Stereodynamics of the reactions $Ne+H_2^+/Ne+D_2^+/Ne+T_2$*

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The vector correlations between products and reagents for the reactions $Ne+H_2^+$, $Ne+D_2^+$, and $Ne+T_2^+$ are calculated by means of the quasi-classical trajectory method on a new potential energy surface constructed by Lü *et al.* [*J. Chem. Phys.* 2010 **132**, 014303]. The polarization-dependent differential cross-sections $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$, and $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$, and the distributions of $P(\theta_r)$, $P(\phi_r)$, and $P(\theta_r, \phi_r)$ are calculated. The isotopic effect, which is associated with the difference in mass factor among the three reactions, is revealed.

Keywords: stereodynamics, quasi-classical trajectory, isotopic effect, vector correlation

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1. Introduction

The investigations of the reactions of ion–molecules containing rare gas atoms are very important to understand many interesting phenomena including interstellar processes, electric discharges, and planetary ionospheres. Moreover, the scattering of protons by rare gas atoms has been the object of numerous studies over the last thirty years. The $Ne+H_2^+ \rightarrow NeH^+ + H$ reaction has been the subject of experimental[1−5] and theoretical studies.[6−13]

From an experimental point of view, we can mention an earlier experiment of the intermolecular isotope effect reported by Klein and Friedman.[1] Bilotta *et al.*[2] conducted a crossed molecular beam experiment, which provided angular distribution and flux contour maps. In a photoelectron-secondary ion coincidence experiment, the relative cross sections for H_2^+ (v = 0–8) was investigated.[3] The relative cross sections for H_2^+ (v = 0–4) as a function of E_{col} were determined in a threshold electron-secondary-ion-coincidence experiment.[4] Finally, the absolute cross section involving an initial rotational number $j = 1$ and initial vibrational number v = 0–17 for 0.7 eV, v = 0–14 for 1.7 eV, and v = 0–12 for 4.5 eV were reported in a very recent experiment.[5]

Regarding the theoretical studies, Kress *et al.*[6] reported on the state-to-state reaction probabilities for zero total angular momentum based on the bending-corrected rotating linear model using the quantum dynamics calculation. The state-selected integral cross sections as a function of energy through use of the coupled-states approximation were reported by Gilibert *et al.*[7,8] Huarte-Larrañaga *et al.*[9,10] using the exact close-coupling hyperspherical determined the energy dependence of the state-to-state and state-to-all integral cross section. Mayneris *et al.*[11] calculated the title reaction probabilities and cross sections over a wide collision energy interval using a time-dependent real wave packet quantum calculation. The influences of vibrational excitation of H_2^+ and D_2^+ on the dynamics were also studied in detail by Mayneris-Perxachs *et al.*[12] They concluded that vibrational energy is more effective than relative translational energy for the reaction to take place. The theoretical studies mentioned above were all based on the potential energy surface (PES) constructed by Pendergast *et al.*[13] However, some dynamic results based on the PES deviate from the experimental data.[5]

As mentioned above, the reaction of $Ne+H_2^+$ and its isotopic variants have attracted considerable attention recently. However, most studies in the previous works dealt basically with the scalar properties. In order to understand the dynamics of the reaction fully, it is important to study not only their scalar properties, but also their vector properties. In our previous work, using a new PES constructed by Lü *et al.*,[14] we investigated the influence of the collision energy on stere-

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odynamics for the reaction $Ne+H_2^+ \rightarrow NeH^+ + H$.[15] According to the importance of the isotopic variants for ion-molecule reaction, here, we study the isotopic effect of vector correlation between products and reagents for the reactions $Ne+H_2^+$/ $Ne+D_2^+$/$Ne+T_2^+$.

