

# Three Dimensional Potential Energy Surface For The F3

**Jing Cao**

Jilin University

**Chunmei Hu**

Jilin University

**Hongmei Yu**

Jilin University

**Yuxuan Bai**

Sichuan Agricultural University

**Yanchun Li**

Jilin University

**Dequan Wang** (✉ [dequan\\_wang@jlu.edu.cn](mailto:dequan_wang@jlu.edu.cn))

Jilin University

**Xuri Huang**

Jilin University

---

## Research Article

**Keywords:** adiabatic, potential energy surface, F3, collision reaction

**Posted Date:** November 9th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-970279/v1>

**License:**  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

---

# Three Dimensional Potential Energy Surface For the F<sub>3</sub>

Jing Cao<sup>a||</sup>, Chunmei Hu<sup>b||</sup>, Hongmei Yu<sup>c</sup>, Yuxuan Bai<sup>d</sup>, Yanchun Li<sup>a</sup>, Dequan Wang<sup>a\*</sup>, Xuri Huang<sup>a\*</sup>

<sup>a</sup>Institute of Theoretical Chemistry, Jilin University, Changchun, People's Republic of China

<sup>b</sup>Hematology and Oncology Department, The Second Hospital, Jilin University, Changchun, People's Republic of China

<sup>c</sup>High Performance Computing Center of Jilin University, People's Republic of China

<sup>d</sup>College of Life Science, Sichuan Agricultural University, Ya'an, People's Republic of China

E-mail: dequan\_wang@jlu.edu.cn;

<sup>||</sup>these authors contributed equally to this work.

Abstract

In order to study the F<sub>3</sub> system, an accurate global adiabatic potential energy surface is reduced in the present work. The high level *ab initio* (MCSCF/MRCI level) methods with big basis set aVQZ are used to calculate 27690 potential energy points in MOLPRO quantum chemistry package using Jacobi coordinate. Meanwhile, B-spline fit method is used to reduce the global potential energy surface in this present work. The shallow well complexes are found in the present work when the angles  $\theta = 30^\circ$ ,  $60^\circ$ , and  $90^\circ$ . Analysing the global potential energy surfaces one can get the conclusion that reactants should overcome at least 0.894 eV energy to cross transition state and reach products.

Keywords: adiabatic, potential energy surface, F<sub>3</sub>, collision reaction.

## 1 Introduction

As the most active element of halogens, fluorine often plays an important role in the chemical reaction process. In the chemical industry, fluorine is widely used in the fields of semiconductors and new energy, which is particularly critical for the future development. Therefore, three dimensional potential energy surface of the F<sub>3</sub> is very interesting. Duggan and Grice have described the approximate shape of the potential energy surface of F<sub>2</sub> + F [1]. Artau and Nizzi [2], who used to determine the dissociation energy of the F<sub>2</sub> bond by the collision-induced dissociation energy method.

Although many studies have been made for the fluorine [1–8], meanwhile, exchange reactions between halogen atoms and halogen atoms have been studied by many scholars [9–16], the exact understanding of three dimensional potential energy surface for the F<sub>3</sub> is so limited. Currently quantum chemistry calculations are able to provide sufficiently reliable data for this system, potential energy surfaces (PESs) can help us to understand possible reaction mechanisms and estimate reaction rates. The potential energy surface of F<sub>3</sub> was studied by classical orbital method combined with direct dynamic electronic structure calculation. By

now, a train of scholars have studied the exchange reaction of trifluoride ions [2–4], but it doesn't have a precise dynamic study for this system. In order to accurately describe this system, three-dimensional PESs for the title system are constructed in this paper.

In the current work, the accurate three-dimensional PESs for this system are deduced. The details of this paper are shown as follow: the computational method will be introduced in the second chapter and the detailed description of PESs will be introduced in the third section. At the last part, the conclusion and discussion will be demonstrated.

## 2 Computational methods

The lowest three adiabatic potential energy surfaces of  $F_3$  system is calculated with *ab initio* method at MCSCF/MRCI level using large basis sets (aVQZ) [17], but only the lowest state is described in this paper. All the calculations are performed in the MOLPRO 2012 package [18]. Total 12 (9  $A'$  + 3  $A''$ ) active orbitals are considered in present work. And 225 (138  $A'$  + 87  $A''$ ) external orbitals are used in this work. Thus the MCSCF function included 360 determinants and 792 intermediate states for the triatomic molecule system. In the MRCI calculated progress, 3 orbitals (3  $A'$  + 0  $A''$ ) are put in core orbital, and 24 electrons are set in valence space. The total number of contracted configurations is 595861, which include the number of internal configurations, singly external configurations, and doubly external configurations are 251, 430002, and 5528358, respectively.

