Commun. Comput. Chem. Vol.**1**, No.**4**, pp. 307-314
doi: 10.4208/cicc.2013.v1.n4.1 December 2013

COMMUNICATION

The Stereodynamics Study of the Reaction S + H_2 (v = 0-3, j = 0, 2, 4, 6) → SH + H

Guang-Ling Shan, Mei-Shan Wang[*] and Chuan-Lu Yang

School of Physics and Optoelectronic Engineering, Ludong University, Yantai, 264025, China

Received 18 Sep 2013; Accepted (in revised version) 7 Nov 2013

Abstract: The stereodynamics of the reaction S + H_2(v = 0-3, j = 0, 2, 4, 6) → SH + H are calculated by means of the quasi-classical trajectory method (QCT) using a recent analytical potential energy surface (PES) of Lv *et al*. [J. Chem. Phys., 136 (2012), 094308]. The reaction probabilities agree well with the previous accurate quantum dynamics results. Vector correlations such as the distributions of the differential cross sections (DCS), the angular distributions of $P(\theta_r)$, and $P(\phi_r)$ are presented at the collision energy of 1.6 eV. The effects of the reagent rovibrational excitation on the stereodynamics of the title reaction are also revealed.

AMS subject classifications: 81U10, 81V45

Keywords: Quasi-classical trajectory, Stereodynamics, Rovibrational excitation, Product polarization

The reaction S + H_2 plays an important role in atmospheric and combustion chemistry as a simplest containing-sulfur atom reaction. This reaction is one chief culprit of acid rain, air pollution, and global climate change [1]. In the past studies, considerable attention was focused on the electronic excitation effect on the reaction dynamics of atomic sulfur and the possible role of intersystem crossing between triplet and singlet potential surface [2-7]. In order to study its reactive dynamics, the construction of an accurate PES is necessary. In 1983, Martin constructed the first PES for the reaction H + HS [8]. The determined transition state was found to be linear with R_{HH} = 2.6 a_0 and R_{HS} = 2.6 a_0. In 2004, Maiti *et al*. constructed the PESs of the two lowest triplet states of SH_2($^3A''$ and $^3A'$) to study the intersystem crossing effects on the S(^1D,^3P) + H_2 → HS + H [9]. In 2007, Klos *et al*. constructed an

---

[*] Corresponding author. *Email address*: mswang1971@163.com (M.-S. Wang)

analytical PES of $H_2S(^3A'')$ at the multi-reference configuration interaction (MRCI)/aug-cc-pVQZ (AVQZ) level [10]. Recently, Lv *et al*. obtained a new high-quality LZHH (Lv-Zhang-Han-He) PES for the lowest triplet state of $H_2S(^3A'')$ at the MRCI/aug-cc-pV5Z level [11]. Based on the PES, they presented an exact QCT calculation and quantum dynamical (QM) studies for the H + HS reaction and the results were supported by each other. Then, Lv *et al*. carried out the quantum scattering dynamics calculation of the title reaction using the time-dependent wave-packet method (TDWP) [12]. They found that both vibrational and rotational excitation of reactant HH would enhance the reactivity of the title reaction. However, it has been so far no answer to what the influence of the vibration and rotational excitation on the stereodynamics of the title reaction is . In the present work, we will investigate this problem.

The QCT calculations have been performed on the $^3A''$ SH_2 ab initio PES constructed by Lv *et al* [11].The ab initio single-point energies are calculated exploiting the aug-cc-pV5Z [13] set of Dunning and the MRCI method [14-16]. As obtained from the PES, the barrier height is 1.043 eV relative to the reactant S + H_2 asymptote, the endoergicity, considering the zero point energy, is 0.854 eV and the transition state for the title reaction is linear with $R_{HH} = 2.54$ a_0 and $R_{SH} = 2.62$ a_0. For more details of the PES, readers can refer to Ref. [11].

