

Time-dependent quantum dynamics study of the $F + CD_4 \rightarrow DF + CD_3$ reaction

Yu-Ping Wang, Peng-Xiu Yan, Yi-Da Li and Dun-You Wang*

School of Physics and Electronics, Shandong Normal University, Jinan, 250014, the People's Republic of China

Received 16 September 2015; Accepted (in revised version) 28 October 2015
Published Online 15 November 2015

Abstract. A four-degrees-of-freedom, time-dependent quantum wave packet propagation method is employed to study the $F + CD_4 \rightarrow DF + CD_3$ 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.

PACS: 34.50.-s; 47.11.Mn; 82.20.Ej; 82.20.Xr

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 an endoergic reaction (later barrier), the vibrational energy is favored for barrier crossing, whereas the translational energy is favored for an 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

*Corresponding author. *Email address:* dywang@sdsu.edu.cn (D.-Y. Wang)

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 H₂O (HOD, D₂O) + 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 H₂D⁺ + H₂ → H₃⁺ + 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 H₂D⁺ 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 CH₄ (CHD₃, CD₄) [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 + CH₄ 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 + CH₄ [9] and another a 7DOF study on the Cl + CHD₃ 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 + CHD₃ → OH + CD₃ [11]. The experimental data show the excitation of C-H vibration in CHD₃ enhances reactivity [12]. However, for the reaction of O with CH₄ [13], bending excitations in CD₄ slightly restrain the reaction. Recently, Czakó and Bowman carried a QCT calculation on the O + CHD₃ 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 + CD₄/CHD₃ → OD/OH + CD₃ reactions [16]. For the O + CHD₃ 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 + CD₄ reaction system, all the vibrational excitations enhance the reactivity, which agrees with the QCT calculation [17] and contradicts the experimental result [13].