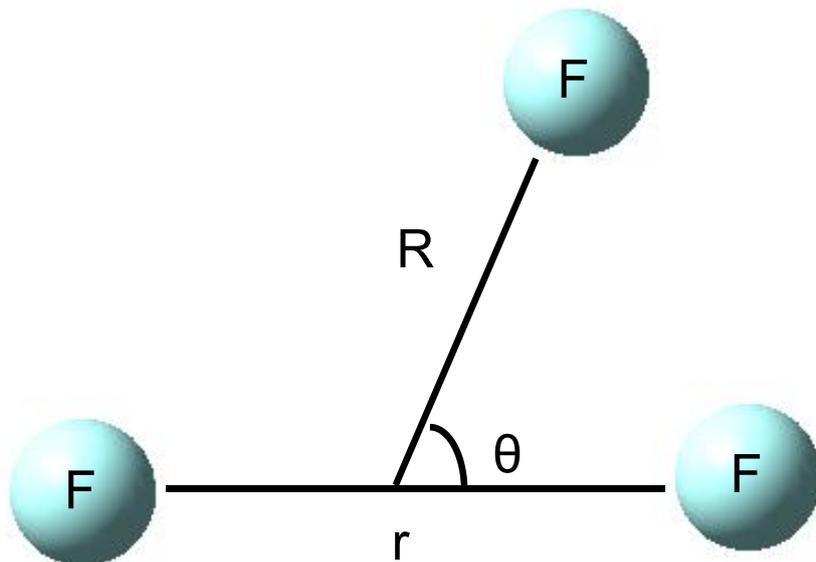


Figure 1: Jacobi coordinate for the  $F_3(^2A'')$  system.

Jacobi coordinate  $(r, R, \theta)$ , which can express the three dimensional PESs well in our previous works on triatomic systems [3, 19–23], is used in the present work.  $r$  is used to show the distance between two fluorine atoms,  $R$  demonstrates the distance from the reduced mass of

the two fluorine atoms to the third fluorine atom, and the angle between these two vectors is presented by  $\theta$  (see figure 1).  $R$  is used in the range of 0.0 Å - 20.0 Å with 69 points, and  $r$  is fixed from 0.4 Å to 5.0 Å with 39 points using different step sizes, and the range of angles  $\theta$  is 0° - 90° with 10° scan step. Therefore, in total of 27690 geometries are calculated. So the large number of scanning points that can warrant the quality of the following fitted the PESs. The three dimension B-spline method [24,25] is used to get the procedures interpolat e surface in the whole scan field.

