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Theoretical study of the stereodynamics of the He+HD^+ reaction*

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This paper investigates the stereodynamics of the reaction He+HD^+ by the quasi-classical trajectory (QCT) method using the most accurate AQUILANTI surface [Aquilanti *et al* 2000 *Mol. Phys.* **98** 1835]. The distribution $P(\phi_r)$ of dihedral angle and the distribution $P(\theta_r)$ of angle between $\boldsymbol{k}$ and $\boldsymbol{j'}$ have been presented at three different collision energies. Four generalized polarization-dependent differential cross-sections $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ are also calculated. Some interesting results are obtained from the comparison of the stereodynamics of the title reaction at different collision energies.

Keywords: quasi-classical trajectory method, stereodynamics, polarization-dependent differential cross-section

PACC: 8200, 8220, 8220T

1. Introduction

The chemical reaction He+HD^+ has been the subject of a great deal of theoretical and experimental research for the past 30 years.[1−11] Remarkable progress on molecular reaction dynamics calculation has been made in recent years due partly to the ability of determining accurate potential energy surfaces (PESs) for simple reactive systems. In 2000, Aquilanti *et al*[5,6] published the most accurate PES for He+H_2^+ reaction. After that, there were a good many theoretical and experimental works for He+H_2^+ reaction and its isotopic variants. By means of the pulse-field ionization-photoelectron-secondary ion coincidence, Tang *et al*[8] studied the translation energy dependence of the He+H_2^+ (v=0–2, 4, 6, j=1) proton transfer cross section and they also performed quasi-classical trajectory (QCT) calculations using the AQUILANTI PES, the results of QCT method are in good agreement with their experimental results. Employing the time-dependent wave-packet method, Chu *et al*[9] computed the probability and cross section of the reaction on the same PES, the results agreed well with the experimental results of Tang *et al*. Lately, Tang *et al*[10] performed time-dependent wave-packet quantum scattering calculations for HD^+ (v=0–3, j_0=1)+He collisions, and the results were in excellent accordance with the experimental results.

It is essential to study the vector properties for the sake of understanding the dynamics of the title reaction fully. The vector properties of chemical reaction can reveal indispensable dynamic information about chemical reaction stereodynamics.[11−18] By investigating the vector properties, we can have a more profound understanding of the scattering dynamics. The paper is organized as follows. In Section 2, we present the theory of the polarization-dependent differential cross-section. Then the results and discussion are given in Section 3. Finally, conclusions are shown in Section 4.

2. Theory

2.1. Polarization-dependent differential cross-sections (PDDCSs)

The reference frame used in this work to express the degree of the polarization of product angular momentum $\boldsymbol{j'}$ is the centre-of-mass (CM) frame, which is shown in Fig.1.

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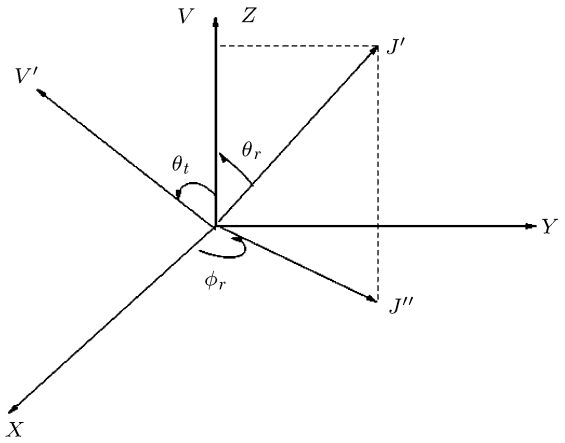


Fig.1. The centre-of-mass coordinate system used to describe the $\boldsymbol{k}$, $\boldsymbol{k}'$ and $\boldsymbol{j}'$ correlations.

The reagent relative velocity vector $\boldsymbol{k}$ is parallel to the z-axis and $x-z$ plane is the scattering plane containing the initial and final relative velocity vectors, $\boldsymbol{k}$ and $\boldsymbol{k}'$. θ is the angle between the reagent relative velocity and product relative velocity. θ_r and ϕ_r are the polar and azimuthal angles of the final rotational momentum $\boldsymbol{j}'$ respectively. The subscripts r and t are employed to distinguish different angles.