2. Computational aspect

In this work the centre-of-mass (CM) reference frame is used to express the degree of the polarization of product angular momentum. The reference frame is shown in Fig. 1. The reagent relative vector $\boldsymbol{k}$ is parallel to the z axis, and the x–z plane is the scattering plane containing the initial and the final relative velocity vectors, $\boldsymbol{k}$ and $\boldsymbol{k}'$. Angle θ_t is the scattering angle between the reagent relative velocity $\boldsymbol{k}$ and product relative velocity $\boldsymbol{k}'$. Angles θ_r and ϕ_r are the polar and the azimuthal angles of the final rotational angular momentum $\boldsymbol{j}'$.

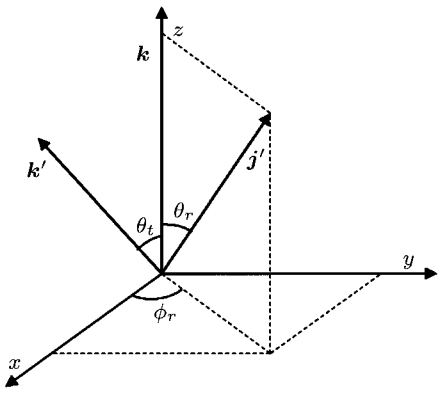


Fig. 1. Centre-of-mass frame used to describe the $\boldsymbol{k}$, $\boldsymbol{k}'$, and $\boldsymbol{j}'$ correlations.

References [16]–[27] described the computational formula of the rotational polarization and the quasi-classical trajectory (QCT) method employed in the present work. The collision energy is chosen as 0.7 eV for the title reactions. The trajectories start at an initial distance of 12.0 Å (1 Å = 0.1 nm) between the Ne atom and the centre of mass of H_2^+ (or D_2^+, T_2^+). In our calculation, batches of 10^5 trajectories are run for each calculation. The Hamiltonian motion equation is solved by the symplectic integration method in integration steps of 0.1 fs, which is sufficient for the total energy conversion and the angular momentum conversion. The initial vibrational and rotational levels of the reactant molecules are taken as $v = 0$ and $j = 0$, respectively. The values of impact parameter, $b_{\max}$, are 2.15, 2.9, and 2.0 Å for the three reactions, respectively.

The *ab initio* potential energy surface (PES) constructed by Lü *et al.*[14] is used in the present work. The PES is computed using the highly correlated complete active space self-consistent field and multireference configuration interaction wave function with a basis set of aug-cc-pV5Z. The *ab initio* energies are fitted to analytical representation using the function proposed by Aguado-Paniagua.[28] The PES is used in quantum reactive scattering dynamics calculation over a collision energy range of 0.5 eV–1.5 eV.[10] The reliability of the PES is confirmed by comparing computational results with the recent experimental values.[5]

3. Results and discussion

The PDDCSs $(2\pi/\sigma)(\mathrm{d}\sigma_{kq}/\mathrm{d}\omega_t)$ contain the information about the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ correlation and the scattering direction of the product molecule. The calculation results of the PDDCSs $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ for the three reactions are shown in Fig. 2. The PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, which is simply the differential cross section (DCS), describes only the correlation or the scattering direction of the product and is not associated with the orientation and the alignment of the product rotational angular momentum vector $\boldsymbol{j}'$. One can see from Fig. 2(a) that the scattering of the products NeH^+/NeD^+/NeT^+ is almost exclusively forward scattering ($\theta_t = 0°$), and the sideward scattering and the backward scattering are very weak. Moreover, the degree of the forward scattering becomes weaker with the increase of the mass of the reagents. The PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$ is the expectation value of the second Legendre moment. We can see from Fig. 2(b) that the trend of $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$ is opposite to that of $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, indicating that $\boldsymbol{j}'$ is strongly aligned in the direction perpendicular to $\boldsymbol{k}$. The trend of $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$ shows that $\boldsymbol{j}'$ is polarized preferentially along the direction perpendicular to $\boldsymbol{k}$ at $\theta_t = 0°$ for the three reactions.

