Effects of collision energy and rotational quantum number on stereodynamics of the reactions: $H(^2S) + NH(v = 0, j = 0, 2, 5, 10) \rightarrow N(^4S) + H_2$*

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The stereodynamical properties of $H(^2S) + NH(v = 0, j = 0, 2, 5, 10) \rightarrow N(^4S) + H_2$ reactions are studied in this paper by using the quasi-classical trajectory (QCT) method with different collision energies on the double many-body expansion (DMBE) potential energy surface (PES) (Poveda L A and Varandas A J C 2005 *Phys. Chem. Chem. Phys.* **7** 2867). In a range of collision energy from 2 to 20 kcal/mol, the vibrational rotational quantum numbers of the NH molecules are specifically investigated on $v = 0$ and $j = 0, 2, 5, 10$ respectively. The distributions of $P(\theta_r)$, $P(\phi_r)$, $P(\theta_r, \phi_r)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$ differential cross-section (DCSs) and integral cross-sections(ICSs) are calculated. The ICSs, computed for collision energies from 2 kcal/mol to 20 kcal/mol, for the ground state are in good agreement with the cited data. The results show that the reagent rotational quantum number and initial collision energy both have a significant effect on the distributions of the $\boldsymbol{k}$–$\boldsymbol{j}'$, the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$, and the $\boldsymbol{k}$–$\boldsymbol{k}'$ correlations. In addition, the DCS is found to be susceptible to collision energy, but it is not significantly affected by the rotational excitation of reagent.

Keywords: quasi-classical trajectory method, stereodynamics, potential energy surface, vector correlation

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1. Introduction

Nitrogen (N) and hydrogen (H) are widespread in the atmosphere and hence have been the focus of a wealth of fundamental and applied research work. Reactions of the nitrogen atom with hydrogen have been a subject of interest among experimental and theoretical chemists for the past three decades. With the development of molecular beam techniques[1] and polarized laser light,[2] an elementary chemical reaction has nowadays become feasible.

Much of the interesting information about an elementary chemical reaction can be summarized according to its excitation function or rate constant. Morley[3] studied the mechanism of NO formation from nitrogen compounds in hydrogen flames by laser fluorescence, and determined the rate constant for the reactions of NH and H atoms at 1790 K–2200 K. In 1990, Koshi and Yoshimura[4] measured the $N(^4S) + H_2$ reaction rate constant at higher temperatures (1950 K–2850 K). Simultaneously, the rate constant for the reaction N + H2→NH + H was first directly measured by Davidson and Hanson, and found to be $1.60 \times 10^{14} \exp(-12650/T)$ (±35%) in a temperature range from 1950 K to 2850 K.[5] In 2005, the rate constant of the reaction NH + H→N + H_2 was determined to be $k = (1.9 \pm 0.5) \times 10^{12}$ $\mathrm{cm^3 \cdot mol^{-1} \cdot s^{-1}}$ in a quasi-static laser-flash photolysis at room temperature by Adam *et al.*[6]

Theoretically, in 2005, Poveda and Varandas[7] reported a repulsive double many-body expansion[8] (DMBE) potential energy surface (PES) for the triatomic fragment of $NH_2(4A')$ reactive system from accurate *ab initio* calculations based on the MRCI/aug-cc-pVQZ level.[9,10] For both the forward reaction $N(^4S) + H_2 \rightarrow H(^2S) + NH$ and reverse reaction $H(^2S) + NH \rightarrow N(^4S) + H_2$, their calculations showed good agreement with experimental results and the best available theoretical estimates. Since the DMBE PES accurately fitted high-level *ab initio* calculations, it was recommended for dynamics, and then a lot of dynamic studies based on DMBE PES for both the forward and reverse reactions were reported one after another. Firstly, Zhang *et al.*[11] investigated the influence of isotopic effect on the stereodynamical properties of the forward reactions at a collision energy of 40 kcal/mol, and presented and discussed the distributions of vector correlations between products and reagents $P(\theta_r)$, $P(\phi_r)$, and $P(\theta_r, \phi_r)$. Yu *et al.*[12] studied the influences of rotational excitation and collision energy on the stereodynamics of the forward reaction $N(^4S) + H_2(v = 0,\ j = 0,\ 2,\ 5,\ 10) \rightarrow NH(X^3\Sigma^-) + H$ using the QCT method. Using the same QCT method, Xia *et al.*[13] investigated the influences of isotopic variants and collision energy on the stereodynamics of the forward reaction. Yu *et al.*[14] presented the QCT study on the product polarization for the forward reactions $N(^4S) + H_2(v = 0\text{–}3,\ j = 0) \rightarrow NH(X^3\Sigma^-) + H$ stereodynamics properties at the investigated energy range from 25 kcal/mol to 140 kcal/mol, and also cal-

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culated four PDDCSs and the distributions of $P(\theta_r)$, $P(\phi_r)$, $P(\theta_r,\phi_r)$, and $\langle P_2(\cos\theta_r)\rangle$ with the rotational ground state and different vibrational excited states of the reagent. For the reverse reactions $H(^2S)+NH\rightarrow N(^4S)+H_2$, Han *et al.*[15] used the QCT and quantum mechanical methods to calculate reaction probabilities at zero total angular momentum, the total reaction cross section and product rotational alignment for the ground ro-vibrational state of the reverse reactions. To date, the research about the stereodynamics of the reverse reactions on the effects of collision energy and rotational quantum number on the DMBE PES has not been found. In order to study the effects of collision energy and rotational quantum number on stereodynamics of the reverse reactions, we perform the QCT calculations on the DMBE PES in this paper. We will calculate the three angular distributions of $P(\theta_r)$, $P(\phi_r)$, $P(\theta_r,\phi_r)$ and differential cross-sections (DCSs) based on this DMBE PES with vibrational ground state and different rotational excited states of the reagent, and investigate the effects of collision energy and rotational excited states of the reagent on stereodynamics properties. It is significant that the title reaction has some interesting results on the $NH_2(4A')$ PES.

