

Quasiclassical trajectory study on the integral cross-section and stereodynamics information of the reaction



TIANYUN CHEN^a, NINGJIU ZHAO^{a,b}, WEIPING ZHANG^{a,*}, DONGJUN WANG^b and XINQIANG WANG^c

^aSchool of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China

^bDepartment of Chemistry, Hebei Normal University of Science and Technology, Qinhuangdao 066600, China

^cCollege of Physics, Chongqing University, Chongqing 400044, China

e-mail: zhangwp@dlut.edu.cn

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Abstract. Integral cross-section and stereodynamics study of the reaction $\text{O} (^1\text{D}) + \text{H}_2 (v = 0, j = 0) \rightarrow \text{OH} + \text{H}$ is undertaken using the quasiclassical trajectory (QCT) method for the collision energy is in the large length of 1.3 to 43 kcal/mol using Dobbyn and Knowles (DK) surface, and the obtained results are compared with those available from earlier available calculated results on the BR surface. The integral cross sections obtained from the quasiclassical trajectory method are in good agreement with those of Chebyshev wave packet method for collision energies above 0.2 eV. We also investigated the vector correlations and polarized dependent differential cross sections (PDDCS) at different collision energies. It is demonstrated that the alignment and state distribution significantly decrease with increase in the collision energy.

Keywords. Polarization dependent differential cross-section (PDDCS); vector correlation; quasiclassical trajectory method; stereodynamics; integral cross section.

1. Introduction

The reaction, $\text{O} (^1\text{D}) + \text{H}_2 \rightarrow \text{OH} (v = 0, j = 0) + \text{H}$ which is one of the most important reactions in atmospheric chemistry, is rapidly maturing as a key model system for insertion mechanisms in reaction dynamics. Because of its fundamental significance, this reaction has been widely investigated during the past 50 years.^{1–16} A number of highly accurate global potential energy surfaces (PES) have been developed for this reaction, and its dynamics is mainly obtained on the ground state potential energy surface (PES) for the water molecule,¹ although the higher $2^1\text{A}'$ state may also be involved through a conical intersection. Many experimental data, including rotation and vibration state distribution^{2,3} of the product, total⁴ and differential^{6,7} reaction cross sections, and isotopic branching ratios,^{8,9}

thermal rate constants,^{5,7,10} and non-adiabatic effects are now available for this system.

Theoretical studies on this system are rendered difficult by the fact that different PESs also become accessible at thermal energies. The lowest one of these PES correlates with the $^1\text{A}_1$ state of H_2O . The ground state PES of water molecules proposed by Joao¹¹ includes a carefully description of long range interaction which plays an important role on the dynamics of the reaction $\text{O} (^1\text{D}) + \text{H}_2 \rightarrow \text{OH} (v=0, j=0) + \text{H}$. There is a barrier to reaction which is the lowest in the linear configuration. Reagents and products rotation and vibration are calculated on different PESs. In most cases, the reaction cross section declines initially with increase in the reagents rotation but then increases with more rotation at excitation. Reagent rotation increases reaction cross section monotonically for a few reactions such as $\text{O} (^3\text{P}) + \text{H}_2$ ^{12–14} and $\text{O} (^3\text{p}) + \text{HCl}$.^{15–17} Recently, Han^{18–21} had used quasiclassical trajectories (QCT) method to investigate not only the reagent, product rotation and vibration but also about the vectors correlation. The

*For correspondence

product relative velocities (\mathbf{k}, \mathbf{k}') and the rotational states (\mathbf{j}, \mathbf{j}') can offer a full picture of the scattering dynamics. The reagent and product relative velocity (\mathbf{k}, \mathbf{k}') characterize the differential cross section. Experimental and theoretical interests in vector correlations in the three atoms reaction $A + BC \rightarrow AB + C$ have increased significantly in the recent years.^{18–36} The vectors \mathbf{k}, \mathbf{k}' and \mathbf{j}' (the product rotational angular momentum) are important since the angular distribution describing the relative orientation of these vectors in space can be characterized by the double and the triple vector correlations. Vector properties, such as velocities and angular momentum, possess not only magnitudes that can be directly related to translational and rotational energies, but also well-defined directions. Clearly, one of the most important things is the determination of the product rotational alignment and orientation about the reagents relative velocity vector. Han and co-workers had used quasiclassical trajectory (QCT) method to calculate the trajectory of heavy–heavy–light (HHL), light–light–light (LLL), heavy–light–light (HLL), and light–heavy–light (LHL) mass combination reactions on the attractive and the repulsive potential surfaces to study the dependence of the product rotational alignment for different collision energies,^{35,36} and obtained the effect of the reaction location of energy barrier on the product alignment of reaction $A + BC$.

