Influence of the reagent vibration on the stereodynamics of the reactions $D^- + H_2$ and $H^- + D_2$*

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Employing the quasi-classical trajectory method and the potential energy surface of Panda and Sathyamurhy [Panda A N and Sathyamurthy N 2004 *J. Chem. Phys.* **121** 9343], the effect of the reagent vibration on vector correlation of the ion–molecule reactions $D^- + H_2$ and $H^- + D_2$ is studied at a collision energy of 35.7 kcal/mol. Four generalized polarization-dependent differential cross sections $(2\pi/\sigma)(d\sigma_{00}/d\omega_t)$, $(2\pi/\sigma)(d\sigma_{20}/d\omega_t)$, $(2\pi/\sigma)(d\sigma_{22+}/d\omega_t)$, and $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ are presented in the centre-of-mass reference frame, separately. At the same time, the effects on the product angular distributions $P(\theta_r)$, $P(\phi_r)$ and $P(\theta_r, \phi_r)$ of the title reactions are also analysed. The calculated results show that the scattering tendencies of the product HD, the alignment and the orientation of $\boldsymbol{j}'$ sensitively depend on reagent molecule vibration.

Keywords: quasi-classical trajectory, generalized polarization dependent differential cross sections, stereodynamics, vector correlation

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1. Introduction

Recently, much attention has been paid to the understanding of the ion–molecule reactions.[1−19] According to the standard Big Bang nucleosynthesis model, the early universe was chemically very simple and only electrons, low energy photons and the lightest nuclei (H, D, etc.) took part in a relatively simple chemical reaction network in an entirely gaseous phase.[20] Being a typical ion–molecule reaction, H^- + H_2 and its isotopic reactions are of interest in understanding the collision processes in interstellar media, the plasma and high-energy physics studies.[3−5] There have been a great variety of experimental and theoretical studies on the reaction cross-section for the collisions of H^- or D^- with H_2, D_2 and HD.[7−10,19] Panda and Sathyamurthy[7] constructed the potential energy surface (PES) of H_3^- system and calculated the reaction probability for the reaction $H^- + H_2$. Subsequently, there are many theoretic studies about the scalar properties of the title reactions using the global *ab initio* PES.[7−10]

As has been discussed in the preceding paragraph, it is adequately important that the reactions of $D^- + H_2$ and $H^- + D_2$ have attracted enormous attention currently. With the intention of fully understanding the dynamics of the $D^- + H_2$ reaction and the $H^- + D_2$ reaction, it is essential to study their vector properties. Li *et al.*[8,9] studied the stereodynamics for (D^-, H_2) and (H^-, D_2) collisions and revealed the isotopic effect in the ion–molecule reactions. For the purpose of providing the complete images of the state-to-state dynamics of the title reactions, the studies of the influence of reagent vibration on the stereodynamics of the $D^- + H_2$ and $H^- + D_2$ reactions are necessary. In the present work, we use the quasi-classical trajectory (QCT) method on the new *ab initio* PES of Panda and Sathyamurhy[7] to study the stereodynamics of the title reactions when the reagent molecules are in the excited vibrational states. Details of the theoretical methodology are given in Section 2 and the obtained results are presented and discussed in Section 3, followed by a summary and conclusion in Section 4.

2. Theory

The specific details of the standard quasi-classical trajectory (QCT) method can be found in Refs. [21]–[23] and the references therein. In the current cal-

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culations, the collision energy (E_c) is chosen to be 35.7 kcal/mol. The vibrational and the rotational levels of the reactant molecule are taken to be $v = 0$, 1, 2 and $j = 0$, respectively. Batches of 10^5 trajectories are run for each reaction. The size of integration step in the trajectories was chosen to be 0.1 fs. The trajectories start at an initial distance of 10.0 Å (1 Å = 0.1 nm) between the D^-/H^- atom and the centre of mass of the H_2/D_2 molecule.