2. Theory

2.1. Rotational polarization of the product

The reference frame used in this work is the center-of-mass (CM) frame, which is shown in Fig. 1. The z axis points to the direction of the relative velocity vector $\boldsymbol{k}$ of the reactant. The x–z plane is the scattering plane containing the reactant and product relative velocity vectors, $\boldsymbol{k}$ and $\boldsymbol{k}'$; the y axis is perpendicular to the scattering plane; θ_r and ϕ_r are the azimuthal and polar angles of the product rotational angular momentum vector $\boldsymbol{j}'$, respectively; θ_t is the scattering angle between $\boldsymbol{k}$ and $\boldsymbol{k}'$.

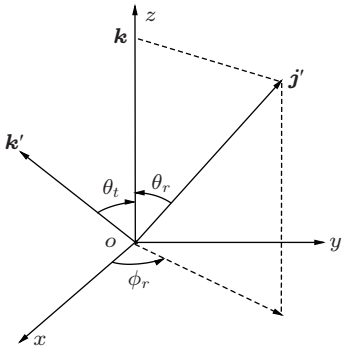


Fig. 1. Center-of-mass coordinate system used to describe the correlation between $\boldsymbol{k}$, $\boldsymbol{k}'$, and $\boldsymbol{j}'$.

The distribution function $P(\theta_r)$ describing the $\boldsymbol{k}$–$\boldsymbol{j}'$ correlation can be expanded into a series of Legendre polynomials as[16–18]

$$P(\theta_r)=\frac{1}{2}\sum_{\mathrm{k}}(2k+1)a_0^{(k)}\mathrm{P}(\cos\theta_\mathrm{r}). \tag{1}$$

The expanding coefficient $a_0^{(k)}$ is called orientation parameter (when k is odd) or alignment parameter (when k is even), and expressed as

$$a_0^{(k)}=\int_0^{\pi}P(\theta_r)\mathrm{P}_k(\cos\theta_\mathrm{r})\sin\theta_\mathrm{r}\mathrm{d}\theta_r=\langle\mathrm{P}_k(\cos\theta_\mathrm{r})\rangle. \tag{2}$$

In the present calculations, $P(\theta_r)$ is expanded up to $k=18$, which shows good convergence.

The dihedral angle distribution function $P(\phi_r)$ depicting the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ correlation can be expanded into a series of Fourier as

$$P(\phi_r)=\frac{1}{2\pi}\left(1+\sum_{\mathrm{even},n\geq2}a_n\cos n\phi_\mathrm{r}+\sum_{\mathrm{odd},n\geq1}b_n\sin n\phi_\mathrm{r}\right), \tag{3}$$

where $a_n=2\langle\cos n\phi_\mathrm{r}\rangle$ and $b_n=2\langle\sin n\phi_\mathrm{r}\rangle$. In the present study, $P(\phi_r)$ is expanded up to $n=24$ for a good convergence.

In the CM reference frame, the direction of $\boldsymbol{j}'$ can be determined by θ_r and ϕ_r, and the spatial distribution function $P(\theta_r,\phi_r)$of the product rotational angular momentum $\boldsymbol{j}'$ can be represented as

$$P(\theta_r,\phi_r)=\frac{1}{4\pi}\sum_k\sum_{q\geq0}\left[a_{q\pm}^k\cos(q\phi_\mathrm{r})-a_{q\mp}^k\sin(q\phi_\mathrm{r})\right]\mathrm{C}_{kq}(\theta_r,0), \tag{4}$$

where $\mathrm{C}_{kq}(\theta_r,\phi_r)$ is a modified spherical harmonics, $a_{q\pm}^k=2\left\langle\mathrm{C}_{k|q|}(\theta_r,0)\cos(q\phi_\mathrm{r})\right\rangle$ when k is odd, and $a_{q\mp}^k=2\mathrm{i}\left\langle\mathrm{C}_{k|q|}(\theta_r,0)\sin(q\phi_\mathrm{r})\right\rangle$ when k is even. In this paper, $P(\theta_r,\phi_r)$ is expanded up to $k=7$, which shows good convergence.

The full three-dimensional angular distribution function $P(\omega_t,\omega_r)$ depicting the $\boldsymbol{k}$–$\boldsymbol{k}'$–$\boldsymbol{j}'$ correlation can be described as

$$P(\omega_t,\omega_r)=\sum_{kq}\frac{2k+1}{4\pi}\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{kq}}{\mathrm{d}\omega_t}\mathrm{C}_{kq}(\theta_r,\phi_r)^*, \tag{5}$$

where the angles $\omega_r=\theta_r,\phi_r$ and $\omega_t=\theta_t,\phi_r$ refer to the coordinates of the unit vectors $\boldsymbol{k}'$ and $\boldsymbol{j}'$ along the directions of the product relative velocity and angular momentum vectors in the CM frame, respectively; $\mathrm{C}_{kq}(\omega_r)$ is a modified spherical harmonics; σ represents the integral cross section; $(1/\sigma)(\mathrm{d}\sigma_{kq}/\mathrm{d}\omega_t)$ denotes the polarization-dependent differential cross sections (PDDCSs) and can be expressed as

$$\frac{1}{\sigma}\frac{\mathrm{d}\sigma_{kq\pm}}{\mathrm{d}\omega_t}=\sum_{k_1}\frac{2k_1+1}{4\pi}S_{kq\pm}^k\mathrm{C}_{k,q}(\theta_t,0), \tag{6}$$

where $k_1>q$,

$$S_{kq\pm}^{k_1}=\left\langle\mathrm{C}_{k_1q}(\theta_t,0)\mathrm{C}_{kq}(\theta_r,0)\times\left[(-1)^q\,\mathrm{e}^{\mathrm{i}q\phi_r}\pm\mathrm{e}^{-\mathrm{i}q\phi_r}\right]\right\rangle, \tag{7}$$

in which, items in angled brackets are averaged over all angles.

