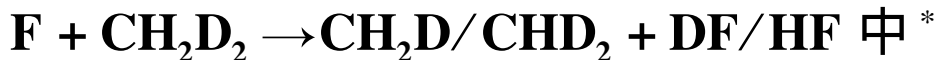


将 SVRT 模型应用到单原子多原子反应



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摘 要: 由于含时波包方法具有经典的直观又不乏量子力学的准确, 选择含时波包方法来处理 $\text{F} + \text{CH}_2\text{D}_2 \rightarrow \text{CH}_2\text{D}/\text{CHD}_2 + \text{DF}/\text{HF}$ 反应. 把半刚性振转子 (SVRT) 模型应用到该反应体系中, 研究了两个通道中该反应从基态反应物开始在修正过的 J1 (MJ1) 势能面上计算出来了反应几率、积分截面、速率常数. 反应几率随能量变化的图的数值结果给出了振荡结构, 这些振荡结构是可以和动力学振荡联系起来. 而这些振荡结构在积分截面随着能量变化的图中就被反应几率求和后的平均结果所掩盖了. 速率常数和实验结果的比较也得到了较好的结果.

关键词: SVRT 模型; TDWP 方法; 反应几率; 速率常数; 积分截面; MJ1 势能面

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The Semirigid Vibrating Rotor Target Model for Atom-polyatom



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Abstract The semirigid vibrating rotor target (SVRT) model is applied for the reaction $\text{F} + \text{CH}_2\text{D}_2 \rightarrow \text{CH}_2\text{D}/\text{CHD}_2 + \text{DF}/\text{HF}$. The time-dependent wave packet approach is also used in the calculation. Reaction probabilities, cross-sections, and rate constants are calculated for the title reaction from the ground state of the reagent on the modified J1 (MJ1) potential energy surface (PES) for both channels. Numerical calculation shows the oscillatory structures in the energy dependence of the calculated reaction probability. Those structures are generally associated with broad dynamical resonances. They are smooth in the energy dependence of integral cross-sections due to summation over partial waves. The calculated rate constants are in good agreement with the experimental measurement.

Keywords SVRT model, TDWP method, Cross-section, Rate constant, MJ1 PES

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1 Introduction

Many theoretical and experimental investigations of the $F + CH_4$ reaction and its isotopic reactions have been performed at various levels of the theory (see Fig. 1). Persky group used the trajectories to compute for thermal reactants at 298 K^[11] and the approach was improved in full-dimension recently^[2-6], in the CH_3/CD_3 product including all vibrational coordinates. The importance of the title reaction in atmospheric and combustion chemistry deserves more study. These studies are devoted mainly to the determination of the energy partitioning among the reaction products^[6,7] and of rate constants^[8-20].

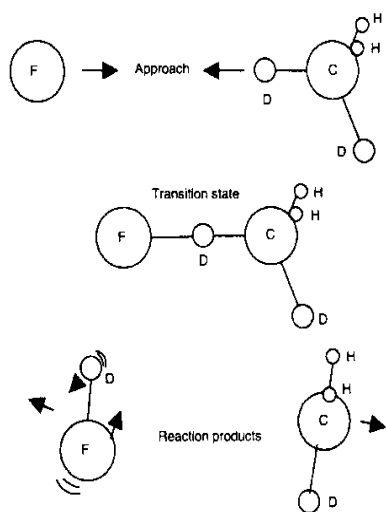


Fig. 1 Simplified view of the $F + CH_2D_2$ hydrogen abstraction reaction

The HF product recoils with a large fraction of the exothermicity in vibrational and rotational energy.

