

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 D₂ and D'S have also been obtained and discussed.

AMS subject classifications: 81U10, 81V45

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

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