

Effects of the reagent rotational excitation on the stereodynamics of the reaction $C(^3P)+CH(X^2\Pi)\rightarrow C_2+H$

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Abstract. Based on the $1^2A''$ global three-dimensional adiabatic potential energy surface [Boggio-Pasqua *et al.*, Phys Chem. Chem. Phys 2:1693-2000], a theoretical study of the stereodynamics of the reaction $C(^3P)+CH(X^2\Pi)$ ($v=0; j=0-6$) has been performed using the quasi-classical trajectories(QCT) method. The cross sections are calculated. The differential cross sections (DCSs) and the distributions of $P(\theta_r)$, $P(\phi_r)$ are presented in detail at the selected collision energy of 0.3 eV. The product rotational alignment parameter $\langle P_2(j' \cdot k) \rangle$ are also obtained as a function of the reagent rotational quantum number. The results show that the reagent rotational excitation plays an important role in the title reaction.

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Key words: stereodynamics; QCT method; rotation excitation; rotational alignment; reaction mechanism.

1 Introduction

The ethanol radical C_2H is one of the most abundant polyatomic species in carbon-rich stars and interstellar clouds [1,2]. C_2H is believed to be the major source of C_2 in comets and interstellar media [3-6]. It's an important intermediate species of numerous combustion reactions [6,7]. It is also the simplest organic triatomic molecule involving a triple $C\equiv C$ bond and has a low-lying electronic state. What's more, C_2H plays an important role in the formation and the destruction of carbon chain molecules C_2H_n (with $n=2-6$)[8]. To shed more light on the details of the formation and destruction of C_2H , it is essential to study the relevant property of the molecular reaction dynamics.

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In experiments, the researchers have done many spectroscopic studies of C_2H and its isotopic species using a variety of techniques, including Laser Magnetic Resonance (LMR) [9, 10], microwave and millimeter-wave spectroscopy [11-13], color center laser spectroscopy [14-16] and Fourier Transform Infrared Spectroscopy (FTIR) [17]. Meanwhile, these experimental studies have been accompanied by the extensive theoretical work and promoted the development of the understanding of the spectroscopy of C_2H [18-20]. However, the experimental work concerning the dynamics of the title reaction is very sparse. To our knowledge, only three estimated values of the rate constant can be found in the literature and databases [22-24]. Theoretically, a series of high-level *ab initio* studies of the X and A state of CCH by Peyerimhoff and co-workers have shown that two A' surface intersect at the C-C distance are near 2.5 bohrs [25, 26]. More recently, Boggio-Pasqua and co-workers [1] build an analytical representation of the three lowest adiabatic potential energy surfaces which correspond to the states $X^2\Sigma^+$ and $A^2\Pi$ of C_2H . These three surfaces belong to the $^2A'$ or $^2A''$ symmetry species [1, 6, 27]. In 2001, Tang *et al.* calculated the dynamics of the title reaction by using a quantum time-dependent wave packet method on the $1^2A'$ and $2^2A'$ surface [6, 27]. In 2010, Yang *et al.* studied the effect of initial rotational quantum number on the $1^2A'$ surface [28]. However, there are only four report on properties of its vector properties about this reaction on $1^2A''$ PES [29-32]. Zhang *et al.* found the cross sections and the value of $\langle P_2(j' \cdot k) \rangle$ of the title reaction decrease with the increase of collision energy [29]. Liu *et al.* reported the product C_2 is mainly backward-forward scattering and the orientation of the product rotational angular momentum tends to point to the negative direction of the y-axis at $E_{col}=0.1eV$ on the $1^2A''$ PES [30]. Wu *et al.* discovered that the title reaction performed a preference of forward scattering and a weak of product rotation alignment considering isotopic effect of CH [31]. Recently, Our team studied the effect of reagent vibrational excitation for this title reaction and it increased the total reaction probability and enhanced the forward scattering [32].

To gain more insight into the detailed dynamics of the title reactions, we have carried out quasiclassical trajectory for the $C(^3P)+CH(X^2\Pi)(v=0, j=0-6) \rightarrow C_2+H$ reaction at 0.3 eV based on the $1^2A''$ PES [1]. The paper is organized as follows: Section 2 provides a brief review of the theoretical methodologies. Section 3 discusses the results. Finally, the main conclusions are presented in Section 4.

2 Theory

2.1 Vector correlations

Fig. 1 illustrates the CM reference frame used in the present investigation. The reagent initial relative velocity vector k is parallel to the z-axis of the CM frame. The scattering plane (x-z plane) contains k and relative velocity vector k' of final product. The scattering angle θ_t is the angle between k and k' . θ_r and ϕ_r are the polar and azimuthal angles of the final rotational angular momentum j' , respectively.

