Time-dependent quantum dynamics study of the F + CD$_4$ → DF + CD$_3$ reaction

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Abstract. A four-degrees-of-freedom, time-dependent quantum wave packet propagation method is employed to study the F + CD$_4$ → DF + CD$_3$ reaction. The calculations show a common resonance peak appears in the reaction probabilities, which verifies the prediction of such resonance from experiment. For F + CD$_4$, the vibrational excitations of the C-H stretching mode enhance the reactivity, whereas the C-X umbrella vibrational excitations hinder the reaction; and the translational energy is more effective than vibrational energy at very lower collision energy, and less effective than the vibrational energy at most energy range. So for this endoergic early barrier reaction, the Polanyi rules cannot be extended to this poly-atomic reaction except at very low collision energy.

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Key words: time-dependent; quantum dynamics; resonance; cross section; energy efficiency; Polanyi rules.

1 Introduction

In 1972, Polanyi proposed the rules on energy efficiency in surmounting the energy barrier based on the A + BC reaction systems, namely the well-known Polanyi rules [1]. For a endoergic reaction (later barrier), the vibrational energy is favored for barrier crossing, whereas the translational energy is favored for a exoergic reaction (early barrier). So far, the rules have been proved to be correct for the atom-diatom reactions. However for the more complex polyatomic reaction systems, it is difficult to determine the energy efficacy in surmounting energy barriers. Therefore, in order to better understand the mode-selective enhancement and energy requirement on reactivity for the polyatomic

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reaction systems, the reaction of Cl, F, and O atoms with methane have been the focus of experimental and theoretical investigations.

In order to study the dynamics of polyatomic reaction systems, chemists and theorists firstly tried a series of studies for the H_2O (HOD, D_2O) + H (D) reaction [2-6]. In 1984, Schatz *et al.* studied the H + HOD reaction using a quasiclassical trajectory (QCT) method, and found the stretching vibration mode of OH is more efficient in enhancing the reactivity than OD [2]. This result is consistent with Crim [3, 4] and Zare's [5] experimental conclusion. In 1997, the quantum dynamics calculation of the H + HOD also gave the same results [6]. In 2010, Wang *et al.* employed a seven-degrees-of-freedom (7DOF), quantum dynamics approach to study the five atomic reaction system $H_2D^+ + H_2 \rightarrow H_3^+ + HD$ [7]. The research shows that reaction probability is not affected by the stretching motion of H^+-HD, and the vibrational excitation of the HD in H_2D^+ hinders the reactivity. On the contrary, compared with the ground state, the rotational excitation of the H^+-HD bond improves the reactivity by a factor of about 2~3 for the higher rotational state. And this is the first time we have observed rotational excitation plays a leading role in the polyatomic reactivity.

In 2000, experimenters and theorists began to study the reactions Cl, F, and O atoms with CH_4 (CHD_3, CD_4) [8-10]. It is still quite challenging to study the dynamics characteristics of such reaction systems using quantum approach, because the methane has nine vibration modes including bending, stretching and torsion. For the Cl + CH_4 reaction with an endoergic late barrier on the PES, Kopin Liu *et al.* in 2007 [8] found that the reactant translational energy is more effective than the stretching motion of CH in surmounting the energy barrier into products, which contradicts the Polanyi rules for a later barrier reaction. And soon after, on the same PES, there are two quantum dynamics studies, one a 6DOF study on the Cl + CH_4 [9] and another a 7DOF study on the CL + CHD_3 reaction [10]. Both results show that only at very low collision energy the Polanyi rules break. In 2010, crossed molecular beam experiments were reported for the reaction O + CHD_3 → OH + CD_3 [11]. The experimental data show the excitation of C-H vibration in CHD_3 enhances reactivity [12]. However, for the reaction of O with CH_4 [13], bending excitations in CD_4 slightly restrain the reaction. Recently, Czakó and Bowman carried a QCT calculation on the O + CHD_3 reaction on a full-dimensional *ab initio* PES [14]. And in the same year, an eight-dimensional (8D) quantum dynamics calculation was reported on this PES [15]. The comparison of their computed integral cross section of the ground state agrees well with experimental results. In 2013, Wang *et al.* employed a 6DOF, time-dependent wave packet method to study the O + CD_4/CHD_3 → OD/OH + CD_3 reactions [16]. For the O + CHD_3 system, the 6DOF ICS agrees well with the QCT results for the ground state [14], and the comparison of the stretching excitations between calculated results and the experimental excitation function agrees with each other quite well [12]. And for the O + CD_4 reaction system, all the vibrational excitations enhance the reactivity, which agrees with the QCT calculation [17] and contradicts the experimental result [13].