In most double molecular experiments, previous research only focused on polarization components, $k=0$ and

$k = 2$. Especially when $k = 0$, equation (6) reduces to $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$. This can be simply interpreted as differential reaction cross section, and it well reflects the product molecular scattering direction. In order to ensure good convergence, the generalized differential polarization reaction cross section is expanded up to $k_1 = 7$ in this paper.

2.2. Integral cross sections

In the framework of QCT, the integral cross sections are assumed to have the following form:

$$\sigma = \pi b_{\max}^2 \frac{N_r}{N}, \tag{8}$$

where N_r is the number of reactive trajectories, N is the total number of trajectories, and $b_{\max}$ is the impact parameter in the QCT program calculation.

2.3. PES properties

The contours of the DMBE PES for the linear arrangement are highlighted in Fig. 2(a). The contours are equally spaced by 20 kcal/mol. The PES was implemented with a complete analytical expression based on a new switch function and the DMBE, which is highly efficient for calculating the QCT. In addition, the PES has a saddle point with the coordinates at (1.17 Å, 1.12 Å).

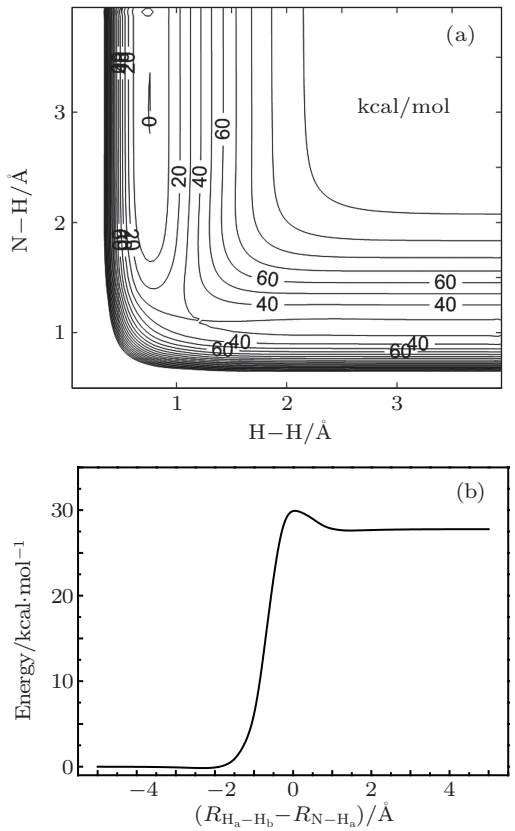


Fig. 2. Potential energy surfaces, showing (a) contours for stretching of N–H–H in linear configurations, and (b) reaction profile along the minimum energy path from the reactants to the products on our chosen PES of the H+NH reaction.

Figure 2(b) shows the reaction profile along the minimum energy path from reactants to products on our selected PES. Forward barrier height of $N + H_2 \rightarrow H + NH$ reaction is about 29.2 kcal/mol, which agrees well with the experimental values,[4,5] thus implying that the title reaction is an endothermic reaction. Conversely, the reverse of $N + NH \rightarrow N + H_2$ reaction has a lower barrier, so the threshold value of the reverse reaction will be lower.

2.4. QCT calculations

The most rigorous theoretical calculation of gas-phase triatomic reaction integral cross section is obtained by quantum dynamics approach based on scattering theory. If quantum effect is negligible, the QCT approach can be used to obtain reasonably reliable results. The standard QCT method is reported in Refs. [19]–[21]. Our study is an adiabatic study without considering the nonadiabatic effects like those reported in Ref. [22]. The more applications of QCT method used for calculating the stereodynamic properties can be found in Refs. [23]–[38]. The vibrational and the rotational levels of the reactant molecules are taken to be $v = 0$ and $j = 0$, 2, 5, 10 respectively in the present paper. The values of selected collision energy (E_c) for the reaction are in a range from 2 kcal/mol to 20 kcal/mol in steps of 2 kcal/mol. In the calculations, batches of 10^5 trajectories are run for each reaction and the integration step size is chosen to be 0.1 fs to guarantee conservations of the total energy and total angular momentum. The initial azimuthal angle and polar angle of the reagent molecule internuclear axis are randomly sampled by using the Monte Carlo method, and the trajectories are started with an initial distance of 15 Å between the H atom and the CM of the NH.

3. Results and discussion

3.1. Influence of reagent rotational excitation on the stereodynamics

Figure 3 shows the calculated $P(\theta_r)$ distributions of the NH product from the reaction $H(^2S) + NH(v = 0, j = 0, 2, 5, 10)$ at a collision energy of 20 kcal/mol on the DMBE PES, which describes the $\boldsymbol{k}$–$\boldsymbol{j}'$ correlation. Apparently, the $P(\theta_r)$ distribution has a maximum and it is symmetric about $\theta_r = 90^\circ$ because of the planar symmetry of the system. The calculated results demonstrate that the excitation of the initial NH rotation has a great influence on the stereodynamics. The maxima of $P(\theta_r)$ are located at θ_r angle close to 90° in the cases of $j = 0$ and $j = 2$, which indicates that the product rotational angular momentum vector is strongly aligned along the direction perpendicular to the relative velocity direction. Furthermore, the peak of the $P(\theta_r)$ distribution becomes rapidly lower as rotational quantum state increases, indicating that the influence of the reagent rotational excitation becomes more

obvious. This result is due to the fact that under a certain collision energy, the higher the rotational excitation, the weaker the aligned effect of the product rotational angular momentum vector is, which aligns along the direction perpendicular to the relative velocity direction.