The distribution function $P(\theta_r)$ describing the $\boldsymbol{k}-\boldsymbol{j}'$ correlation can be expanded in a series of Legendre polynomials as[19−22]

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

where

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

The expanding coefficients $a_0^{(k)}$ are called orientation (k is odd) and alignment (k is even) parameter.

The dihedral angle distribution function $P(\phi_r)$ describing $\boldsymbol{k}-\boldsymbol{k}'-\boldsymbol{j}'$ correlation can be expanded in Fourier series as

$$\begin{aligned}P(\phi_r)=&\frac{1}{2\pi}\left(1+\sum_{\mathrm{even},n\geq 2}a_n\cos(n\phi_r)\right)\\&+\sum_{\mathrm{odd},n\geq 1}b_n\sin(n\phi_r),\end{aligned} \tag{3}$$

where

$$a_n=2\langle\cos(n\phi_r)\rangle, \tag{4}$$

$$b_n=2\langle\sin(n\phi_r)\rangle. \tag{5}$$

The full three-dimensional angular distribution associated with $\boldsymbol{k}-\boldsymbol{k}'-\boldsymbol{j}'$ can be represented by a set of generalized PDDCSs in the CM frame which is the same as that in the Ref.[19]. The fully correlated CM angular distribution is written as

$$P(\omega_t,\omega_r)=\sum_{kq}\frac{[k]}{4\pi}\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega_t}C_{kq}(\theta_r,\phi_r)^*, \tag{6}$$

where $\dfrac{1}{\sigma}\dfrac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega_t}$ is a generalized PDDCS, and $\dfrac{1}{\sigma}\dfrac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega_t}$ yields

$$\begin{aligned}&\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{k0}}{\mathrm{d}\omega_t}=0\quad(k\ \text{ is }\ \text{odd}),\\&\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{kq+}}{\mathrm{d}\omega_t}=\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega_t}+\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{k-q}}{\mathrm{d}\omega_t}=0\\&(k\ \text{even},\ q\ \text{odd or},k\ \text{odd},\ q\ \text{even}),\end{aligned} \tag{7}$$

$$\begin{aligned}&\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{kq-}}{\mathrm{d}\omega_t}=\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega_t}-\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{k-q}}{\mathrm{d}\omega_t}=0\\&(k\ \text{even},\ q\ \text{even or},\ k\ \text{odd},\ q\ \text{odd}).\end{aligned} \tag{8}$$

2.2. Quasi-classical trajectory calculations

The AQUILANTI surface[5,6] was used to perform the QCT[19,23−25] calculations. The quasi-classical algorithm which is sixth order symplectic routine with energy conservation checked[26] is employed for the numerical solution with Hamilton's classical equations. Three collision energies (E_{T}=1.0, 1.5 and 2.0 eV) were chosen for the title reaction. The vibrational and rotational levels of HD^+ molecule were taken as v= 0, and j = 0, respectively. In our study, batches of 100000 trajectories were run for each reaction. The trajectories were started at an initial distance of 2.5 nm between the He atom and the centre of the mass of the HD^+ molecule.

3. Results and discussion

The $P(\theta_r)$ distribution of the products which describes the $\boldsymbol{k}-\boldsymbol{j}'$ correlation is associated with the collision energy. Figure 2(a) shows that the peak of $P(\theta_r)$ is at $\theta_r=90^\circ$ and symmetric with respect to 90°, which suggests that $\boldsymbol{j}'$ is strongly aligned along the direction perpendicular to $\boldsymbol{k}$. The peak of $P(\theta_r)$ becomes higher when the collision energy increases.