Because the F + CH$_4$ and its isotopic reactions play an important role in atmospheric chemistry, a lot effort has been put on studying the reaction. For the F + CH$_4$ reaction system, Liu and co-workers made the outstanding contribution in experimental. And theirs research found resonances signatures near the reaction threshold for the F + CH$_4$ reaction [18], besides, the resonance peak also showed up in the integral cross section [19]. For the F + CHD$_3$ reaction, experimental study on the CH stretching excitation revealed that one quantum excitation of CH stretch mode of CHD$_3$ slows down the reactivity and favors the DF + CHD$_2$ products [20]. Then, the QCT calculations [21, 22] explained this unexpected experimental finding. The calculations shows a long-range stereodynamical interaction induced by the CH stretching excitation steers the slow F atom to one of the CD bonds, thereby promoting the D-abstraction channel at low collision energies. Recently, Liu *et al.* [23] also found the antisymmetric stretch of CH$_4$ inhibits the CH bond rupture for the F + CH$_4$ reaction. In 2007, a 3DOF time-independent calculation [24] and a 5DOF SVRT [25] study in 2009 [26] were carried out on the PES-2006. In the 5DOF study, a single resonance peak was found in the reaction probability for $J \leq 55$ and rate constants were also reported. However, over the temperature range of 180-400K, the 5DOF results underestimated the experimental results at low temperature by factors of 1.71 and overestimated the experimental results by factors of 1.21 at high temperature. Zhang *et al.* performed a 5DOF SVRT model calculation [27] for the F + CH$_4$ reaction using two different PESs constructed based on the analytical form. The study concluded the resonance was observed on one of the PESs near the threshold and disappeared when the partial wave J is greater than 30. In addition, resonance was also found on the isotopic reaction of F + CHD$_3$ by Clary and co-workers [28]. In 2013, Wang *et al.* performed a 4DOF quantum reactive dynamics on the F + CH$_4$ reaction [29] using an *ab initio* full-dimensional PES developed by Czakó and Bowman [30]. The study indicated that there is a common resonance peak showing up on the reaction probabilities near the reaction threshold. The calculations also showed the vibrational umbrella motion of C-X hinders the reactivity, and the translational energy enhances the reactivity more than the vibrational energy at lower collision energy, but less effective than the vibrational energy at higher collision energy.

In this paper, we performed a 4DOF, time-dependent wave-packet quantum scattering approach for the F + CD$_4$ on the full dimensional PES developed by Czakó and Bowman. Here our purpose is to compare our computed integral cross sections with experimental measurements, and to investigate the energy efficiency on reactivity for the title reaction systems.

This paper is organized as follows. In Section 2 we give details of the 4DOF quantum reactive dynamics approach for this reaction system. Section 3, we present the initial state selected integral cross section and the discussion of the energy efficacy on surmounting the early barrier. The conclusions are given in Section 4.

2   Theoretical methods

We employed a 4DOF reduced dimensional quantum dynamics study on the F + CD$_4$ $\rightarrow$ DF + CD$_3$ reaction. In the 4DOF model, as shown in Fig. 1, we regarded the three nonreactive D atoms in the CD$_4$ as one pseudo-atom X which locates at the center of mass of the three D atoms. Thus this title reaction becomes a pseudo atom-triatom reaction system F + DCX $\rightarrow$ DF + CX. And, the 4DOF includes the CX vibrational motion (r), which approximately represents the umbrella motion of CD$_3$ with CD bond lengths fixed at the saddle point values, the bond-breaking motion (ρ), and the translational motion (R); besides we also consider one bending motion (γ).
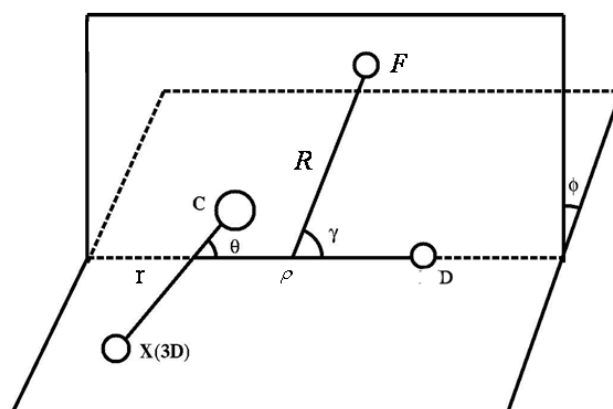

Figure 1: Reactant Jacobi coordinates for the reaction F + CD$_4$ $\rightarrow$ DF + CD$_3$. Reaction. In the 4DOF model, the active coordinates are R,r,ρ and γ, whereas θ and ϕ are fixed at their saddle point values.