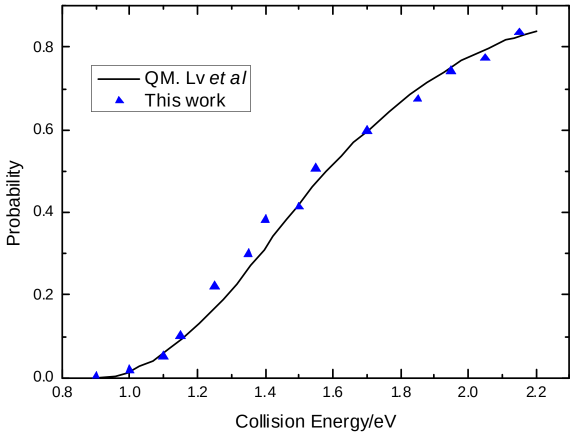

Figure 1: Comparison of the reaction probabilities between our QCT result and TDWP calculations for the S (^3P) + H_2 ($v = 0, j = 0$) reaction.

The employed QCT methodology is standard and its theoretical details are described elsewhere [17-23], so only some brief details will be given here. 100000 trajectories have been calculated on $^3A''$ PES for the title reaction. The collision energy is set to 1.6 eV for the present calculations and the rovibrational states of the reagent H_2 molecule are taken as v = 0-3 and j = 0, 2, 4, 6, respectively. In our calculation, the integration step is chose to be 0.1 fs, which can ensure good convergence of the results. In order to ensure no interaction between the attacking atom H and the center-of-mass (CM) of the molecule H_2, the distance between them is set to 20 Å. The orientation of the diatomic molecule and the phase of the diatomic vibrational motion are randomly sampled by a Monte Carlo method.

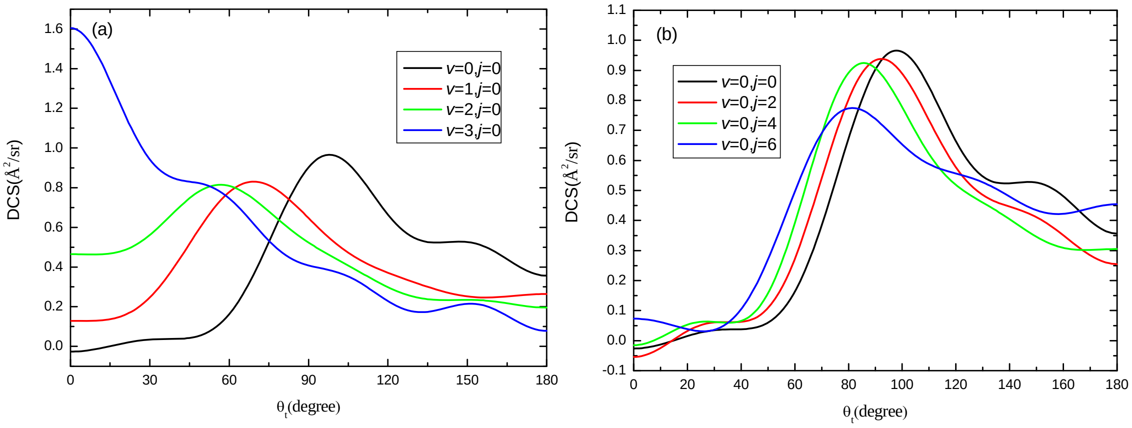

Figure 2: DCSs for the S(^{3}P) + H$_2$ → HS + H reaction at E$_{col}$ =1.6 eV and for rovibrational states (a) v = 0-3, j = 0. (b) v = 0, j = 0, 2, 4, 6.

Table 1 Distributions of impact parameters b_{max}, numbers of reaction trajectories N_r for the reaction S (^{3}P) + H$_2$(v = 0-3, j = 0, 2, 4, 6) → HS + H.

