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

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Abstract: The stereodynamics of the reaction $S + H_2 (v = 0-3, j = 0, 2, 4, 6) \rightarrow SH + H$ 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 $P(\theta)$, and $P(\phi)$ 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 $S(^1D, ^3P) + H_2 \rightarrow HS + H$ [9]. In 2007, Klos *et al.* constructed an

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analytical PES of $\text{H}_2\text{S}(^3\text{A}'')$ 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 $\text{H}_2\text{S}(^3\text{A}'')$ 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 $\text{H} + \text{HS}$ 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 H_2 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 $^3\text{A}''$ 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 $\text{S} + \text{H}_2$ asymptote, the endoergicity, considering the zero point energy, is 0.854 eV and the transition state for the title reaction is linear with $R_{\text{HH}} = 2.54 a_0$ and $R_{\text{SH}} = 2.62 a_0$. For more details of the PES, readers can refer to Ref. [11].

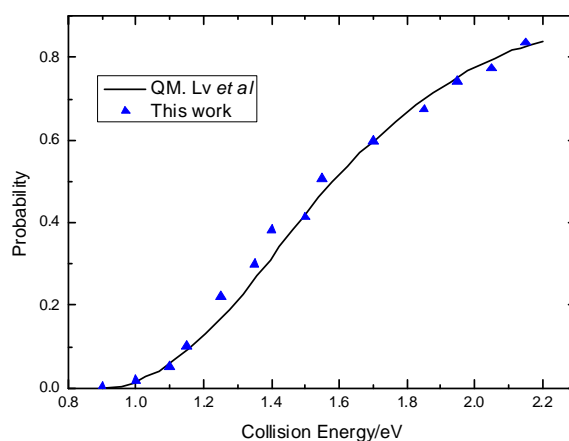


Figure 1: Comparison of the reaction probabilities between our QCT result and TDWP calculations for the $\text{S}(^3\text{P}) + \text{H}_2(v=0, j=0)$ reaction.

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 $^3\text{A}''$ 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 chosen 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