The 4DOF Hamiltonian expressed in the reactant Jacobi coordinates, shown in Fig. 1, can be written as

$$H = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{(J-j)^2}{2\mu R^2} + h_r(r) + h_\rho(\rho) + \frac{j^2}{2\mu_\rho r_\rho^2} + V_{4D}(\hat{R},\hat{r},\hat{\rho},\gamma). \tag{1}$$

Here, the first term is the translational energy of the reaction system, μ is the reduced mass of the whole system, and R is the distance between the center of mass CDX and the F atom. The r is the bond length from the X(3D) pseudoatom to C, ρ is the distance from the center of mass of CX to D, γ is the Jacobi angle formed by ρ and R, J is the total angular momentum operator, and j is the rotational angular momentum operator of D-CX.

The vibrational reference Hamiltonians $h_r(r)$ and $h_\rho(\rho)$ are given as,

$$h_r(r) = -\frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} + V_{1D}(r) \tag{2a}$$

$$h_\rho(\rho) = -\frac{\hbar^2}{2\mu_\rho}\frac{\partial^2}{\partial \rho^2} + V_{1D}(\rho) \tag{2b}$$

where $V_{1D}(r)$ and $V_{1D}(\rho)$ are one-dimensional reference potentials for r and ρ. These potentials are cuts in the respective coordinates, and the other coordinates are fixed at equilibrium geometry of the asymptotic region. The time-dependent wave function satisfies the Schrödinger equation $i\hbar[\partial/(\partial t)]\Psi(t)=H\Psi(t)$ can be expanded in terms of the body-fixed (BF) ro-vibrational eigenfunctions defined in terms of the reactant Jacobi coordinates as

$$\Psi_{v_0 j_0 K_0}^{JM\varepsilon}(\hat{R},\hat{r},\hat{\rho},t) = \sum_{nvjK} F_{nvjK,v_0 j_0 K_0}^{JM\varepsilon}(t) \times u_n^v(R)\varphi_{v_1}(r)\varphi_{v_2}(\rho)Y_{jK}^{JM\varepsilon}(\hat{R},\hat{r},\hat{\rho}), \qquad (3)$$

where n is the translational basis label, and ε is the parity of the system defined as $\varepsilon=(-1)^{j+L}$ (L is the orbital angular momentum quantum number of F atom with respect to the center of mass of DCX). The $Y_{jK}^{JM\varepsilon}(\hat{R},\hat{r},\hat{\rho})$ is the BF total angular momentum eigenfunction. The reference vibration eigenfunction $\varphi_{v_1}(r)$ and $\varphi_{v_2}(\rho)$ respectively satisfy

$$h_r(r)\varphi_{v_1}(r)=E_{v_1}(r), \quad h\rho(\rho)\varphi_{v_2}(\rho)=E_{v_2}(\rho). \qquad (4)$$

We employed the split-operator method [31] here to propagate the wave packet on the PES for the quantum dynamics calculation,

$$\Psi^{JM\varepsilon}(\hat{R},\hat{r},\hat{\rho},t+\Delta)=e^{-iH_0\Delta/2}e^{-iU\Delta}e^{-iH_0\Delta/2}\Psi^{JM\varepsilon}(\hat{R},\hat{r},\hat{\rho},t), \qquad (5)$$

where the reference Hamiltonian H_0 is defined as,

$$H_0=-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2}+h_r(r)+h_\rho(\rho), \qquad (6)$$

and the effective potential operator U in Eq. (5) is defined as

$$U=\frac{(J-j)^2}{2\mu R^2}+\frac{j^2}{2\mu_\rho\rho^2}+V_{4D}(\hat{R},\hat{r},\hat{\rho},\hat{\gamma}), \qquad (7)$$