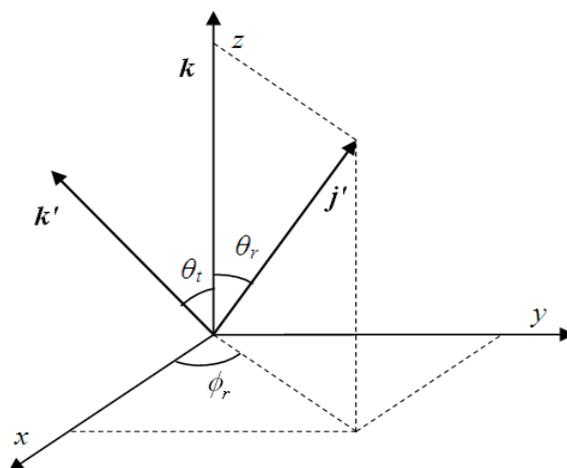


Figure 1: The center-of-mass frame used to describe the k , k' and j' correlations.

The distribution $P(\theta_r)$ describes the correlation of the two vectors $k-j'$, which can be expanded in a series of Legendre Polynomials:

$$P(\theta_r) = \frac{1}{2} \sum_k (2k+1) a_0^{(k)} P_k(\cos\theta_r). \tag{1}$$

The polarization parameter are given by

$$a_0^{(k)} = \int_0^\pi P(\theta_r) P_k(\cos\theta_r) \sin\theta_r d\theta_r = \langle P_k(\cos\theta_r) \rangle. \tag{2}$$

The coefficients a_0^k is called orientation parameter (when k is odd) or alignment parameter (when k is even). As $k=2$, the expression for the expansion coefficient $a_0^{(k)}$

$$a_0^2 = \langle P_2(\cos\theta_r) \rangle = \frac{1}{2} \langle 3\cos^2\theta_r - 1 \rangle \tag{3}$$

which expresses the degree of the product rotational alignment, therefore, it is also called the rotational alignment parameter of the product.

The dihedral angle distribution function $P(\phi_r)$ describing $k-k'-j'$ correlation can be expanded as a Fourier series:

$$P(\phi_r) = \frac{1}{2\pi} \left(1 + \sum_{\text{even}, n \geq 2} a_n \cos n\phi_r + \sum_{\text{odd}, n \geq 1} b_n \sin n\phi_r \right) \tag{4}$$

with

$$a_n = 2 \langle \cos n\phi_r \rangle \quad \text{and} \quad b_n = 2 \langle \sin n\phi_r \rangle. \tag{5}$$

In this work, $P(\phi_r)$ is expanded up to $n=24$, which shows a good convergence.

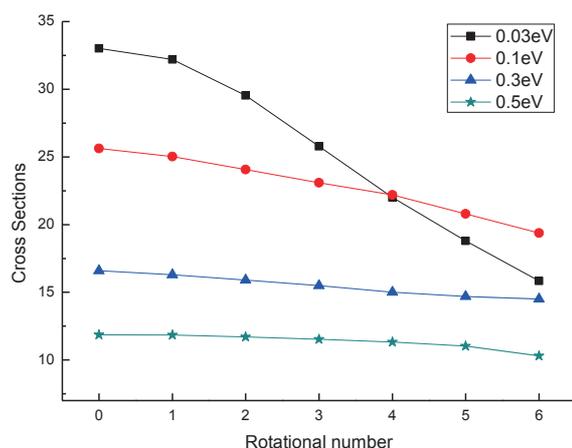


Figure 2: Total reaction cross section for $C(^3P)+CH(X^2II)(v=0, j=0-6)\rightarrow C_2+H$ as a function of j at different collision energies.

2.2 Quasiclassical trajectory calculations

We employ the standard quasi-classical trajectory (QCT) method to study the stereodynamics of the title reaction. The QCT methodology here employed is standard, and only some brief details will be given here. During the calculation, the classical Hamilton's equations are numerically integrated for the motion in three dimensions, and the accuracy of the integration is verified by checking the conservation of the total energy and total angular momentum for every trajectory. Batch of 100,000 trajectories have been calculated on the $1^2A''$ PES for the title reaction. The selected collision energy E_{col} is chosen as 0.3 eV and the initial CH rovibrational states are taken as $v=0$ and $j=0-6$, respectively. The integration step is chosen as 0.1 fs. In order to ensure no interaction between attacking atom C and the center-of-mass (CM) of the molecule CH, the distance between them is set to be 10 Å. The impact parameters are optimized before running the trajectories.