States	N	b_{max}(Å)	N_r
v=0, j=0	100000	1.3944	15387
v=1, j=0	100000	1.9900	29225
v=2, j=0	100000	2.3130	39849
v=3, j=0	100000	2.5500	46748
v=0, j=2	100000	1.3950	17611
v=0, j=4	100000	1.4650	21976
v=0, j=6	100000	1.6200	27347

We compare our QCT results of the reaction probability with the corresponding TDWP results given by Lv *et. al* [12]. **Figure 1** present the reaction probabilities of the reaction S (^{3}P) + H$_2$(v = 0, j = 0) as a function of collision energy. Clearly, the threshold energy of the title reaction is about 0.9 eV, and the reaction probabilities tend to increase monotonically with increasing the collision energy. The QCT results are slightly bigger than the quantum results at some collision energies, however, the QCT values are in good agreement with the quantum results on the whole. One can conclude that the QCT calculations for the title reaction are reliable. Because of the simple feature of the PES: there is a straight uphill route and downhill route in S (^{3}P) + H$_2$ → HS + H reaction, and the reaction probability increase monotonically with the increasing collision energy. Therefore, we'll only focus our attention on the stereo-dynamics of the title reaction at the middle energy E_{col} = 1.6 eV in the present studies. The effect of other collision energies on the stereo-dynamics of the title reaction can be found in our future work.

The DCSs for the reaction S (^{3}P) + H_2 → HS + H describing ***k*-*k*′** correlation at E_{col} = 1.6eV are presented in **Figure 2(a)** and **2(b)**. It is clearly that the peak of DCS distribution appears at $\theta_t = 100^o$ for v = 0, j = 0, which is indicates that the product SH molecules prefers both sideway scattering and backward scattering. From **Figure 2(a)**, one can see that the degree of the sideway and backward scattering decreases and the degree of the forward scattering increases obviously as the increase of v. In other words, the angular distribution of the product evolves from the sideway and backward into the forward direction as the increase of v. As shown in **Figure 2(b)**, the title reaction prefers both the sideway scattering and backward scattering for the rotational excitation from j = 0 to 6. With the increase of j, the degree of the backward scattering also decreases and the sideway scattering increases. Clearly, one can see from **Table 1**, as v or j increases, the maximum value of the impact parameter grows obviously. The range of impact parameter for which reaction is possible is evidently enlarged. It is well known, larger impact parameters imply a lower radial energy. Consequently, the degree of the backward scattering decreases. Moreover, the vibration and rotation of the H_2 seem to couple very efficiently with the motion on the barrier, compensating the lack of radial energy and helping to surmount the barrier. Consequently, the number of reaction trajectories increasing with v or j increase, which can be seen from **Table 1**.

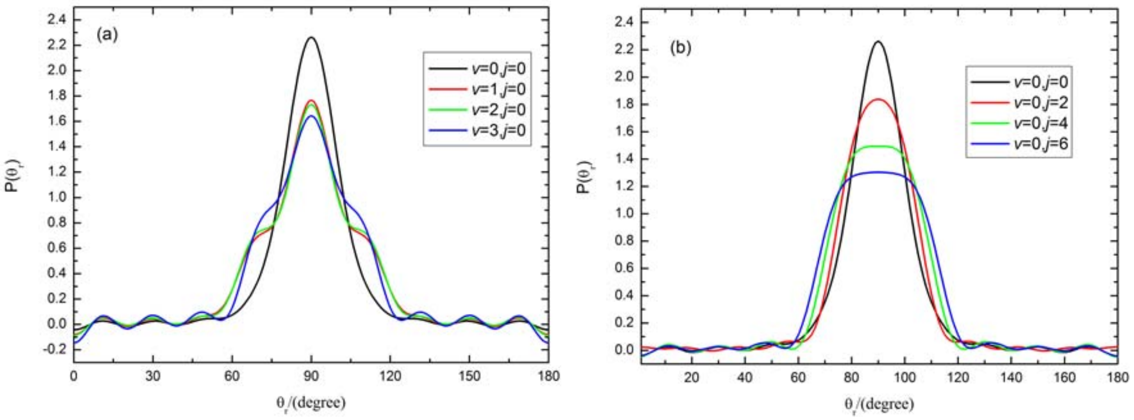

Figure 3: Distributions of $P(\theta_r)$ for the S(^{3}P) + H_2 → HS + H reaction at E_{col} = 1.6 eV and for rovibrational states (a) v = 0-3, j = 0. (b) v = 0, j = 0, 2, 4, 6.