The PDDCSs $(2\pi/\sigma)(\mathrm{d}\sigma_{kq}/\mathrm{d}\omega_t)$ with $q \neq 0$ are depicted in Figs. 2(c) and 2(d). All PDDCSs with $q \neq 0$ are equal to zero at the extremities of forward and backward scatterings. At these limiting scattering angles, the $\boldsymbol{k}$–$\boldsymbol{k}'$ scattering plane is not determined and the values of these PDDCSs with $q \neq 0$ must be zero. The PDDCSs with $q \neq 0$ at the scattering angles away from the extremities in the forward ($\theta_t = 0°$)

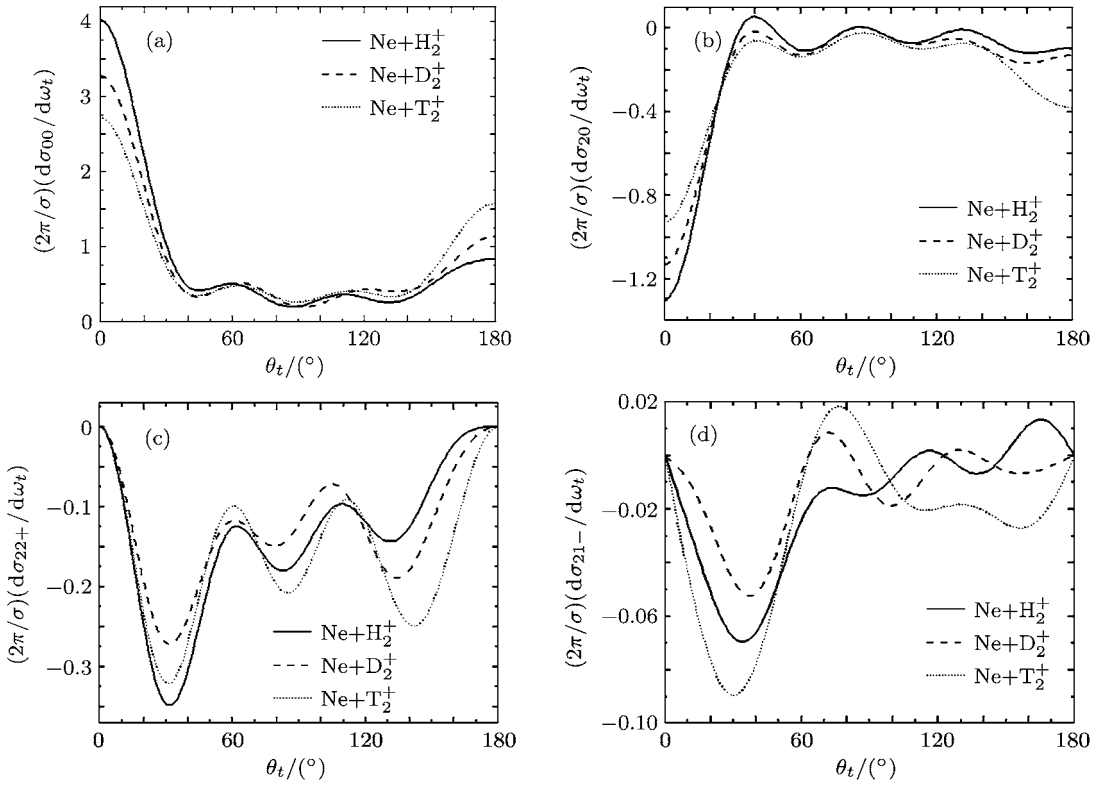


Fig. 2. PDDCSs for the three reactions, showing the distributions of $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$ (a), $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$ (b), $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ (c), and $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ (d).

and backward ($\theta_t = 180^\circ$) directions provide information about the ϕ_r dihedral angle distribution, and indicate that the $P(\theta_r,\ \phi_r)$ is not isotropic for sideward and backward scattering products. It is obvious that the values of $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ are negative for all scattering angles, which indicates that the product alignment prefers to be along the y axis. We also find that the polarization trends of the three reactions are similar and all the strongest polarizations of the products appear at about $\theta_t = 30^\circ$. The PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$, which is related to $\langle \sin 2\theta_r \cos\phi_r \rangle$, is depicted in Fig. 2(d). The values of the $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ for the three reactions are negative in the forward hemisphere, indicating that $\boldsymbol{j}'$ is aligned along the direction of vector x–z in the forward hemisphere. Figure 2(d) also shows that $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ is close to zero in the backward hemisphere for the reactions Ne+H$_2^+$ and Ne+D$_2^+$, showing obvious isotropicity in the backward hemisphere.