In our previous work,³⁴ we have investigated the effect of initial vibration state \mathbf{v} of H_2 on the title reaction $O(^1D) + H_2 \rightarrow OH + H$ at collision energy of 19.0 kcal/mol on 2^1A state, and we found that with increasing the value of \mathbf{v} from 0 to 3 mainly leads to the forward scattering of the product. In order to get more dynamics information for the reaction, we choose four collision energies 5.5 kcal/mol, 14.4 kcal/mol, 26 kcal/mol, 38 kcal/mol, respectively. Li *et al.*³³ had studied this reaction on the same PES at five lower collision energies: 1.1 kcal/mol, 1.8 kcal/mol, 2.0 kcal/mol, 2.2 kcal/mol and 2.4 kcal/mol. The title reaction involves the formation of a short-lived water intermediate that decays before the in reactive energy has any chance to randomize completely. Also the OH products are produced mainly in the H–O–H molecular plane.

In this study, we use the quasiclassical trajectory method to investigate the dynamics of the reaction $O(^1D) + H_2 (\mathbf{v} = 0, \mathbf{j} = 0) \rightarrow OH + H$ for the DK PES. Collision energies from 1.3 kcal/mol (= 0.0564 eV) to 43 kcal/mol (= 1.865 eV). The cross sections are compared with those of Lin's.²⁸ The vector correlation are also studied at four collision energies, 5.5 kcal/mol,

14.4 kcal/mol, 26 kcal/mol, 38 kcal/mol, and polarized dependent differential cross sections (PDDCSs) have been obtained to get more information about the reaction. In the calculation, a batch of 20 000 trajectories has been run for each of the collision energy with the integration step of 0.1 fs.

2. Theory

Figure 1 shows the center-of-mass (CM) coordinate system used to describe the $\mathbf{k}, \mathbf{k}', \mathbf{j}'$ correlations. θ is the angle between the reagent relative velocity and product relative velocity. θ_r and ϕ_r are the polar and azimuthal angles of final rotational momentum \mathbf{j}' .

The rationale of the reaction is calculated by the formula:

The fully correlated (CM) angular distribution is written as the sum

$$P(\cos \theta, \cos \theta_r, \phi_r) = \frac{1}{4\pi} \sum_{k=0}^{\infty} \sum_{q=-k}^k (2k+1) \times \frac{2\pi}{\sigma} \frac{d\sigma_{kq}}{d\omega} C_{kq}(\theta_r, \phi_r), \quad (1)$$

where $\omega = \theta, \phi$ and $\omega_r = \theta_r, \phi_r$ refer to the coordinates of the unit vectors \mathbf{k}' and \mathbf{j}' along the directions of the product relative velocity and rotational angular momentum vectors in the CM frame, respectively. $\frac{1}{\sigma} \frac{d\sigma_{kq}}{d\omega}$ is the generalized polarization dependent differential cross-section (PDDCS).^{19,20,27}

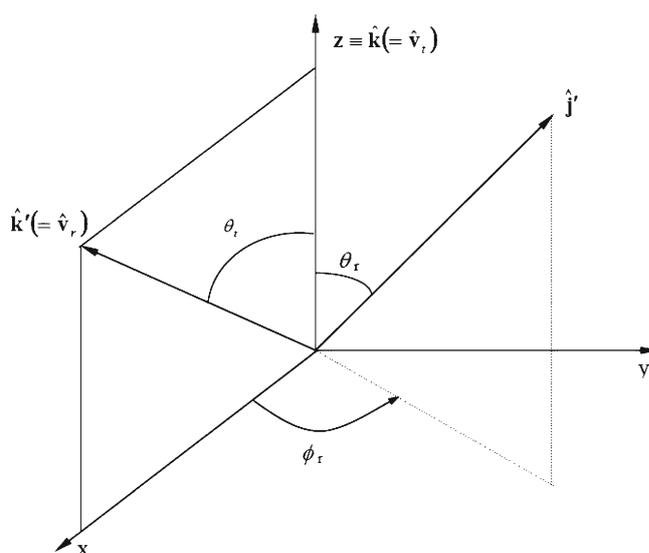


Figure 1. The center-of-mass coordinate system used to describe the $\mathbf{k}, \mathbf{k}', \mathbf{j}'$ correlations.