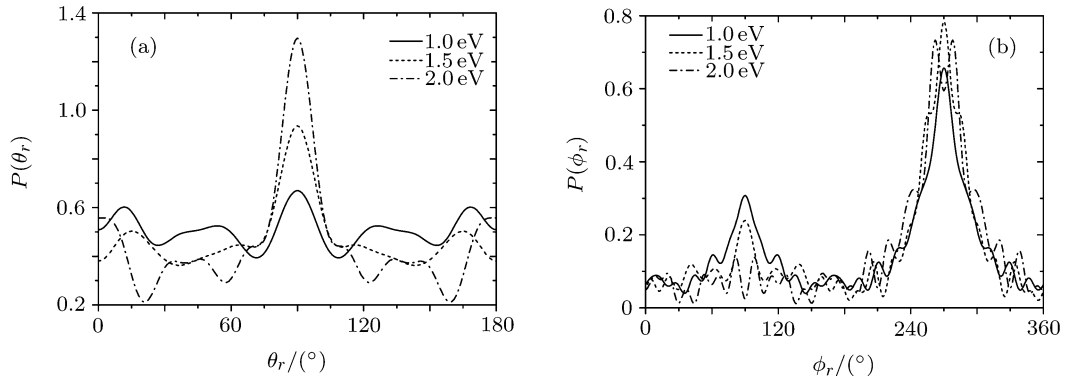


Fig.2. The angular distribution of $P(\theta_r)$ and $P(\phi_r)$ at three collision energies. The $P(\theta_r)$ in panel (a) describes the $\boldsymbol{k}-\boldsymbol{j}'$ correlation. The $P(\phi_r)$ in panel (b) shows the dihedral angle distribution of $\boldsymbol{j}'$ with respect to the $\boldsymbol{k}-\boldsymbol{k}'$ plane.

The dihedral angle distribution $P(\phi_r)$ depicted in Fig.2(b) describe $\boldsymbol{k}-\boldsymbol{k}'-\boldsymbol{j}'$ correlations. The peaks of $P(\phi_r)$ appear at $\phi_r = 90°$ and 270°, which demonstrates that $\boldsymbol{j}'$ is primarily aligned along y-axis of the CM frame. Because the peak at $\phi_r = 180°$ is unequal to that at $\phi_r = 270°$ for a specified collision energy, $\boldsymbol{j}'$ is not only aligned, but also oriented along the y-axis. The peak at $\phi_r = 270°$ is evidently higher than that at $\phi_r = 90°$ of three collision energies, $\boldsymbol{j}'$ is preferentially oriented along the positive direction of y-axis, and shows a stronger orientation at E_{T}=1.5 eV. We also plot the angular momentum polarization in the form of polar plot θ_r and ϕ_r at three collision energies in Fig.3. The distributions of $P(\theta_r,\ \phi_r)$ whose peak at (90°, 90°) and (90°, 270°) are in good accordance with the distributions of $P(\theta_r)$ and $P(\phi_r)$ of the products.

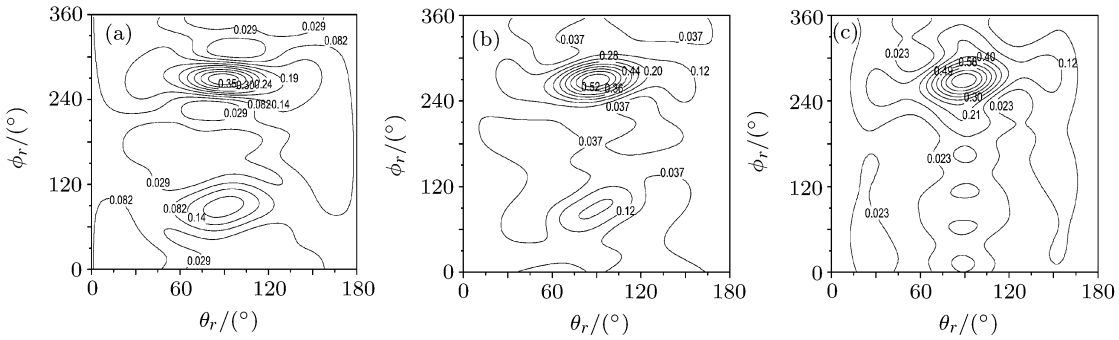


Fig.3. Polar plots of $P(\theta_r, \phi_r)$ distribution. Panels (a)–(c) describe the distributions at the collision energies of 1.0 eV, 1.5 eV and 2.0 eV, respectively.

The generalized PDDCSs describe the $\boldsymbol{k}-\boldsymbol{k}'-\boldsymbol{j}'$ correlation and the scattering direction of the product molecule. The PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$ only describes the $\boldsymbol{k}-\boldsymbol{k}'$ correlation, namely, the scattering direction of the product. The scattering direction of the product is related to the collision energy. It can be seen from Fig.4(a) that the product is strongly scattered backward ($\theta_t = 180°$)and weakly scattered forward ($\theta_t = 0°$) for the collision energies of 1.0 and 1.5 eV. When E_{T}=2.0 eV, the product is mainly scattered backward. The PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$ is painted in Fig.4(b). The behaviour of $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$ shows the opposite trend to that of $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, which indicates that $\boldsymbol{j}'$ is strongly aligned along the direction perpendicular to $\boldsymbol{k}$. The $\boldsymbol{j}'$ is preferentially polarized along the direction perpendicular to $\boldsymbol{k}$ at 180° for the three collision energies.

