Intrinsic product polarization and branch ratio in the S(^{1}D, ^{3}P) + HD reaction on three electronic states

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The intrinsic product polarization and intramolecular isotope effect of the S(^{1}D, ^{3}P) + HD reaction have been investigated on both the lowest singlet state (1A′) and the triplet state (3A′ and 3A″) potential energy surfaces by using quasi-classical trajectory and quantum mechanical methods. The calculations indicate that intramolecular isotope effects are different on the three electronic states. The stereodynamics study shows that the $P(\theta_r)$ distributions, $P(\phi_r)$ distributions, and polarization-dependent differential cross sections (PDDCSs) (00) are sensitive to mass factor and the product angular momentum vectors are not only aligned but also oriented.

Keywords: quasi-classical trajectory, quantum mechanics, product polarization, branch ratio

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1. Introduction

The S(^{1}D, ^{3}P) + H_2 reaction and its deuterated variants are known as paradigms for reactions that proceed via the insertion dynamics.[1–3] Thus, they have been an important subject of many experimental and theoretical studies. The reaction dynamics of these systems have been investigated by the molecular beam experiments that are carried out at low collision energies.[4–6] A number of detailed quasi-classical trajectory (QCT) and quantum mechanical (QM) reactive-scattering calculations have also been reported for the reactions on the lowest singlet state (1A′) potential energy surface,[7–17] while their dynamical properties on the triplet state (3A′ and 3A″) potential energy surfaces have rarely been studied. Moreover, detailed investigation of their stereodynamical reaction properties, such as the intrinsic product polarizations, has not been performed so far.

Most of the previous research on the reaction dynamics of the SH_2 system has focused on its scalar properties, such as the rate constants, cross sections, product population distributions.[7–17] However, in order to fully understand the dynamics and get the complete information on the reaction mechanism, it is necessary to investigate the vector properties, such as the velocities and the angular momenta. This is because the vector properties possess not only the magnitudes directly relating to translational and rotational energies, but also the well-defined directions. The vector properties are the key indicators of the intrinsic angular momentum orientation and polarization in molecular scattering processes, in connection with the anisotropy of the potential energy surface involved in the reaction.[18–20] Thus, it is important to study both scalar and vector properties together to derive a complete understanding of the dynamics underlying molecular reactions. Among the recent dynamical studies,[21–48] two studies have focused on the reverse H+HS reaction and its isotope reaction D+DS on the triplet electronic state.[23,24]

For the title reaction, the intramolecular isotope effect, defined as $r' = \sigma_{SH+D}/\sigma_{SD+H}$ (σ is the integral cross section), is another important and interesting issue to be studied, for this branch ratio may provide a sensitive probe of the reaction dynamics.[17,21,22]

In this paper, we present a detailed QCT study of the S(^{1}D, ^{3}P) + HD reaction on both the lowest singlet state (1A′) potential energy surface and the triplet state (3A′ and 3A″) potential energy surfaces. Using this methodology, we first computed the integral cross sections at different collision energies and investigated the intramolecular isotope effect. Then, going beyond the scalar properties, we further studied the stereodynamics of this system and focused on depicting a vector-correlation picture. For these purposes, the calculations of the polarization-dependent differential cross sections (PDDCSs) and the product rotational angular momentum alignment or orientation were performed to clarify the dynamical mechanism of intrinsic product polarization.

2. Methods

The general method for the QCT calculation is the same as those used previously,[23–40] where the equations for the classical Hamiltonians are integrated numerically for motion in three dimensions. In the present work, the calculations of the lowest singlet state (1A′) were performed on the potential energy surface from Ho *et al.*,[10] and the triplet state (3A′

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and 3A″) potential energy surfaces were described by using an LEPS function, based on parameters obtained through fitting Morse functions to the diatomic *ab initio* points.[11] As described in the above two articles,[10,11] the triplet state surfaces are endoergic by about 23.5 kcal/mol and have a 25.3 kcal/mol barrier for an abstraction reaction; the singlet state surface is strongly attractive and has a −94.4 kcal/mol potential well for an insertion reaction. Therefore, less energy is needed for the reactive system to be trapped into the singlet potential well than to overcome the triplet barriers.

The rotational number and vibrational number of the reagent HD were both zero and the initial separation distance between S and the mass center of HD was 10 Å. The initial azimuthal orientation angle and polar angle of the molecule frame were randomly sampled using the Monte Carlo method with the two angles ranging from 0° to 180° and from 0° to 360°, respectively. In this calculation, a batch of 100000 trajectories was run for each of the S(^{1}D, ^{3}P) + HD reactions and the integration step size in the numerical solution was chosen to be 0.1 fs, which is sufficient to guarantee the conservation of the total energy and total angular momentum.

