Stereodynamics study of the exchange reaction $O(^3P) + CH_4 \rightarrow H + OCH_3$*

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A new London–Eyring–Polanyi–Sato potential energy surface is employed in this work to study the stereo properties of the $O(^3P) + CH_4 \rightarrow H + CH_3O$ reaction in its rovibrationally ground state using the quasiclassical trajectory method (QCT). Our calculations are performed at a range of collision energies, $E_c = 1.5$ eV$\sim$ 3.5 eV, and the excitation function obtained by the QCT method accords well with the experimental data. The product rotational polarization is calculated, and the product shows a strong rotational polarization in the centre-of-mass coordinate system. The orientation of the product rotational angular momenta is sensitive to the increase in collision energy, and the alignment of the product rotational angular momenta shows some of the properties of the heavy heavy–light mass combination reactions. In the isotopic substituted reaction study, when the H atoms in methane are replaced by D atoms, the rotational polarization is obviously reduced. The polarization-dependent differential cross section is also studied by this QCT calculation to provide detailed information about the rotational alignment and orientation of the product.

Keywords: quasiclassical trajectory method, potential energy surface, product polarization, isotope effect

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1. Introduction

The reaction of the electronic ground state of the oxygen atom $O(^3P)$ with hydrocarbons plays an important role in many chemical environments, such as combustion, air pollution, atmospheric chemistry,[1] and low earth orbit (LEO) conditions.[2] The $O(^3P) + CH_4$ reaction is the simplest reaction that is used as a model system for the reactions of hyperthermal and polymeric hydrocarbon with $O(^3P)$, and so has aroused interest in recent studies.[2–6]

Because of the highest energy barrier among the different hydrocarbon reactions, experimental studies of these systems have proved rather difficult using past techniques such as flash photolysis-shock tubes, flow tubes, and laser photolysis with laser-induced fluorescence.[7] There are not many dynamic experimental studies in either the abstraction or exchange channel of this system.[8–10] In recent years, Kowalski and Pranszke[3] used a beam of fast oxygen atoms in the $O(^3P)$ state to impact the CH_4 target, and obtained the OH(A-X) product excitation function. But the collision energy they chose was too high (10 eV–300 eV).[3] Zhang and Liu[6] also conducted a cross beam experiment for this reaction, and found that compared with the ground-state reagent, bend-excited methane yields more vibrational excitations of the hydroxyl coproduct.[6] Troya *et al.*,[9] and Troya and Garcia-Molina[10] studied both the abstraction and exchange of this system experimentally and theoretically, and gave the experimental excitation function of the exchange channel.

In the theoretical studies, the main difficulties came from the polyatomic characteristic of the reaction. This leads to difficulties in obtaining accurate potential energy surfaces and using high level simulations. Recently, Martinez *et al.*[11] made an *ab initio* pseudotriatomic potential energy surface to research the abstract reaction of $O + CH_4$, and the obtained results were in good agreement with the experimental results.

Earlier studies of the thermal conditions and dynamics were not sufficient, and stereodynamics is needed to understand more of the properties of the exchange channel of this reaction. In this work, we investigate the stereo properties of the title reaction. We use the triatomic approximation to treat the methyl as a pseudo-atom.[12] Then, a new triatomic potential energy surface (PES) is applied to the quasiclassical trajectory method (QCT).[13–17] The reaction $O(^3P) + CH_4 \rightarrow H + CH_3O$ is simulated in a collision energy range from 1.5 eV to 3.5 eV to study vector properties such as the product rotational polarization. In Section 2, a brief review of the theoretical methodologies is provided. The calculated results in this work are discussed in Section 3, and some conclusions are drawn from the present study in Section 4.

2. Theory

2.1. Potential energy surface

A three-atom model PES called extended-LEPS (London–Eyring–Polanyi–Sato)[18,19] is employed in this work, where the CH_3 in this reaction is treated as a pseudo-atom. This approximation has been used in some other similar works, such as the abstraction channel reaction $O + CH_4 \rightarrow$

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OH + CH_3, and the calculation results are in good agreement with the experimental measurements.[11,20] All the parameters used in this surface are shown in Table 1.