3 Results and discussion

Fig. 2 shows the influence of the initial reagent rotational excitation on the reaction cross sections for $C(^3P)+CH(X^2II)(v=0-6, j=0)$ at the relative collision energies $E_{col}=0.03, 0.1, 0.3, 0.5$ eV, respectively. Considering the four energies, it is easy to conclude that the reaction cross sections decrease with the increase of the collision energies, which is due to no energy barriers on the PES of the title reaction. For the given collision energy, it can be seen that the values of cross section decrease when the rotational quantum number. What's more, the effect of reagent rotational excitation at lower energy 0.03 eV is more obviously than other one's. The cross sections changes little at higher energy. This phenomenon may due to the ratio of rotational energy and collision energy. The higher ratio of rotational energy, the more obvious the tendency becomes.

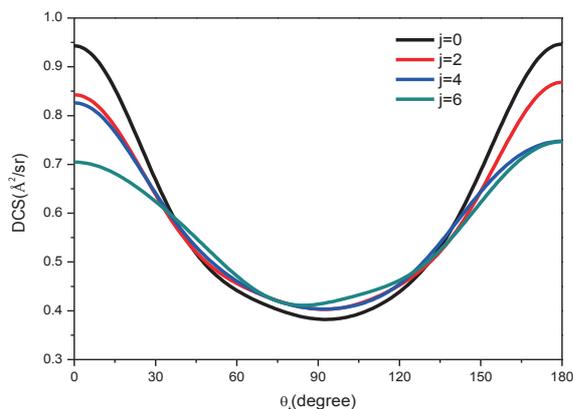


Figure 3: Differential cross section for $C(^3P)+CH(X^2\Pi)(v=0, j=0, 2, 4, 6)$ at the collision energy $E_{col}=0.3$ eV.

Fig. 3 represents the calculated DCSs for $C(^3P)+CH(X^2\Pi)(v=0, j=0, 2, 4, 6)$ at the collision energy $E_{col}=0.3$ eV. We can see clearly that the C_2 molecules scattered mainly in the forward-backward direction. Owing to the effect of the potential well of PES, a long-life complex compounds are formed [40], which leads to the same chance between the forward scattering and the backward scattering when the initial rotational quantum number $j_{CH}=0$. However, when rotational energy increases, it changes the scattering directions. Overall, the reagent rotational excitation enhances the strength of the backward scattering.

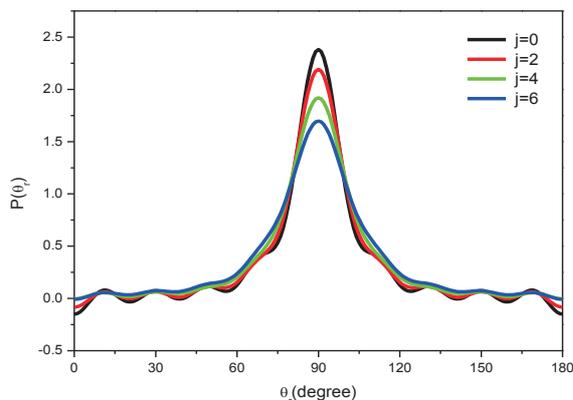


Figure 4: The distribution of $P(\theta_r)$ for $C(^3P)+CH(X^2\Pi)(v=0, j=0, 2, 4, 6)$ at the collision energy $E_{col}=0.3$ eV.

The $P(\theta_r)$ distribution of the product C_2 is shown in Fig. 4, which describes the $k-j'$ correlation. One can see that the peaks of $P(\theta_r)$ distribution are at the angle $\theta_r = 90^\circ$ and they are symmetric with respect to $\theta_r = 90^\circ$. It implies that the product rotational angular momentum vector j' is strongly aligned along the direction at a right angle to the relative velocity direction k [33]. We also observed that the peak of the $P(\theta_r)$ distributions becomes lower and wider with the increasing of the reagent rotational excitation of the

