

## REGULAR ARTICLE

# Collision Energies Effect on Cross Sections and Product Alignments for the D+DS Reaction

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**Abstract:** Quasi-classical trajectory calculations were performed to study the abstraction and exchange processes in the title reaction on the lowest triplet state ( $^3A''$ ) potential energy surface [J. Chem. Phys. 136 (2012), 094308]. The reaction probabilities and integral cross sections, computed over the collision energies ( $E_c$ ) of 0.1-2.0eV, agree very well with the previous accurate quantum dynamics results. Alignments of the product molecules  $D_2$  and  $D'S$  have also been obtained and discussed.

**AMS subject classifications:** 81U10, 81V45

**Keywords:** Quasi-classical trajectory, Reaction probability, Integral cross section, Alignment

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## 1 Introduction

In the past several decades, chemical reactions involving sulfur atoms and sulfur-containing species have attracted much attention due to their importance role in combustion and atmospheric chemistry. Among them, the HHS system is considered to be one of the model systems for open shell reactions on account of its relatively simple electronic structure as well as its rich nonadiabatic singlet-triplet crossing effects [1-4]. The reaction  $H(^2S)+HS(^2\Pi)$  involves two singlet states ( $^1A',^1A''$ ) and two triplet states ( $^3A',^3A''$ ) and many ab initio electronic structure studies have been carried out concerning on this reaction. In 1983, using the configuration interaction (CI) method based on the ab initio self-consistent-field (SCF) with an extended Gaussian basis set, Martin constructed the

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potential energy surface (PES) for the reaction H+HS [5]. The determined transition state is found to be linear with  $R_{HH} = 2.6a_0$  and  $R_{HS} = 2.6a_0$ . Later, Maiti et al. constructed the PES of the lowest adiabatic state  $H_2S(^3A'')$  as they analysed the intersystem crossing effects in the  $S(^3P, ^1D) + H_2 \rightarrow SH + H$  reaction [6]. The 3D-spline interpolation method was utilized to construct the PES in the interaction areas and the asymptotic areas were constructed by a London-Eyring-Polanyi-Sato (LEPS) function. Carrying out trajectory surface-hopping calculations, they have found importance of intersystem crossing effect on the thermal rate constant at low temperature. In 2007, Klos et al. obtained a new global PES of the ground  $^3A''$  adiabatic electronic state at the MRCI/ aug-cc-pVQZ level [7].

Recently, Lv et al. reported a new LZHH (Lv-Zhang-Han-He) PES for the ground triple state  $^3A''$  of the H+HS reaction from accurate ab initio data on MRCI/aug-cc-pV5Z level [8]. Based on this PES, they performed an exact quantum dynamical (QM) study and quasi-classical trajectory (QCT) calculations of the total reaction dynamic properties. The results are in good agreement with each other and they have also found that the initial vibrational excitation of reactant HS would enhance the reactivity of both abstraction  $H(^2S) + HS(^2\Pi) \rightarrow H_2(X^1\Sigma^+) + S(^3P)$  and exchange  $H(^2S) + HS(^2\Pi) \rightarrow H(^2S) + HS(^2\Pi)$  channels. Later, on their newly-constructed global adiabatic PES for the excited  $^3A'$  triplet state of the HHS system, Lv et al. further studied the dynamical behavior of  $S(^3P) + H_2 \rightarrow HS + H$  utilizing the time-dependent wave packet quantum scattering method within the centrifugal sudden approximation and Coriolis Coupling approach [9].

As the isotope effects can provide significant and different dynamical view of chemical reaction on the same potential surface [10,11], Lv et al. also have done an exact quantum scattering investigation of the D+DS reaction and computed the scalar properties: reaction probability and integral cross section most recently [12]. As we know, with the development of laser techniques, the accurate measurement of the reagent/product orientation and alignment in molecular reactions has been available. The QCT calculation has been proved to be a powerful procedure to simulate the measured profiles. To the best of our knowledge, there has no QCT study of reaction dynamics for D+DS system. In this work, we have calculated the reaction probability and integral cross sections (ICS) as well as product alignment for collision energies ( $E_c$ ) below 2.0eV utilizing the newly LZHH  $^3A''$  ground PES for a better knowledge of the rich dynamical features of the title three-atom reaction.