### 3 RESULTS AND DISCUSSION

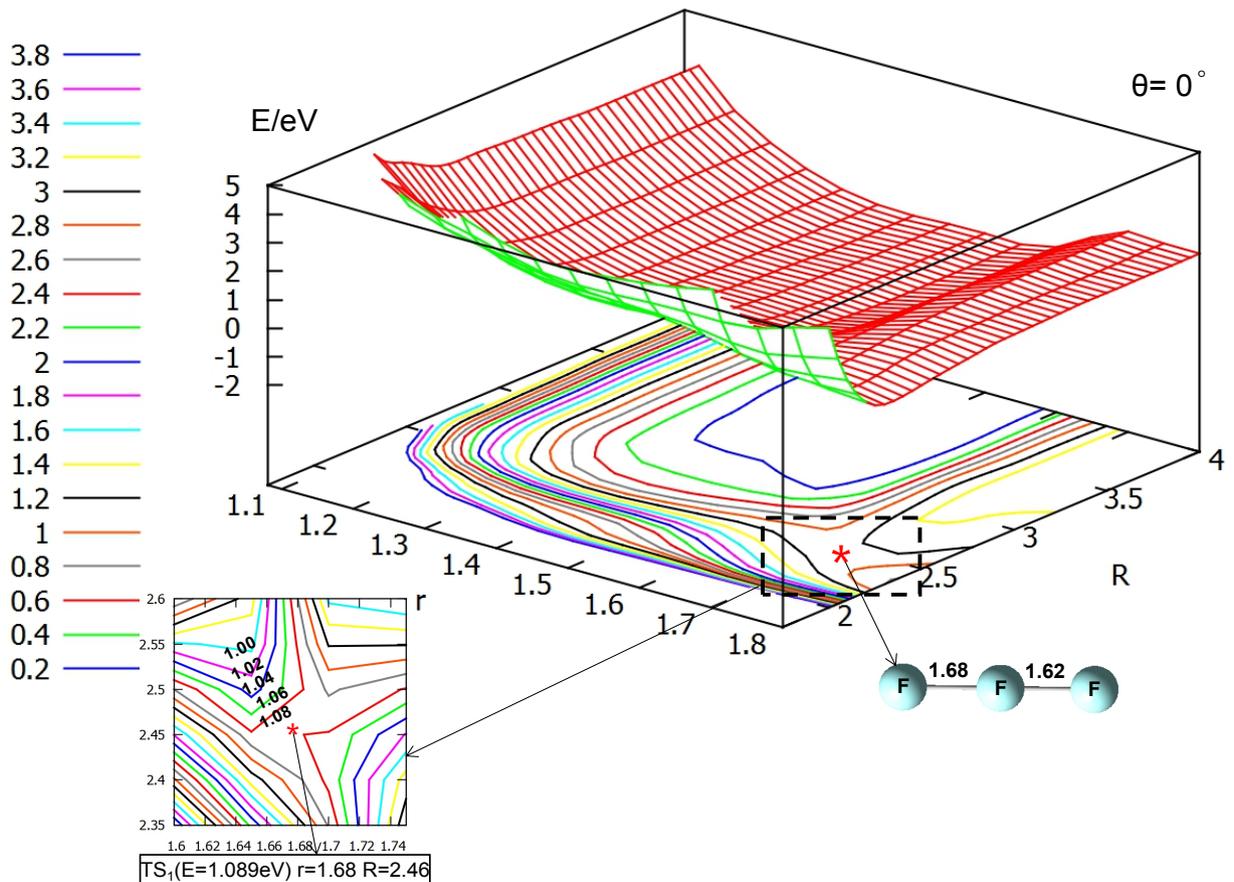


Figure 2: Adiabatic potential energy surface (in eV) and contour plots of the potential energy surface for the lowest energy state of  $F_3(^2A'')$  as the function of  $r$  and  $R$  (in Å) in  $C_\infty$  symmetry.

The three dimensional adiabatic potential energies of the lowest energy state for the  $F_3(^2A'')$  system is deduced in the present work, for a more clear understanding of the character of this system, the two dimensional(2D) PES is shown in the following part. For a more clear discussing of these PESs, the energy of  $F + F_2$  is shift to 0.00 eV.

The one-dimensional potential energy surface for  $F_2$  is studied in the present work. The dissociation energy is 1.40 eV, which compares well to the former theoretical and experimental results (1.25 eV, 1.60 eV) [2, 26].