The PDDCSs are written as follows.³⁷⁻⁴⁰

$$\begin{aligned} \frac{2\delta}{\sigma} \frac{d\sigma_{k0}}{d\omega} &= 0 && \text{when } k \text{ is odd} \\ \frac{2\delta}{\sigma} \frac{d\sigma_{kq+}}{d\omega} &= \frac{2\delta}{\sigma} \frac{d\sigma_{kq}}{d\omega} + \frac{2\delta}{\sigma} \frac{d\sigma_{k-q}}{d\omega} = 0 && \text{when } k \text{ is even and } q \text{ is odd or when } k \text{ is odd } q \text{ is even} \\ \frac{2\delta}{\sigma} \frac{d\sigma_{kq-}}{d\omega} &= \frac{2\delta}{\sigma} \frac{d\sigma_{kq}}{d\omega} - \frac{2\delta}{\sigma} \frac{d\sigma_{k-q}}{d\omega} = 0 && \text{when } k \text{ is even and } q \text{ is odd or when } k \text{ is odd } q \text{ is even.} \end{aligned}$$

We can also summarize these as⁴¹⁻⁴³

$$\frac{2\delta}{\sigma} \frac{d\sigma_{kq\pm}}{d\omega} = \sum_{k_1} \frac{[k_1]}{4\delta} S_{kq\pm}^{k_1} C_{k_1-q}(\theta, 0).$$

And $S_{q\pm}^{k_1}$ was expressed as

$$S_{kq\pm}^{k_1} = \langle c_{k_1q}(\theta, 0) c_{kq}(\theta_r, 0) [(-1)^q e^{iaxq\phi_r} \pm e^{-iaxq\phi_r}] \rangle.$$

Double vector correlations ($\mathbf{k} - \mathbf{j}'$, $\mathbf{k} - \mathbf{k}'$, or $\mathbf{k}' - \mathbf{j}'$) can be expanded into a series of Legendre polynomials. The $P(\theta_r)$ distribution corresponding to the $\mathbf{k} - \mathbf{j}'$ correlation is written as

$$P(\theta_r) = \frac{1}{2} \sum_k [k] a_0^k P_k(\cos\theta_r). \quad (2)$$

The a_0^k coefficients (polarization parameters) are given by

$$a_0^k = P_k(\cos\theta_r).$$

The brackets represent an average of over all the reactive trajectories. The dihedral angular distribution of the $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ triple vectors correlation is characterized by the angle $P(\phi_r)$. The distribution of the dihedral angular discussion $P(\phi_r)$ could be expanded as a Fourier series

$$P(\phi_r) = \frac{1}{2\delta} \left(1 + \sum_n a_n \cos n\phi_r + \sum_n b_n \sin n\phi_r \right),$$

with a_n and b_n given by

$$a_n = 2 \langle \cos n\phi_r \rangle$$

$$b_n = 2 \langle \sin n\phi_r \rangle.$$

In the work, when $P(\phi_r)$ is expended up to $n = 24$ to get convergence results.

The joint of probability density function of angles θ_r and ϕ_r defining the direction of \mathbf{j}' , can be written as⁴⁴⁻⁵⁰

$$\begin{aligned} P(\theta_r, \phi_r) &= \frac{1}{4\pi} \sum_{kq} [k] a_q^k C_{kq}(\theta_r, \phi_r)^* \\ &= \frac{1}{4\pi} \sum_k \sum_{q \geq 0} [a_{q\pm}^k \cos q\phi_r - a_{q\mp}^k i \sin q\phi_r] \\ &\quad \times C_{kq}(\theta_r, 0). \end{aligned} \quad (3)$$

The parameter a_q^k is evaluated by

$$a_{q\pm}^k = 2 \langle C_{k|q|}(\theta_r, 0) \cos q\phi_r \rangle \quad k \text{ even}, \quad (4)$$

$$a_{q\pm}^k = 2i \langle C_{k|q|}(\theta_r, 0) \sin q\phi_r \rangle \quad k \text{ odd}. \quad (5)$$

During the calculation, $P(\theta_r, \phi_r)$ is expanded up to $k = 7$, which is sufficient for good convergence.