Table 1. The parameters in the extended-LEPS PES of the reaction O + CH_4 $\rightarrow$ H + OCH_3, 1 Å = 0.1 nm.

Parameter	H–O	H–CH_3	O–CH_3
β^{a}/Å^{-1}	2.294	1.83	1.96
D^{a}/(kcal/mol)	106.4	106.9	91.86
r_0^{a}/Å	0.9706	1.093	1.44
S^{b}/(Sato)	0.74	0.10	–0.50

[a] cited from Refs. [1] and [21].

[b] from this work.

2.2. Rotational polarization of the product

The centre-of-mass (CM) frame is used in this work, where the z axis is parallel to the reagent relative velocity $\boldsymbol{k}$, and the y axis is perpendicular to the plane containing $\boldsymbol{k}$ and $\boldsymbol{k}'$; $\boldsymbol{k}'$ is the relative velocity of the products. The distribution function of the vector correlation between $\boldsymbol{k}$ and $\boldsymbol{j}'$ ($\boldsymbol{j}'$ is the angular momentum of the O-methyl product) is expanded in a series of Legendre polynomials as[22]

$$P(\theta_{\rm r}) = \frac{1}{2}\sum_{l}[l]a_0^{(l)}{\rm P}_l(\cos\theta_{\rm r}),$$

where $\theta_{\rm r}$ is the angle between $\boldsymbol{j}'$ and $\boldsymbol{k}$. The coefficients $a_0^{(l)}$ are called polarization parameters, and $a_0^{(l)} = \langle {\rm P}_l(\cos\theta_{\rm r})\rangle$, where the average is taken over all the reactive trajectories.

The dihedral angle distribution $P(\phi_{\rm r})$, which describes the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ correlations, can be expanded in Fourier series as[22]

$$P(\phi_{\rm r}) = \frac{1}{2\pi}\left(1 + \sum_{\text{even},n>2} a_n\cos n\phi_{\rm r} + \sum_{\text{odd},n\geq 1} b_n \sin n\phi_{\rm r}\right),$$

where $a_n = 2\langle\cos n\phi_{\rm r}\rangle$ and $b_n = 2\langle\sin n\phi_{\rm r}\rangle$, and where the average is taken over all the reactive trajectories. To obtain a fine convergence in the calculation of this work, $P(\theta_{\rm r})$ is expanded up to l =18, while $P(\phi_{\rm r})$ is expanded up to $n = 24$.

The resulting probability density function of angles $P(\phi_{\rm r})$ and $\phi_{\rm r}$ can be written as[22]

$$P(\theta_{\rm r},\phi_{\rm r}) = \frac{1}{4\pi}\sum_{k}\sum_{q\geq 0}[k][a_{q\pm}^{k}\cos(q\phi_{\rm r}) - a_{q\mp}^{k}{\rm i}\sin(q\phi_{\rm r})]C_{kq}(\theta_{\rm r},0).$$

The polarization parameter a_q^k is given by

$$a_{q\pm}^{k} = 2\left\langle C_{k|q|}(\theta_{\rm r},0)\cos(q\phi_{\rm r})\right\rangle, \quad \text{for even } k,$$
$$a_{q\mp}^{k} = 2i\left\langle C_{k|q|}(\theta_{\rm r},0)\sin(q\phi_{\rm r})\right\rangle, \quad \text{for odd } k.$$

In this work, $P(\theta_{\rm r},\phi_{\rm r})$ is expanded up to $k = 7$ to obtain a good convergence.

The full three-dimensional angular distribution associated with $\boldsymbol{k}$, $\boldsymbol{k}'$, and $\boldsymbol{j}'$ is represented by a set of generalized polarization-dependent differential cross sections (PDDCS) in the CM frame, and the fully correlated CM angular distribution can be written as

$$P(\omega_{\rm t},\omega_{\rm r}) = \sum_{kq}\frac{[k]}{4\pi}\frac{1}{\sigma}\frac{{\rm d}\sigma_{kq}}{{\rm d}\omega_{\rm t}}C_{kq}(\theta_{\rm r},\phi_{\rm r}),$$

where $[k] = 2k+1$, $1/\sigma({\rm d}\sigma_{kq}/{\rm d}\omega_{\rm t})$ is a generalized PDDCS, and $C_{kq}(\theta_{\rm r},\phi_{\rm r})$ are modified spherical harmonics. The differential cross section is given by

$$\frac{1}{\sigma}\frac{{\rm d}\sigma_{00}}{{\rm d}\omega_{\rm t}} = P(\omega_{\rm t}) = \frac{1}{4\pi}\sum_{k_1}[k_1]h_0^{k_1}(k_1,0){\rm P}_{k_1}(\cos\theta_{\rm t}).$$