## 2 Method

### 2.1 Potential energy surface

The potential utilized here is the ground-state adiabatic  $^3A''$  surface constructed by Lv et al. This analytical global surface was calculated exploiting the ang-cc-pV5Z basis set of Dunning and the MRCI method. As obtained from the analytical  $^3A''$  PES, the transition state for the abstraction channel is linear with  $R_{HH}=2.54a_0$  and  $R_{HS}=2.62a_0$  and the barrier height is 2.07kcal/mol (0.09eV) with respect to the reactant H+HS asymptote, while the exchange channel barrier is 7.15kcal/mol (0.31eV) and the transition state lies at linear geometry with  $R_{HS}=R_{HS}=2.87a_0$ . For more details of the PES, readers can refer to Ref. [8].

## 2.2 Quasiclassical trajectory calculations

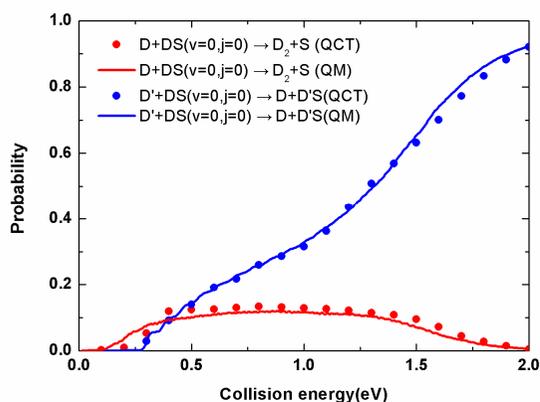
The calculation method of QCT is the same as that of Ref. [13-15]. The classical Hamilton's equations are numerically integrated in three dimensions. The collision energy ranges from 0.1 to 2.0eV in a step of 0.1eV. The reactants were prepared with initial vibrational and rotational quantum numbers  $v=0$  and  $j=0$ , respectively. A batch of 100000 trajectories was run for each energy for the title reaction and the time step is chosen to be 0.1fs which is sufficient for obtaining the converged results. The initial distance between the D atom and the DS molecule is 10 Angstroms. The impact parameter  $b$  is an important input parameter. The maximum value of it,  $b_{\max}$ , was determined by calculating 100000 trajectories at fixed values systematically increasing the value of  $b$  until no reactive trajectories were obtained [16]. The reaction probability,  $N_r/N$ , is the ratio of the number of reactive trajectories to the total number of trajectories, while the reactive cross section is defined as  $\sigma_r = \pi b_{\max}^2 (N_r / N)$ . The sampling error is defined as  $\sigma_r = \sqrt{\frac{N - N_r}{NN_r}} \times 100$  %, and the reactive cross section error in our calculation is defined as  $\sigma_{rs} = \sigma \sigma_r$ .

## 3 Results and discussion

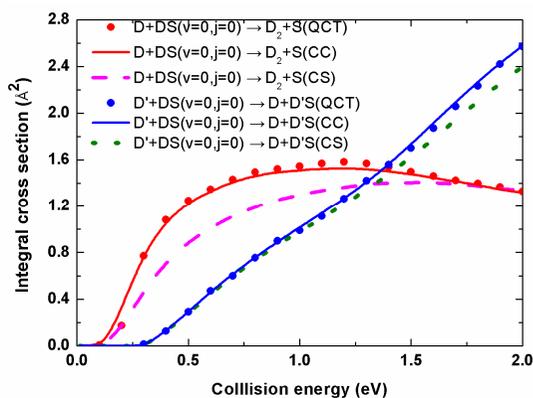
### 3.1 Reaction probabilities

**Figure 1** presents the D+DS ( $v=0, j=0$ ) reaction probabilities for the abstraction and exchange channels as a function of the collision energy. The quantum results calculated by Lv et al. was also plotted in the figure where the red line and the blue line correspond to the quantum results of  $D_2+S$  and  $D'S+D$  product branch, respectively. Our QCT results are found to be in good agreement with the quantum values [8]. That is to say, our QCT computations can describe the fine structures of the title reaction the same good as the QM numerations. It can be observed in **Figure 1** that the reaction probabilities of two product channels exhibit a