3. Results and discussion

Figure 2 describes the four polarized dependent differential cross sections (PDDCSs) of the OH product for the $O(^1D) + H_2(v=0, j=0) \rightarrow OH + H$ reaction calculated on the DK surface^{51,52} or the collision energies are 5.5 kcal/mol, 14.4 kcal/mol, 26 kcal/mol, 38 kcal/mol, respectively. PDDCSs describe the correlation of $\mathbf{k}-\mathbf{k}'-\mathbf{j}'$ and the scattering direction of the product molecule. The PDDCS $(2\delta/\sigma)(d\sigma_{00}/d\omega_t)$, which is simply the differential cross-section (DCS) describes only the $\mathbf{k}-\mathbf{k}'$ correlation or the scattering direction of the product and is not associated with the orientation and alignment of the product rotational angular momentum vector. It is seen that for all the four collision energies the product molecules are scattered mostly in the forward and backward direction.

The PDDCS $(2\delta/\sigma)(d\sigma_{20}/d\omega_t)$ is the expectation value of the second Legendre moment, it can be clearly seen that all of PDDCSs $(2\delta/\sigma)(d\sigma_{20}/d\omega_t)$ are negative, and the trends are opposite to $(2\delta/\sigma)(d\sigma_{00}/d\omega_t)$, indicating that \mathbf{j}' is strongly aligned perpendicular to \mathbf{k} . This phenomenon may be resulted in the $(2\delta/\sigma)(d\sigma_{20}/d\omega_t)$ related to alignment moment $\langle P_2(\mathbf{cos}\theta) \rangle$. The detailed discussion of the product rotation alignment effect will be taken up while discussing figures 3 and 4. With $q \neq 0$ the values of PDDCSs are near to zero, which can be seen in figure 2. On the DK surface, The PDDCS $(2\delta/\sigma)(d\sigma_{22+}/d\omega_t)$ strongly scattering depends with angle. As we can see from figure 2, all the values of $(2\delta/\sigma)(d\sigma_{22+}/d\omega_t)$

