_4. Both S_1 and S_4 satisfy the symmetry permutation requirements for XY_3, so T^{XYYY} is written as follows:

$$T^{XYYY}(S_1) = [1 - \tanh(C_{12} \cdot S_1)] \cdot [1 - \tanh(C_{13} \cdot S_4)]. \quad (20)$$

Five- and six-body terms can also be constructed using a similar policy. However, we truncate the four-body term in the present work. More terms will increase the fitting accuracy, but the effects of five-body and six-body terms should be small compared with those of the three- and four-body terms.

It should be noted that all parameters for the polynomials use C_n, regardless of the different meanings in different functions. However, they will not be confused in the entire APES because each function will be programmed by a separate subroutine.

4. Results and discussion

According to the above expression, there are 239 parameters and 16 variables (15 variables are involved in internuclear distances and 1 variable is involved in energy) in the final function for the present APES. Thirty of them are of linear variation, 198 are the parameters of polynomial and the other one is used to represent the energy of the single body. The parameters are determined using the nonlinear least square fitting method (Levenberg–Marquardt) involving 7127 geometries calculated by *ab initio* calculations. The fitting calculations are carried out with a Fortran 90 subroutine from a Web page of Miller[29] and a main drive program by ourselves. However, we perform a little improvement on the download subroutine. For the numerical derivative of the fitting function, we substitute the one-point formula of numerical derivatives with a two-point formula in our fitting in order to improve the fitting accuracy. Generally, the initial parameters can be chosen arbitrarily, but the convergent problem is often encountered in the present case because of the numbers of variables and parameters. Therefore, we use a policy of freezing some parameters in the beginning, then gradually add more changeable parameters. The initial values of the parameters in a new fitting with more fitting parameters are chosen according to the last successful fitting. The thirty nonlinear fitting parameters are the last ones joining to fit, and they are limited to give the rational dissociation radicals of the molecule in the tentative fitting. Finally, we let all the 239 parameters join fitting. After many tedious calculations, all 239 parameters are determined. The final fitted parameters are not listed here for the sake of brevity, but are included in the FORTRAN subroutine provided via e-mail. All the 7127 energy points from *ab initio* and fitted APES as well as the errors for each point are also be available via e-mail. It is surprising that the root-mean-square error is 3.2 cm^{-1} and the minimum error is only 8.1×10^{-5} cm^{-1}, which even is smaller than those of many systems containing three or two atoms. There are 10 points whose energies derivate from their *ab initio* counterparts over 10 cm^{-1}. These facts imply that the present fitting is of high quality.

To satisfy the necessity of dynamic calculations, we construct the analytical energy derivatives for our APES in the Cartesian coordinate system. They are also implemented in the FORTRAN subroutine. Using POLYRATE 9.7[30] and our APES, we calculate the geometries and frequencies of the reactants, products, and saddle points. Tables 1 and 2 collect the geometries and frequencies for CH_4 and CH_3, respectively. The experimental values and other theoretical work in the literature are also included. It is found that the C–H bond lengths of the two radicals are in agreement with the corresponding *ab initio* counterparts. However, three C–H stretch vibrational frequencies of CH_3 are obviously smaller than those of their *ab initio* counterparts, and one is larger than that of CH_4. The main cause is that the present energies in the fitting process focus on the reactive section around the reaction path but not in the region of incident or output limit. This implies that the fit-

ting results for CH_4 and CH_3 are from extrapolation but not interpolation. Therefore, there appear some deviations between the data from the fitted function and the data used for fitting are expectable. Of course, improvement can be realized via joining more energies in the incident or output regions to describe the reactant or product accurately.

It should be noted that the present geometry and frequencies of the saddle point as shown in Table 3, are in good consistence with those of the *ab initio* counterpart. Although the geometry of APES by Czakó *et al.*[8] coincides well with the one at UCCSD(T)/aug-cc-pVTZ, there are obvious deviations in frequencies, particularly the imaginary and low vibrational frequencies, which are very important for the reaction. The imaginary and low vibrational frequencies of the two recent model APES calibrated by the Espinosa–García group[5,6] are also too small compared with those of the *ab initio* counterpart at UCCSD(T)/cc-pVTZ or UCCSD(T)/aug-cc-pVTZ. Therefore, it is safe to say that the present APES can accurately reproduce the characteristic of the saddle point, and it is better than the other APESs in the literature.

With the improved canonical version of the variational transition-state theory (ICVT) in POLYRATE 9.7, we calculate the rate constants using our APES. The results are presented in Table 5 and Fig. 3. The present rate constants are close to the experimental values obtained by Moore *et al.*[31] but are obviously different from the other two experimental data.[32,33] However, our rate constants near 250 K are in good agreement with all the three experimental values. Figure 3 also shows that the present rate constants are larger at a low temperature (T) and decrease with T increasing. However, the rate constants increase again when the T is over 406 K. This tendency is different from those for the experimental data of Atkinson *et al.*[32] and Persky,[33] but similar to that for the experimental data of Moore *et al.*[31] and those of the two models of APES by the Espinosa-Garcia group.[3,4] After comparing the frequencies of the saddle point on different APESs

Table 5. Spectroscopic parameters of two-body terms based on the present APEF.