Recently, the SVRT model has been applied to a number of chemical reactions including $H + HOH$ (D)^[21], $H + CH_4$ ^[21], $O + CH_4$ ^[22], and in good agreement with full-dimensional results. It is reasonable for us to study the reaction $F + CH_2D_2 \rightarrow CH_2D/CHD_2 + DF/HF$ for a six atoms system employing the SVRT model. Currently, no exact full-dimensional quantum dynamical calculations are available for $F + CH_2D_2$ reaction and such exact dynamics calculations are not expected in the near future. Thus, we believe that the $F + CH_2D_2$ reaction provides an excellent benchmark

system for testing new dynamical methods developed to treat polyatomic reactions. For this purpose, we carry out dynamics calculation for the title reaction applying the four mathematical dimensions (4D) SVRT model on MJ1 PES.

2 The basic SVRT model for the atom-polyatom reaction

2.1 The SVRT Hamiltonian

In this work, we use the SVRT model to carry out the computational study of the six-atom reaction $F + CH_2D_2 \rightarrow CH_2D/CHD_2 + DF/HF$. In the basic SVRT model for the atom-polyatom reactions, we treat the target molecule CH_2D_2 as a semirigid rotor composed of two rigid fragments H/D and CHD_2/CH_2D ^[23]. The Hamiltonian for reactive collision between the atomic projectile F and the SVRT molecule CH_2D_2 takes the form^[23],

$$\hat{H} = -\frac{\eta^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hat{L}^2}{2\mu R^2} + \hat{H}_T + V \quad (1)$$

where μ is the reduced translational mass,

$$\mu = \frac{M_F M_{CH_2D_2}}{M_F + M_{CH_2D_2}} \quad (2)$$

R is the relative radial distance between the center-of-mass (CMS) of F and CH_2D_2 . \hat{L} is the orbital angular momentum operator. The definition of other parameters can be found in reference [23]. The internal Hamiltonian \hat{H}_T describing the SVRT molecule T is given by^[23]

$$\hat{H}_T = \frac{1}{2} \sum_{ij} \hat{\Pi}_i G_{ij} \hat{\Pi}_j - \frac{\eta^2}{2\mu_T} \frac{\partial^2}{\partial r^2} + V_T(\mathbf{r}) \quad (3)$$

where \mathbf{r} is the radial distance, $V_T(\mathbf{r})$ the interaction potential, and μ_T the reduced mass between CHD_2/CH_2D and H/D fragments of molecule CH_2D_2 ,

$$\mu_T = \frac{M_H M_{CH_3}}{M_H + M_{CH_3}} \quad (4)$$

Where $M_T = M_H + M_{CH_3}$. The detail definition of the parameters in Eq.(3) can be found in Ref.[23].

2.2 TD wavepacket approach

The numerical calculation for the atom-polyatom reactive collision using the SVRT Hamiltonian of Eq. (1) can be carried out using the time-dependent (TD)

wavepacket approach for the reaction^[22]. In the TD approach, one solves the TD Schrödinger equation

$$i\eta \frac{\partial}{\partial t} \Psi(t) = H\Psi(t) \quad (5)$$

with the Hamiltonian defined in Eq.(1). With an appropriate choice of basis set, the expansion of $\Psi(t)$ can take the form^[21 23]

$$\Psi(t) = \sum_{pvjK_n} \mathbf{u}_p^v(\mathbf{R}) Z_{jk(n)}^{JM}(\Omega, \theta, \chi) \phi_v(\mathbf{r}) C_{pvjK_n}(t) \quad (6)$$

where $\mathbf{u}_p^v(\mathbf{R})$ is the translational basis function whose definition is given^[22]. $C_{pvjK_n}(t)$ is the time function. $\phi_v(\mathbf{r})$ is vibrational basis function given by the solution of the one-dimensional eigenequation

$$\left[-\frac{\eta^2}{2\mu_T} \frac{\partial^2}{\partial r^2} + V_T(r) \right] \phi_v(r) = \varepsilon_v \phi_v(r) \quad (7)$$

and $Z_{jk(n)}^{JM}(\Omega, \theta, \chi)$ is the body-fixed (BF) total angular momentum eigenfunction. The angular momentum function for the atom-polyatom system is given by^[23]

$$Z_{jk(n)}^{JM}(\Omega, \theta, \chi) = \bar{D}_{MK}^J(\Omega) \bar{d}_{k_n}^{j*}(\theta) \frac{1}{\sqrt{2\pi}} e^{in\chi} \quad (8)$$

The detailed definition of the parameter of the former formula can be found in Ref. [21 23]. The TD wave function is propagated by employing the split-operator method, and the detail information can be found^[23 24].