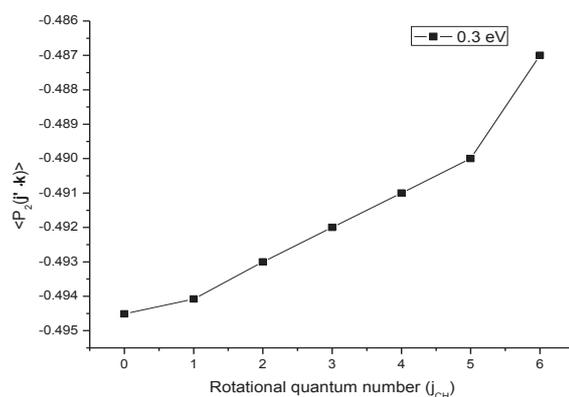


Figure 5: Rotational alignment parameter of the product $C_2 \langle P_2(j' \cdot k) \rangle$ for the reaction $C(^3P) + CH(X^2\Pi)$ ($v=0, j=0-6$) at the collision energy $E_{col}=0.3$ eV.

title reaction. This means that the increase of the reagent rotational energy will decrease the anisotropic distribution of the product rotational angular momentum vector j' .

To obtain a better understanding of the product rotational alignment distribution of C_2 , we calculate the product rotational alignment parameter $\langle P_2(j' \cdot k) \rangle$, which shows in Fig. 5 $\langle P_2(j' \cdot k) \rangle$ can give us a quantitative description of the degree of the product rotational alignment. The value of $\langle P_2(j' \cdot k) \rangle$ changes from 1 to -0.5. The smaller the expectation value of $\langle P_2(j' \cdot k) \rangle$ is, the stronger the degree of the product rotational alignment is. It can be seen from Fig. 5 that the value of $\langle P_2(j' \cdot k) \rangle$ increases when the reagent rotational quantum number increases. It is consistent with the $P(\theta_r)$ distribution.

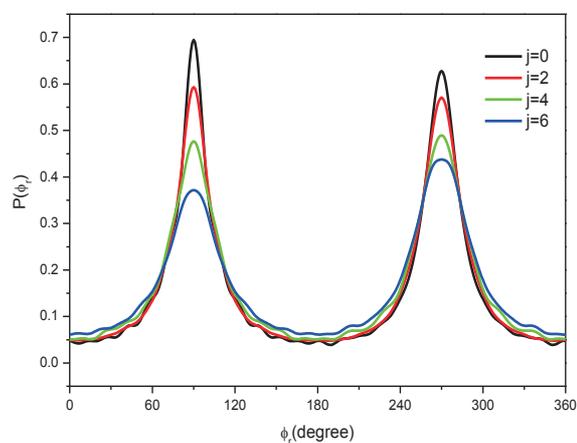


Figure 6: The dihedral angle distribution of the product C_2 for the reaction $C(^3P) + CH(X^2\Pi)$ ($v=0, j=0, 2, 4, 6$) at the collision energy $E_{col}=0.3$ eV.

Fig. 6 shows the calculated $P(\phi_r)$ distribution for product C_2 at the reagent rotational quantum number of 0, 2, 4, 6, respectively. We can see that the $P(\phi_r)$ distributions are asymmetric with respect to the $k-k'$ scattering plane, with the peaks appearing at

$\phi_r = 90^\circ$ and 270° , which reveals that there is a strong polarization of the product angular momentum j' of the title reaction [34]. It is clear that the peak at $\phi_r = 90^\circ$ decreases with the increase of rotational number. This behavior implies that the product rotational angular momentum vector j' is not only aligned, but also the oriented directions changes from the positive to negative y-axis. As a general view, the peak of $P(\phi_r)$ distribution decreases and becomes a little wider with the increase of the reagent rotational quantum number, which reflects that the rotational polarization of the product is weakened with the increase of the reagent vibrational quantum number. Therefore, the reagent vibrational excitation has a negative influence on the polarization of the product rotational angular momentum.

4 Conclusions

In this work, we study the stereodynamics of $C(^3P)+CH(X^2\Pi)(v=0, j=0-6)\rightarrow C_2+H$ reaction using a QCT method on the $1^2A''$ PES constructed by Boggio-Pasqua *et al.* The Cross Sections and DCSs are obtained. The cross sections decrease with the increase of the reagent rotational quantum number. The calculated DCSs show that it enhances the trend of the backward scattering of the title reaction. The distributions of $P(\theta_r)$, and $P(\phi_r)$ in the different rotational states of the reagent are also discussed. The $P(\theta_r)$ distribution shows that the alignment degree of the product angular momentum is weakened with the increase of j_{CH} . The $P(\phi_r)$ distribution indicates that the product rotational angular momentum vector j' is not only aligned, but also the oriented directions changes from the positive to negative y-axis. The increase of j_{CH} reduces the orientations degree of the product rotational angular momentum. We concluded that the stereodynamics of the title reaction is sensitively affected by the reagent vibrational excitation.

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