We find from the PDDCSs that the mass of the target atom has a considerable influence on the angular distribution and each distribution can show a different aspect of the isotopic effects for the three reactions. In order to obtain a better graphical representation of the vector correlation between products and reagents for the three reactions, we also plot the $P(\theta_r)$ and $P(\phi_r)$ distributions.

The calculated $P(\theta_r)$ distributions for the three reactions are shown in Fig. 3. The $P(\theta_r)$ distribution of the product describes the $\boldsymbol{k}$–$\boldsymbol{j}'$ vector correlation with $\boldsymbol{j}'$. $\boldsymbol{k} = \cos\theta_r$. It can be seen from Fig. 3 that the peak of $P(\theta_r)$ is located approximately at $\theta_r = 90^\circ$ and symmetric with respect to 90°, indicating that the product angular momentum $\boldsymbol{j}'$ tends to align in the direction perpendicular to $\boldsymbol{k}$. For the three reactions, as the mass of the substituted atom increases, there appears a contraction in the calculated $P(\theta_r)$ distributions with the peak moving upward, which suggests that the product alignment becomes stronger at a heavy target atom. This phenomenon is strongly correlated to the expectation values of $\langle P_2(\boldsymbol{j}' \cdot \boldsymbol{k}) \rangle$ which are –0.149, –0.192, and –0.269 for reactions Ne+H$_2^+$, Ne+D$_2^+$, and Ne+T$_2^+$, respectively (the smaller the expectation value of $\langle P_2(\boldsymbol{j}' \cdot \boldsymbol{k}) \rangle$, the stronger the rotational alignment is). As discussed in Refs. [29]–[31], the character of the PES and the mass factors will affect the distribution of $P(\theta_r)$. Considering that the PESs used in the three reactions are the same, we conclude that the difference in $P(\theta_r)$ distribution is prob-

ably attributed to the difference in mass factor (i.e., $\cos^2\beta = m_A m_C/(m_A + m_B)(m_B + m_C)$ for the reaction A+BC → AB+C) among the three reactions. As is well known, $\boldsymbol{j}' = \boldsymbol{L}\sin^2\beta + \boldsymbol{J}\cos^2\beta + \boldsymbol{J}_1 m_B/m_{AB}$. The difference in mass between m_B and m_C results in different values of $\sin^2\beta$ and $\cos^2\beta$, then, different values of $\boldsymbol{j}'$ are obtained. So $P(\theta_r)$ distribution will be different because it is determined by $\boldsymbol{j}'$ and $\boldsymbol{k}$. The mass factor and the product rotational alignment parameter $\langle P_2(\boldsymbol{j}'\cdot\boldsymbol{k})\rangle$ are listed in Table 1.

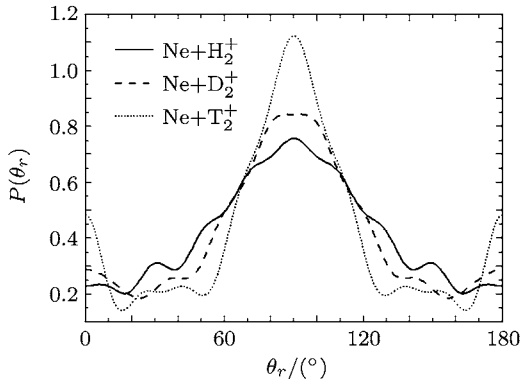


Fig. 3. Curves for product polarization distribution $P(\theta_r)$ versus θ_r for the reactions Ne+H_2^+, Ne+D_2^+, and Ne+T_2^+.