3 Results and discussion

Only four of the 12 internal coordinates for the $F + CH_2D_2$ system are treated explicitly in the dynamics calculation using the basic SVRT model. Fig. 2 shows that the reagent molecule CH_2D_2 that consists of a H/D atom and a CHD_2/CH_2D fragment is treated as a semi-rigid vibrating rotor. The fragment CHD_2/CH_2D fixed in the geometry in the basic SVRT model. The reaction of $F + CH_2D_2$ is believed to be direct, and the geometry of the transition state is a linear F-H-C/F-D-C configuration with a stretched F-H/D bond length^[2].

As shown in Fig. 2, the bond angle α between H-C and D-C bonds in the CH_2D_2 group is the only parameter to be adjusted. We assign the angle α equaling to the transition state value 109.47° , and the contour plot of the MJ1 PES in the saddle point is shown in Fig. 3 in both channels with the left one for $F + CH_2D_2$

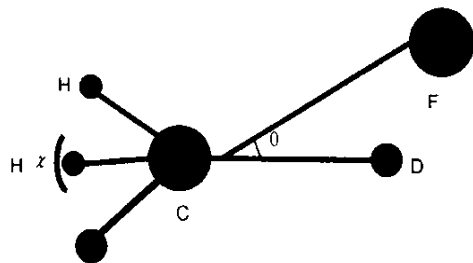


Fig. 2 The SVRT model for $F + CH_2D_2$ reaction using Jacobi coordinates

\mathbf{R} is the distance between F and the center-of-mass of the CH_2D_2 molecule, \mathbf{r} is the distance between H and the center-of-mass of CH_3 , and θ is the angle formed by \mathbf{R} and \mathbf{r} . The geometry of CH_3 is fixed at the values at the transition state on the MJ1 PES.

$\rightarrow HF + CHD_2$ and the right one for $F + CH_2D_2 \rightarrow DF + CH_2D$, which result in a barrier height both about 8.4 kJ/mol (0.073 eV), among the experimental estimate of 4.02 ~ 10 kJ/mol^[21].

Fig. 4 shows the calculated total reaction probability of CH_2D_2 as a function of collision energy for total angular momentum $J = 0, 10, 20, 40, 60, 80, 100, 120, 140, 160$ for both channels. It should be mentioned that since the two hydrogen atoms and the two deuterium atoms in the group CH_2D_2 are treated as distinguishable, respectively, we multiply a factor of two to each reaction probability for both channels from the dynamics calculation to account for equal. Firstly, we note that the quantum tunneling effects are quite pronounced. The barrier height of MJ1 PES is very low, so the probabilities are increasing sharply as the energy is lower than 0.05 eV. The descendant probability at the range 0.2 ~ 0.4 eV perhaps own to the tropism of the CH_2D_2 . Secondly, the resonancelike oscillatory structures are shown for reaction probability in its dependence on the collision energy. The potential influence of collisions in previous arrested relaxation studies merits further clarification. In fact, the oscillatory structure in Fig. 4 is a similar feature noted previously for the least exothermic channel in several three-atom reactions such as $H + D_2$ ^[24-29], $F + H_2$ ^[21 26], $F + HD \rightarrow HF + D$ ^[14] and $F + CD_4 \rightarrow CD_3 + DF$ ^[16]. However, counter examples also exist, such as $F + D_2$ ^[17] and