threshold at low collision energy and the representations of them with collision energy are quite different. The reaction probability of the exchange channel shows an overall increasing trend as the collision energy increases. In the case of the abstraction channel, nevertheless, the probability decreases slightly with increasing collision energy after a platform between 0.5 and 1.2 eV. All these features in **Figure 1** can be ascribed to the fact that both the abstraction and exchange reactions have respective energy barriers along their minimum energy paths. The threshold behavior is in well accordance with the barrier height difference of two product channels. For the probability of the abstraction and exchange channels, it is also noticeable that the former is dominant at low collision energy while the latter is taking the leading role as the collision energy exceeds the barrier height. This phenomenon shows that translation energy has active impact on the exchange reactivity and passive effect on the abstraction reactivity resulting from the larger acceptance cone of the exchange reaction with increasing reaction energy [17]. As we know, the QCT method has a shortage of its inability to handle the quantum tunneling effect of the reactive system and remarkable consistency of quantum and QCT results here indicates that no significant quantum effects exist in the title reaction.



**Figure 1:** Comparison of the calculated reaction probabilities as a function of collision energy for the abstraction and exchange reaction.



**Figure 2:** A comparison between the QCT and QM-CC/QM-CS cross section in the collision energy range of 0.0-2.0 eV for the abstraction and exchange reactions.

### 3.2 Integral cross sections

Now we focus on another important parameter—the integral cross section to interpret the internal mechanism of the  $D+DS$  reaction. **Table 1** and **Table 2** summarize the trajectory details (maximum impact parameter, number of computed and reactive trajectories) and the

resulting cross sections of the abstraction and exchange channels. The total reaction cross section as a function of collision energies for both abstraction and exchange channels are plotted in **Figure 2**. As presented in the panel, for the exchange channel, the QM-CC result is slightly overestimated with respect to the QM-CS one and our QCT value is closer to the QM-CC result. For the abstraction branch, the QM-CC curve is also higher than the QM-CS line and our QCT cross section is again in good agreement with the QM-CC one. Here, we can see that the reaction threshold of the QCT results is almost the same as that of the quantum outcomes, implying once again that the quantum effects have negligible influence on this system. The well consistence between QCT and QM outcomes demonstrated that the QCT method provides a rather reliable way to study the dynamical behavior for the title reaction system with computational efficiency and accuracy, just as the cases in many systems [18-22]. On further inspection it can be found that the QCT calculations well reproduce the quantum upward behavior for the exchange channel, it is also clear that the small cross section near 0.4eV is arising from the 0.31eV barrier height. As regards the abstraction channel, the cross section is rising sharply from  $0.15\text{\AA}^2$  to  $1.575\text{\AA}^2$  at the relative low energy range, and then is slightly falling to  $1.374\text{\AA}^2$  at high collision energy. This is because the  $D+DS \rightarrow D_2+S$  reaction is exothermic, and has an early barrier of 0.09eV. In addition, the larger cross sections of the exchange channel than that of abstraction pathway indicate that formation of the  $D'S$  product is easier than that of the  $D_2$  product in this reactive system.