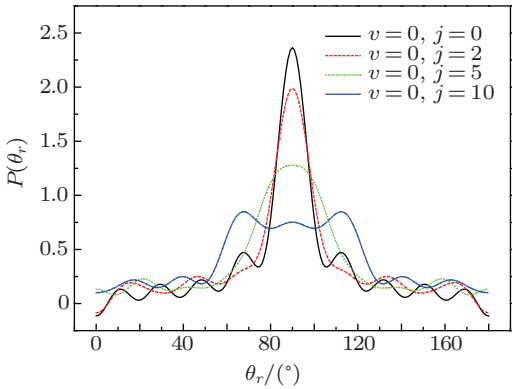


Fig. 3. (color online) Calculated results of distribution for $\boldsymbol{k}$–$\boldsymbol{j}'$ correlation for H(^{2}S) + NH($v = 0,\ j = 0,\ 2,\ 5,\ 10$) at collision energy of 20 kcal/mol.

The distributions of $P(\phi_r)$ at a collision energy of 20 kcal/mol on the DMBE PES are shown in Fig. 4, and the $P(\phi_r)$ shows the dihedral angle distribution of $\boldsymbol{j}'$ with respect to the $\boldsymbol{k}$–$\boldsymbol{k}'$ plane, in which the $\boldsymbol{k}$–$\boldsymbol{k}'$ scattering plane is at ϕ_r of about 180°. Apparently, one can find that $P(\phi_r)$ tends to be asymmetric about $\phi_r = 180°$, reflecting the strong polarization of the angular momentum. The peak or the centre of maximum value of $P(\phi_r)$ at ϕ_r angle close to 270° indicates that the rotational angular momentum vector $\boldsymbol{j}'$ of the product is oriented mainly along the negative direction of y axis in the CM frame. Moreover, further supporting information from the peak positions of the $P(\phi_r)$ with different rotational quantum number values shows that the increase of the value of rotational quantum number leads to the rapid decrease of the peak of $P(\phi_r)$. The results demonstrate that the orientation of the dihedral angle distribution of $\boldsymbol{j}'$ depends sensitively on the rotational quantum number.

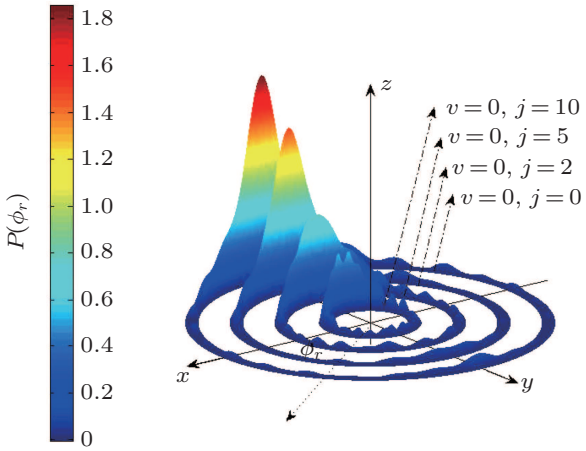


Fig. 4. (color online) Distributions for the H(^{2}S) + NH($v = 0,\ j = 0, 2, 5, 10$)→N(^{4}S) + H_2 reaction, calculated on the DMBE PES at a collision energy of 20 kcal/mol.

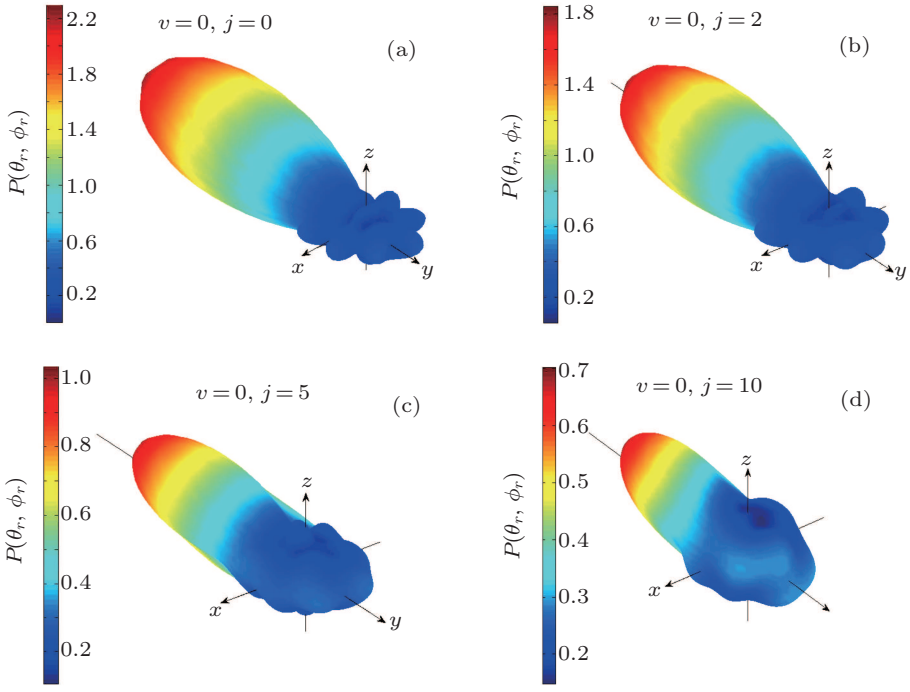


Fig. 5. (color online) Distributions representing the reactions at $E_c = 20$ kcal/mol for (a) $v = 0$ and $j = 0$, (b) $v = 0$ and $j = 2$, (c) $v = 0$ and $j = 5$, and (d) $v = 0$ and $j = 10$.