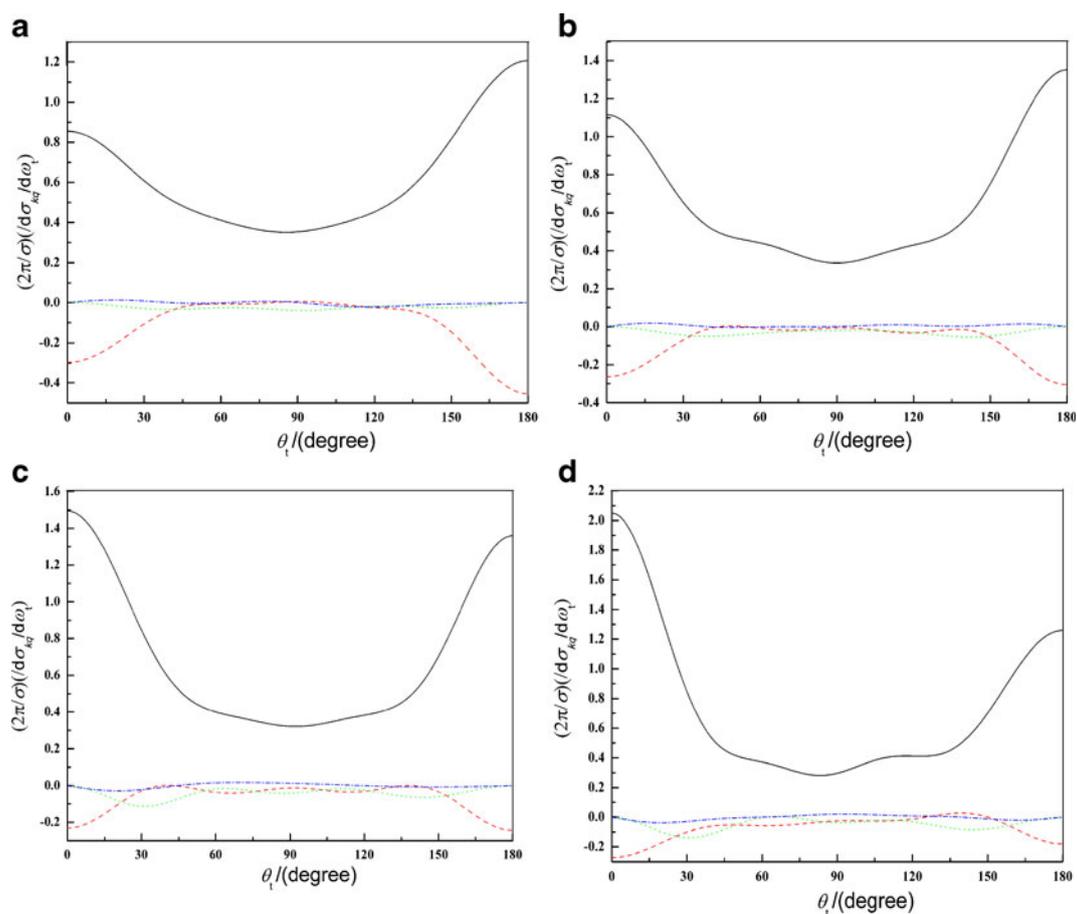


Figure 2. Four polarization dependent differential cross-sections of the reaction $O(^1D) + H_2 \rightarrow OH + H$ for different collision energies. (a) 5.5 kcal/mol, (b) 14.4 kcal/mol, (c) 26 kcal/mol, (d) 38 kcal/mol; $(2\pi/\sigma) (d\sigma_{00}/d\omega_t)$ solid line, $(2\pi/\sigma) (d\sigma_{20}/d\omega_t)$ dash line, $(2\pi/\sigma) (d\sigma_{22+}/d\omega_t)$ dot line, $(2\pi/\sigma) (d\sigma_{21-}/d\omega_t)$ dash dot line.

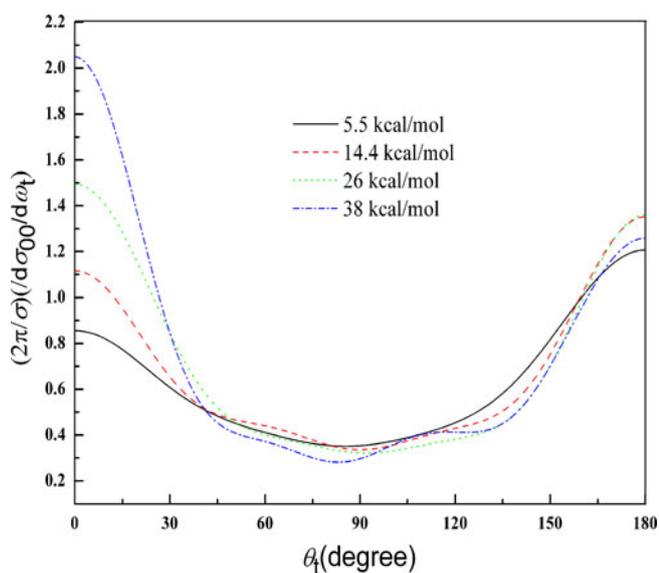


Figure 3. PDDCSs $(2\pi/\sigma) (d\sigma_{00}/d\omega_t)$ of the reaction $O + H_2 \rightarrow OH+H$.

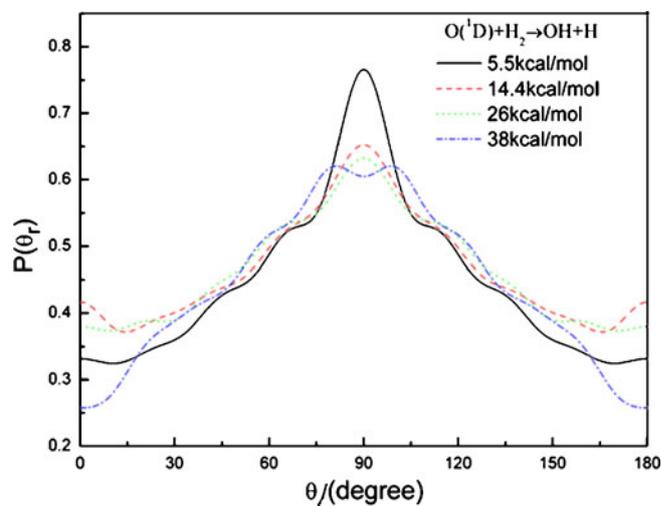


Figure 4. The distribution of $P(\theta_r)$ reflecting the $k-j'$ correlation for $O(^1D) + H_2 \rightarrow OH + H$ reactions.

for the title reaction are negative for all scattering angles, thus revealing a noticeable preference for an alignment of \mathbf{j}' along the y axis as opposed to the x axis. The distribution of $(2\delta/\sigma)(d\sigma_{21-}/d\omega_t)$ which is related to $(\sin^2\theta_r, \cos^2\phi_r)$ is close to zero on the surface and almost a straight line. That is to say the $(2\delta/\sigma)(d\sigma_{21-}/d\omega_t)$ is obviously isotropic and almost independent of surface.