The calculated distributions of $P(\theta_r)$ of the product SH, which describes the ***k*-*j*′** correlation for different rovibrational states are shown in **Figure 3**. In all cases, The $P(\theta_r)$

distributions exhibit a maximum at $\theta_r = 90^{\circ}$ and symmetric with respect to $\theta_r = 90^{\circ}$, which indicated that the product rotational angular momentum vector $\boldsymbol{j}'$ is strongly aligned along the direction perpendicular to the reactant relative velocity $\boldsymbol{k}$. **Figure 3(a)** corresponds to the $P(\theta_r)$ distributions for v = 0-3, j = 0, and **Figure 3(b)** for v = 0, j = 0, 2, 4, 6. As shown in the **Figures 3(a)** and **3(b)**, the $P(\theta_r)$ distributions become lower and broader with the increase of the reagent vibrational or rotational excitation, which means that the alignment degree of the product becomes weaker when the reagent is in the higher excited vibrational or rotational state. The same phenomena can be found in the O(^{3}P) + H_2 reaction [24]. It is well known, the alignment parameter $\langle P_2(\boldsymbol{j}'\cdot\boldsymbol{k})\rangle$ is another way to express the degree of product rotational polarization [22], the closer the value of $\langle P_2(\boldsymbol{j}'\cdot\boldsymbol{k})\rangle$ reachs -0.5, the stronger the product rotational alignment is along the direction perpendicular to the reagent relative velocity direction $\boldsymbol{k}$. One can see clearly that the calculated values of $\langle P_2(\boldsymbol{j}'\cdot\boldsymbol{k})\rangle$ shown in **Table 2**, are consistent with the $P(\theta_r)$ distributions. With the increase of the rotation-vibration coupling of the H_2 molecule, the centrifugal barrier of the title reaction is enlarged. The centrifugal barrier causes the memory losses of the angular momentum alignment with the various directions of the products in space, and then the alignment degree of the product becomes weak.

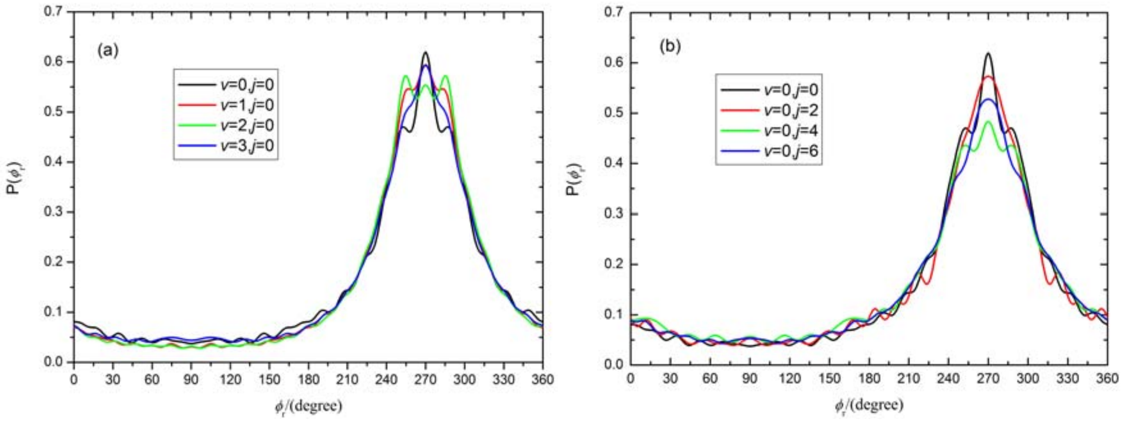

Figure 4: Distributions of $P(\phi_r)$ for the S(^{3}P) + H_2 → HS + H reaction at E_{col} = 1.6 eV and for rovibrational states (a) v = 0-3, j = 0. (b) v = 0, j = 0, 2, 4, 6.

