The effects of collision energy and isotope on stereodynamics for the reactions $O^+ + H_2/D_2/T_2$

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Abstract. The vector correlations between products and reagents for the chemical reactions $O^+ + H_2/D_2/T_2$ at different collision energies (1.0eV-2.8eV) have been studied by means of the quasi-classical trajectory (QCT) method based on the RODRIGO potential energy surface(PES) [Rodrigo *et al* 2004 *J. Chem. Phys.* 120 4705]. The four generalized polarization-dependent differential cross-sections (PDDCSs) $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$, $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$, $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$ and $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ have also been calculated at seven different collision energies respectively. The isotope effect comparing with the effect of collision energies has been discussed further. The results indicate that the reaction is sensitive to the mass factors. Meanwhile the collision energies have a greater effect than the mass factors.

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Key words: Stereodynamics; Vector correlation; Quasi-classical trajectory method; Polarization-dependent differential cross-section; Isotope effect.

1 Introduction

The ion-molecule reaction has been of great importance recently [1-10]. The $O^+ + H_2$ reaction has played a great role in the development of ion-molecule reaction dynamics [1-5]. It has attracted extensive attention both experimentally and theoretically. The hydrogen atom transfer reaction $O^+ + H_2$ has served as a prototypic example for the study of the kinetics and dynamics of moderately exothermic ion-molecule systems. What's more interesting is that it presents a well for collinear OHH arrangements. It also plays an important role in interstellar chemistry and in the Earth's ionosphere [1-2, 6-8].

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The most accurate PES for $O^+ + H_2$ reaction is constructed by Rodrigo *et al.* in 2004. Following, there are many theoretical and experimental works for the $O^+ + H_2$ reaction. For example, Rodrigo *et al* reported rate constants and cross sections based on this PES using the quasi-classical trajectory method. Then he studied the reaction and its isotopic variants using the time dependent wave packet method [3]. Moreover, rate constant, cross section and angle-velocity distribution have also been studied experimentally. Experimental studies about the $O^+ + H_2$ reaction show that electronically nonadiabatic processes are only important at high relative translational energies [4, 5].

As is known, the vector properties of a chemical reaction can provide valuable information about stereodynamics of chemical reaction, so it is very important to study a reaction's vector properties. However, most studies in former work deal substantially with the scalar properties, which leads to much useful information missed. In order to get full information of the ion-molecule reaction, the scalar and vector properties should be considered together [11-19]. As far as we know, there are already some investigations about the $O^+ + H_2$ reaction and its isotopic variants, yet most of which are about their scalar characters, such as rate constant, cross section, reaction probability, etc. In order to obtain more information of this system, especially its vector characters and the effect of comparing the mass factors with collision energies, the title reactions are chosen for this paper.

2   Quasi-classical trajectory calculations

In our calculations, the RODRIGO PES [3] has been employed. The collision energy is chosen from 1.0 eV to 2.8 eV (the step is 0.3 eV) for the three title reactions. The vibrational and rotational numbers of the reactants molecule are all chosen as v=0, j=0. In the calculation method of QCT we use here is the same as that of references [20-22]. The initial azimuthal orientation angle and polar angle of the reagent molecule inter-nuclear axis are randomly sampled using Monte Carlo method, and the range of the angle θ_r and ϕ_r is from $0°$ to $180°$ and from $0°$ to $360°$, respectively. In the calculation, batches of 20000 trajectories are run for each reaction and the integration step size is chosen as 0.1 fs which can leads to good results.

3   Results and discussion

The four commonly polarization-dependent differential cross-sections (PDDCSs) $(2\pi/\sigma)$ $(d\sigma_{00}/d\omega_t)$, $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$, $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$ and $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ as a func-

Table 1: The mass factor $\cos^2\beta$ calculated for different isotopic variants H_2, D_2 and T_2.

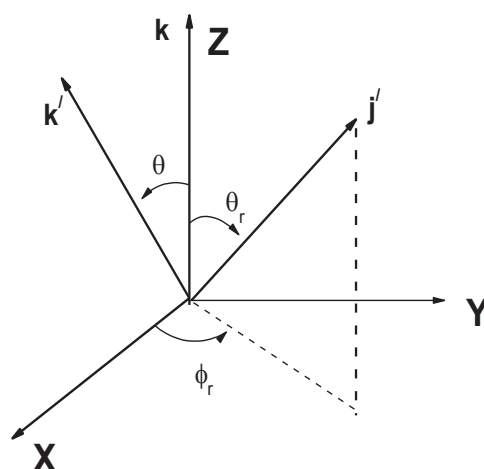| Reaction system	$O^+ + H_2$	$O^+ + D_2$	$O^+ + T_2$
$\cos^2\beta$	0.4704	0.4441	0.4206