In order to obtain more information on how the reaction scattering depend with increasing the collision energy, the PDCCSs $(2\delta/\sigma)(d\sigma_{00}/d\omega_t)$ of the four collision energies are compared. It can be clearly seen from figure 3, though the four $(2\delta/\sigma)(d\sigma_{00}/d\omega_t)$ display the same trend, there is a little difference with increasing of collision energy, the forward scattering becomes stronger and backward scattering becomes weaker.

The distribution of $P(\theta_r)$ is show in figure 4, which represents the $\mathbf{k}-\mathbf{j}'$ correlation, and it can be concluded that the product rotation alignment is strongly correlated. Comparing the results of the four collision energies, it can be obtained that with increasing collision energy, the rotation alignment is becoming weaker. It can be clearly seen that there is a significant discrepancy between the peaks distribution of $P(\theta_r)$ when the collision energy is increased. The distribution peaks at θ_r angles close to 90° and is symmetric with respect to 90° because of the planar symmetry of the system.

In the previous work, Chen *et al.*^{19,21} have studied the $\text{Cl} + \text{H}_2$ system and found that the distribution of the product angular momentum vectors is very sensitive to the mass factor. The effect of mass factor $\cos^2\beta = m_L m_{L'}/(m_L + m_{L'})(m_{L'} + m_{L''})$ on product rotation alignment is also notable for the LLL mass combination reaction. During the reactive encounter, total angular momentum is conserved, $\mathbf{j} + \mathbf{L} = \mathbf{j}' + \mathbf{L}'$ (\mathbf{L} and \mathbf{L}' are the reagent and product orbital angular momenta). According to the impulse model, $\mathbf{j}' = \mathbf{L} \sin^2\beta + \mathbf{j} \cos^2\beta + \mathbf{J}_1 m_B/m_{AB}$, the larger product will take more angular momentum away, so the increase of the mass factor reduces the anisotropic distribution of \mathbf{j}' .

The dihedral angle distribution $P(\phi_r)$ is depicted in figure 5. It tends to be asymmetric with respect to the scattering plane, directly reflecting the strong polarization of angular momentum induced by the PES. It is a crucially sensitive indicator of the stereodynamics of the $\text{O}(^1\text{D}) + \text{H}_2(v=0, \mathbf{j}=0) \rightarrow \text{OH} + \text{H}$ reaction. The asymmetry in the $P(\phi_r)$ distributions reflects the strong orientation. Peaks of $P(\phi_r)$ at $\phi_r = \pi/2$, connect with molecular products with counter clockwise rotation. But there is another peak at $\phi_r = 3\pi/2$, which

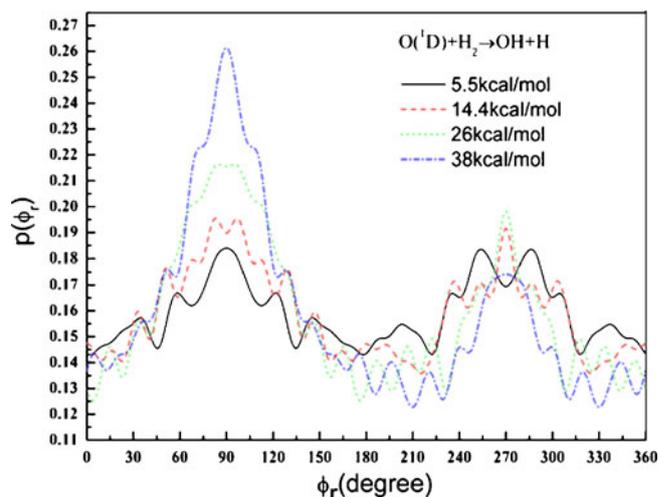


Figure 5. Dihedral angle distribution of \mathbf{j}' , $P(\phi_r)$ with respect to the $\mathbf{k}-\mathbf{k}'$ plane.

