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Time-dependent wave packet state-to-state quantum dynamics study of the abstraction reaction $S(^3P) + H_2(v = 0, j = 0)$ on $1^3A''$ electronic state

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ABSTRACT

The state-to-state quantum dynamics of the abstraction channel of $S(^3P) + H_2(v = 0, j = 0)$ reaction is studied on the potential energy surface (PES) constructed by Lv et al. (2012), utilizing the product Jacobi coordinate based time-dependent wave packet method. Reaction probabilities and total integral cross section (ICS) agree well with previous results (Lv et al., 2012) for collision energies ranging from 0.8 to 1.4 eV. Results show that total differential cross sections (DCSs) for small collision energies have backward structures, whereas those for large collision energies are sideways peaked. Although the summed-over-all-final-state DCS for single collision energy is smoothly varied, the DCS of the product HS of a selected final state shows strong oscillations. For the selected final state, the opacity function derived by reaction probability multiplied by $(2J + 1)$, shows that different mechanisms relevant to several sets of J partial waves lead to the maxima in the differential cross section in the collision process.

1. Introduction

Sulfur compounds are important in combustion, atmospheric and environmental chemistry. Thus, their reactions have been well studied both experimentally and theoretically. The reaction of $S(^1D, ^3P) + H_2$, as well as its reverse reaction, is the simplest reaction that can be used to study sulfur properties. Due to spin-orbit coupling between singlet and triplet states, the importance of intersystem crossing between the two states in the $S(^1D, ^3P) + H_2$ reaction attracted great interest [1,2]. Meanwhile, the reagent excitation reaction $S(^1D) + H_2$ has been well investigated [2–10]. However, studies about the reaction $S(^3P) + H_2$ are rare. Shiina et al. [11] were the first to experimentally measure the rate constants for the reaction $S(^3P) + H_2 \rightarrow H + HS$ in a temperature range of 1050–1660 K by laser photolysis-shock tube atomic resonance spectrometry. They also pointed out that at low pressures below 2 atm, the main reaction path is an abstraction process that leads to the products of HS and H rather than the insertion process leading to the product H_2S. Shiina et al. [12] later showed that at the lower temperature range of 900–1050 K and a high pressure of up to 4 atm, the abstraction channel of the reaction $S(^3P) + H_2$ dominated over the insertion channel.

Shiina et al. [11] also constructed an ab initio potential energy surface (PES) to clarify the reaction mechanism of the reaction $S(^3P) + H_2$. As it can be seen from the potential energy surface (PES) [11], the activation energy of the simple hydrogen atom abstraction reaction $S(^3P) + H_2 \rightarrow H + HS$ is 82.5 kJ/mol. Tsuchiya et al. [13] reported a collinear $^3\Pi$ direct-abstraction potential energy surface. They showed that the reaction $S(^3P) + H_2 \rightarrow H + HS$ has a very small “late” barrier along the reaction coordinate, which is only 8.3 kJ/mol above the H +HS asymptote. Maiti et al. [1] proposed that the reaction $S(^3P) + H_2$ involves three PES($1^3A''$, $2^3A''$ and $^3A'$) and constructed the two lowest triplet states ($^3A''$ and $^3A'$). They studied intersystem crossing effects with a trajectory-hopping method. Calculations [1] show that intersystem crossing plays an important role particularly for the reaction starting from the collision energy close to the threshold of $S(^3P) + H_2$. This finding is due to the fact that intersystem crossing allows the reaction encounter with the singlet potential well rather than the triplet barrier. Recently, a high-quality ab initio PES for the abstraction reaction $S(^3P) + H_2$ of the lowest $1^3A''$ has been presented [14] and both calculations with Close-coupling (CC) and Centrifugal-Sudden approximations (CS) are achieved using time-dependent wave-packet (TDWP) method [15]. Calculations [15] show that collision energy enhances the reactivity of the title reaction. This finding has been confirmed by Shan et al. [16,17] in the investigation of stereodynamics of the title reaction with quasi-classical trajectory calculations.

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Table 1
The numerical parameters on the L-shaped grid used in the calculations

$S(^3P) + H_2$	
Diatomic coordinate range (R_{HH})	$R \in [0.5, 14.5]$
Number of grid points in R	$N_R^{total} = 108$, $N_R^{int} = 99$
Diatomic coordinate range (r_{HS})	$r \in [0.5, 14.5]$
Number of grid points in r	$N_r^{total} = 200$, $N_r^{int} = 100$
Number of angular basis function	$j_{max} = 140$
Number of vibrational basis function	$Vr^{Int} = 100$, $Vr^{asy} = 4$
Absorbing potential parameters	IPABS(R, r) = 2.0
	RABS(R/r) = 0.12/0.03
Initial wave packet	$Z_0 = 10.5$, $\delta = 0.7$, $E_0 = 1.1$
Total propagation time	$T_{total} = 10{,}000$, $\Delta t = 5$

All parameters are given a.u.

To our best knowledge, no nonadiabatic dynamic calculation has been performed for the reaction of $S(^1D, ^3P) + H_2$. Moreover, no study has been reported on the state-to-state dynamics of $S(^3P) + H_2(v = 0, j = 0)$ abstraction process on the lowest $1^3A''$. As a reference for future work, we present in this paper a detailed calculation of the title reaction implemented on graphics processing units (GPUs). GPUs provide hundreds of cores for efficient parallel computing and being used for nongraphic computing, such as in quantum chemistry. Baraglia et al. [18] recently developed a time-independent quantum reactive scattering code implemented on three central processing units (CPUs) and three GPUs which showed a 6.98 speedup. The speedup test on the reactive probability of the quantum scattering dynamics of $Cl + H_2$ and $N + N_2$ [19] is 2–20. In our work, the state-to-state quantum dynamics of $S(^3P) + H_2$ reaction is carried by a recently developed GPU code with TDWP method. Compared with the traditional serial CPU computation, the global speedup of the GPU version of TDWP code is 22–45 [20]. Product Jacobi coordinate [21] is chosen, and the Coriolis coupling effect [22–24] is completely considered. Integral cross sections (ICSs) and differential cross sections (DCSs) for collision energies from 0.8 to 1.4 eV are presented.