**Table 1:** Distributions of impact parameters  $b_{\max}$ , numbers of reactive trajectories  $N_r$  integral cross sections  $\sigma_r \pm \sigma_{rs}$  for the reaction  $D + DS \rightarrow D_2 + S$

Collision energies(eV)	$N$	$b_{\max}(\text{\AA})$	$N_r$	$\sigma_r \pm \sigma_{rs}$
0.1	100000	1.4	119	0.0073±0.0916
0.2	100000	2.48	900	0.1739±0.0332
0.3	100000	2.6	3635	0.7720±0.0163
0.4	100000	2.62	5016	1.0817±0.0138
0.5	100000	2.655	5635	1.2479±0.0130
0.6	100000	2.655	6079	1.3462±0.0124
0.7	100000	2.65	6487	1.4312±0.0120
0.8	100000	2.665	6704	1.4958±0.0118

0.9	100000	2.6701	6802	1.5235±0.0117
1.0	100000	2.65	7012	1.5470±0.0115
1.1	100000	2.67	7010	1.5700±0.0115
1.2	100000	2.67	7070	1.5834±0.0115
1.3	100000	2.67	7004	1.5686±0.0115
1.4	100000	2.67	6872	1.5391±0.0117
1.5	100000	2.65	6798	1.5000±0.0117
1.6	100000	2.6518	6617	1.4618±0.0119
1.7	100000	2.66	6406	1.4240±0.0121
1.8	100000	2.665	6272	1.3994±0.0122
1.9	100000	2.667	6125	1.3687±0.0124
2.0	100000	2.67	5941	1.3306±0.0126

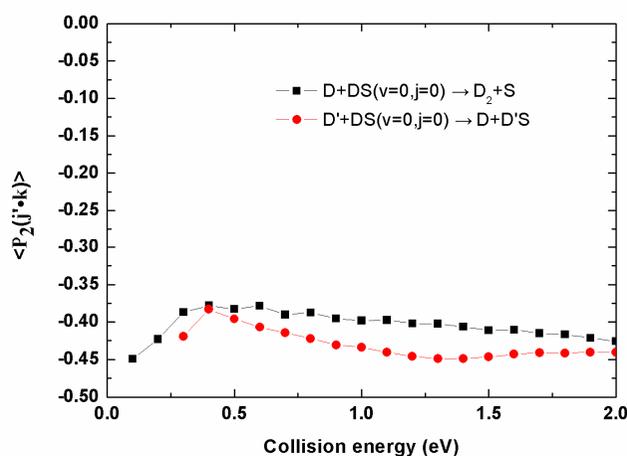
**Table 2:** Distributions of impact parameters  $b_{\max}$ , numbers of reactive trajectories  $N_r$  integral cross sections  $\sigma_r \pm \sigma_{rs}$  for the reaction  $D' + DS \rightarrow D'S + D$

Collision energies(eV)	$N$	$b_{\max}(\text{Å})$	$N_r$	$\sigma_r \pm \sigma_{rs}$
0.3	100000	0.606	1258	0.0145±0.0280
0.4	100000	0.97	4261	0.1260±0.0150
0.5	100000	1.144	7047	0.2897±0.0115
0.6	100000	1.2674	9330	0.4708±0.0099
0.7	100000	1.332	10724	0.5977±0.0092
0.8	100000	1.402	12213	0.7542±0.0085
0.9	100000	1.442	13772	0.8997±0.0079
1.0	100000	1.458	14812	0.9892±0.0076
1.1	100000	1.54	14927	1.1122±0.0075
1.2	100000	1.62	15349	1.2655±0.0074
1.3	100000	1.67	16213	1.4205±0.0072
1.4	100000	1.79	15492	1.5594±0.0074

1.5	100000	1.81	16551	1.7035±0.0071
1.6	100000	1.85	17403	1.8712±0.0069
1.7	100000	1.94	17403	2.0577±0.0069
1.8	100000	1.9	19687	2.2327±0.0064
1.9	100000	2.02	18871	2.4191±0.0066
2.0	100000	2.04	19680	2.5730±0.0064

### 3.3 Rotational alignment parameter

Besides the scalar properties, the vector characters about the reaction dynamics can be also obtained by using the QCT approaches. In the present work, we calculate only the rotational alignment parameter  $\langle P_2(j' \cdot k) \rangle$  of the product, as it alone can be measured in most experiments up to now. Here,  $j'$  represents the product angular momentum vector and  $k$  is the reagent initial relative velocity vector; the detail descriptions can be consulted Ref. [23].