The bipolar moments $h_0^{k_1}(k_1,0)$ are evaluated using the expectation values of the Legendre moments of the differential cross section,

$$h_0^{k_1}(k_1,0) = \left\langle {\rm P}_{k_1}(\cos\theta_{\rm t})\right\rangle.$$

2.3. Quasiclassical trajectory calculations

A standard QCT calculation was carried out in three dimensions, and the CH_4 molecule was initialized in the rovibrational ground state ($v = 0$ and $j = 0$). The trajectory simulations were performed in a collision energy range of 1.5 eV–3.5 eV with a time integration step of 0.1 fs, and 2×10^5 trajectories were sampled for each energy level. All the calculations in this QCT were under adiabatic approximation, and the zero point energy (ZPE) was not contained.

3. Results and discussion

The contour plot of our three-atom model extended-LEPS PES is shown in Fig. 1(a), and the energy along the reaction path is shown in Fig. 1(b). The PES shows a minimal barrier in a collinear configuration O–CH_3–H′. The saddle point (at about O–C=1.9 Å, H′–C=1.3 Å) in Fig. 1(a) indicates that the title reaction is a repulsive one and has an early barrier, which means that the reaction probability is sensitive to the collision energy. From Fig. 2, we can see that the calculated excitation functions (integral cross section) accord well with the experimental data. This means that the extended-LEPS PES employed in this work is very good. So in the following calculations, this extended-LEPS PES is used to study the stereodynamical properties of the title reaction and its isotopic substituted reaction.

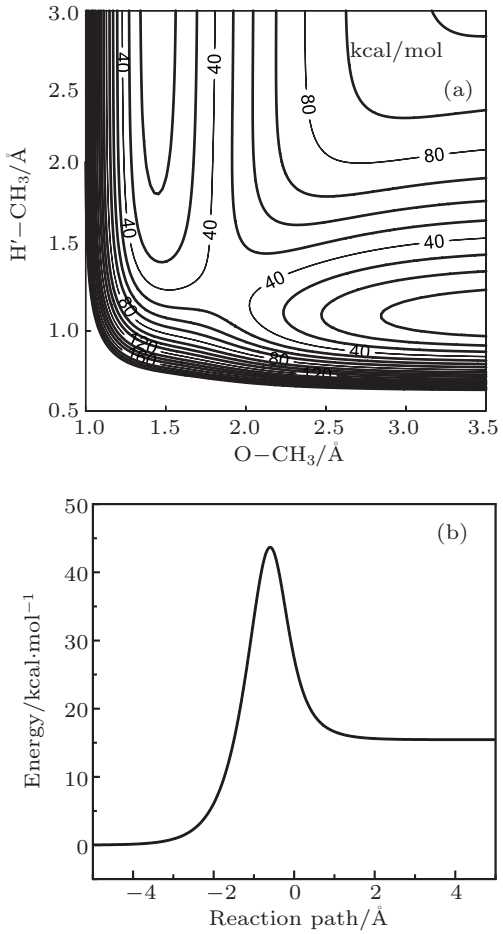


Fig. 1. (a) Contour plot for the O + CH_4 → H + OCH_3 surface at the reaction configuration. The contours are equally spaced by 10 kcal/mol and the C–O and H–C bonds are in Å. (b) The energy along the reaction path of the extended-LEPS surface.