As shown in Fig. 1, the centre-of-mass (CM) reference frame is chosen. The three-dimensional angular distribution associated with $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ correlation can be written as a set of generalized polarization-dependent differential cross sections (PDDCSs) in the CM frame. The fully correlated CM angular distribution is written as[24]

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

where

$$[k] = 2k + 1. \qquad (2)$$

Many photon-initiated bimolecular reaction experiments are sensitive only to those polarization moments with $k = 0$ and $k = 2$. In the present work, $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$, and $(2\pi/\sigma)(\mathrm{d}\sigma_{21-}/\mathrm{d}\omega_t)$ are calculated. In the above calculations, PDDCSs are expanded up to $k = 7$, which is sufficient for good convergence.

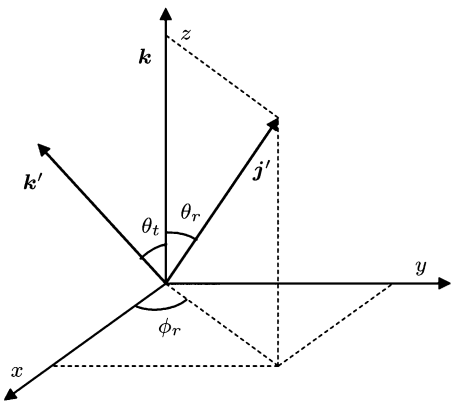


Fig. 1. The centre-of-mass frame describing the $\boldsymbol{k}$, $\boldsymbol{k}'$, and $\boldsymbol{j}'$ correlations.

The distribution function $P(\theta_r)$ describing the $\boldsymbol{k}$–$\boldsymbol{j}'$ correlation can be expanded into a series of Legendre polynomials as[24–27]

$$P(\theta_r) = \frac{1}{2} \sum_k (2k+1) a_0^{(k)} \mathrm{P}_k(\cos\theta_r). \qquad (3)$$

The dihedral angle distribution $P(\phi_r)$ of the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ three-vector correlation is calculated by its expansion into a Fourier series, which can be expressed as follows:

$$P(\phi_r) = \frac{1}{2\pi}\Big(1 + \sum_{\mathrm{even},n\geq 2} a_n \cos n\phi_r + \sum_{\mathrm{odd},n\geq 1} b_n \sin n\phi_r\Big). \qquad (4)$$

The joint probability density function $P(\theta_r, \phi_r)$ of angles θ_r and ϕ_r, which defines the direction of $\boldsymbol{j}'$, can be written as

$$P(\theta_r, \phi_r) = \frac{1}{4\pi} \sum_{kq} (2k+1) a_q^k C_{kq}(\theta_r, \phi_r)^*. \qquad (5)$$

3. Results and discussion

The PDDCSs give the rich information about the polarization of angular momentum and the scattering direction of the product molecule, which can help us to completely understand the reaction. As shown in Figs. 2 and 3, we firstly calculate the PDDCSs of the product HD for the reactions $D^- + H_2$ $(v = 0, 1, 2, j = 0) \rightarrow H^- + HD$ and $H^- + D_2$ $(v = 0, 1, 2, j = 0) \rightarrow D^- + HD$ on the *ab initio* PES,[7] respectively. The selected collision energy (E_c) for the reactions is 35.7 kcal/mol. The PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, which is simply the differential cross section (DCS), describes the $\boldsymbol{k}$–$\boldsymbol{k}'$ correlation or the scattering direction of the product. The DCS is shown in Figs. 2(a) and 3(a). One can find that there exist prominent changes with the enhancement of the vibration excitation of the reactant diatomic molecules. Obviously, when the vibration of reagent molecules is excited to the $v = 1, 2$ energy levels, the scattering trend of the product HD of the $D^- + H_2$ reaction is remarkably changed and the scattering is almost exclusively forward scattering. However, it turns into the backward scattering when the vibration of the reagent molecules is in the ground vibration state. By contrast, the scattering trend for the $H^- + D_2$ $(v = 0, 1, 2, j = 0)$ reactions is still the backward scattering, though the probability of the forward scattering is increased with the enhancement of the vibration excitation of D_2. From Figs. 2(b) and 3(b), one can find that the distribution of the PDDCS $(2\pi/\sigma)(\mathrm{d}\sigma_{20}/\mathrm{d}\omega_t)$ of the reaction $D^- + H_2$ $(v = 0, 1, 2, j = 0)$ differs from that of the reaction $H^- + D_2$ $(v = 0, 1, 2, j = 0)$.[28,29] For $D^- + H_2$ $(v = 2, j = 0)$, $\boldsymbol{j}'$ is preferentially polarized along the direction perpendicular to $\boldsymbol{k}$ at 0°. However, $\boldsymbol{j}'$ is