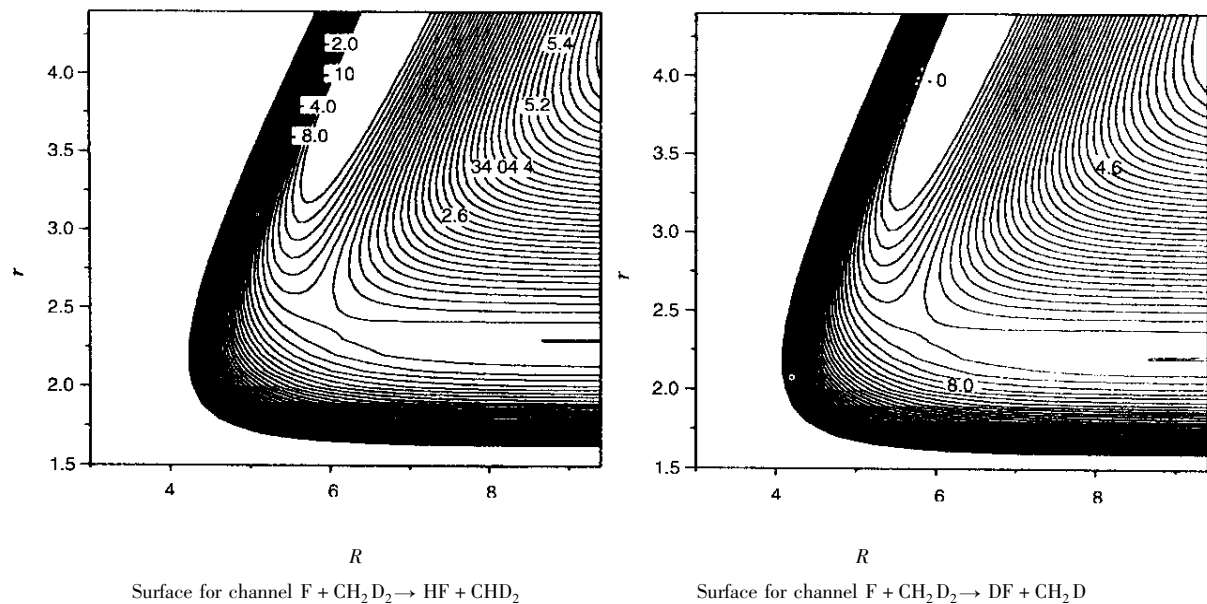


Fig. 3 The contour plot of PES for $F + CH_2D_2 \rightarrow CH_2D/CHD_2 + DF/HF$

Where the angle θ is set to zero. The energies are in kcal/mol. Bend length is 1.090 \AA , the F-H-C is collinear.