The $P(\phi_r)$ distributions shown in **Figure 4** describe the $\boldsymbol{k}$-$\boldsymbol{k}'$-$\boldsymbol{j}'$ vectors correlations at E_{col} = 1.6eV, revealing the product SH rotational polarization and its rovibrational-dependent behaviors. Clearly, the $P(\phi_r)$ distributions are asymmetric with respect to the $\boldsymbol{k}$-$\boldsymbol{k}'$ scattering plane (or about $\phi_r = 180^{\circ}$) and a conspicuous peak appears at $\phi_r = 270^{\circ}$for all the rotational and vibration states, which indicate a marked product alignment along the y-axis and a marked product orientation pointing to the negative direction of the y-axis. It also indicates that there is a preference for the right-hand rotation of the product in the plane which is parallel to the scattering plane. One can see from **Figure 4(a)**, the effect of the vibrational excitation on the product alignment is not obvious. As **Figure 4(b)** depicted, for the different rotational states, the peak of $P(\phi_r)$ distribution decreases and becomes a little narrower with the increasing rotational quantum number, which reflects that the polarization of the product's rotational angular momentum is reduces with the increase of reagent's rotational quantum number. Therefore, the reagent's rotational excitation has a negative influence on the polarization of the product's rotational angular momentum.

Table 2 Values of product rotational alignment parameter calculated for initial rotation and vibration states $v = 0$, $j = 0$-3 and $v = 0$-3, $j = 0$.

State(v, j)	(0,0)	(1,0)	(2,0)	(3,0)	(0,2)	(0,4)	(0,6)
$\langle P_2(\boldsymbol{j}'\cdot\boldsymbol{k})\rangle$	-0.438	-0.395	-0.386	-0.384	-0.433	-0.418	-0.401

In the present paper, we study the vector corrections between the reagent and product for $S + H_2 \rightarrow SH + H$ reaction using a QCT method on the new PES constructed by Lv *et al*. The DCS and the distributions of $P(\theta_r)$, and $P(\phi_r)$ in the different rovibrational states are discussed. The calculated DCSs show that the title reaction changes from the side-backward scattering to the forward scattering with the increase of v, and the trend of the product sideway-scattering becomes stronger and the trend of the product backward-scattering becomes weaker with the increase of j. The $P(\theta_r)$ distribution shows that the alignment degree of the product of the title reaction decrease with the increase of v or j. Besides, the reagent's rotational excitation has a negative influence on the polarization of the product's rotational angular momentum.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos.11074103, 10974078 and 11174117). All calculations were carried out in the Shuguang Super Computer (sscc) of Ludong University. The author thanks Dr. Shuang-Jiang Lv for providing the potential energy surface.

References

[1] Y.Z. Song, P.J.S.B. Caridade and A.J.C. Varandas, Potential energy surface for ground-state H_2S via scaling of the external correlation, comparison with extrapolation to complete basis set limit, and use in reaction dynamics J. Phys. Chem. A., 113 (2009), 9213-9219.

[2] H. Shiina, M. Oya, K. Yamashita, A. Miyoshi and H. Matsui, Kinetic studies on the pyrolysis of H_2S, J. Phys. Chem., 100 (1996), 2136-2140.

[3] T.S. Chu, K.L. Han and G.C. Schatz, Significant nonadiabatic effect in the S(^{1}D) + HD reaction, J. Phys. Chem. A., 111 (2007), 8286-8290.

[4] T.S. Chu, Y. Zhang and K.L. Han, The time-dependent quantum wave packet approach to the electronically nonadiabatic processes in chemical reaction, Int. Rev. Phys. Chem., 25 (2006), 20-235.

[5] H. Yang, K.L. Han, G.C. Schatz, S.C. Smith and M. Hankel, Exact and truncate Coriolis coupling calculation for the S(^{1}D) plus HD reaction employing the ground adiabatic electronic state, Phys. Chem. Chem. Phys., 12 (2010), 12711-12718.

[6] H. Shiina, A. Miyosh and H. Matsui, Investigation on the insertion channel in the S(^{3}P) + H_2 reaction, J. Phys. Chem. A., 102 (1998), 3556-3559.

[7] K. Tsuchiya, K. Yamashita, A. Miyoshi and H. Matsui, Study on the reaction of atomic sulfur (^{3}P) with H_2, D_2, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, and i-C_4H_{10}, J. Phys. Chem., 100 (1996), 17202-17206.