**Figure 3:** product rotational alignment parameter as a function of collision energy for the abstraction and exchange reactions.

**Figure 3** displays the dependence of the product rotational alignment on collision energies. It is clear that the values are almost invariant with respect to collision energies. This is well consistent with previous calculations by Han group [14]. It is generally realized that a classical limiting value of -0.5 has existed for this product alignment parameter. Moreover, the larger the absolute value is, the stronger the product rotational alignment is along perpendicular to the reagent relative velocity direction  $k$ . An inspection of the **Figure 3**

shows that has a tiny peak at  $E_c=0.4\text{eV}$  for both the abstraction and exchange channels, and then becomes slightly negative with increasing collision energies for the two channels. The product D'S shows the sharpest alignment when is  $E_c=1.4\text{eV}$  and exhibits a more strongly aligned trend than the product  $D_2$  in the whole range.

## 4 Conclusion

In this paper we have employed the QCT method to study the influence of collision energy on the abstraction and exchange channels of the D+DS reaction based on the new global *ab initio* LZHH PES. It has been found that our QCT results about the reaction probabilities and the integral cross sections for the two channels are in good consistent with the quantum calculations presented by Lv et al. In addition, the rotational alignment of the product is calculated, and  $\langle P_2(j' \cdot k) \rangle$  values are almost invariant with respect to collision energies. Experimental studies about reaction probabilities, integral cross sections, and product rotational alignment effect on the title reaction are expected for further comparison of the experiment and theory.

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## References

- [1] L. Banares, J.F. Castillo, P. Honvault and J.M. Launay, Quantum mechanical and quasi-classical trajectory reaction probabilities and cross sections for the  $S(^1D)+H_2, D_2, HD$  insertion reactions, *Phys. Chem. Chem. Phys.*, 7 (2005), 627-634.
- [2] C. Berteloite, M. Lara, A. Bergeat, S.D. Le Picard, F. Dayou, K.M. Hickson, A. Canosa, C. Naulin, J.-M. Launay, I.R. Sim and M. Costes, Kinetics and Dynamics of the  $S(^1D) + H_2 \rightarrow SH + H$  Reaction at Very Low Temperatures and Collision Energies, *Phys. Rev. Letts.*, 105 (2010), 203201(1)-(4).
- [3] M. Lara, P.G. Jambrina, A.J.C. Varandas, J.M. Launay and F.J. Aoiz, On the role of dynamical barriers in barrierless reactions at low energies:  $S(^1D)+H_2$ , *J. Chem. Phys.*, 135 (2011), 134313(1)-(14).
- [4] T.S. Ho, T. Hollebeek, H. Rabitz, S. Der Chao, R.T. Skodje, A.S. Zyubin and A.M. Mebel, A globally smooth *ab initio* potential surface of the  $1A'$  state for the reaction  $S(^1D)+H_2$ , *J. Chem. Phys.*, 116 (2002), 4124-4134.
- [5] R.L. Martin, A theoretical study of the reaction  $H + HS \rightarrow H_2 + S$ , *Chem. Phys.*, 82 (1983), 337-341.