The initial wave function is chosen as the product of a specific rovibrational eigenfunction and a localized translational wave packet,

$$\Psi_i(0)=\varphi(\hat{R})\Psi_{vjK}^{JM\varepsilon}(\hat{R},\hat{r},\hat{\rho}), \qquad (8)$$

where $\varphi(\hat{R})$ is chosen to be a standard Gaussian function and $\Psi_{vjK}^{JM\varepsilon}(\hat{R},\hat{r},\hat{\rho})$ is the eigenfunction of the pseudotriatom DCX's Hamiltonian $\hat{H}_{DCX}$. And the $\hat{H}_{DCX}$ is defined as

$$\hat{H}_{DCX}=h_r(r)+h_\rho(\rho)+V_{2D}(\rho,r). \qquad (9)$$

After the wave function is propagated into the product region, the standard time-dependent reactive flux [32, 33] method is employed to extract the initial-state-selected reaction probability.

To obtain the integral cross section, we calculate the partial wave reaction probabilities of the total angular momentum J. The initial-state-selected integral cross section $\sigma_{v_0 j_0}(E)$ is obtained by summing over all the initial-state-selected reaction probability $P^J_{v_0 j_0 K_0}$ for all partial waves

$$\sigma_{v_0 j_0}(E) = \frac{1}{2j_0+1} \frac{\pi}{k^2} \sum_J (2J+1) P^J_{v_0 j_0 K_0}(E), \tag{10}$$

where E is the translational energy, v_0 and j_0 are, respectively, the initial vibrational and rotational quantum numbers, K_0 is the projection of J onto BF Z axis of the atom-triatom system, and k is the wave number defined as $\sqrt{2\mu E}$.

3 Results and discussions

3.1 Computational parameters

For the translational coordinate R in the range from 3.3-12.3 bohr, we expand the wave function using 170 sine basis functions, among these 78 are used to expand the wave function in the interaction region. We used 60 potential-optimized vibrational discrete variable representation (DVR) points for the r coordinates in the range from 0.7-6.5 bohr; 10 potential-optimized vibrational DVR points are used for CX covering the range of 0.0-2.0 bohr, and 51 spherical harmonic rotational functions for γ. To converge the calculation, the time-dependent wave packet is propagated with a time step of 15 a.u. for a total time of about 18000 atomic unit time.

3.2 Comparisions of the ICSs

Fig. 2 shows nine different partial waves of the F + DCX ro-vibrational ground state for $J = 0, 20, 40, 60, 80, 100, 120, 140$ and 160. It is worth mentioning that Liu *et al.* observed there is a reaction threshold at 0.5Kcal/mol (0.022eV) in the F + CH_4 experiment [34]. As shown in Fig. 2, our 4DOF quantum dynamics calculation show the reaction threshold is also around 0.02eV. Besides, we also found the common resonance peak shows up in every partial wave ($J \geq 0$) reaction probability after the threshold, and this found confirms the prediction for the F+CD_4 reaction exists resonance peak by Liu *et al.* [35, 36]. And the reactive resonances was found in the isotope reaction F + CH_4(v=0) and F + CHD_3(v=0). Therefore, it is not a surprise that the resonance peak was observed in here.

Due to each D atom in CD_4 should have an equal opportunity to react, the ground vibrational state integral cross section obtained by Eq. (10) is multiplied by a factor of 4 before plotted in Fig. 3. In total, for the ground state ICS, 169 partial wave reaction probabilities were needed to converge the translational energy up to 0.7 eV. In Fig. 3, we made a comparison between the ground state integral cross section and the ICS of the
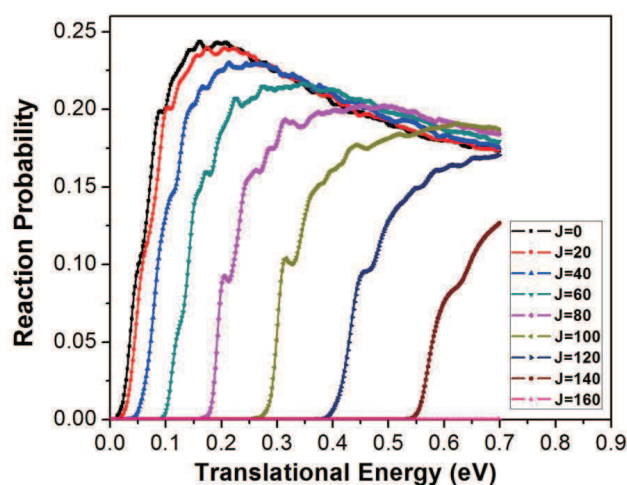
Figure 2: The reaction probabilities of theF $+$ CD$_4$ reaction for different partial waves $J = 0, 20, 40, 60, 80,$ 100, 120, 140 and 160 as a function of the translational energy.