preferentially polarized along the direction perpendicular to $\boldsymbol{k}$ at 180° for $H^- + D_2$ ($v = 0, 1, 2, j = 0$). It is worth while noting that the degree of the polarization decreases except for $D^- + H_2$ ($v = 2, j = 0$) with the enhancement of vibration excitation of the reactant diatomic molecule. For the distributions of $(2\pi/\sigma)(\mathrm{d}\sigma_{22+}/\mathrm{d}\omega_t)$ shown in Figs. 2(c) and 3(c), their values are almost negative for all scattering angles, which indicates that the notable preference of product alignment is polarized along the y axis. The strongest polarizations of the product for $D^- + H_2$ ($v = 0, 1, 2, j = 0$) reactions display at θ_t close to 120°, 100°, and 35°, while the same behaviours emerge

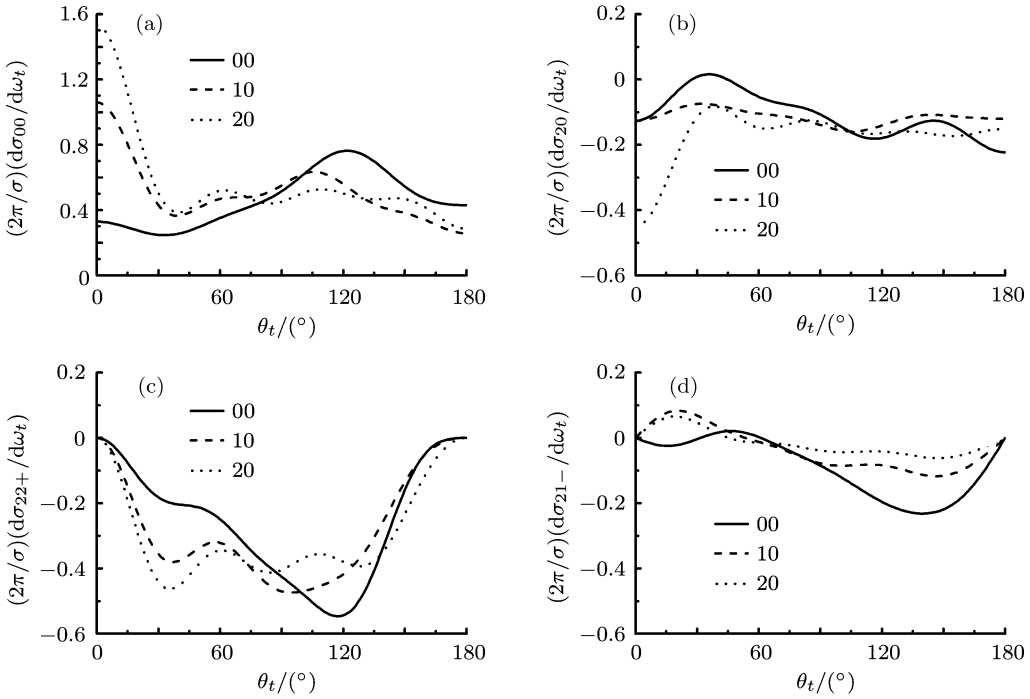


Fig. 2. Four PDDCSs for the reactions $D^- + H_2$ ($v = 0, 1, 2, j = 0$) at $E_c = 35.7$ kcal/mol.