In order to further investigate the effect of rotational excitation on the reaction and validate more information about the angular momentum polarizations, we calculate the spatial distribution function $P(\theta_r, \phi_r)$ of the rotational angular momentum $\boldsymbol{j}'$ of the product molecule, and we plot the result in the form of polar plots θ_r and ϕ_r averaged over all scatter-

ing angles at collision energy $E_c = 20$ kcal/mol as shown in Fig. 5. Clearly, the $P(\theta_r, \phi_r)$ distributions peaked at 90° and 270° are in good accordance with the distributions of $P(\theta_r)$ and $P(\phi_r)$ at the collision energy $E_c = 20$ kcal/mol aforementioned. From the $P(\theta_r, \phi_r)$ distributions, it can be observed that j' is oriented preferentially along the negative direction of the y axis in the rotational ground state and all the excitation states. Therefore, the distributions $P(\theta_r, \phi_r)$ show that the product H_2 is strongly polarized in the direction perpendicular to the scattering plane and rotates mainly in the plane parallel to the scattering plane.

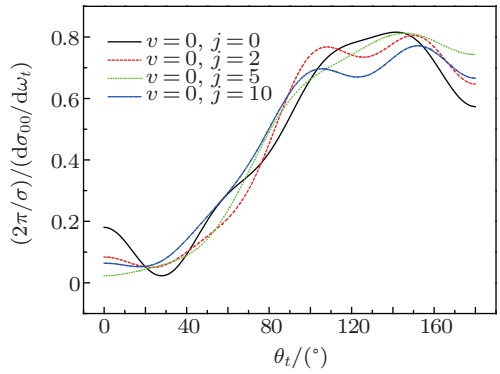


Fig. 6. (color online) Variations of $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$ with θ_t at $E_c = 20$ kcal/mol for the cases: $v = 0$ and $j = 0$; $v = 0$ and $j = 2$; $v = 0$ and $j = 5$; $v = 0$ and $j = 10$.

The DCS supplies the most detailed information about the reaction stereodynamics and describes only the k–k' correlation or the scattering direction of the product. The DCSs for the reactions $H(^2S) + NH(v = 0,\ j = 0, 2, 5, 10) \rightarrow N(^4S) + H_2$ at $E_c = 20$ kcal/mol, plotted each as a function of scattering angle are shown in Fig. 6. However, the DCS displays the distribution in the backward direction. In comparison with the case of rotational ground state, in addition, the DCS is not affected obviously by the rotational quantum number ($j = 0$, 2, 5, 10) of the reactants. That is because the ratio between the reduced mass of product H_2 and the mass of N is a main factor in the scattering direction of H_2, which is less affected by the initial dynamics of the reactant NH.

3.2. Influence of collision energy on the stereodynamics of reaction

Figures 7(a)–7(d) display the $P(\theta_r)$ distributions of four different rotational quantum states and the vibrational ground state on the PES with the collision energy change in a range of 2 kcal/mol–20 kcal/mol, which also validates the above-mentioned ordering. For the vibrational ground state and a constant rotational quantum state on the PES, except for the case of v = 0 and $j = 10$ at lower collision energy (less than 5 kcal/mol) (Fig. 7(c)), a higher peak value of the $P(\theta_r)$ distribution can be obtained with a bigger collision energy; for the case of $v = 0$ and $j = 10$ (Fig. 7(d)), the peak of $P(\theta_r)$ distribution disappears and the alignment of the product rotational angular momentum vector becomes the weakest among the four cases. The result indicates that the rotational angular momentum of the product has a strong orientation effect, and the degree of planning increases with the increase of the collision energy.

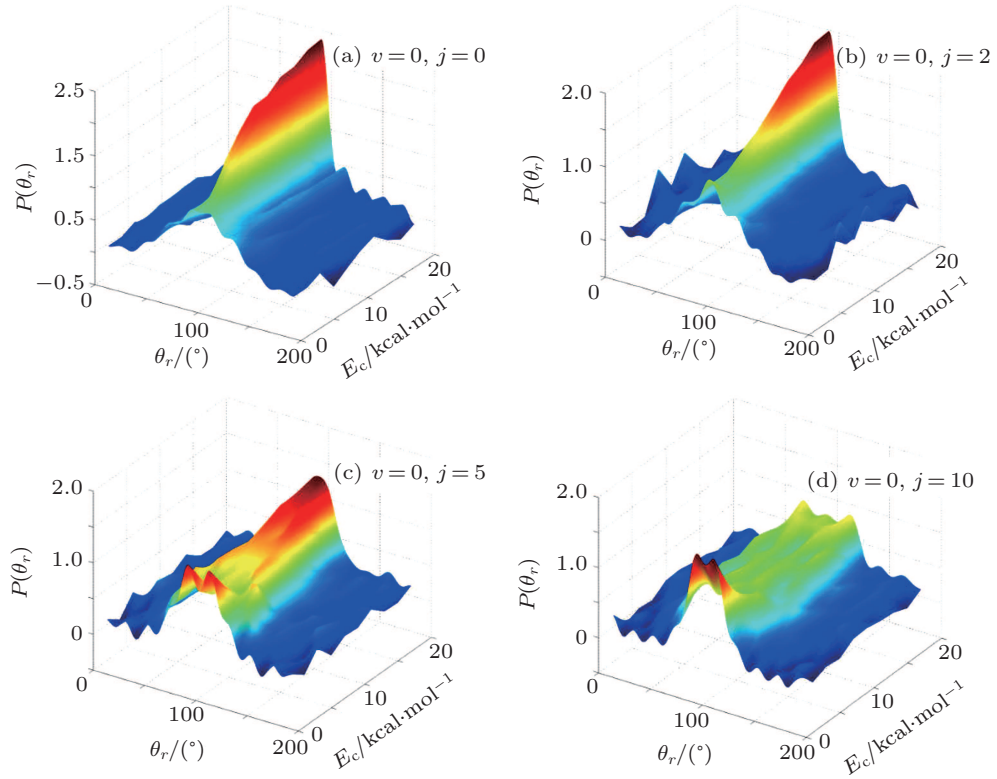


Fig. 7. (color online) Distributions of each as a function of the polar angle θ_r and collision energy for the title reactions with (a) $v = 0$ and $j = 0$, (b) $v = 0$ and $j = 2$, (c) $v = 0$ and $j = 5$, and (d) $v = 0$ and $j = 10$.