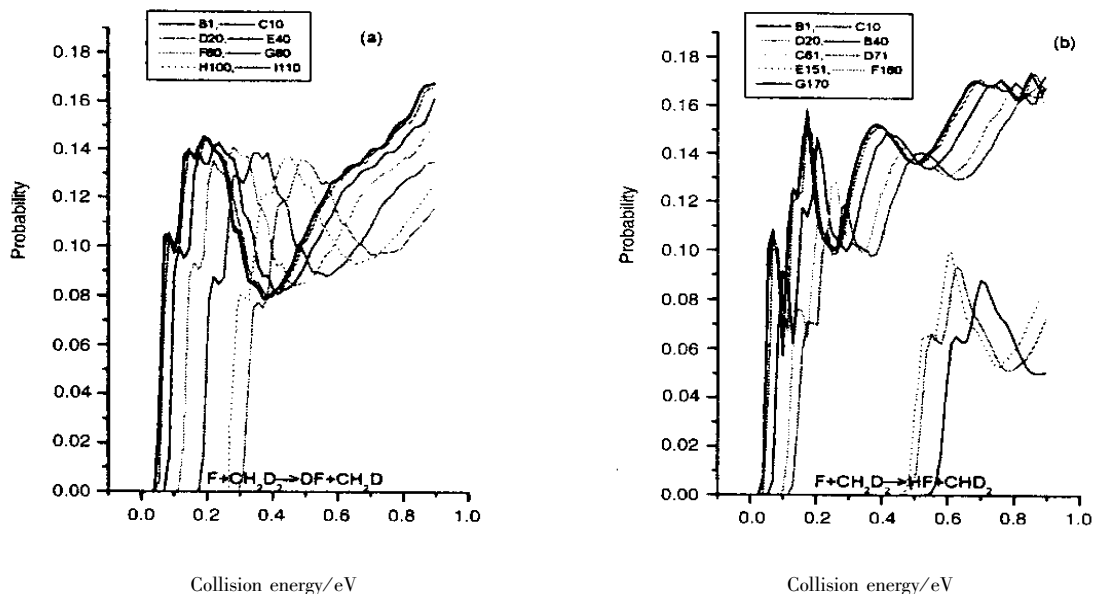


Fig. 4 Total reaction probabilities for $\nu=0, j=0, J=0, 10, 20, 50, 70, 100$ of the CH_2D_2 reactant on the MJ1 PES

The solid line is for $J=0$, dashed line is for $J=10$, dotted line is for $J=20$, dashed-dotted line is for $J=50$, dashed-dotted-dotted line is for $J=70$, short-dashed line is for $J=100$.

$OH + D_2^{[27]}$. There are much similarities between the current $F + CH_2D_2$ reaction and the $H + CH_4 \rightarrow CH_3 + H_2$ and the $F + HD$ reactions^[21]: The reactions involve direct abstraction of the hydrogen or deuterium atom. There is a slow change in geometry of the CH_2D/CHD_2 group from pyramidal to planar during these reactions.

In addition, the shape and width of the oscillatory structure of the reaction probability in Fig. 4 are strikingly similar to those in the $F + HD$ reaction^[21]. Based on these similarities, we strongly believe that the oscillatory structures in Fig. 4 are associated with broad dynamical resonances that exist in the $F + CH_2D_2$ reac-

tion. This resonance-like feature deserves our further theoretical investigations in the future.

Furthermore, transferred H/D atom between the two heavy "particles" (the F atom and the CH_2D/CHD_2 moiety) in the transition-state region may serve to mediate the energy flow between the vibration of HF/DF and the umbrella motion of CH_2D/CHD_2 , resulting in the resonances of the two receding products. In addition, the reaction probability shows a peak near the collision energy of 0.04 eV, which is very close to the reaction barrier 0.073 eV on the MJ1 PES. Although we are quite sure that tunneling must be involved here, we do not know the exact cause of this peak. Whether it corresponds to any physical resonance state near the threshold energy or is simply an artifact of the potential remains to be explored further.

The centrifugal sudden (CS) approximation is employed and the dynamics calculation is carried out for J up to 190 for the calculation with total angular momentum $J > 0$. These calculations yield total integral cross-sections from the initial ground state using the standard formula

$$\sigma_g(E) = \frac{\pi}{k_g^2} \sum_J (2J+1) P_g^J(E) \quad (9)$$

The integral cross-sections of both channels are shown in Fig. 5 as a function of the translational energy. No experimental cross sections have been reported for the reaction. Because of the effect of partial wave averaging, the resonance will be observed smoothly at about 0.08 eV in the integral cross sections in Fig. 5. Generally, the reaction cross section of the channel of $F + CH_2D_2 \rightarrow DF + CH_2D$ is much higher than that of the channel $F + CH_2D_2 \rightarrow HF + CHD_2$ over the range of the collision energy 0.02 ~ 0.9 eV. It is therefore interesting to investigate the resonance contribution to the computed $F + CH_2D_2 \rightarrow CH_2D/CHD_2 + DF/HF$ cross-section in a little more details. The most effective way is to combine the expected resonance contribution to the reaction probability at $J=0$.^[29]