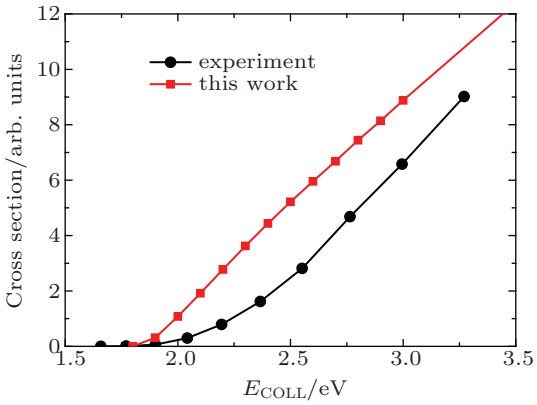


Fig. 2. (color online) A comparison between the experimental and our theoretical excitation functions (integral cross section versus collision energy) for the reaction O + CH_4 → H + OCH_3.

The reaction has a threshhold at about 1.7 eV from the experimental report,[9] which accords well with the energy barrier shown in Fig. 2. Although the title reaction is in the exchange channel, we can still define this reaction as a heavy heavy–light (HHL) mass combination reaction. This mass combination indicates that the rotational alignments of the products are almost independent of either attractive or repulsive PES, and the rotational angular momenta of the products will show strong polarizations[18] Figure 3 shows the $P(\theta_r)$ distributions at the three selected collision energies, 2.0 eV, 2.5 eV, and 3.0 eV, respectively. Each of the distributions has a symmetrical form with respect to $\theta_r = 90°$, and the large peak around $\theta_r = 90°$ can demonstrate that $\boldsymbol{j}'$ has a cylindrically symmetric distribution in the product scattering frame and that the vector of $\boldsymbol{j}'$ prefers to be perpendicular to $\boldsymbol{k}$. In this mass combination reaction, almost all the orbital momenta will turn into the angular momenta of the products. When the collision energy gets larger, more orbital momenta will turn into the angular momenta of the products ($\boldsymbol{L} \to \boldsymbol{j}'$).[18] So the peak at $\theta_r = 90°$ gets larger when E_c increases from 2.0 eV to 3.0 eV in Fig. 3.

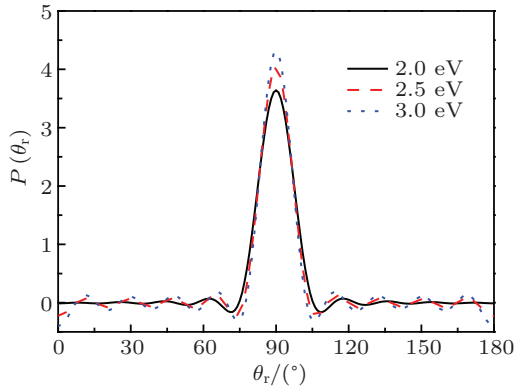


Fig. 3. (color online) A comparison of $P(\theta_r)$ among different collision energies for the reaction O + CH_4 → H + OCH_3.

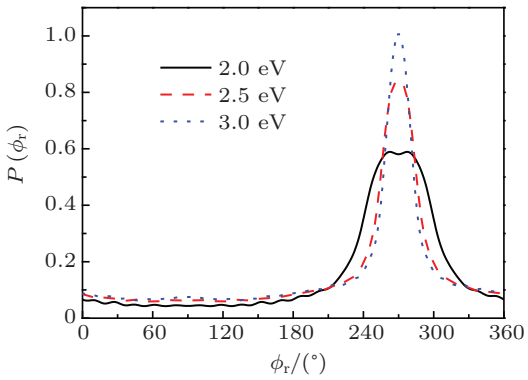


Fig. 4. (color online) A comparison of $P(\phi_r)$ among different collision energies for the reaction O + CH_4 → H + OCH_3.