Figures 8(a)–8(d) display the $P(\phi_r)$ distributions of four different rotational quantum states and the vibrational ground state on the PES, respectively. One can find that $P(\phi_r)$ tends to be asymmetric about $\phi_r = 180°$, reflecting the strong polarization of the angular momentum. In the figures, each surface has only one evident peak at ϕ_r close to 270°, which implies that the product H_2 prefers to show a left-handed rotation in the plane parallel to the scattering plane ($\boldsymbol{k}$–$\boldsymbol{k}'$), and the rotational angular momentum vector of the product is oriented along the negative direction of y axis. For the higher reactant rotational state ($j = 5$, 10), an interesting trend can be obtained from Figs. 8(c)–8(d), the peak values of $P(\phi_r)$ increase with the increase of the collision energy. The findings indicate that out-of-plane mechanism at a higher collision energy and in a rotational excitation state of the reactant dominates the abstract reaction. In addition, the study also finds that the greater the collision energy, the larger the relative velocity vector is, the smaller the probability of the molecule being ejected back is; the degree of backward scattering will become smaller.

The $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$ is the simple DCS only describing the $\boldsymbol{k}$–$\boldsymbol{k}'$ correlation and the scattering direction of the product, and not associated with the orientation nor alignment of the product rotational angular momentum vector $\boldsymbol{j}'$, which is shown in Fig. 9 for initial rotational states of the reactant molecule of NH with (a) $v = 0$ and $j = 0$, (b) $v = 0$ and $j = 2$, (c) $v = 0$ and $j = 5$, and (d) $v = 0$ and $j = 10$. From the results of $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, we can draw the conclusion that the products are scattered backward strongly for all the initial rotational states of NH at the lower collision energy, and the increase of the collision energy will reduce this tendency. But the DCS is not significantly affected by the rotational quantum number ($j = 0$, 2, 5, 10) of reactants. This phenomenon of DCS can be attributed to the contribution of the abstract reaction.

The integral reaction cross-section results each as a function of collision energy calculated for the H + NH ($v = 0$, j) reaction for four different values of j as marked in the figure are shown in Fig. 10. The cross section values increase monotonically with increasing collision energy. It can be seen from Fig. 10 that the cross section values decrease with the increase of rotational excitation of the reactant diatom at the lower collision energy, which indicates that the ICS is in reasonable agreement with the cited data at vibration rotation ground state, calculated by Adam *et al.*[6] Our calculation method is similar to the classical trajectory method in Ref. [6]. As a result of the barrier in the entrance channel, the ICS steeply rises with the collision energy increasing. The threshold value is lower for $j = 0$, the threshold occurs around 0.5 kcal/mol and shifts to higher energies with j increasing. This shift is the result of the narrow transition state; faster and faster rotation of NH makes the crossing of the transition state region less and less possible. Therefore, the cross section of the title reaction increases monotonically with energy increasing due to the threshold, indicating that it is an abstraction reaction.