We also calculated the reaction rate constant from the initial ground state cross section by the formula.

$$r_g(T) = \left(\frac{8kT}{\pi\mu}\right)^{1/2} (kT)^{-2} \int_0^\infty dE_l E_l \times$$

$$\exp\left(-\frac{E_l}{kT}\right) \sigma_g(E_l) \quad (10)$$

Fig. 6 shows comparison of our calculated rate constants of both channels with the experimental results^[9] for the reaction $F + CH_4$, while there are no experimental results for the title reaction. Clearly, the current calculated rate constant using the SVRT model is in reasonable agreement with the experimental result over a wide range of temperatures as shown in Fig. 6. The rate constants of this work are much lower than the experimental results of $F + CH_4$. In the whole temperature the rate constant of the channel $F + CH_2D_2 \rightarrow DF + CH_2D$ is the smallest one. Firstly, the tunneling effect in the high temperature is much higher than that in the low temperature. Secondly, the symmetric and asymmetric stretch and umbrella bend modes also enhance the reaction rate in the higher temperature. Thirdly, it should be pointed out here that our calculated rate constant only includes the initial ground state. The effect of rotational and vibrational excitations on rate constant has not been investigated in this work. If this factor is taken into account, the rate constant of this work can be increased more in the low temperature. Fourthly, the rate constant of $F + CH_2D_2 \rightarrow DF + CH_2D$ is lower than the other channel of this reaction in the high temperature, it must be caused by the tunneling effect of the light H atom, which is higher than the

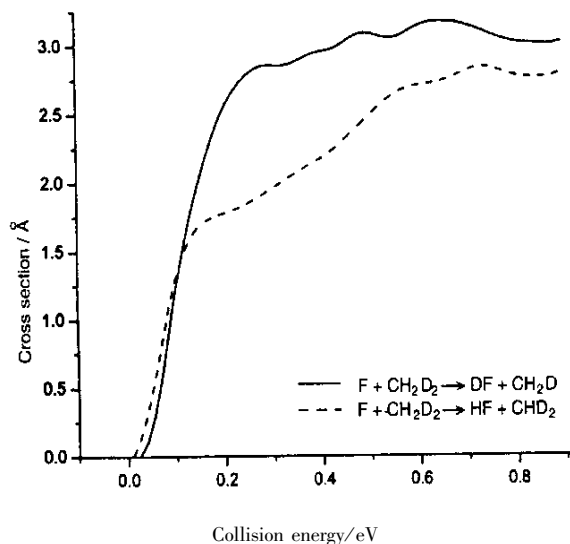


Fig. 5 Reaction Cross section as a function of collision energy for the $F + CH_2D_2$ reaction using SVRT on the MJ1 PES

weighty D atom. And an isotope-specific factor, which represents a kinetic isotope effect favoring H-atom elimination from activated complexes, has been reported to be 1.360.^[18] The kinetic H/D isotope effect is also examined. Finally, the difference is perhaps due to the leak of the MJ1 PES. The PES is being improved in our group. The current calculated rate constant using the SVRT model is almost in reasonable agreement with experimental result over a wide range of temperatures as shown in Fig. 6.

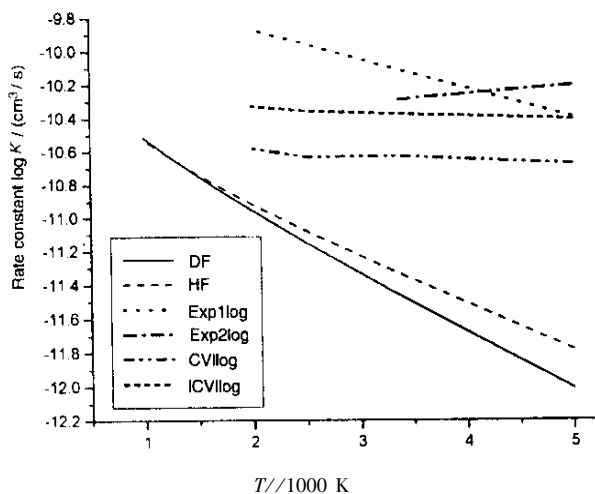


Fig. 6 The Rate Constant for $v=0, J=0$ of the CH_2D_2 reactant for the $\text{F} + \text{CH}_2\text{D}_2$ reaction on the MJ1 potential