is related to the product molecules with clockwise rotation. The peaks at $\phi_r = \pi/2$ are not equaled to those at $\phi_r = 3\pi/2$, which shows that the rotational angular momentum vectors of the products of the reaction are mainly aligned along y -axis of the CM frame. As can be seen from the figure 5, The peaks of $P(\phi_r)$ is increased with increasing collision energies, which imply that product orientation become stronger. We examine trajectories and that determine the reactant and product orbital momenta have propensity for being parallel to each other. The strong propensity for parallel orientation of \mathbf{l} and \mathbf{l}' , combined with the angular momenta conservation and the fact that \mathbf{j}' lie perpendicular to the $\mathbf{k}-\mathbf{k}'$ plane, at ϕ_r angles close to $\pi/2$ and $3\pi/2$, suggest that the reaction proceeds preferentially when the reactant velocity vector lies in a plane containing all three atoms.

The integral cross section is show in figure 6. The inset in figure 6 shows the cross section we have calculated for the collision energy from 0.056 eV ($= 1.3$ kcal/mol) to 1.865 eV ($= 43$ kcal/mol), and the figure 7 is the inset of figure 6 zoomed in. The cross section is obtained by a full partial wave summation without any empirical interpolation or extrapolation. It is clearly seen that near zero collision energies, the cross sections are very large and decrease sharply in the low energy region when $E_c < 0.2$ eV, reflecting on the barrierless nature of the insertion reaction. However, at higher collision energies, the cross section values remain almost constant.

In order to get more dynamics information, we compare the reaction cross section for the $\text{O}(^1\text{D}) + \text{H}_2(v=0, \mathbf{j}=0) \rightarrow \text{OH} + \text{H}$ reaction obtained on the

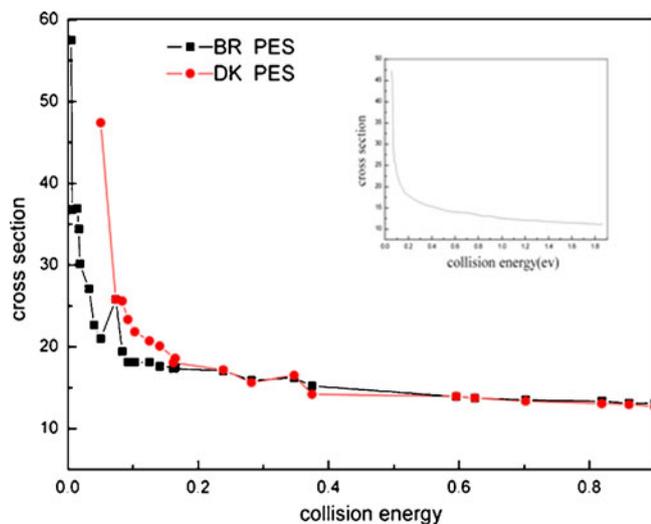


Figure 6. Collision energy dependence of the reaction cross section for the $O(^1D) + H_2 \rightarrow OH + H$ reaction. Solid line with circle: Chebyshev wave packet method of Lin *et al.*²⁸ Solid line with square circle: QCT calculations. The inset shows the details about cross section from 0.0564 eV ($= 1.3$ kcal/mol) to 1.865 eV ($= 43$ kcal/mol) on the DK surface. And the units of cross section is (A^2).

DK PES using the QCT method with those obtained on the BR surface using Chebyshev wave packet method²⁸ in figure 6. In our program, we can not calculate cross sections when collision energy is smaller than 0.01 eV, so we compare them for energies above 0.01 eV. It is