- [6] B. Maiti, G.C. Schatz and G. Lendvay, Importance of intersystem crossing in the  $S(^3P,^1D)+H_2 \rightarrow SH+H$  reaction, *J. Phys. Chem. A*, 108 (2004), 8772-8781.
- [7] J.A. Klos, P.J. Dagdigian and M.H. Alexander, Theoretical study of the multiplet branching of the SD product in the  $S(^1D)+D_2 \rightarrow SD(^2II)+D$  reaction, *J. Chem. Phys.*, 127 (2007), 154321(1)-(10).
- [8] 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)-(7).
- [9] S.J. Lv, P.Y. Zhang and G.Z. He, Time-dependent Wave Packet Quantum Scattering Study of Reaction  $S(^3P)+H_2 \rightarrow HS+H$  on a New ab initio Potential Energy Surface  $^3A'$ , *Chin. J. Chem. Phys.*, 25 (2012), 291-296.
- [10] T.S. Chu, A.J.C. Varandas and K.L. Han, Nonadiabatic effects in  $D^+ + H_2$  and  $H^+ + D_2$ , *Chem. Phys. Lett.*, 471 (2009), 222-228.
- [11] W.L. Li, M.S. Wang, C.L. Yang, X.G. Ma, D.H. Wang and W.W. Liu, Quasi-classical trajectory study of the cross sections of the reactions of  $D^+ + H_2 \rightarrow H+HD$  and  $H^+ + D_2 \rightarrow D^+ + HD$ , *Chem. Phys. Lett.*, 445 (2007), 125-128.
- [12] S.J. Lv, P.Y. Zhang and G.Z. He, Exact Quantum-Scattering Study of the  $D(^2S) + DS(^2II)$  Reaction, *Chin. Phys. Lett.*, 29 (2012), 073401(1)-(4).
- [13] K.L. Han, G.Z. He and N.Q. Lou, The theoretical studies of product alignment of the reactions of Na, F with  $CH_3I$ , *Chin. Chem. Lett.*, 4 (1993), 517-520.
- [14] 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.
- [15] M.L. Wang, K.L. Han and G.Z. He, Product rotational polarization in the photoinitiated bimolecular reaction  $A+BC \rightarrow AB+C$  on attractive, mixed and repulsive surfaces, *J. Chem. Phys.*, 109 (1998), 5446-5454.
- [16] V.W.-K. Wu, Product rotational angular momentum polarization in the  $H+FCl(v=0-5, j=0,3,6,9) \rightarrow HF+Cl$  reaction, *Phys. Chem. Chem. Phys.*, 13 (2011), 9407-9417.
- [17] B.N. Fu and D.H. Zhang, A Time-Dependent Quantum Dynamical Study of the  $H + HBr$  Reaction, *J. Phys. Chem. A*, 111 (2007), 9516-9521.
- [18] T.S. Chu, Quantum Mechanics and Quasiclassical Study of the  $H/D + FO \rightarrow OH/OD + F, HF/DF + O$  Reactions: Chemical Stereodynamics, *J. Comput. Chem.*, 31 (2009), 1385-1396.
- [19] T.S. Chu, H. Zhang, S.P. Yuan, A.P. Fu, H.Z. Si, F.H. Tian and Y.B. Duan, A Comparative Study of the  $H + FO (v=0, j=0) \rightarrow (OH + F)/(HF + O)$  Reaction from QM and QCT Methods, *J. Phys. Chem. A*, 113 (2009), 3470-3475.
- [20] J. Zhao, Y. Xu, D.G. Yue and Q.T. Meng, Quasi-classical trajectory study of the reaction  $H + FO \rightarrow OH + F$ , *Chem. Phys. Lett.*, 471 (2009), 160-162.
- [21] B.R. Han, H. Yang and Y.J. Zheng, A.J.C. Varandas, Quasi-classical trajectory and quantum mechanics study of the reaction  $H(^2S) + NH \rightarrow N(^4S) + H_2$ , *Chem. Phys. Lett.*, 493 (2010), 225-228.

- [22] Z.X. Duan, W.L. Li and M.H. Qiu, Influence of collision energy and reagent rotation on the cross sections and product polarizations of the reaction  $F + HCl$ , *J. Chem. Phys.*, 136 (2012), 144309(1)-(12).
- [23] F.J. Aoiz, M. Brouard and P.A. Enriquez, Product rotational polarization in photon-initiated bimolecular reactions, *J. Chem. Phys.*, 105 (1996), 4964-4982.