3. Results and discussion

Figure 1 shows the QCT calculated $J = 0$ reaction probabilities as a function of collision energy in the range of 0.01–0.60 eV for the SH + D and SD + H products in the S(^{1}D) + HD ($v = 0$, $j = 0$) reaction on the singlet electronic state, and these values are also compared with those from the QM reactive-scattering calculations.[17] As can be seen, the overall agreement between the QCT and QM calculations is satisfactory. For the SH + D product, the reaction probabilities derived by QCT calculations show an overall increasing trend with the increase of the collision energies in the whole of this energy range, whereas the SD + H product shows a decreasing trend in their reaction probabilities. In addition, at very low collision energies, the reaction probabilities of the SD + H product are slightly larger than those of the SH + D product, while the branching is reversed at high collision energies. Note here that the branch ratio at very low energy on the singlet electronic state is astray from the statistical value of 1, which is partially due to the nonadiabatic effect that occurred in this reactive system.[17] Overall, it can be seen from here that this QCT calculation works well for this system and can be applied for further investigation of the intrinsic product polarization and intramolecular isotope effect on different electronic states.

Using this QCT methodology, we then computed the integral cross sections and branch ratios for the S(^{1}D, ^{3}P) + HD ($v = 0$, $j = 0$) reaction at different collision energies and on three different electronic states, and the results are shown in Table 1. For the lowest singlet state (1A′), the total cross sections for the SH + D and SD + H products are almost the same and the intrinsic branch ratio slightly increases with the increasing collision energies, which is in agreement with the precious study.[17] For the triplet state (3A′), the SD + H product is more favored over SH + D, and this dominance is caused by the larger number of open channels of the SD + H product owing to its smaller vibrational frequency. For the other triplet state (3A″), the SH + D product is more favored over SD + H at the collision energy of 1.5 eV but the SD + H product is more favored at other collision energies. This phenomenon may be due to the intramolecular isotope effect where the major contribution may come from the reorientation of HD molecule as the S atom approaches.[21]

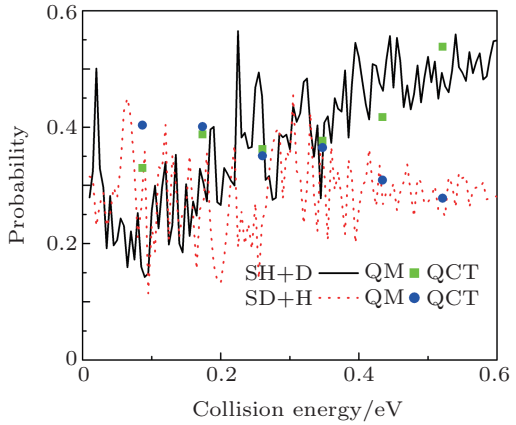


Fig. 1. (color online) The calculated $J = 0$ reaction probabilities as a function of collision energy (a) in the range of 0.01–0.60 eV and on singlet 1A′ state for the S(^{1}D) + HD ($v = 0$, $j = 0$) reaction, Here, green square points refer to the QCT calculated SH + D product compared with the QM calculation [taken from Ref. [17]] shown in the black solid line, and black circle points refer to the QCT calculated SD + H product compared with the QM calculation shown in the red dotted line.

Next, we studied the stereodynamics of the S(^{1}D, ^{3}P) + HD ($v = 0$, $j = 0$) reaction and derived the graphical representation[27] of the product polarizations in order to get a better understanding of the mechanism of the reaction dynamics. Figure 2 shows the distribution of $P(\theta_r)$ for the SH + D and SD + H products on both the singlet state (1A′) and the triplet states (3A′ and 3A″), respectively. Each of the $P(\theta_r)$ distributions shows a strong product polarization alignment and peaks at θ_r angles close to $\pi/2$. The distributions are also symmetric with respect to $\pi/2$, which is caused by the planar symmetry of this system. The distributions of SD+H product show narrower peaks than those of SH+D product, indicating that the distribution of the product angular momentum vector is sensitive to the mass factor. The increasing of mass factor will enhance the anisotropic distribution of the product rotational angular momentum.

Table 1. The integral cross sections and branch ratios with influences of different collision energies and electronic states of the S(^{1}D, ^{3}P) + HD ($v = 0$, $j = 0$) reaction on both the lowest singlet state (1A′) potential energy surface and the triplet state (3A′ and 3A″) potential energy surfaces.