2. Theory

For a given total rotational angular momentum $\hat{J}$, the Hamiltonian of the title reaction $S(^3P) + H_2 \rightarrow H + HS$ in the body-fixed (BF) product Jacobi coordinate can be represented as [25]:

$$\hat{H} = -\frac{\hbar^2}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} + \frac{\left(\hat{J}-\hat{j}\right)^2}{2\mu_R R^2} + \frac{\hat{j}^2}{2\mu_r r^2} + V_{pes} \tag{1}$$

where R is the distance between H and the center of mass of HS, while r is the bond length of HS. The corresponding reduced mass μ_r is expressed as $\mu_r = m_H \times m_S/(m_H + m_S)$, and μ_R can be written as $\mu_R = m_H \times (m_H + m_S)/(2m_H + m_S)$. $\hat{J}$ is the total angular momentum operator, and $\hat{j}$ is the rotational angular momentum operator of HS. V_{pes} is the potential energy of the SH_2 system.

The initial Gaussian wave packet for the reactant in the space-fixed (SF) reactant Jacobi coordinate is expanded as:

$$|\chi_i\rangle = \varphi^{JM\varepsilon}_{\alpha v_0 j_0 l_0} = G(R_\alpha)\phi_{v_0 j_0}(r_\alpha)|JMj_0 l_0 \varepsilon\rangle \tag{2}$$

where $\phi_{v_0 j_0}(r_\alpha)$ is the rovibrational eigenfunction of H_2. $|JMj_0 l_0 \varepsilon\rangle$ represents the SF rotational basis and describes angular motion, with M being the projection of the total angular momentum J in SF coordinates for the initial state $v_0 j_0 l_0$. Afterwards, the initial wavepacket is projected from spaced-fixed representation to the BF representation, with rotational function $|JMj_o K\rangle$. K is the projection of total angular momentum J in BF coordinates. Then the initial wave packet in BF product Jacobi coordinate at the grid $(R_{v0}, r_{vi}, \theta_{vj}, K_\beta)$ is propagated on GPU by the split-operator scheme:

$$\varphi^{JMp}\left(\vec{R},\vec{r},t+\Delta\right) = exp\left(-i\hat{H}_0\frac{\Delta}{2}\right)exp\left(-i\hat{V}_{rot}\frac{\Delta}{2}\right)exp(-iV\Delta)exp\left(-i\hat{V}_{rot}\frac{\Delta}{2}\right) exp\left(-i\hat{H}_0\frac{\Delta}{2}\right)\varphi^{JMp}(\vec{R},\vec{r},t) \tag{3}$$

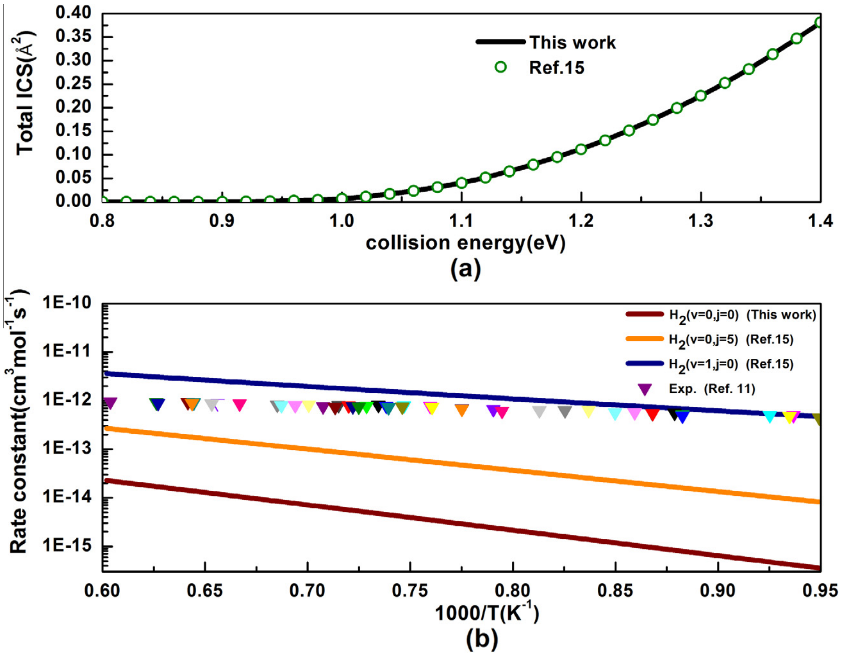

Fig. 1. (a) Comparison of the total integral cross section for the abstraction channel (dashed line) with the previous CC result (circles) [15] obtained from total reaction probability calculation. (b) Comparison of calculated thermal rate constants for the reaction $S(^3P) + H_2$ in different reagents ro-vibrational states on the lowest $1^3A''$ in the temperature range of 1052–1661 K with previous experimental results in the temperature range of 1050–1660 K by Shiina et al. [11]. (Wine line: our results for the $H_2(v = 0, j = 0)$; Orange line: rate constants for $H_2(v = 0, j = 5)$ calculated by the integral reaction cross sections in Ref. [15]; rate constants for $H_2(v = 1, j = 0)$ calculated by the integral reaction cross sections in Ref. [15]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)