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

tion of both collision energy and scattering angle are depicted in Fig. 2. As mentioned above, the generalized PDDCS is used to describe the k-k'-j' correlation and the scattering direction of the product molecule (that is OH^+, OD^+, OT^+ in this paper, respectively, see Fig. 1). However, the PDDCS $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$ only describe the k-k' correlation or the scattering direction of the product and is not associated with the orientation and alignment of the product rotational angular momentum vector j'. At the same time, it is called the differential cross section (DCS) instead. It can be seen clearly from Fig. 2 that the products are strongly scattered backward at lower collision energies, however it is mainly sideways scattered at higher collision energies. Moreover, the polarization trend is consistent for the three reactions O^++H_2/D_2/T_2. That means with the increase of the substitutional atom's mass the polarization trend changes little. The PDDCS $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$ drawn in Fig. 2 is the expectation value of the second Legendre moment $\langle p_2(\cos\theta_r)\rangle$. As can be seen from Fig. 2 that the behavior of $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$ shows that the tendency is opposite to that of $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$, which indicates that j' is strongly aligned perpendicular to k. Moreover, the distribution of $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$ for the three reactions is almost the same. This trend can be explained by the mass factor between the three reactions. When the two H atoms are replaced by two D atoms or two T atoms at the same time, the mass factor $\cos^2\beta$ ($\cos^2\beta = \frac{m_A m_C}{(m_A+m_B)(m_B+m_C)}$ for the reaction $A+BC \rightarrow AB+C$ which is shown in Table.1) is very near to each other which leads to the similar distribution of the $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$. It can be deduced reasonably that the collision energy has greater influence on the two PDDCSs $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$ and $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$ than the mass factors.

It can also be seen in Fig. 2 that the PDDCSs with $q \neq 0$ are zero at the extremities of forward and backward scattering. At these limiting scattering angles, the k-k' scattering plane is not determined and the value of these PDDCSs with $q \neq 0$ must be zero. The
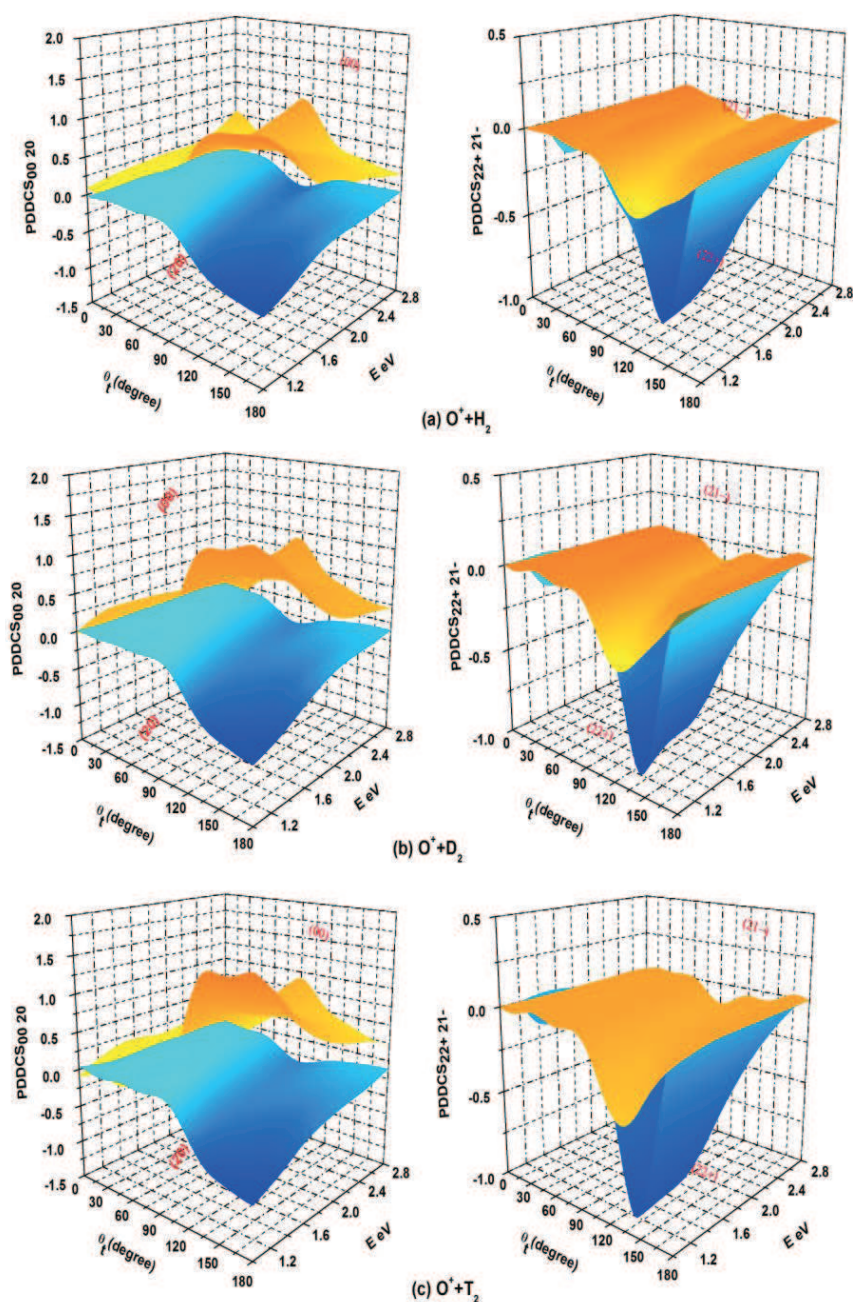
Figure 2: The four PDDCSs as a function of both the scattering angle θ_r and collision energy for the three reactions $O^+ + H_2$, $O^+ + D_2$ and $O^+ + T_2$.