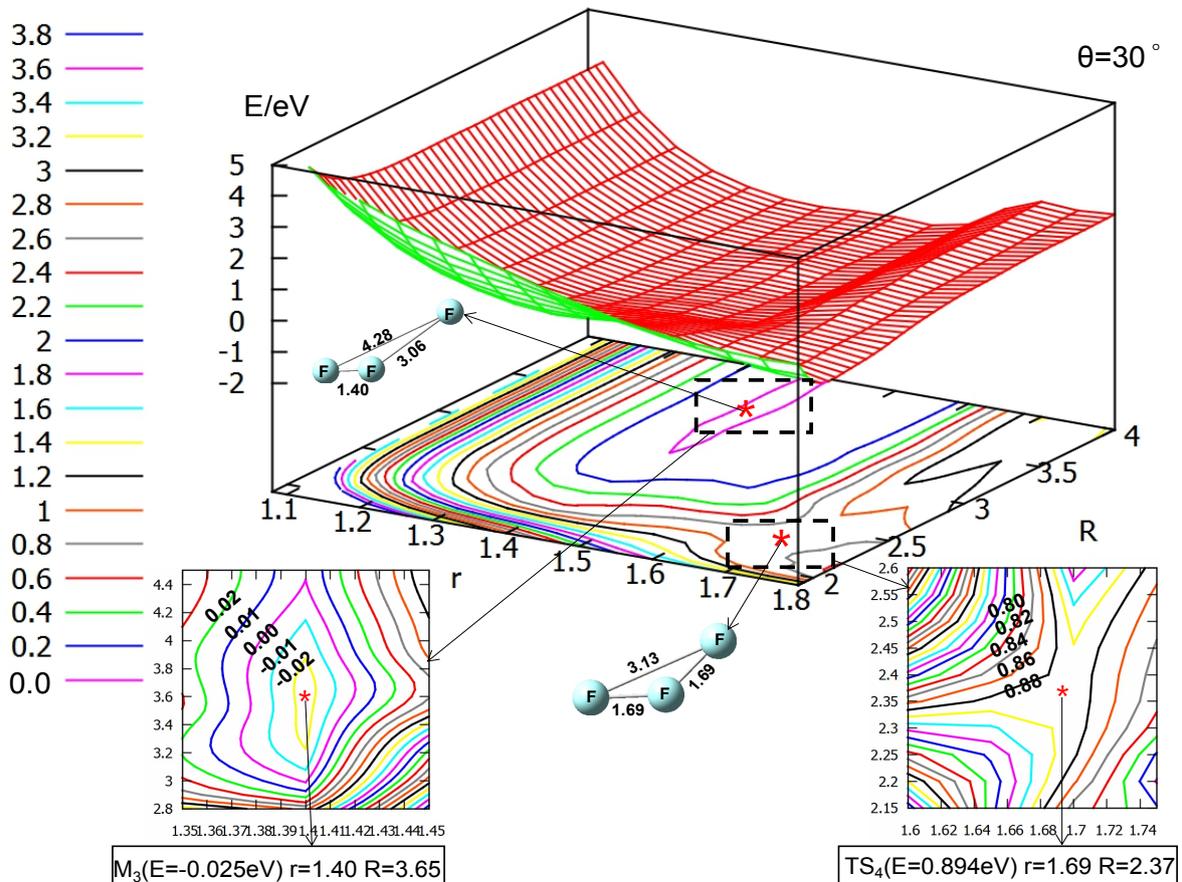


Figure 3: Adiabatic potential energy surface (in eV) and contour plots of the potential energy surface for the lowest energy state of  $F_3(^2A'')$  as the function of  $r$  and  $R$  (in Å) for  $\theta = 30^\circ$ . The importance isomer and transition state are shown in the lower panels.

The 2D lowest energy state adiabatic potential energy surfaces (2D-PESs) have been shown in different angles for  $F_3(^2A'')$  energy surface. The different four angles ( $\theta = 0^\circ, 30^\circ, 60^\circ, 90^\circ$ ) are used to describe the vividly change of the PES. The upper part of each figure is the 2D image PES, and the corresponding contour plot of each 2D-PES are shown in the lower part of each figure. In the contour plotted part, the difference of the energy between two adjacent curves is 0.20 eV, the short distance between two adjacent curves means big energy changes with distance ( $R$  or  $r$ ) and vice versa. Some important parts (isomers or transition state parts) are enlarged plotted in each figure.

The 2D-PES for  $F_3(^2A'')$  in linear symmetry is plotted in figure 2. From this figure one can see that the potential energies increase with the decrease the distance of the  $R$ . There is no minimum in this figure. The PES of  $F_3(^2A'')$  system in linear symmetry is flat when the  $r$  in the range of  $1.3 \text{ \AA} < r < 1.6 \text{ \AA}$ , and  $R > 3.0 \text{ \AA}$ . In this area, the energy is lower than 0.2 eV and larger than 0.0 eV so this area is embraced by the blue curve (the blue curve is the contour line of the energy of 0.2 eV). An enlarged figure is plotted to show the transition state (TS) area. The geometry of this TS is  $r = 1.68 \text{ \AA}$  and  $R = 2.46 \text{ \AA}$ . The linear symmetry of reactants  $F_a + F_bF_c$  overcome 1.089 eV energy crossing the TS then transforming to the