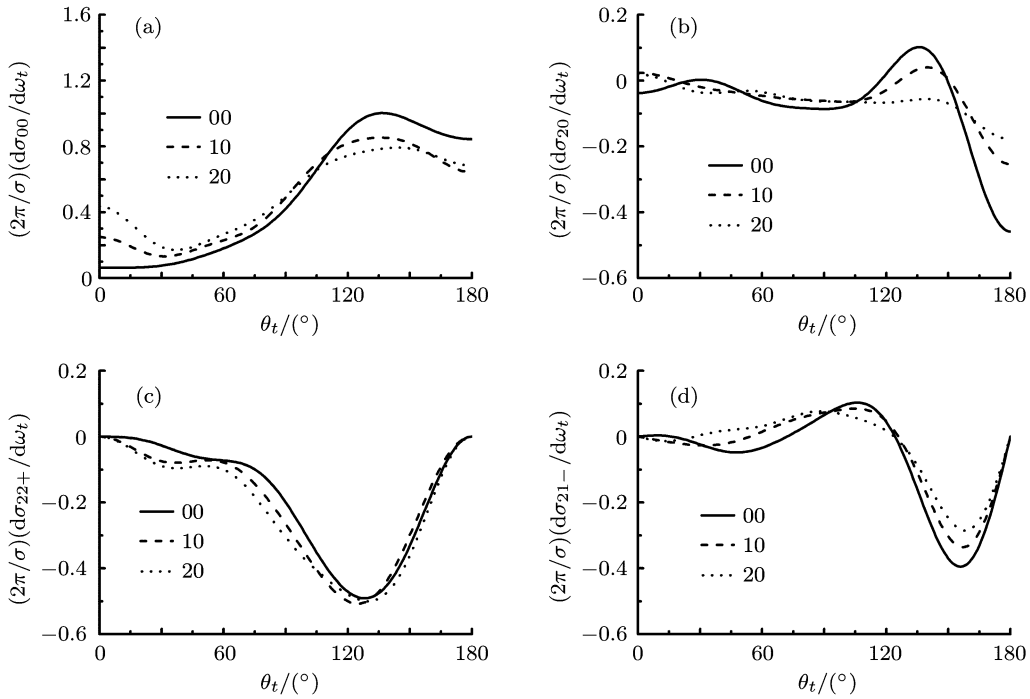


Fig. 3. Four PDDCSs for the reactions $H^- + D_2$ ($v = 0, 1, 2, j = 0$) at $E_c = 35.7$ kcal/mol.

at θ_t close to 130°, 130°, and 125° for the $H^- + D_2$ ($v = 0, 1, 2, j = 0$) reactions. In addition, the distributions of $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ are considerably affected by enhancing vibration excitation of the reactant diatomic molecules. As shown in Figs. 2(d) and 3(d), the values of $(2\pi/\sigma)(d\sigma_{21-}/d\omega_t)$ present a positive peak separately at θ_t close to 20° ($v = 1, 2, j = 0$) for the former reaction as the reagent H_2 molecule vibrations are excited to the $v = 1$, 2 energy levels.

As a means of achieving a better graphical representation of the polarization of the products for the reactions $D^- + H_2$ ($v = 0, 1, 2, j = 0$) and $H^- + D_2$ ($v = 0, 1, 2, j = 0$), we plot $P(\theta_r)$ and $P(\phi_r)$ distributions at the selected collision energy in Fig. 4. It is clearly seen that both the distribution of the $P(\theta_r)$ and the distribution of the $P(\phi_r)$ of the product HD change dramatically when the vibration of reactant molecule are excited to the $v = 1$, 2 energy levels. One can also see that the $P(\theta_r)$ distributions each have a maximum for θ_r at 90° and are symmetric with respect to 90°, which demonstrates that the rotational angular momentum vector $\boldsymbol{j}'$ of the product is distributed with the cylindrical symmetry in the product scattering frame and the direction of $\boldsymbol{j}'$ is preferentially perpendicular to the relative velocity direction $\boldsymbol{k}$.

From Fig. 4, the peak of $P(\theta_r)$ distribution for the reaction $D^- + H_2$ becomes higher and broader when the reagent vibration is excited to the $v = 1$, 2, which implies that the degree of the rotational alignment of the product increases with the increase of the quantum number of the vibration state. However, it will become lower for the reaction $H^- + D_2$, which is opposite to the former reaction. The dihedral angle distributions tend to be asymmetric with respect to the $\boldsymbol{k}$–$\boldsymbol{k}'$ scattering plane (or about $\phi_r = 180°$), directly reflecting the strong polarization of angular momentum of the product HD for the title reactions. There are two peaks of $P(\phi_r)$ distribution for both reactions at 90° and 270°, when the vibration of reagent molecule is in the ground vibration state or excited vibration states, which shows that the rotational angular momentum vectors of the product of the reactions are mainly aligned along y axis of the CM frame. The orientations of the product for the title reactions are evidently different. With regard to the reaction $D^- + H_2$, the peaks at $\phi_r = 270°$ become apparently stronger and those at $\phi_r = 90°$ nearly remain the same value with the enhancement of the vibration excitations of H_2, indicating that $\boldsymbol{j}'$ is more preferentially oriented along the negative direction of y axis. With respect to the reaction $H^- + D_2$, $\boldsymbol{j}'$ tends to be oriented along the positive direction of y axis when the reactant D_2 is in the ground vibration state. Again, the trend has the distinct changes as the reagent vibration is excited. The peaks at $\phi_r = 90°$ become