product CD$_3$ (the total of the ground state and the three vibration excited state) measured by the team of Liu [36]. Because the experiment did not report absolute cross section, the data of computed ICS was divided by 10.98 (the ratio of the maximum of ICS between computed and measured data), we rescaled the computed excitation function by a factor of 10.98 in order to help the comparison between the computed and measured data. As shown in Fig. 3, both the calculated and measured excitation functions has a sharp rise after the threshold, but the computed excitation function rised more rapid than that in the experimental, the theoretical peak occurs at 0.276eV, then declined very slowly.
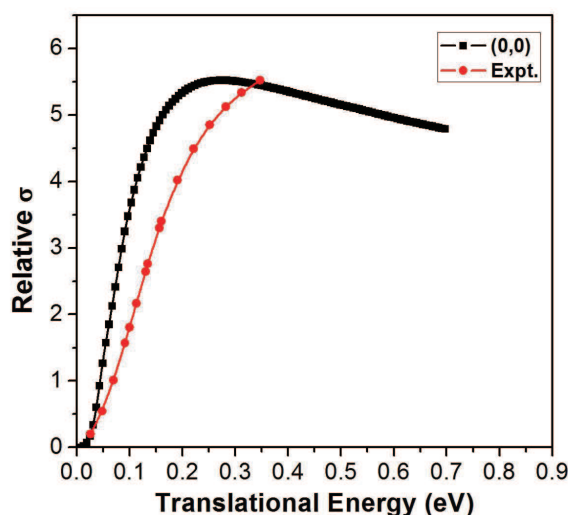

Figure 3: Comparison of the 4DOF integral cross section for the ground state F $+$ CD$_4$ reaction with the experimental results.

Whereas, the experimental excitation function has been has a slower increase when the translational energy is between 0.262eV and 0.347eV. The difference between the two results caused by the following reasons: first, the measured excitation function is only for the CD_3 (vNK) umbrella motion product; second, in the present model, there are no internal rotational motion included for CD_4 expect the external rotational motions of the F atom with respect to the CD_4 center of mass rotation. So, the vibrational energy of CD_4 cannot be efficiently transferred to the rotational motions and to the other neglected vibrational DOFs, which makes the CD vibration more active than that in reality (experimental); thus, the ICS of the ground state shows a slower decay after the position of the peak.

3.3   Energy efficiency on reactivity

170 and 179 partial waves are needed to converge the initial-state selected ICSs for the umbrella (0,1) and stretching (1,0) modes of CD_4, respectively. And in Fig. 4, we give the ICSs for the umbrella (0,1) and stretching (1,0) modes of CD_4 as a function of the translational energy. As shown in the picture, with the increase of the collision energy E_C, the three states (0,0), (0,1) and (1,0) both have a sharp rise first, and then slow down to a plateau. But the (1,0) state has a faster rising rate to reach the peak at the $E_C = 0.136$ eV, and the ICS of (1,0) state is always the biggest among the (0,0) and (0,1) states. For the umbrella state (0,1), the value of ICS is the smallest. Based on the above results, we can conclude, the translational energy is more effective in promoting the reaction when the collision energy is less than 0.136eV; and the vibrational energy's effect is more obvious at the high collision energy. Compared with the ground state, the stretching modes of CD improve the reactivity, while the umbrella modes of CX hinder the reactivity. And
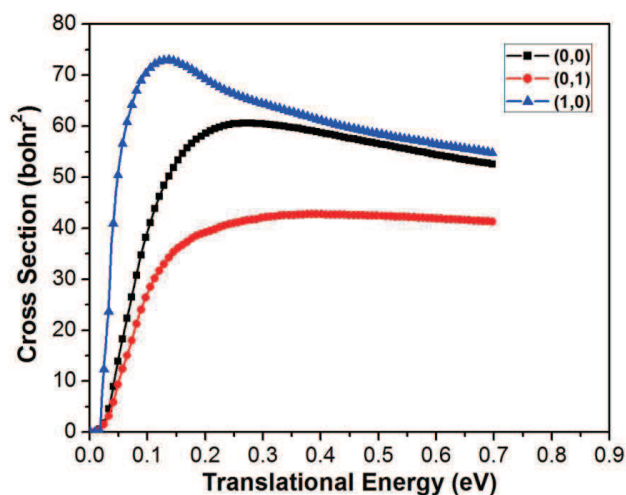