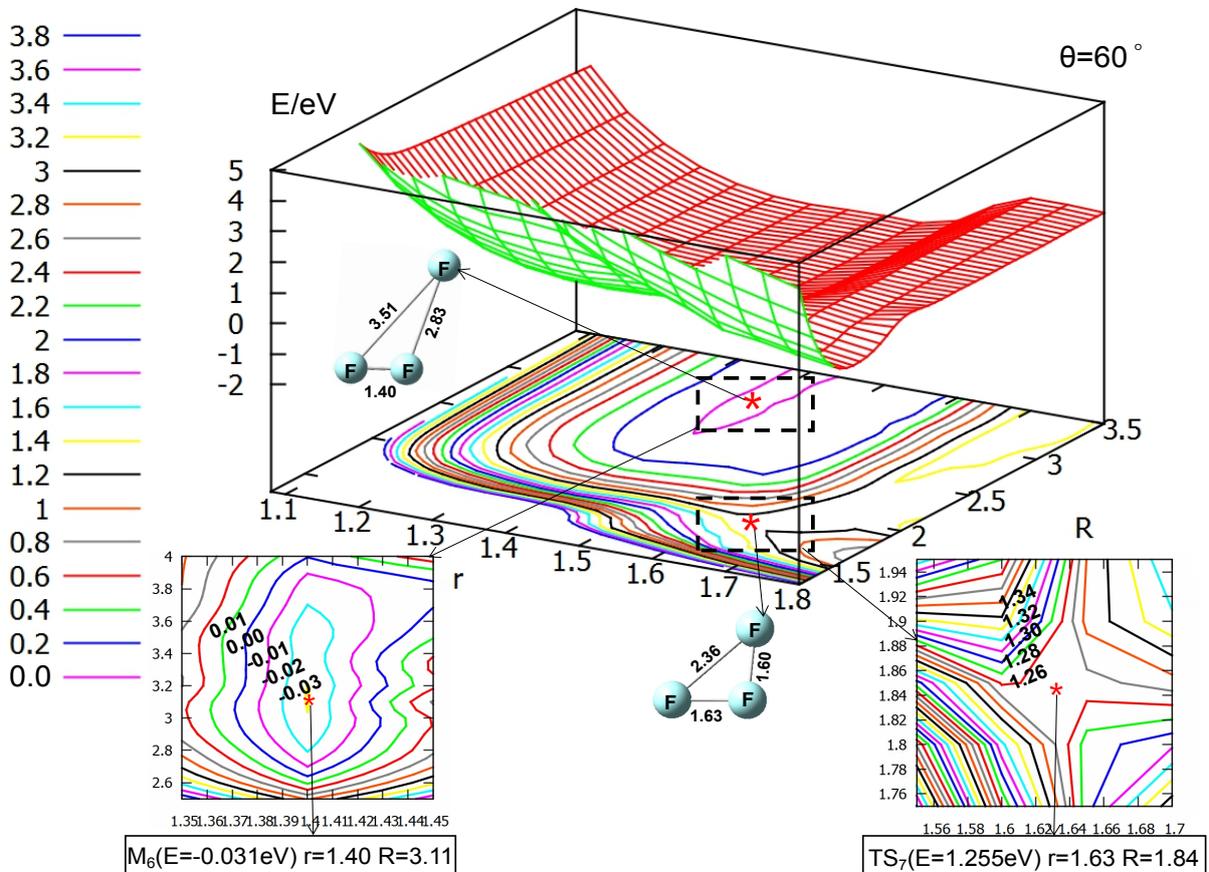


Figure 4: Adiabatic potential energy surface (in eV) and contour plots of the potential energy surface for the lowest energy state of  $F_3(^2A'')$  as the function of  $r$  and  $R$  (in Å) for  $\theta = 60^\circ$ . The importance isomer and transition state are shown in the lower panels.

products  $F_a F_b + F_c$ .

The character of the PES for the  $\theta = 30^\circ$  is shown in the figure 3. There is a minimum in this angle, the geometry of the minimum is  $r = 1.40$  Å, and  $R = 3.65$  Å. The energy of this minimum is  $-0.025$  eV, which is slight lower than that of reactants. The difference of these two energies is so small that the minimum is not stable. If one wants the reactants transform to the products along  $\theta = 30^\circ$ , the system should over come  $0.88$  eV energy through the TS, the geometry of the TS is  $r = 1.69$  Å and  $R = 2.37$  Å.

The character of the PES with  $\theta = 60^\circ$  (see Figure 4) is similar to that of  $\theta = 30^\circ$ : Firstly, both of these two figures have a shallow minimum; the energy of the minimum for  $\theta = 60^\circ$  is  $-0.03$  eV and the geometry of this minimum is  $r = 1.40$  Å and  $R = 3.11$  Å. Secondly, the reactants want to change to the products through these two angles reaction pathway, the additional energies should be given to this system to over come the transition state. The energy of the TS for  $\theta = 60^\circ$  is  $1.255$  eV, which is higher than that of  $\theta = 30^\circ$ . The geometry of the TS is  $r = 1.63$  Å and  $R = 1.84$  Å.

Figure 5 shows the adiabatic PES of the title system for the  $\theta = 90^\circ$ . When the F atom attacks the  $F_2$  molecule along  $\theta = 90^\circ$ , and for the same  $r$ , the energy is nearly no changed