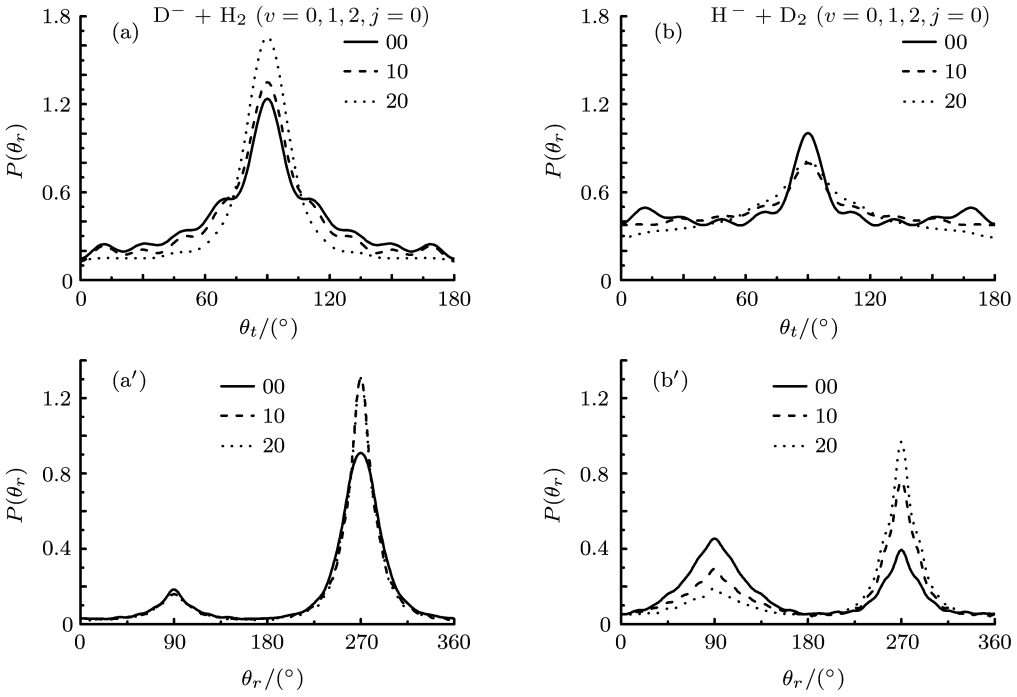


Fig. 4. Product polarization distributions $P(\theta_r)$ and $P(\phi_r)$ for the reactions $D^- + H_2$ ($v = 0, 1, 2, j = 0$) and $H^- + D_2$ ($v = 0, 1, 2, j = 0$) at $E_c = 35.7$ kcal/mol.

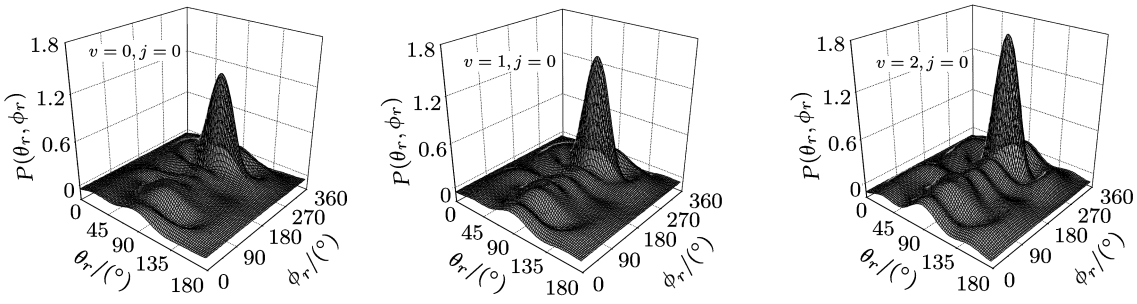


Fig. 5. Polar plots of $P(\theta_r, \phi_r)$ distributions averaged over all scattering angles for the reactions $D^- + H_2$ ($v = 0, 1, 2, j = 0$) at $E_c = 35.7$ kcal/mol.