Figure 4: The 4DOF integral cross section for the F + CD_4 reaction, as a function of the translational energy. (0,1) and (1,0) are the umbrella and stretching modes of CD_4, respectively.
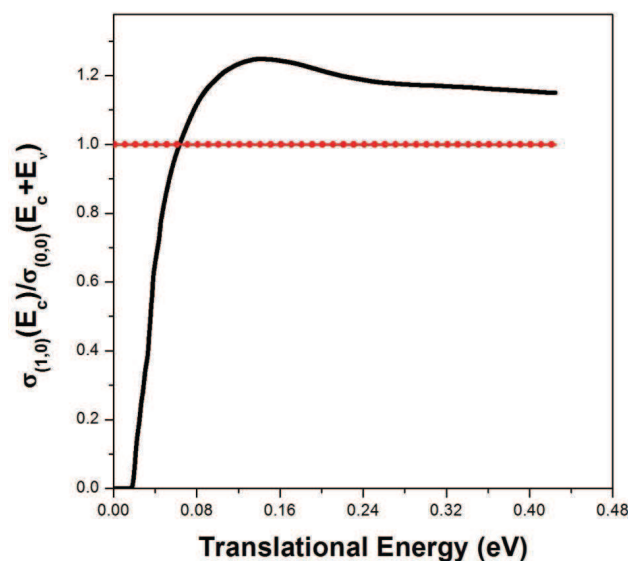
Figure 5: Cross section ratio of the ICS for the F + CD$_4$ reaction, $\sigma(1,0)/\sigma(0,0)$, between the C-D stretching mode and the ground state as a function of collision energy based on an equal amount of total energy, where the vibrational energy difference E_v between the two states is 0.27413eV.

this results is consistent with the dynamics study of F + CH$_4$ by Wang *et al.* [29].

Fig. 5 gives the ICS ratio, $\sigma_s(E_C)/\sigma_g(E_C+E_V)$, of the CD stretching excited state (1,0) to the ground state (0,0) on the basis of the equal amounts of total energy. This figure shows that, with the increase of the translational energy, the ratio increases quickly to reach 1.0 at E_C = 0.064 eV, after that the increase of the ratio becomes slow. Then, the ratio begins to decline slowly and keep the same value finally. This indicates, at the $E_C < 0.064$ eV, translational energy is more efficient than vibrational energy. And when collision energy is larger than 0.064 eV, the vibrational energy is slightly more efficient than translational energy, because the biggest ratio is only about 1.248. Overall, for this early-barrier reaction, the translational energy is much more effective in promoting the reaction than at the very low vibrational energy, and the vibrational enery is more effective than the translational energy at higher energy. And the result is the similar to the results of the reaction F + CH$_4$ [33]. So the Polanyi rules can only be extended to this reaction for the low energy.

4   Conclusions

In this study, we have carried out reduced-dimensional quantum reaction dynamics, time-dependent wavepacket propagation computations to study the F + CD$_4$ → DF + CD$_3$ reaction. A 4DOF approach is employed to study the reactant energy efficiency in surmounting the early energy barrier on the *ab initio* PES developed by Czakó and Bowman.

For the F + CD$_4$ reaction system, we found the reactant stretching excitations promote the reactivity; whereas, the umbrella modes of CX hinder the reactivity. Besides, at $E_C <$ 0.064 eV, the translational energy is more efficient in enhancing the reactivity than CD vibrational energy; at $E_C >$ 0.064 eV, the vibrational energy is slightly more efficient than translational energy. In addition, the emergence of the resonance peak in reaction probability and ICS confirms the prediction for the F + CD$_4$ reaction exists resonance peak by Liu *et al.* [35, 36].

The Polanyi rules, which were summarized on the basis of the atom-diatom reaction systems, show which form of energy is effective in surmounting an early barrier or a late barrier. And the Polanyi rules are hold for some poly-atomic reactions. As in this study, for the early barrier reaction, the translational energy is more efficient in enhancing the reactivity than vibrational energy only at very low translational energy. So the Polanyi rules still cannot be simply extended to the polyatomic reaction system. We think more theoretical and experimental investigations are needed to better understand the energy requirement on reactivity for more complex polyatomic reaction systems.

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