Electronic state	Collision energy/eV	Maximum impact parameter/Å		Number of reaction trajectories		Integral cross section/Å^2		Intrinsic branch ratio
		SH + D	SD + H	SH + D	SD + H	SH + D	SD + H	
1A′	1.5	2.42	2.38	39 469	40 043	7.2617	7.1257	1.0191
	1.8	2.36	2.31	40 711	39 956	7.1475	6.6982	1.0671
	2.1	2.31	2.25	41 464	40 568	6.9510	6.4521	1.0773
3A′	1.5	0.75	0.54	168	956	0.0030	0.0088	0.3390
	1.8	0.95	0.87	465	4 736	0.0132	0.1126	0.1171
	2.1	1.25	1.09	1 146	10 698	0.0563	0.3993	0.1409
3A″	1.5	0.85	0.57	673	852	0.0153	0.0087	1.7566
	1.8	1.15	0.88	1 105	4 634	0.0459	0.1127	0.4072
	2.1	1.35	1.09	2 142	10 572	0.1226	0.3946	0.3108

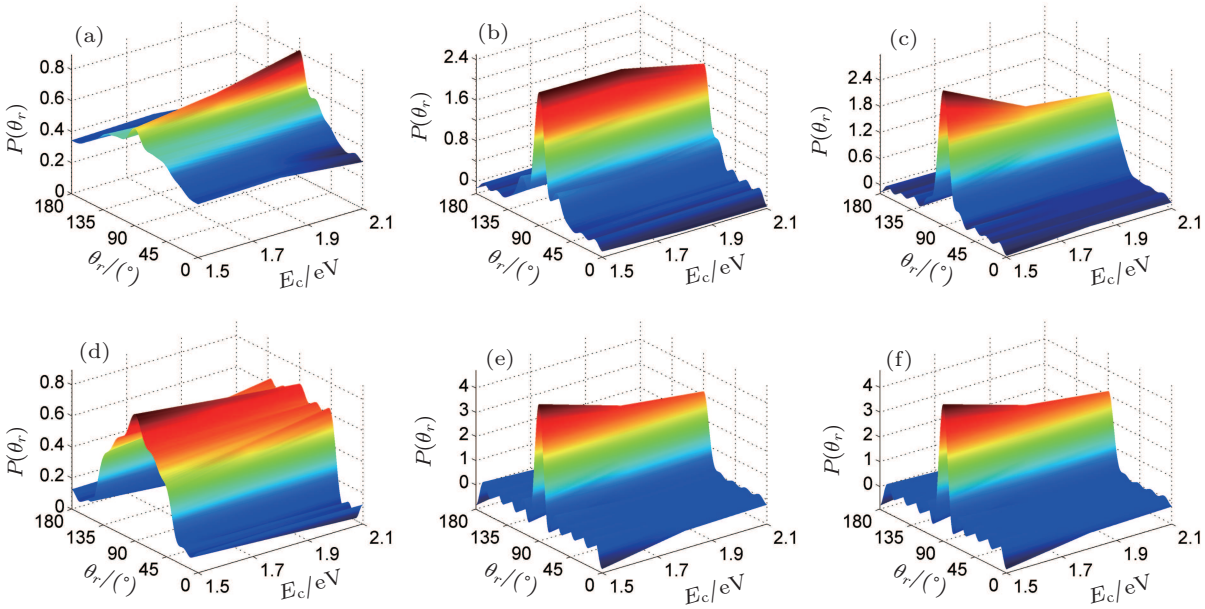


Fig. 2. (color online) The distribution of $P(\theta_r)$ for the SH + D and SD + H products of the S(^{1}D, ^{3}P) + HD ($v = 0$, $j = 0$) reaction on both the singlet state (1A′) and the triplet states (3A′ and 3A″) at the collision energies ranging from 1.5 eV to 2.1 eV. (a) SH + D, 1A′, (b) SH + D, 3A′, (c) SH + D, 3A″, (d) SD + H, 1A′, (e) SD + H, 3A′, (f) SD + H, 3A″.