The solid line is for the $\text{F} + \text{CH}_2\text{D}_2 \rightarrow \text{CH}_2\text{D} + \text{DF}$ channel in this work, dashed line is for the $\text{F} + \text{CH}_2\text{D}_2 \rightarrow \text{CH}_2\text{D}/\text{CHD}_2 + \text{DF}/\text{HF}$ channel, dotted line is for experimental values of Moore *et al.*: $k = 3 \times 10^{-10} \exp \frac{400^{[9]}}{T}$, dashed-dotted line is for the experimental values^[8]: $k = 3.41 \times 10^{-11} \exp \frac{121.5}{T}$, dashed-dotted-dotted line is for CVT-CDSCSAG based on the QCI/b3 shifted curve, short dashed for ICVT-CDSCSAG method based on the QCI $s_d(t)/b3$ shifted curve^[21].

4 Conclusion

The title reaction is calculated through the time-dependent quantum scattering, which has been carried out using the SVRT model, based on the analytic MJ1 potential energy surface^[21]. In the SVRT model, the C-H bond angle α of the H-CH₃ group is fixed at its transition state, which gives rise to a reaction barrier of 8.4 kJ/mol. This is in close the energy dependence of

the reaction probability shows familiar oscillatory structure similar to those observed in the $\text{F} + \text{HD}$ and $\text{F} + \text{H}_2$ reactions. In particular, the distinct peak in the present calculated probabilities in Fig. 4 is also very apparent in the simulation. However, this peak is somewhat much larger in the simulation than expected. These structures give a strong indication that the dynamical resonance is present in this reaction. Generally, Fig. 6 shows the reaction cross section of the channel $\text{F} + \text{CH}_2\text{D}_2 \rightarrow \text{DF} + \text{CH}_2\text{D}$ is much higher than that of the channel $\text{F} + \text{CH}_2\text{D}_2 \rightarrow \text{HF} + \text{CHD}_2$. It is clear from the comparison that the simulation is in agreement with experiment rate constants for the $\text{F} + \text{CH}_2\text{D}_2 \rightarrow \text{CH}_2\text{D}/\text{CHD}_2 + \text{DF}/\text{HF}$ reaction, and also in fairly good agreement with the theoretical result for $\text{F} + \text{CH}_2\text{D}_2 \rightarrow \text{CH}_2\text{D}/\text{CHD}_2 + \text{DF}/\text{HF}$ reaction. As usual, however, the resonance structure weakens in the energy dependence of integral cross-section, and this resolution of the partial wave sum clearly shows the effect of partial wave averaging, which tends to lower the peak in the integral cross section. Finally, the current study of the $\text{F} + \text{CH}_2\text{D}_2$ reaction shows that quantitatively reliable dynamics results for polyatomic reactions can be obtained using the SVRT model in just a few mathematical dimensions.