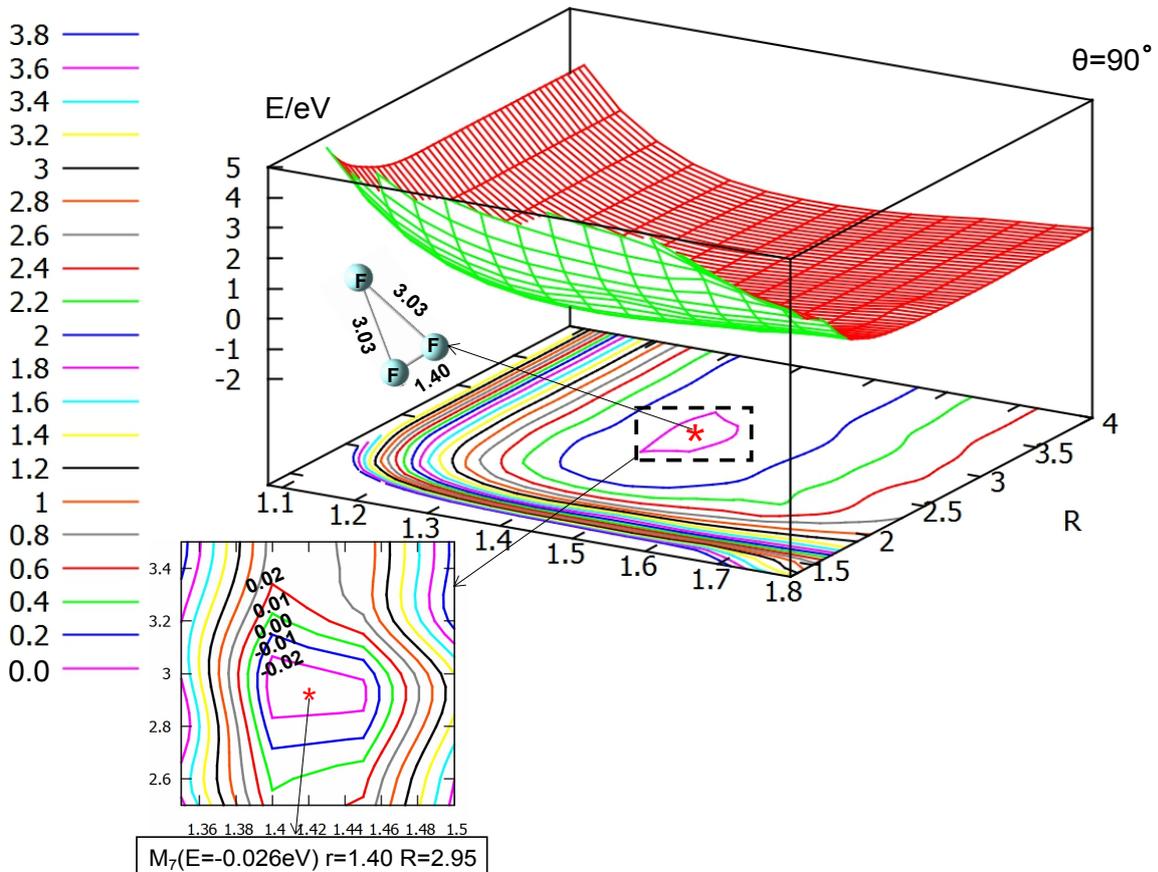


Figure 5: Adiabatic potential energy surface (in eV) and contour plots of the potential energy surface for the lowest energy state of  $F_3(^2A'')$  as the function of  $r$  and  $R$  (in Å) for  $C_{2v}$  symmetry. The importance isomer is shown in the lower panel.

with the function of  $R$  when  $R > 3.5$  Å, when  $R$  decreasing to 2.95 Å and the  $r = 1.40$  Å, the system reaches the shallow well complex, the energy of this complex is -0.026 eV. After this complex, the energy of this system becomes higher and higher with decrease the  $R$  distance further.

The figures for other degrees also have been plotted. The details are shown in supplement files.

The 2D-PES for  $F_3(^2A'')$  as the function with two bond lengths of  $r(F_aF_b)$  and  $r(F_bF_c)$  (in Å) with the angle, between these two bonds, fixed at  $\alpha = 180^\circ$  is shown in Figure 6. The important region is magnified plotted in the same figure. The blue dotted line shows the easiest reaction pathway for the title reaction. Meanwhile, the sketch map of this dotted line is plotted in the lower panel, which shows the reaction barrier is 104.715 kJ/mol, compared with Duggan and Grice's work [1](108 kJ/mol), the results are almost consistently. The geometry of the transition state for the reaction pathway is  $r(F_aF_b) = 1.66$  Å and  $r(F_bF_c) = 1.65$  Å.