PDDCS $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$ at the scattering angles away from extremities forward and backward directions provide information on the θ_t scattering angle distribution and the fact that the values are nonzero at the scattering angles away from $\theta_t = 0°$ and $180°$ indi-
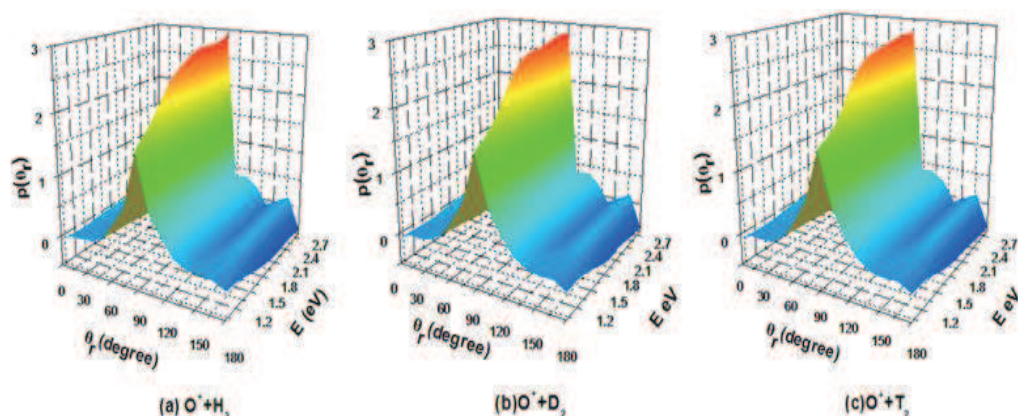
Figure 3: The $P(\theta_r)$ distributions as a function of both the polar angle and the collision energy for the three reactions O^++H_2, O^++D_2 and O^++T_2.

cates that $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$ is not isotropic for sideways and forwards scattering products. From the PDDCS $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$, we can get some more useful information. The $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$ distributions are related to $\langle\sin^2\theta_r\cos2\varphi_r\rangle$, it can be seen from Fig. 2 that the values of $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$ are negative for all scattering angles of the title reactions which indicates that the product is strongly aligned along the y-axis. Fig. 2 also shows that the polarization trend of the three reactions is displayed consistently. It represents the polarization changes little with the mass factors. It can also be seen that the strongest polarization appears at around 145° with the collision energy bellow 2.0 eV, however, the strongest polarization appears at 70° to 90° when the collision energy is above 2.0 eV. It shows that collision energy has greater influence on the strongest polarization than the mass factors. The distributions of $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ related to $\langle-\sin^2\theta_r\cos2\phi_r\rangle$ are plotted in Fig. 2. As can be seen clearly from Fig. 2, the tendency of the polarization for the three reactions is consistent. The strongest polarization is at around 120° and decreases with the increase of the collision energies when the collision energy is below 2.0 eV, However, the strongest polarization appears at around 90° and changes little with different collision energies when the collision energy is above 2.0 eV. Meanwhile, the strongest polarization changes little with different mass factors. It means that the collision energy has stronger influence on the PDDCS $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ than the mass factors.