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Reference

- [1] Persky A. *J. Phys. Chem.*, 1996, **100**:689
- [2] Corchado J C, Espinosa-Garcia J. *J. Chem. Phys.*, 1996, **105**:3160; Corchado J C, Espinosa-Garcia J. *J. Chem. Phys.*, 1996, **105**:3152
- [3] Elran Y, Kay K G. *J. Chem. Phys.*, 2002, **116**:10577
- [4] Gauss A Jr. *J. Chem. Phys.*, 1976, **65**:4365
- [5] Kornweitz H, Persky A, Levine R D. *Chem. Phys. Lett.*, 1998, **289**:125
- [6] Yao L, Han K L, Song H S, Zhang D H. *J. Phys. Chem. A*, 2003, **107**:2781; Yao L, Han K L, Song H S, Zhang D H. *J. Chin. Chem. Soc.*, 2003, **50**:565
- [7] Maneshkarimi M, Heydtmann H. *Chem. Phys. Lett.* 1995, **234**:182

- [8] Moore C F , Smith I W M , Stewart D W A. *Int. J. Chem. Kinet.* 1994 , **26** : 813
- [9] Atkinson R , Baulch D L , Cox R A , Hampson R F Jr , Kerr J A , Troe J. *J. Phys. Chem. Ref. Data* , 1992 , **21** : 1380
- [10] Clyne M A A , Hodgson A. *Chem. Phys.* , 1983 , **79** : 351
- [11] Nazar M A , Polanyi J C. *Chem. Phys.* , 1981 , **55** : 299
- [12] Wickramaaratchi M A , Setser D W , Hildebrandt H , Korbitzer B , Heydtmann H. *Chem. Phys.* , 1985 , **94** : 109
- [13] Jonathan N B H , Sellers P V , Stace A J. *J. Mol. Phys.* , 1981 , **43** : 215
- [14] Skodje R T , Skouteris D , Manolopoulos D E , Lee S H , Dong F , Liu K. *J. Chem. Phys.* , 2000 , **112** : 4536
- [15] Møgelberg T E , Platz J , Nielsen O J , Sehested J , Wallington T J. *J. Phys. Chem.* , 1995 , **99** : 5373
- [16] Cong Shulin , Li Yamin , Yin Hongming , Sun Julong , Han Keli. *Chin. J. Chem. Phys.* , 2002 , **15** : 198
- [17] Jones W E , Skolnik E G. *Chem. Rev.* , 1976 , **76** : 563
- [18] Michael J V. *Chem. Phys. Lett.* , 1980 , **76** : 129
- [19] Wallington T J , Hurley M D , Shi J , Maricq M M , Sehested J , Nielsen O J , Ellermann T. *Int. J. Chem. Kinet.* , 1993 , **25** : 651
- [20] Zhang D H , Zhang J Z H. *J. Chem. Phys.* , 2000 , **112** : 585 ; Zhang D H , Zhang J Z H. *J. Chem. Phys.* , 1994 , **101** : 3671 ; Zhang D H , Lee Soo-Y , Baer M. *J. Chem. Phys.* , 2000 , **112** : 22
- [21] Wang M L , Li Y M , Zhang J Z H , Zhang D H. *J. Chem. Phys.* , 2000 , **113** : 5 ; Wang M L , Li Y M , Zhang J Z H. *J. Phys. Chem. A* , 2001 , **105** : 2530
- [22] Zhang J Z H. *J. Chem. Phys.* , 1999 , **111** : 3929
- [23] Fleck J A Jr , Morris J R , Feit M D. *Appl. Phys.* , 1976 , **10** : 129
- [24] Fernandez-Alonso F , Zare R N. *Annu. Rev. Phys. Chem.* , 2002 , **53** : 67
- [25] Tamagake K , Setser D W , Sung J P. *J. Chem. Phys.* , 1980 , **73** : 2203
- [26] Neumark D M , Wodtke A M , Robinson G N , Hayden C C , Lee Y T. *J. Chem. Phys.* , 1985 , **82** : 3045
- [27] Strazisar B R , Lin C , Davis H F. *Science* , 2000 , **290** : 958
- [28] Duncan W T , Truong T N. *J. Chem. Phys.* , 1995 , **103** : 9642 ; Yu H G , Nyman G. *Phys. Chem. Chem. Phys.* , 1999 , **1** : 1181
- [29] Williams R L , Rowland F S. *J. Phys. Chem.* 1973 , **77** : 301