The dihedral angle distributions $P(\phi_r)$ and their comparison at three selected collision energies for the reaction are shown in Fig. 4. The $P(\phi_r)$ distributions tend to be asymmetric with respect to the $\boldsymbol{k}$–$\boldsymbol{k}'$ scattering plane; this reflects the strong rotational polarization of the products. We often use the term "in-plane" to refer to the product molecule rotation preference in the plane parallel to the scattering plane, and the term "out-of-plane" to refer to the product molecule rotation preference in the plane perpendicular to the scattering plane at the same time. The peak in the distribution at the angle close to 270° in Fig. 4 implies a preference for left-handed product

rotation in the plane parallel to the scattering plane. It is noteworthy that no peak appears at the angle close to 90°, which means that $\boldsymbol{j}'$ tends to be oriented along the negative direction of the y axis of the CM frame. As the E_c decreases, the peak around 270° becomes small, and when $E_c = 2.0$ eV the peak becomes flat. When E_c decreases, the polarization is weakened and the product molecule rotation prefers to change from the in-plane reaction mechanism to the out-of-plane mechanism.

The polarization in the isotope effect is then investigated, and a comparison between reaction O + CH_4 → H + OCH_3 and reaction O + CD_4 → D + OCD_3 at collision energy $E_c = 2.5$ eV is shown in Figs. 5 and 6. The polarization of $\boldsymbol{j}'$ decreases when the H atom in the title reaction is substituted by a D atom. The distribution has a peak at $\theta_r = 90°$, which is shown in Fig. 5. This peak means that the angular momenta of the products prefer to be perpendicular to $\boldsymbol{k}$. The peak changes obviously with the mass factor (defined as $\cos^2\beta = m_A m_C/(m_A+m_B)(m_B+m_C)$);[23] and the alignment of the products decreases. Figure 6 shows a comparison of $P(\phi_r)$ between the two reactions. In reaction O + CH_4 → H + OCH_3, there is a sharp and high peak at $\phi_r = 90°$, and in the O + CD4 → D + OCD_3 reaction, a small and flat peak appears. This means that more products turn to be "out-of-plane" and oriented along the negative direction of the y axis of the CM frame.

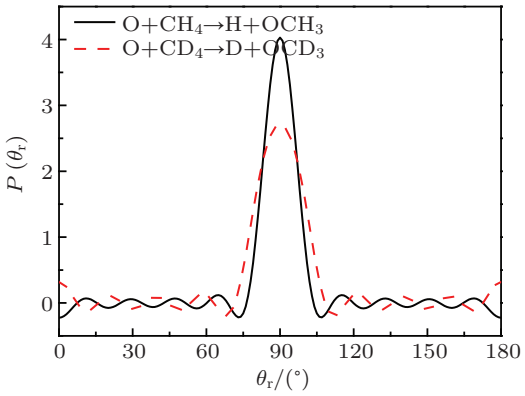


Fig. 5. (color online) A comparison of $P(\theta_r)$ between reactions O + CH_4 → H + OCH_3 and O + CD_4 → D + OCD_3.

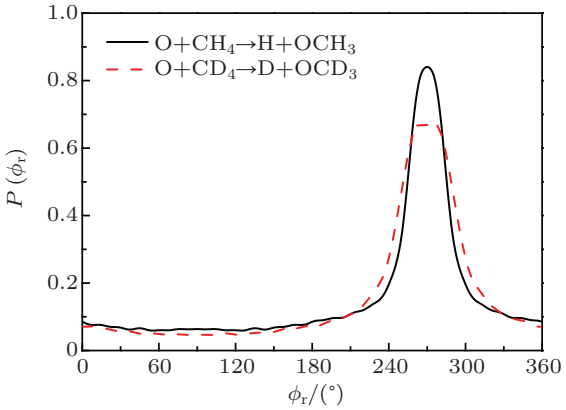


Fig. 6. (color online) A comparison of $P(\phi_r)$ between reactions O + CH_4 → H + OCH_3 and O + CD_4 → D + OCD_3.

The differential cross sections (DCSs) for the O + CH_4 reaction at $E_c = 2.0$, 2.5, and 3.0 eV are shown in Fig. 7. At the low collision energy of 2.0 eV, the DCS shows forward-sideway distribution. When the collision energy increases, the angular distributions shift towards more a forward direction. This reflects the characteristics of the repulsive potential energy surface of this title reaction. The trajectories come from the direct reactions and stay near the minimum energy reaction path at a low collision energy. When the energy increases, more trajectories will come from the indirect reactions.