We have already gotten rich information about the angular momentum polarization from the PDDCSs shown in Fig. 2. In order to get more information, we have plotted $P(\theta_r)$ and $P(\phi_r)$ in Fig. 3 and Fig. 4, respectively. The $P(\theta_r)$ distributions describing the k-j' correlation of the products OH^+, OD^+, OT^+ are shown in Fig. 3. It is clearly that the peak of $P(\theta_r)$ distribution is at $\theta_r = 90°$ and symmetric with respect to 90°, which indicates that the product rotational angular momentum vector j' is strongly aligned along the direction perpendicular to k. However, there is a discrepancy among the $P(\theta_r)$ distribution of the three reactions. That is the peak of $P(\theta_r)$ distribution becomes higher with
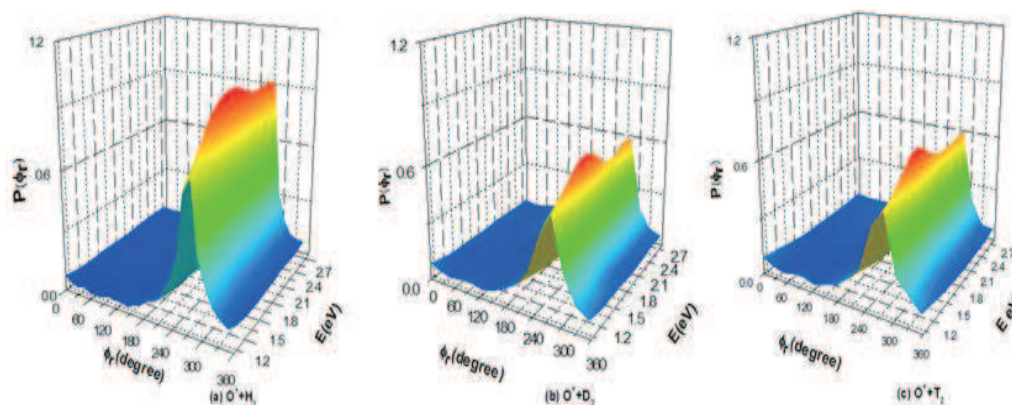
Figure 4: The $P(\varphi_r)$ distributions as a function of both the polar angle and the collision energy for the three reactions $O^+ + H_2$, $O^+ + D_2$ and $O^+ + T_2$.

the increase of the isotopic atomic mass. According to the reference [14, 24], the $P(\theta_r)$ is sensitive to two factors: one is the characters of surfaces; the other is the mass factors (i.e., $\cos^2\beta = m_A m_C / (m_A + m_B)(m_B + m_C)$ for the reaction A + BC → AB + C). It is based on the same PES (Rodrigo *et al.* 2004 *J. Chem. Phys.* 120 4705) for the three reactions in our calculation, so we can deduce that the difference of the $P(\theta_r)$ distributions comes from the difference of mass factor among the reaction $O^+ + H_2 \rightarrow OH^+ + H$ [$\cos^2\beta$=0.4704], $O^+ + D_2 \rightarrow OD^+ + D$ [$\cos^2\beta$=0.4441] and $O^+ + T_2 \rightarrow OT^+ + T$ [$\cos^2\beta$=0.4206]. We can easily find that the width of the distribution hardly changes with the increase of the atomic mass. It means that the product rotational alignment effect is almost the same as the H atom is substituted either by D or by T. What should be noticed specially is that with the increase of collision energies the products' alignment becomes stronger. However, when the collision energy is above 2.0 eV, the trend is not obvious. That means higher collision energy has little influence on the products' alignment for this reaction system. It also means that the mass factors have a greater effect than collision energies when collision energy is above 2.0 eV.