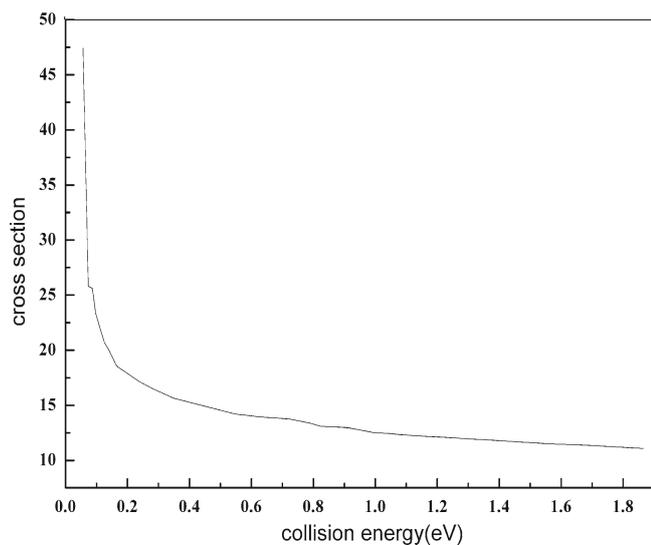


Figure 7. The details about cross section from 0.0564 eV ($= 1.3$ kcal/mol) to 1.865 eV ($= 43$ kcal/mol) on the DK surface. The units of cross section is (A^2).

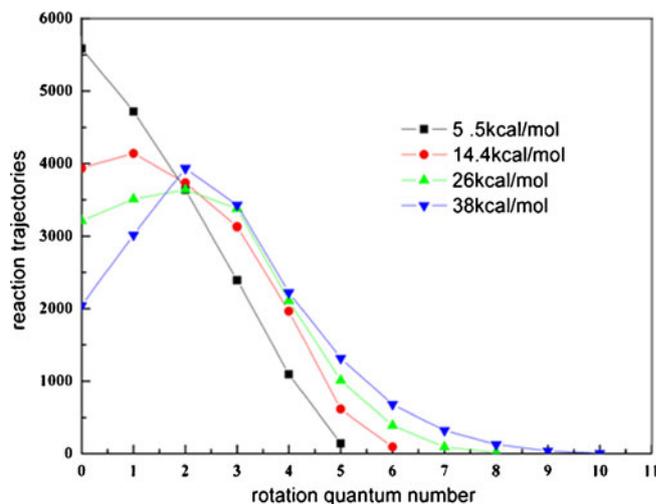


Figure 8. The correlation of reactive trajectories and rotation quantum number for the four collision energies.

seen that for collision energies above 0.2 eV, the results are obtained on the two PES are almost identical, but an important difference appears for collision energy lower than 0.1 eV, where the cross section obtained using the DK surface are larger than those obtained using the BR surface. The difference of reactive cross section between the BR surface and DK surface at low collision energies may arise from differences on the long range regions of the potentials. The gradients on the van der Waals valley are expected to have some consequences in the dynamics of the $O(^1D) + H_2 \rightarrow OH + H$ reaction at low collision energies. It should promote the reorientation of the hydrogen molecule towards the collinear geometry, relating to the O atom's direction. But at higher collision energies, the influence of the long-range force on the reaction seems to become less significant and the total reactivity is largely controlled by the short range features of the PES near the reaction barrier.

In figure 8, one can note that there are different product rotation quantum numbers for different collision energies from 5.5 kcal/mol to 38 kcal/mol. In addition, the rotation quantum number is increased with increase in collision energy. We can also see that at different collision energies, the reaction probability is different. At 5.5 kcal/mol, about 5600 trajectories reacted with $j = 0$ and 4200 trajectories reacted with $j = 1$ at 14.4 kcal/mol, while 4600 trajectories with $j = 2$ at 26 kcal/mol, and 3900 trajectories when $j = 2$ at 38 kcal/mol. These imply that the reaction is more active for these values of j .

4. Conclusion

In this study, integral cross-section and stereodynamics information of the reaction $O(^1D)+H_2(v=0, j=0) \rightarrow OH + H$ were studied by the quasiclassical trajectory (QCT) method on the DK potential energy surface for collision energy in the range of 1.3 kcal/mol to 43 kcal/mol. Our calculated results were compared with Lin's results obtained by the Chebyshev wave packet method on the BR surface.²⁸ Our results agree well with results on BR surface for collision energy is above 0.2 eV. We have also shown the rotation quantum number and reaction trajectories correlation and is found that rotation quantum number is increased with increase in collision energy. Also, the four collision energy values, (5.5 kcal/mol, 14.4 kcal/mol, 26 kcal/mol, 38 kcal/mol), are chosen to show the vector correlations for the $O(^1D) + H_2 \rightarrow OH(v=0, j=0) + H$ reaction. It has been demonstrated that that with the increase of the collision energy, dihedral angle distribution of $P(\phi_r)$ becomes larger and the rotation alignment becomes weaker. Furthermore, the forward scattering becomes stronger than the backward scattering.

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