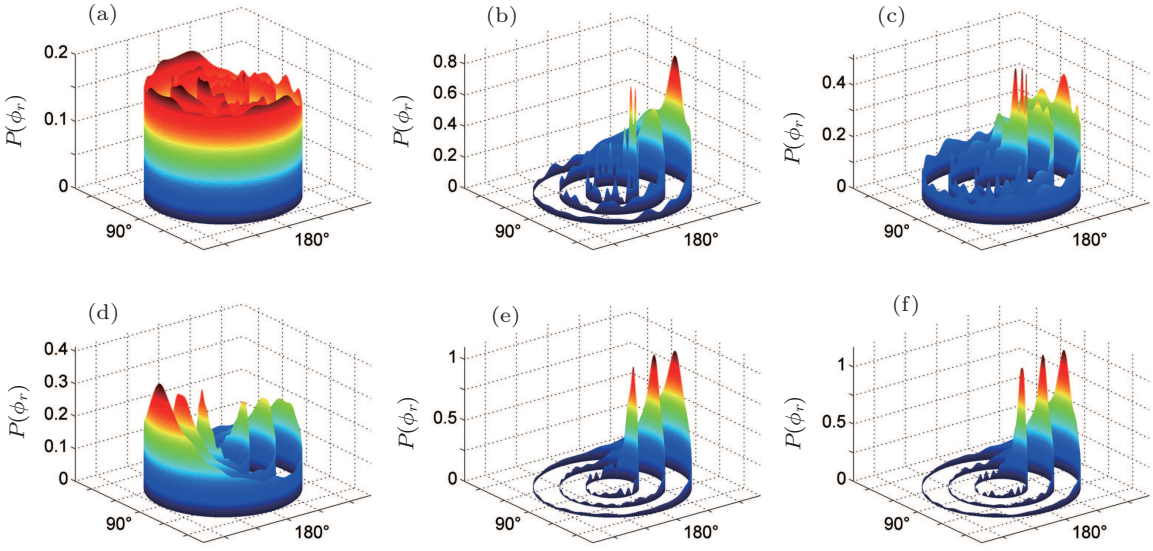


Fig. 3. (color online) The dihedral angle distribution of $P(\phi_r)$ for the SH + D and SD + H products of the S(^{1}D, ^{3}P) + HD ($v = 0$, $j = 0$) reaction on both the singlet state (1A′) and the triplet states (3A′ and 3A″) at the collision energies of 1.5, 1.8 and 2.1 eV, respectively. (a) SH + D, 1A′, (b) SH + D, 3A′, (c) SH + D, 3A″, (d) SD + H, 1A′, (e) SD + H, 3A′, (f) SD + H, 3A″.

The dihedral angle distribution of $P(\phi_r)$ for the SH + D and SD + H products on both the singlet and triplet states are shown in Fig. 3. For the SH + D product on the singlet state ($1A'$), the distribution probabilities show the isotropic feature with the dihedral angle ϕ_r, which indicates little product orientation in this state. For the SD + H product on the singlet state ($1A'$), the dihedral angle distribution of $P(\phi_r)$ tends to be weakly asymmetric about $\phi_r = \pi$, while the distributions of both SH + D and SD + H products on the triplet states ($3A''$) are strongly asymmetric. These asymmetric distributions directly reflect the strong product polarization of angular momentum, which is not only aligned along the y axis (i.e., the distributions have peaks at $\phi_r = \pi/2$ and $3\pi/2$), but also oriented (i.e., the peak at $\phi_r = 3\pi/2$ is larger than the peak at $\phi_r = \pi/2$). The asymmetric distribution of $P(\phi_r)$ implies a preference for left-handed HD rotation in planes parallel to the scattering plane. The effect of mass factor can also be seen from this perspective, the higher peaks and more anisotropic distributions of the rotational angular momentum of SD + H product are caused by the larger mass factor.

Figure 4 shows the polarization-dependent differential cross sections (PDDCSs) (00) of the S(^{1}D, ^{3}P) + HD ($v = 0$, $j = 0$) reaction for the SH + D and SD + H products on the singlet and triplet states. For the singlet state ($1A'$), the PDDCSs (00) tend to be almost symmetric about $\theta_t = \pi/2$, indicating the forward and backward scattering are similarly favored. While the PDDCSs (00) on the triplet states ($3A''$) are strongly asymmetric, indicating a preference of backward scattering. Furthermore, the asymmetry of PDDCSs (00) on the triplet states is stronger at low collision energy, and both channels of each electronic state show little preference of sideway scattering.