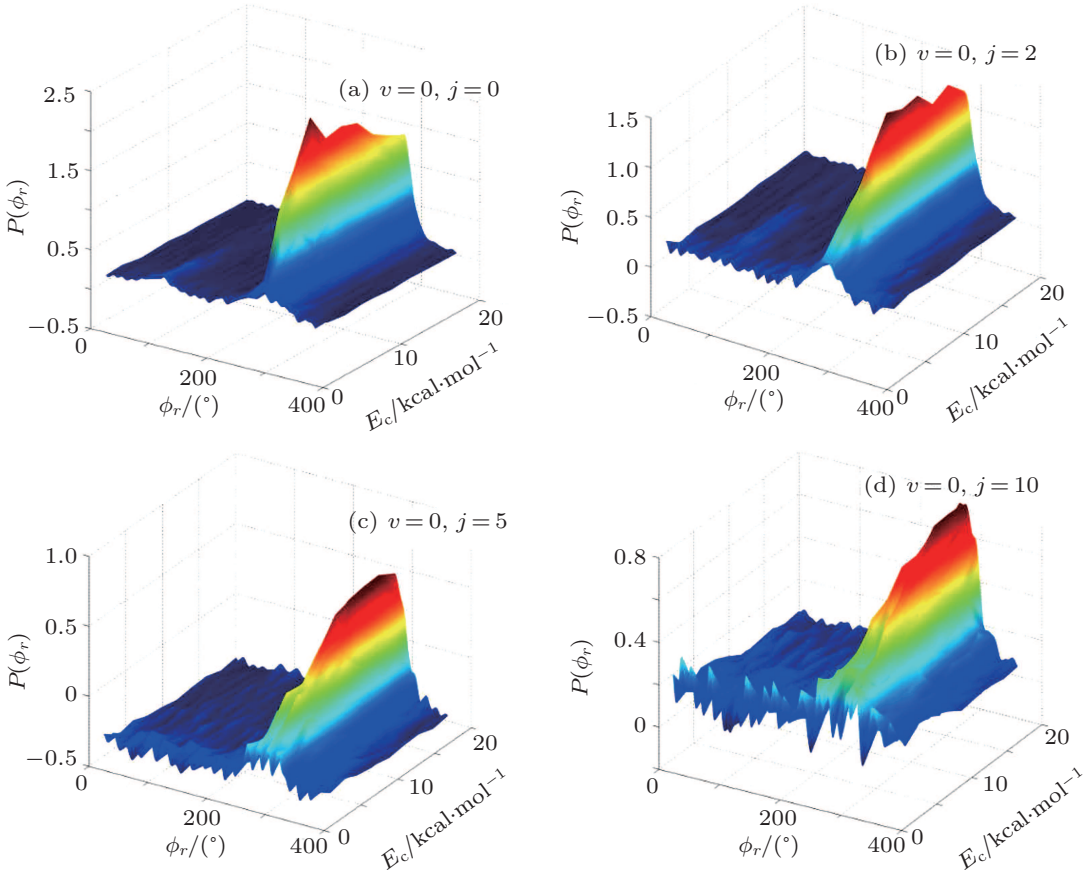


Fig. 8. (color online) Distributions of each as a function of polar angle ϕ_r and collision energy for the title reactions with (a) $v = 0$ and $j = 0$, (b) $v = 0$ and $j = 2$, (c) $v = 0$ and $j = 5$, and (d) $v = 0$ and $j = 10$.

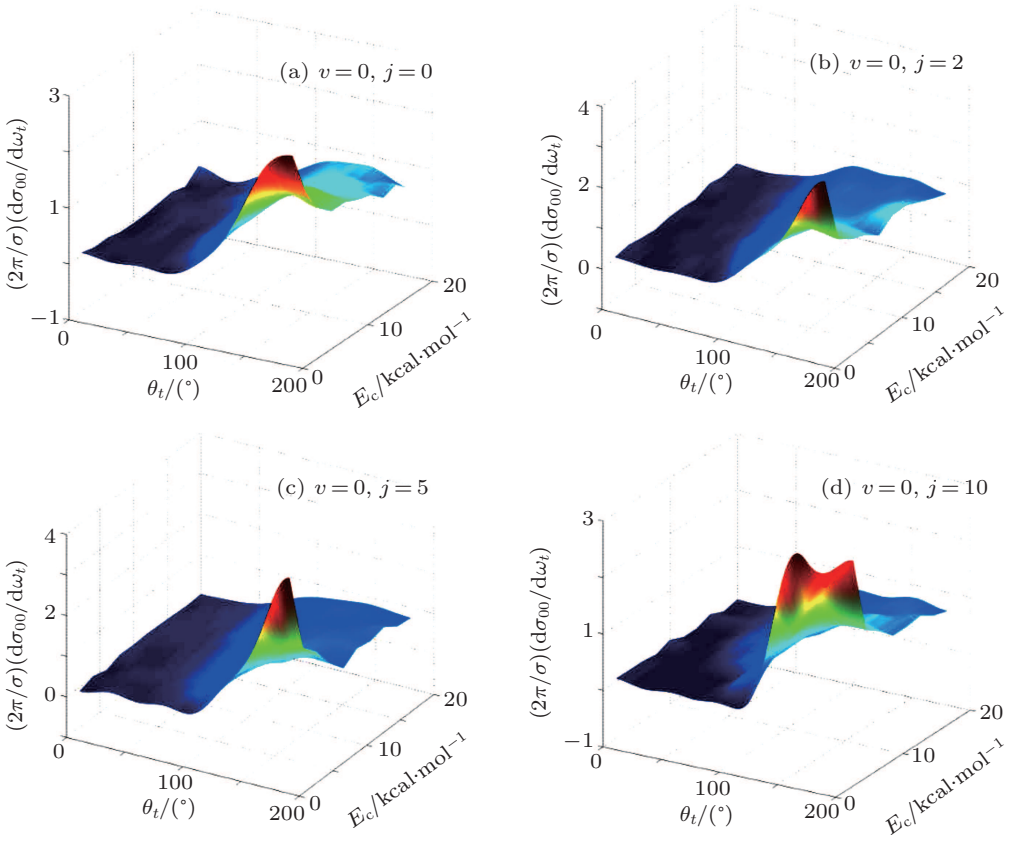


Fig. 9. (color online) Differential cross sections each as a function of scattering angle θ_t and collision energy for the reactions H + NH decomposed into initial rotational states of NH with (a) $v = 0$ and $j = 0$; (b) $v = 0$ and $j = 2$; (c) $v = 0$ and $j = 5$; (d) $v = 0$ and $j = 10$.

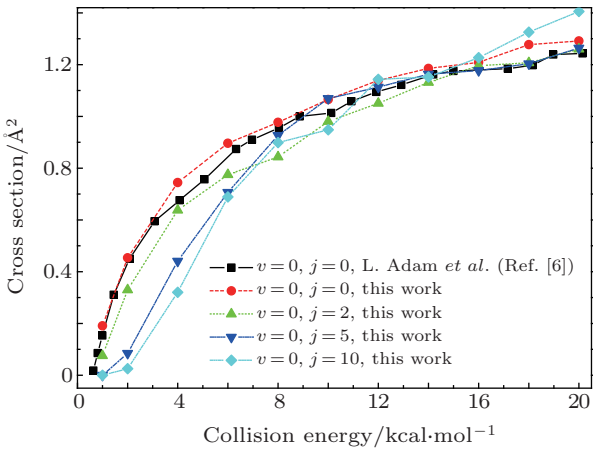


Fig. 10. (color online) Initial state-selected integral cross sections of the H + NH($v = 0$, j) reaction each as a function of the collision energy. The cross sections for various j values are shown by different lines and symbols. The integral cross section results for $j = 0$ (black squares) cited from Ref. [6].