[8] R.L. Martin, A theoretical study of the reaction H + HS → H_2 + S, Chem. Phys., 82 (1983), 337-341.

[9] B. Maiti, G.C. Schatz and G. Lendvay, Importance of intersystem crossing in the S(^{3}P, ^{1}D) + H_2 → SH + H reaction, J. Phys. Chem. A., 108 (2004), 8772-8781.

[10] J.A. Klos, P.J. Dagdigian and M.H. Alexander, Theoretical study of the multiplet branching of the SD product in the S(^{1}D) + D_2 → SD($^2\Pi$) + D reaction, J. Chem. Phys., 127 (2007), 154321(1)-154321(10).

[11] S.J. Lv, P.Y. Zhang, K.L. Han and G.Z. He, Exact quantum scattering study of the H + HS reaction on a new ab *initio* potential energy surface $H_2S(^3A'')$ J. Chem. Phys., 136 (2012), 094308(1)-094308(7).

[12] S.J. Lv, P.Y. Zhang, M.Y. Zhao and G.Z. He, Quantum wave packet dynamics study of the S(^{3}P) + H_2 reaction on the lowest $SH_2(1^3A'')$ state, Comp. Theor. Chem., 997 (2012), 83-87.

[13] P. A. Kendall, T. H. Dunning and R. J. Harrison, Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions, J. Chem. Phys., 96 (1992), 6796-6807.

[14] P. J. Knowles and H. J. Werner, An efficient method for the evaluation of coupling coefficients in configuration interaction calculations, Chem. Phys. Lett., 145 (1988), 514-522.

[15] H. J. Werner and P. J. Knowles, An efficient internally contracted multiconfiguration-reference configuration interaction, J. Chem. Phys., 89 (1988), 5803-5815.

[16] P. J. Knowles and H. J. Werner, Internally contracted multiconfuguration-reference configuration interaction calculations for excited states, Theor. Chim. Acta., 84 (1992), 95-103.

[17] K.L. Han, G.Z. He and N.Q. Lou, Effect of location of energy barrier on the product alignment of reaction A + BC, J. Chem. Phys., 105 (1996), 8699-8704.

[18] K.L. Han, L. Zhang, D.L. Xu, G.Z. He and N.Q. Lou, Experimental and theoretical studies of the reaction of excited calcium atoms with ethyl and n-propyl bromides, J. Phys. Chem. A., 105 (2001), 2956-2960.

[19] M.L. Wang, K.L. Han and G.Z. He, Product rotation polarization in photo-initiated bimolecular reactions A + BC: Dependence on the character of the potential energy surface for different mass combination, J. Phys. Chem. A., 102 (1998), 10204-10210.

[20] M.D. Chen, K.L. Han and N.Q. Lou, Theoretical study of stereodynamics for the reaction Cl + H_2/HD/D_2, J. Chem. Phys., 118 (2003), 4463-4470.

[21] F.J. Aoiz, L. Banares and V.J. Herrero, Recent results from quasiclassical trajectory computations of elementary chemical reactions, J. Chem. Soc., Faraday Trans., 94 (1998), 2483-2500.

[22] F.J. Aoiz, M. Brouard and P.A. Enriquez, Product rotational polarization in photon-initiated bimolecular reactions, J. Chem. Phys., 105 (1996), 4964-4982.

[23] F.J. Aoiz and L. Banares, J.F. Castillo and V.J. Herrero, Comment on "Reaction cross sections for the H + $D_2(v = 0,1)$ system for collision energies up to 2.5 eV: A multiconfiguration time-dependent Hartree wave-packet propagation study", J. Chem. Phys., 111 (1999), 9891-9892.

[24] Z.H. Xu, F.J. Zong, B.R. Han, S.H. Dong, J.Q. Liu and F. Ji, Effects of reagent's rotational and vibrational excitations on reaction $O(^3P) + H_2(v = 0, 3, j = 0, 3, 5, 7, 9, 12, 15) \rightarrow OH + H$, Chin. Phys. B., 21 (2012), 093103(1)-093103(9).