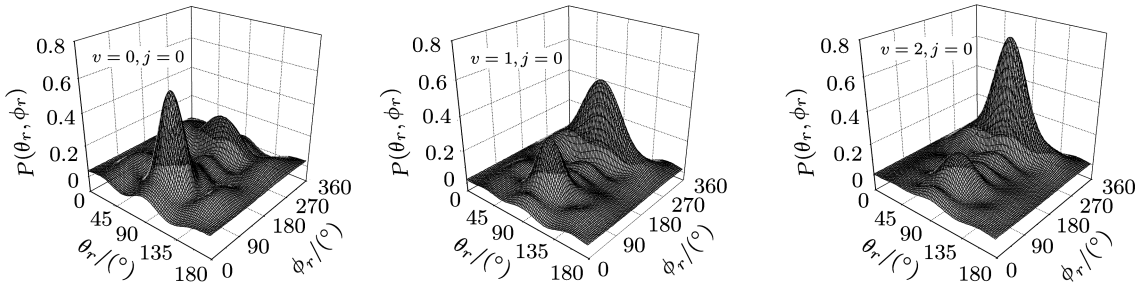


Fig. 6. Polar plots of $P(\theta_r, \phi_r)$ distributions averaged over all scattering angles for the reactions $H^- + D_2$ ($v = 0, 1, 2, j = 0$) at $E_c = 35.7$ kcal/mol.

weaker and those at $\phi_r = 270°$ stronger. That is to say, the values of $\boldsymbol{j}'$ of the $H^- + D_2$ ($v = 1, 2, j = 0$) reactions become more preferentially oriented along the negative direction of y axis. The difference in the preferred oriented direction of the product between the former and the latter reactions may be ascribed to the differences in effective potential barrier height[2,8] and the effect of the repulsive energy[8,30−31] between H and H or D and D. This can be explained by impulse model[30−32] of the A+BC reaction.

For the sake of further validation, the polarizations of angular momentum in the form of polar plots θ_r and ϕ_r, which represent the average of the scattering angles of the distributions, are also plotted. As can be seen from Figs. 5 and 6, the peaks of the distributions $P(\theta_r, \phi_r)$ are close to (90°, 90°), and (90°, 270°), which are in good accordance with those of the distributions of $P(\theta_r)$ and $P(\phi_r)$. According to the distributions of $P(\theta_r, \phi_r)$, one can also conclude that the products of the reactions are preferentially polarized in the direction perpendicular to the scattering plane and the products mainly rotate in planes parallel to the scattering plane.

4. Conclusion

In this paper, we studied the influence of the reagent vibration on the stereodynamics of the D^- + H_2 and H^- + D_2 reactions using the QCT method. We calculated the generalized PDDCSs and the distributions of $P(\theta_r)$, $P(\phi_r)$ and $P(\theta_r, \phi_r)$ for the title reactions on the PES constructed by Panda and Sathyamurthy.[9] The two reactions are both dominated by the direct reaction mechanism. When the H_2 molecules are in the low-lying excited vibrational states, the tendency of the forward scattering of HD becomes stronger for the D^- + H_2 reaction. However, the scattering trend for the H^- + D_2 reactions still presents that of the backward scattering and the degrees of distribution decrease with the increment of vibration state. The values of rotational angular momentum vector j' of the products from the two reactions are not only aligned, but also oriented. Meanwhile, $\boldsymbol{j}'$ values of the two reactions become more preferentially oriented along the negative direction of y axis with the increase of vibrational quantum number. The calculated results imply that the vibration of the reagent H_2 (D_2) plays an important role in the stereodynamics of the title reactions.

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