4. Conclusions

In this new theory developed in this paper, a QCT dynamics study on the product polarizations for the reaction $H(^2S) + NH(v = 0,\ j = 0, 2, 5, 10) \rightarrow N(^4S) + H_2$ is carried out by using the DMBE PES. The distributions of $P(\theta_r)$, $P(\phi_r)$, $P(\theta_r, \phi_r)$, $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$, and DCSs are calculated in a collision energy range of 2 kcal/mol–20 kcal/mol and four different rotational excitation states. The results show that the influences of different collision energies and different rotational excitation states on the rotational polarizations of the product present different characteristics. The following conclusions can be drawn. The distribution $P(\theta_r)$ indicates that the product rotational alignment is susceptible to rotational quantum number and collision energy, and the product rotational angular momentum vector $\boldsymbol{j}'$ of the product for the reaction is strongly aligned in the vertical direction of the relative velocity $\boldsymbol{k}$. The distributions of $P(\phi_r)$ and $P(\theta_r, \phi_r)$ demonstrate that the product rotational angular momentum vector $\boldsymbol{j}'$ is oriented along the negative direction of y-axis of the CM frame. In addition, the $(2\pi/\sigma)(\mathrm{d}\sigma_{00}/\mathrm{d}\omega_t)$ shows that as the collision energy increases, the product rotational alignment becomes stronger. The DCS also indicates that at collision energy ($E_c = 20$ kcal/mol) of the reagents, the scattering of the product H_2 is in the backward direction, but the DCS is not significantly affected by the rotational quantum number ($j = 0$, 2, 5, 10) of reactants.

References

[1] Mcclelland G M and Herschbach D R 1979 *J. Phys. Chem. A* **83** 1445
[2] Jonah C D, Zare R N and Ottinger C 1972 *J. Chem. Phys.* **56** 263
[3] Morley C 1981 *Sym. Combust.* **18** 23
[4] Koshi M and Yoshimura M 1990 *J. Chem. Phys.* **93** 8703
[5] Davidson D F and Hanson R K 1990 *Int. J. Chem. Kinet.* **22** 843
[6] Adam L, Hack W, Zhu H, Qu Z W and Schinke R 2005 *J. Chem. Phys.* **122** 114301
[7] Poveda L A and Varandas A J C 2005 *Phys. Chem. Chem. Phys.* **7** 2867

[8] Varandas A J C 1988 *Adv. Chem. Phys.* **74** 255
[9] Werner H J and Knowles P J 1988 *J. Chem. Phys.* **89** 5803
[10] Knowles P J and Werner H J 1988 *Chem. Phys. Lett.* **145** 514
[11] Zhang J, Chu T S, Dong S L, Yuan S P, Fu A P and Duan Y B 2011 *Chin. Phys. Lett.* **28** 93403
[12] Yu Y J, Xu Q and Xu X W 2011 *Chin. Phys. B* **20** 123402
[13] Xia W Z, Yu Y J and Yang C L 2012 *Acta Phys. Sin.* **61** 223401 (in Chinese)
[14] Yu Y J, Wang D H, Feng S X and Xia W Z 2012 *J. Theor. Comput. Chem.* **11** 763
[15] Han B R, Yang H, Zheng Y J, Varandas A J C 2010 *Chem. Phys. Lett.* **493** 225
[16] Wang M L, Han K L and He G Z 1988 *J. Phys. Chem. A* **102** 10204
[17] Shaferray N E, Orrewing A J and Zare R N 1995 *J. Phys. Chem.* **99** 7591
[18] Li X H, Wang M S, Pino I, Yang C L and Ma L Z 2009 *Phys. Chem. Chem. Phys.* **11** 10438
[19] Han K L, He G Z and Lou N Q 1996 *J. Chem. Phys.* **105** 8699
[20] Li R J, Han K L, Li F E, Lu R C, He G Z and Lou N Q 1994 *Chem. Phys. Lett.* **220** 281
[21] Lu R F, Wang Y H and Deng K M 2013 *J. Comput. Chem.* **34** 1735
[22] Chu T S, Zhang Y and Han K L 2006 *Int. Rev. Phys. Chem.* **25** 201
[23] Wang Y H, Xiao C Y, Deng K M and Lu R F 2014 *Chin. Phys. B* **23** 043401
[24] Chen M D, Han K L and Lou N Q 2002 *J. Chem. Phys.* **283** 463
[25] Zhang X and Han K L 2006 *Int. J. Quantum Chem.* **106** 1815
[26] Tan R S, Liu X G and Hu M 2012 *Chin. Phys. Lett.* **29** 123101
[27] Wei Q 2013 *Chin. Phys. Lett.* **30** 073101
[28] Xie T X, Zhang Y Y, Shi Y, Li Z R and Jin M X 2015 *Chin. Phys. B* **24** 043402
[29] He D, Wang M S, Yang C L and Jiang Z J 2013 *Chin. Phys. B* **22** 068201
[30] Li Y Q, Yang Y F, Yu Y, Zhang Y J and Ma F C 2016 *Chin. Phys. B* **25** 023401
[31] Zhai H S and Han K L 2011 *J. Chem. Phys.* **135** 104314
[32] Wei Q 2015 *Chin. Phys. Lett.* **32** 13101
[33] Chu T S and Han K L 2008 *Phys. Chem. Chem. Phys.* **10** 2431
[34] Chen X P and Li X L 2013 *Chin. Phys. Lett.* **30** 064702
[35] Ju L P, Han K L and Zhang J Z H 2009 *J. Comput. Chem.* **30** 305
[36] Wang M X, Wang M S, Yang C L, Liu J, Ma X G and Wang L Z 2015 *Acta Phys. Sin.* **64** 043402 (in Chinese)
[37] Chi X L, Zhao J F, Zhang Y J, Ma F C and Li Y Q 2015 *Chin. Phys. B* **24** 053401
[38] Li H Z, Liu X G, Tan R S and Hu M 2015 *Chin. Phys. Lett.* **32** 83102