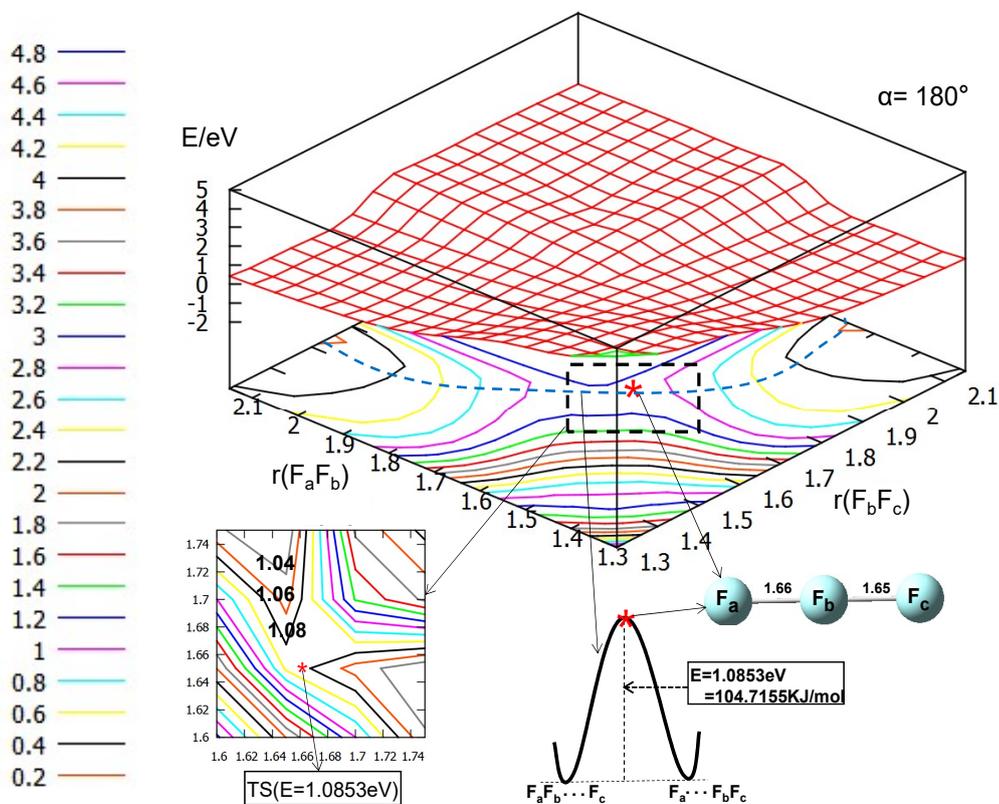


Figure 6: Adiabatic potential energy surface (in eV) and contour plots of the potential energy surface for the lowest energy state of  $F_3(^2A'')$  as the function of  $r(F_aF_b)$  and  $r(F_bF_c)$  (in Å) in  $C_\infty$  symmetry.

## 4 CONCLUSIONS

The electronic adiabatic state PESs for the lowest energy state of  $F_3$  are presented with high level *ab initio* (MCSCF/MRCI level) method by MOLPRO quantum chemistry package in Jacobi coordinate. The potential energies are calculated using aVQZ basis set over larger region of configuration space. 27690 potential energy points are calculated for getting the global accurate PESs, which is deduced by an accurate B-spline fit method. There is no minimum in the PES with  $\theta = 0.0^\circ$ , but there is a transition state in this PES. The process of  $F_a + F_bF_c \rightarrow F_aF_b + F_c$  along the angle  $\theta = 0.0^\circ$  should be given additional energy of 1.089 eV; but for  $\theta = 30.0^\circ$ , this energy is reduced to 0.894 eV; when the angle increase to  $60^\circ$ , the reaction barrier will reach 1.255 eV. There are shallow complexes in the PES for  $\theta = 30^\circ$ ,  $60^\circ$ , and  $90^\circ$  and the energies are -0.025 eV, -0.031 eV, and -0.026 eV.

### Notes

The authors declare no competing financial interest.

## Acknowledgements

This work is supported by the National Natural Science Foundation of China (Nos. 21573090), Jilin Province Science and Technology Development Plan (20150101005JC). This work completed under cooperation between Institute of Theoretical Chemistry and High Performance Computing Center of Jilin University, China.

## Declarations

## Conflicts of interest

The authors declare no competing interests.

## Availability of data and material

Data are available, that are included in the code.

## Code availability

Private custom codes relevant to the content of this paper were generated for personal use.

## Author contribution

**Jing Cao:** data curation, fitting the data, optimised configurations, investigation, methodology and writing-original draft.

**Chunmei Hu and Hongmei Yu:** investigation, methodology and fitting the data.

**Yuxuan Bai and Yanchun Li:** data curation, investigation and methodology.

**Dequan Wang and Xuri Huang:** optimised configurations, investigation, methodology and writing-original draft.

## References

- [1] Duggan JJ, Grice R(1984)Topography of Potential-energy Surfaces DIM (Diatomics-in-molecules) Surface for  $F + F_2$ . J Chem Soc.80:795-808.
- [2] Artau A, Nizzi KE, Hill BT, Sunderlin LS, Wenthold PG(2000)Bond Dissociation Energy in Trifluoride Ion. J AM Chem Soc 122:10667-10670.
- [3] Wang DQ, Wang DG, Fu LW, Wang JY, Shi G, Li YC, Huang XR(2019)An accurate ground state potential surface for the scattering reaction  $F^- + F_2(v,j) \rightarrow F_2(v',j') + F^-$ . RSC Adv 9:1929-1932.
- [4] Tuinman AA, Gakh AA, Hinde RJ, Compton RN(1999)The First Direct Observation of the Trifluoride Anion ( $F_3^-$ ) in the Gas Phase. J Am Chem Soc 121:8397-8398.
- [5] Mota F, Novoa JJ(1996)The symmetry breaking problem in the trifluoride anion: A multireference approach. J Chem Phys 105:8777-8785.
- [6] Takayanagi T, Kurosaki Y(1997)Theoretical Calculations of Potential Energy Surface and Thermal Rate Constants for the  $H(\text{Mu}) + F_2$  Reaction. J Phys Chem A 101:7098-7104.