Table 1. Values of product rotational alignment parameter $\langle P_2(\boldsymbol{j}'\cdot k)\rangle$ and mass factor for the three reactions.

Reaction systems	$\langle P_2(\boldsymbol{j}'\cdot\boldsymbol{k})\rangle$	Mass factor
Ne+H_2^+ → NeH$^+$+H	–0.149	0.476
Ne+D_2^+ → NeD$^+$+D	–0.192	0.447
Ne+T_2^+ → NeT$^+$+T	–0.269	0.435

The dihedral angle distributions of $P(\phi_r)$ for the three reactions are shown in Fig. 4. Since ϕ_r is the dihedral angle between the planes consisting of $\boldsymbol{k}$–$\boldsymbol{k}'$ and $\boldsymbol{k}$–$\boldsymbol{j}'$, the $P(\phi_r)$ distribution is correlated to the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ vector correlation and can provide stereodynamical information about both product alignment and product orientation. It can be clearly seen that the $P(\phi_r)$ tends to be asymmetric with respect to the $\boldsymbol{k}$–$\boldsymbol{k}'$ scattering plane (or about $\phi_r = 180^\circ$), directly reflecting the strong polarization of the product angular momentum for the title reactions. This can be explained by impulse model[32,33] of the A+BC reaction. For reaction A+BC → AB+C, we have $\boldsymbol{j}' = \boldsymbol{L}\sin^2\beta + \boldsymbol{J}\cos^2\beta + \boldsymbol{J}_1 m_B/m_{AB}$, where $\boldsymbol{L}$ is the reagent orbital augular momentum, $\boldsymbol{J}$ is the reagent rotational angular momentum, and $\boldsymbol{J}_1 = \sqrt{\mu_{BC}R}(\boldsymbol{r}_{AB}\times\boldsymbol{r}_{CB})$ with r_{AB} and r_{CB} being unit vectors, and μ_{BC} the reduced mass of BC molecule, and R the repulsive energy between BC. During the chemical-bond forming and breaking for reactions, the term $\boldsymbol{L}\sin^2\beta + \boldsymbol{J}\cos^2\beta$ in the equation is symmetric, while the term $\boldsymbol{J}_1 m_B/m_{AB}$ shows a preferential direction because of the effect of the repulsive energy, which makes the product show orientation. One can see from Fig. 4 that each distribution has two evident peaks, indicating strong polarization and alignment along the y axis of the CM frame. The peak close to $\phi_r = 270^\circ$ implies a preference for left-handed product rotation in the plane parallel to the scattering plane and the peak at $\phi_r = 90^\circ$ indicates a preference for right-handed product rotation. As shown in Fig. 4, the peak at $\phi_r = 90^\circ$ for Ne+H_2^+ reaction is a little higher than that at $\phi_r = 270^\circ$, which reveals that the rotational angular momentum vector of product NeH$^+$ is not only aligned but also oriented along the positive direction of the y axis. However, the peak at $\phi_r = 90^\circ$ becomes lower, but higher at $\phi_r = 270^\circ$ as the mass of the reactant molecules increases. For reactions Ne+D_2^+ and Ne+T_2^+, the peaks of $\phi_r = 270^\circ$ are higher than those of $\phi_r = 90^\circ$, which indicates that the rotational angular momentum vectors of products NeD$^+$ and NeT$^+$ are not only aligned but also oriented along the negative direction of y axis and the orientation becomes more apparent as the mass of the reactant molecule increases. Now, we conclude that the difference in the mass factors among the three reactions can result in obviously different orientations and alignments.

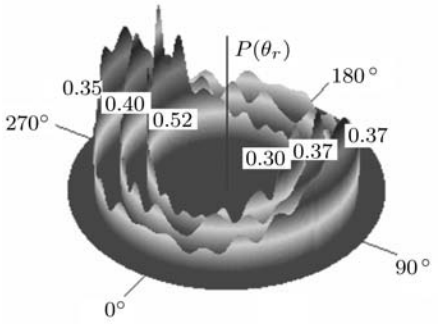


Fig. 4. Profiles of dihedral angle distribution $P(\phi_r)$ for the three reactions Ne+H_2^+/Ne+D_2^+/Ne+T_2^+ (from outer to inner).