		R_e/Å	D_e/eV	B_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	α_e/cm^{-1}
H_2	Present	0.7415	4.7444	60.843	4400.11	121.29	3.053
	Expt.[22]	0.7416	4.476	60.809	4395.2	117.99	2.993
	Expt.[23]	0.741441	4.4781*	60.853	4401.21	121.33	3.062
CH	Present	1.1205	3.5926	14.4393	2856.06	66.7174	0.534871
			($E_0 = 0.1750$)				
	Expt.[22]*	1.1199	3.465	14.457	2858.5	63.02	0.534
HF	Present	0.9176	6.1131	20.918	4149.4	89.2642	0.776783
			($E_0 = 0.2544$)				
	Expt.[22]*	0.9168	5.869	20.51	4138.32	89.88	0.798
CF	Present	1.2851	5.8536	1.38712	1306.0	11.0646	0.0175811
			(E_0= 0.0176)				
	Expt.[22]*	1.2718	5.67	1.4172	1308.1	11.0	0.0184

*D_0 is the experimental value, including no zero point energy E_0. * Reference [24]

Table 6. Forward thermal rate constants for the $F + CH_4 \rightarrow HF + CH_3$ reaction (in 10^{-11} cm^3 molecule$^{-1}\cdot$s^{-1}).

	ICVT/ZCT	ICVT PM3–SRP/IC	ICVT/MJ1	TMB[5]	Expt.[30]	Expt.[29]	Expt.[28]
100.00	19.15	4.58	2.47				
150.00	8.94	3.76	2.05	2.68			7.66
184.00	6.67				3.95±0.35		
198.00	6.09				4.15±0.35		
200.00	6.02	3.64	1.94	3.20		4.06	6.26
216.00	5.53				4.80±0.35		
237.00	5.05				5.30±0.35		
250.00	4.82	3.70	1.95	3.71		6.05	5.54
262.00	4.64				6.05±0.35		
298.00	4.26	3.82	2.00	4.16	6.65±0.35	7.84	5.13
340.00	4.01				7.45±0.35		
400.00	3.85	4.11	2.18	5.17		11.04	
406.00	3.85				8.55±0.35		
500.00	3.87	4.47	2.43	5.95		13.47	
600.00	4.05						
700.00	4.31						
800.00	4.61						
900.00	4.93						
1000.00	5.25						

reported in the literature, we find that the rate constants exhibiting the minimum correspond to those of the APES with larger imaginary and low vibrational frequencies. Generally, the present APES can give better information about the saddle point, although the frequencies of the product CH_3 and reactant CH_4 are not reproduced completely. Obvious disaccord between the different theoretical rate constants and the experimental counterparts still exist, which calls for more theoretical and experimental investigations for the title reaction.

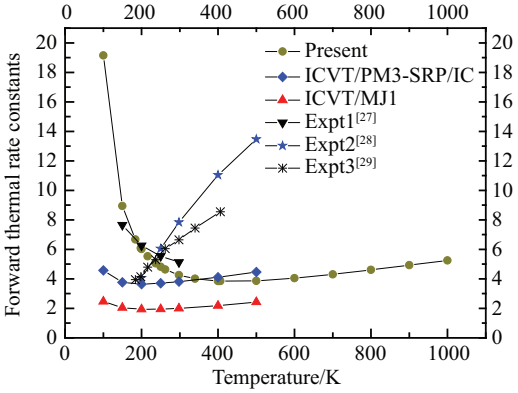


Fig. 3. (color online) The forward thermal rate constants for the $F+CH_4 \rightarrow HF+CH_3$ reaction (in 10^{-11}cm^3 molecule$^{-1}\cdot$s^{-1}).

5. Conclusion

A full-dimensional APES of the $F+CH_4 \rightarrow HF+CH_3$ reaction is developed by fitting 7127 energy points calculated at the UCCSD(T)/cc-pVTZ level. The present APES is represented by many-body expansion with 15 variables of internuclear distances; it includes 239 fitted parameters. The APES is symmetrized for the permutation of H atoms in the reactive system.

Compared with the reported APES in the literature, the present APES can better reproduce the geometry and frequencies of the saddle point, although the frequencies for CH_3 and CH_4 deviate from the *ab initio* values because they are not given special treatment in the grid of calculational geometries. All two-body terms are constructed from the potential energy curve at a high theoretical level, so the product HF can be described accurately. Moreover, APES is implemented with a completely analytical derivative, which is highly efficient and likely to perform dynamic calculations, particularly quasi-classical trajectory dynamics calculations. A deeper understanding of the title reaction is expected based on the new APES.

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