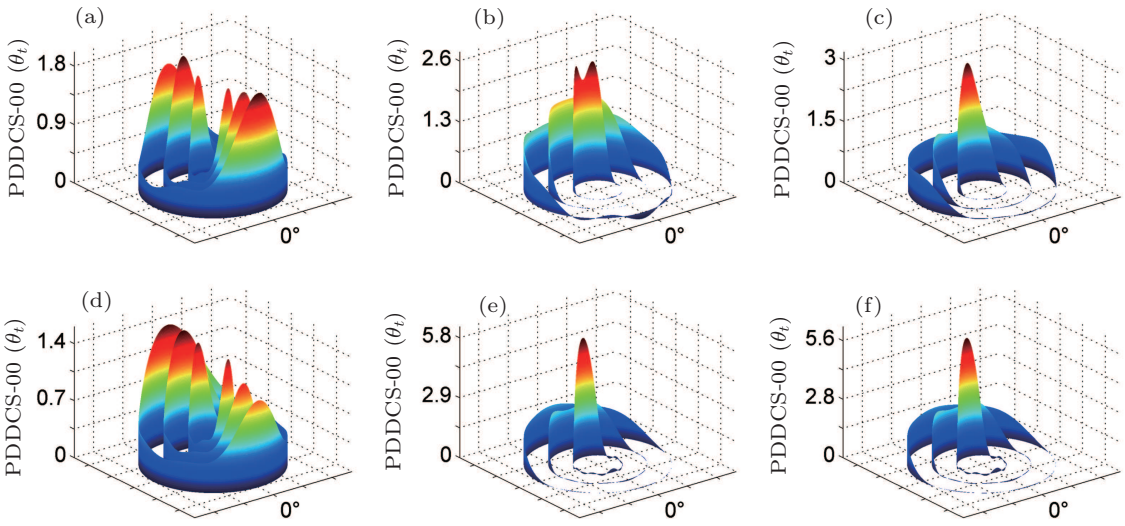


Fig. 4. (color online) The polarization-dependent differential cross sections (PDDCSs) (00) for the SH + D and SD + H products of the S(^{1}D, ^{3}P) + HD ($v = 0$, $j = 0$) reaction on both the singlet state ($1A'$) and the triplet states ($3A'$ and $3A''$) at the collision energies of 1.5, 1.8 and 2.1 eV, respectively. (a) SH + D, $1A'$, (b) SH + D, $3A'$, (c) SH + D, $3A''$, (d) SD + H, $1A'$, (e) SD + H, $3A'$, (f) SD + H, $3A''$.

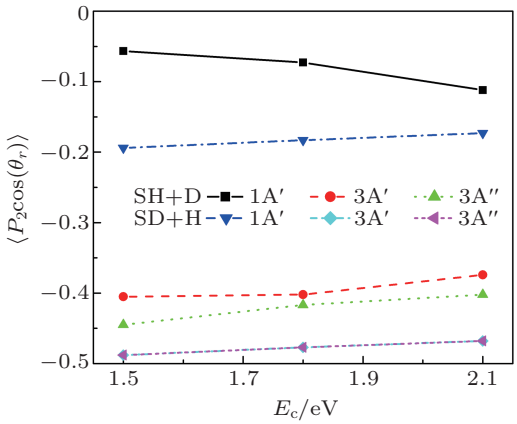


Fig. 5. (color online) The product rotational alignment parameter $\langle P_2\cos(\theta_r)\rangle$ as a function of collision energy in the range of 1.5–2.1 eV for the SH + D and SD + H products of the S(^{1}D, ^{3}P) + HD ($v = 0$, $j = 0$) reaction on the singlet state ($1A'$) and the triplet states ($3A'$ and $3A''$), respectively.

Figure 5 shows the QCT calculated product rotational alignment parameter $\langle P_2\cos(\theta_r)\rangle$, as a function of collision energy in the range of 1.5–2.1 eV, and these shown values are directly measurable with experiments. Seen in the figure, the rotational alignment parameter $\langle P_2\cos(\theta_r)\rangle$ of each product on both the singlet and triplet states monotonously increases very little with the increase of the collision energy, except for that the alignment parameter of the SH + D product on the singlet state decreases monotonously. Finally, we note that our QCT calculations are carried out separately on the three electronic states, therefore, the nonadiabatic effects in chemical reactions[46–48] have not been considered here.

4. Conclusion

We carried out a detailed QCT study of the S(^{1}D, ^{3}P) + HD reaction on both the lowest singlet state ($1A'$) potential energy surface and the triplet state ($3A'$ and $3A''$) potential energy surfaces. The integral cross sections, branch ratio, the polarization-dependent differential cross sections, and the product angular momentum alignment or orientation of different collision energies and different electronic states have been computed and investigated. The QCT-calculated reaction probabilities on the singlet state are inconsistent with the results of earlier QM reactive-scattering calculations. The integral cross sections indicate that the intramolecular isotope effect plays an important role in this system. The stereodynamics study shows that the $P(\theta_r)$ distributions, $P(\phi_r)$ distributions, and PDDCSs (00) are sensitive to mass factor and the product rotational angular momentum vectors are not only aligned but also oriented. Moreover, the degree of the product orientation and alignment is different for the three different electronic states.

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