The angular momentum polarization in the form of polar plots θ_r and ϕ_r is also plotted in Fig. 5. The peaks of the distribution $P(\theta_r, \phi_r)$ are closely at (90°, 90°) and (90°, 270°), which are in good accordance with those of the distributions of $P(\theta_r)$ and $P(\phi_r)$. One can also conclude from the distribution of $P(\theta_r, \phi_r)$ that the products from the three reactions are polarized preferentially in the direction perpendicular to

the scattering plane and the products rotate mainly in planes parallel to the scattering plane. The topographical features of the $P(\theta_r, \phi_r)$ distributions further support the above-mentioned findings about the vector correlations between products and reagents for the reactions Ne+H_2^+, Ne+D_2^+, and Ne+T_2^+ associated with the different masses of target atom.

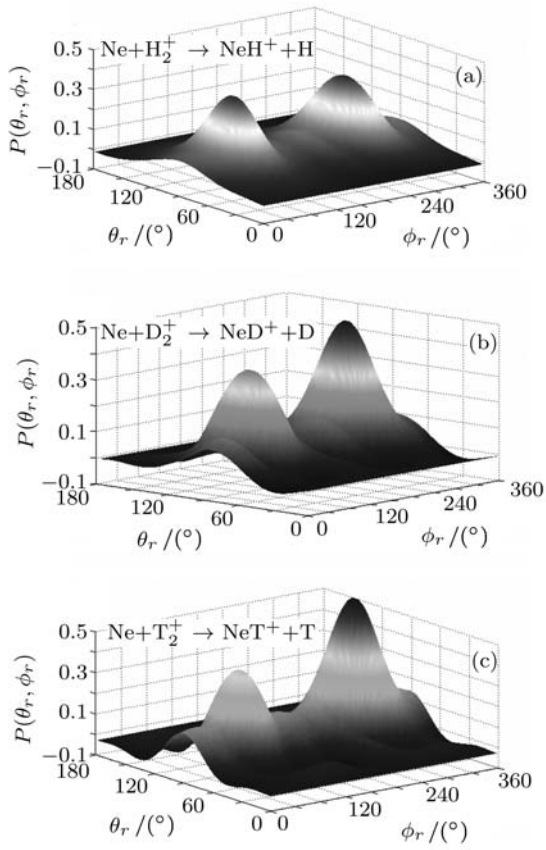


Fig. 5. Polar plots of $P(\theta_r, \phi_r)$ distribution averaged over all scattering angles for the three reactions.

4. Conclusion

In this paper, we study the vector correlations between products and reagents for Ne+H_2^+, Ne+D_2^+, and Ne+T_2^+ reactions via the QCT method on the new PES constructed by Lü *et al.*[14] The normalized PDDCSs and the distributions of $P(\theta_r)$, $P(\phi_r)$, and $P(\theta_r, \phi_r)$ are discussed in detail. The calculated DCS shows that the forward scattering decreases to some extent as the mass of the reagent increases although the forward scattering for the products of the title reactions is preferable. The product rotational angular momentum vector $\boldsymbol{j}'$ for each of the three reactions is strongly aligned along the direction perpendicular to $\boldsymbol{k}$ and such an alignment is found to be stronger in the heavier mass isotope system. The $P(\phi_r)$ distribution shows that both the product alignment along the y axis and the product orientation occur obviously. The product polarization behaviour is supported by the $P(\theta_r, \phi_r)$ distribution and the PDDCSs. If the target molecule H_2^+ is substituted either by D_2^+ or by T_2^+, the oriented direction of rotational angular momentum vector of product becomes different. Therefore, the isotopic effects of the three reactions are obviously revealed by the stereodynamics properties.

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