The dihedral angle distributions describing k-k'-j' correlation are shown in Fig. 4. The $P(\phi_r)$ tends to be asymmetric with respect to ϕ_r=180° directly reflecting the strong polarization of angular momentum for the three reactions. It can be seen clearly that there is a peak at about ϕ_r=270°, which means that the rotational angular momentum vector j' of the products for the three reactions has a preferentially orientation effect. We can also see that the peaks of $P(\phi_r)$ change little as the atomic mass increases. However, the peaks change more obviously with different collision energies. What should be noticed specially is that the orientation becomes stronger and stronger with the increase of collision energies as the collision energies are below 2.0 eV. The orientation changes less obviously with the increasing energies when the collision energies are above 2.0 eV. It is obvious that the collision energies have a greater effect than the atomic mass, which may be caused by the character of the PES. According to the previous theoretical study for A+BC
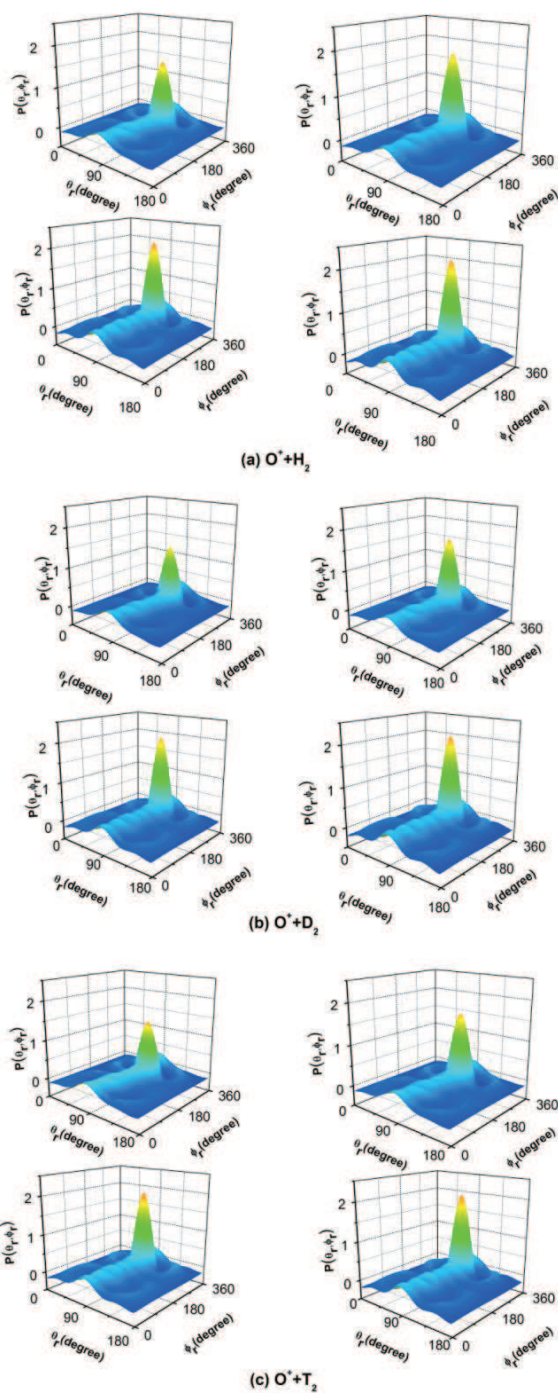
Figure 5: $P(\theta_r,\phi_r)$ distributions as a function of both the polar angle θ_r and φ_r at four collision energies for the three reactions $O^+ + H_2$, $O^+ + D_2$ and $O^+ + T_2$.

$\rightarrow$ AB+C reaction [25-28], j' can be represented as $j' = L\sin^2\beta + j\cos^2\beta + J_1 m_B/m_{AB}$, where L is the reagent orbital angular momentum and $J_1 = \sqrt{\mu_{BC}R}(r_{AB} \times r_{CB}).(r_{AB}$ and r_{CB} are unit vectors where B points to A and B points to C, respectively. μ_{BC} is the reduced mass of BC molecule and R is the repulsive energy). During the process of the chemical-bond forming and breaking for the $O^+ + H_2/D_2/T_2$ reactions, the part of $L\sin^2\beta + J\cos^2\beta$ is symmetric in the equation. However, the left term of j' ($J_1 m_B/m_{AB}$) shows a preferring direction as a result of the effect of the repulsive energy, which leads to the orientation of the product. In order to valid more information of the angular momentum polarization, we also plot it in the form of polar plots θ_r and ϕ_r, averaged all scattering angles in Fig. 5. As can be seen from Fig. 5, the distributions of $P(\theta_r, \phi_r)$ peak at $(90°, 270°)$ which are in good accordance with the distributions of $P(\theta_r)$ and $P(\phi_r)$ calculated in this paper.

4   Conclusions

Calculations of the product rotational polarization for the $O^+ + H_2$ and its isotopic reaction have been performed based on the RODRIGO surface at a collision energy of 1.0-2.8 eV. Four PDDCSs and the distributions of $P(\theta_r)$, $P(\phi_r)$ and $P(\theta_r, \phi_r)$ are calculated respectively. The results indicate that the degrees of alignment and orientation of the three products rotational angular momentum vectors j' may ascribe to the different collision energies or difference of the mass factors in the three reactions. What's more, the collision energy has greater effect on alignment and orientation of the three products rotational angular momentum vectors j' than mass factor. In a word, the influence of the collision energy on stereodynamics characters of the reaction system $O^+ + H_2$ and its isotopic reaction $O^+ + D_2/O^+ + T_2$ is more obvious than that of mass factor.

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