- [7] Ault BS, Andrews L(1976)Matrix Reactions of Alkali Metal Fluoride Molecules with Fluorine. Infrared and Raman Spectra of the Trifluoride Ion in the  $M + F_3^-$  Species. *J Am Chem Soc* 98:1591-1593.
- [8] Balint-Kurti GG(1973)Potential energy surfaces for simple chemical reactions: $Li+F_2 \rightarrow LiF+F$ . *Molecular Physics* 11:393-435.
- [9] Lee YT, McDonald JD, LeBreton PR, Herschbach DR(1968)Molecular-Beam Kinetics: Evidence for Short-Range Attraction in Halogen Atom-Molecule Exchange Reactions. *J Chem Phys* 49:2447.
- [10] Beck D, Engelke F and Loesch HJ(1968)Reaktive Streuung in Molekularstrahlen:  $Cl+Br_2$ . *Ber Bunsenges Phys Chem* 72:1105.
- [11] Lee YT, LeBreton PR, McDonald JD and Herschbach DR(1969)Molecular Beam Kinetics: Evidence for Preferred Geometry in Interhalogen Exchange Reactions. *J Chem Phys* 51:455.
- [12] Blais NC and Cross JB(1970)Molecular Beam Kinetics: The Differential Cross Section of the Reaction  $Cl + Br_2$ . *J Chem Phys* 52:3580.
- [13] Valentini JJ, Lee YT and Auerbach DJ(1977)A crossed molecular beam study of the translational energy dependence of  $Cl + Br_2 \rightarrow BrCl + Br$  reaction. *J Chem Phys* 67:4866.
- [14] Duggan JJ, Grice R(1983)Topography of potential-energy surfaces. DIM (diatomics-in-molecules) surfaces for  $F + HF$  and  $Cl + HCl$ . *J Chem Soc Faraday Trans 2* 80:739-744.
- [15] Duggan JJ, Grice R(1984)Topography of Potential-energy Surfaces. DIM (Diatomics-in-molecules) Surface for  $Cl + Cl_2$ . *J Chem Soc Faraday Trans 2* 80:809-816.
- [16] Firth NC and Grice R(1987)Topography of Potential-energy Surfaces. Spin-Orbit Interaction for  $H + F_2, Cl_2$ . *J Chem Soc Faraday Trans 2* 83:1011-1022.
- [17] Dunning TH(1989)Gaussian basis sets for use in correlated molecular calculations.I.The atoms boron through neon and hydrogen. *J Chem Phys* 90:1007-1023.
- [18] Werner HJ, Knowles PJ, Knizia G, Manby FR, Schütz and others; MOLPRO, version 2012.1, a package of ab initio programs <http://www.molpro.net>.
- [19] Wang DQ, Shi G, Fu LW, Yin RL, Ji YB(2019)Accurate Potential Energy Surfaces for the Three Lowest Electronic States of  $N(^2D) + H_2(X^1\Sigma_g^+)$  Scattering Reaction. *ACS Omega* 4:12167-12174.
- [20] Wang DQ, Fu LW, Qu ZX, Chen YK, Huang XR(2017)Accurate potential surfaces for the ground state of  $H + C_2$  reaction. *Eur Phys J D* 71:252-258.
- [21] Fu LW, Wang DQ, Chen YK, Huang XR(2018)Accurate potential surfaces for the first two lowest of  $Li + H_2$  reaction. *RSC Adv* 8:15595-15602.

- [22] Wang DQ, Wang DG, Fu LW, Huang XR(2019)Accurate potential surfaces for the first three lowest states of reaction  $O(^3P) + C_2(a^3\Pi_u) \rightarrow CO(X^1\Sigma) + N(^1D)$ . Chem Phys 517:228-236.
- [23] Yin RL, Gao N, Zhang RM, Wang DQ, Huang XR(2020)Accurate potential energy surfaces for the excited state of  $CF_2$  molecule. Chem Phys 538:110906-110913.
- [24] Sathyamurthy N, Raff LM(1975)Quasiclassical trajectory studies using 3D spline interpolation of ab initio surfaces. J Chem Phys 63:464-473.
- [25] Patrício M,Santos JL, Patrício F, Varandas AJC(2013)Roadmap to spline-fitting potentials in high dimensions. J Math Chem 51:1729-1746.
- [26] Huber KP, Herzberg G(2000)Constants of Diatomic Molecules(data prepared by Gallagher JW and Johnson RD, III). In NIST Chemistry WebBook, NIST Standard Reference Database 69; Mallard WG, Linstrom PJ, Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 20899(<http://webbook.nist.gov>)