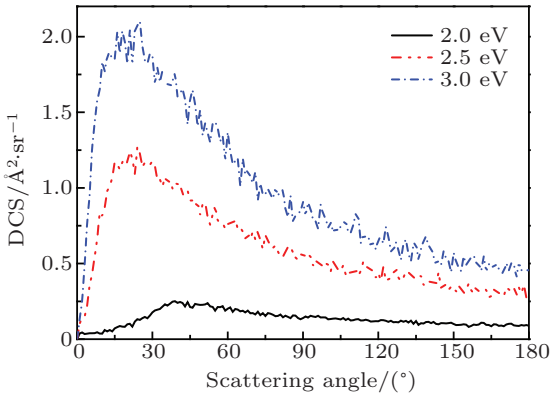


Fig. 7. (color online) Total differential cross sections (DCSs) for the reaction O + CH_4 → H + OCH_3 for collision energies of 2.0, 2.5, and 3.0 eV.

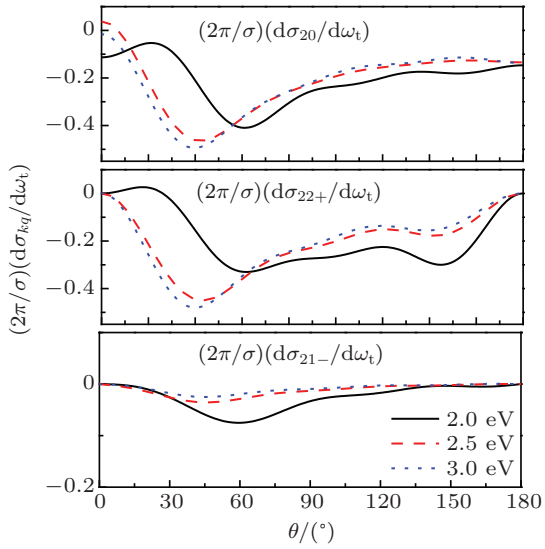


Fig. 8. (color online) PDDCS: $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$, $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$, and $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ of three different collision energies.

The generalized PDDCSs describe the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ correlation and the scattering direction of the product molecule. Figure 8 shows the PDDCSs of reaction O + CH_4 → H + OCH_3 at three different values of collision energy, E_c = 2.0, 2.5, and 3.0 eV. $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$ shows an opposite trend to that of the DCS, which results from the fact that the $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$ is related to alignment parameter $\langle P_2(\boldsymbol{j}'\boldsymbol{k})\rangle$. And when E_c increases, $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$ becomes smaller, and this distribution suggests that the

product rotational angular momentum j' polarization becomes more preferential along the direction perpendicular to k at a larger collision energy. $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ and $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ in Fig. 8 shows the PDDCS distributions with $q \neq 0$. All of these distributions are equal to zero at the ends of forward and backward scatterings. At these two scattering angles the k–k' scattering plane is not determined, so the values of the PDDCSs with $q \neq 0$ must be zero. The $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ is related to $\langle \sin^2\theta_r \cos 2\phi_r \rangle$. The negative value of $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ indicates the strong product rotational alignment along the y axis. And the polarization is enhanced when the collision energy is larger. $(2\pi/\sigma)(\mathrm{d}\sigma_{22-}/\mathrm{d}\omega_t)$ is related to $\langle -\sin 2\theta_r \cos\phi_r \rangle$. But we see in Fig. 8 that all the values at three energy levels are almost zero.

4. Conclusion

The $O(^3P) + CH_4 \rightarrow H + CH_3O$ reaction is investigated using a quasiclassical trajectory method in the three-atom approximation on a new extended-LEPS potential energy surface. The calculation is performed to obtain the integral cross sections and product rotational polarization for this exchange reaction through the collision energy from 1.5 eV to 3.5 eV, and the calculated excitation function is in good agreement with the experimental values. Using this new surface, the product rotational polarization is then investigated. The distribution is not sensitive to the collision energy, and $P(\phi_r)$ shows that the orientation is obviously stronger when the collision energy is larger. The isotopic effect study shows that when H atoms in methane are substituted by D atoms, the polarization of the rotational momenta of products decreases obviously. The PDDCSs of the title reaction are also calculated, and provide detailed information about the rotational alignment and orientation of the product.

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