The collision energies have great effect on the angular distribution PDDCSs with $q \neq 0$. All PDDCSs with $q \neq 0$ are equal to zero at the extremities of forward and backward scattering. The value of

$(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ is negative for all scattering angles, as shown in Fig.4(c), indicating that the remarkable preference of product alignment along the y-axis. It is very interesting that the reaction presents a consistent polarization trend, however there is a little disagreement. The strongest polarization of the product of the three collision energies are at about 90°, 92° and 100°, respectively. The distributions of $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ are presented in Fig.4(d). The polarization trend is also displayed consistently. The strongest polarizations of the products of the three collision energies are at about 130°, 140° and 150°, respectively.

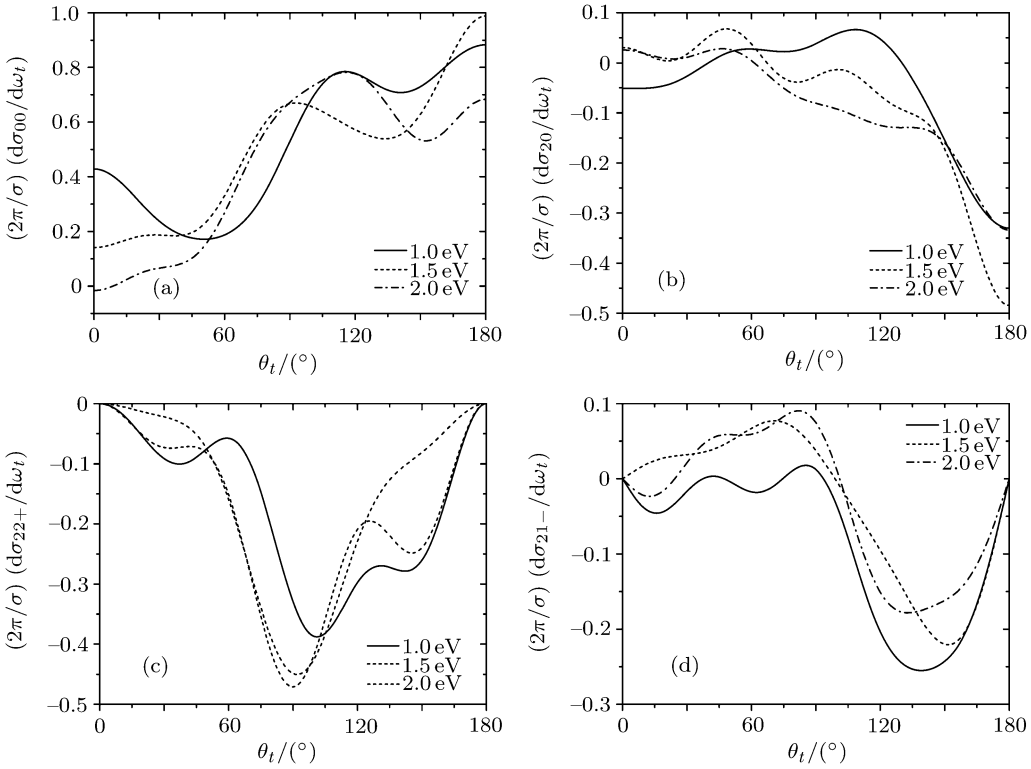


Fig.4. Four PDDCSs at three collision energies.

4. Conclusion

In this paper, the stereodynamics of the reaction $\mathrm{He+HD^+}$ has been investigated by the QCT method. The distribution $P(\phi_r)$ of dihedral angle, the distribution $P(\theta_r)$ of angle between $\boldsymbol{k}$ and $\boldsymbol{j'}$, and four generalized PDDCSs were calculated at three collision energies. The results demonstrate that the rotational polarization of product presents different characters for different collision energies. The rotational angular momentum vectors $\boldsymbol{j'}$ of the products are not only aligned, but also oriented. The product tends to be scattered backward at the different collision energies.

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