



Effect of reagent vibrational excitation on reaction $S(^3P) + D_2$ in $^3A''$ and $^3A'$ states



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ABSTRACT

Time dependent wave packet method is applied to study the influence of reagent vibrational excitation on $S + D_2$ reaction in the new adiabatic triplet $^3A''$ and $^3A'$ potential energy surfaces, respectively. The reaction probabilities and integral cross sections as a function of collision energies are presented. The ν -dependent behavior of the integral cross sections on the two surfaces shows that the vibrational energy drives the reactivity more than the translational energy for this reaction. The comparison of the influences of vibrational excitation for different surfaces reveals that the vibrational energies of $^3A'$ state are more effective than that of $^3A''$ in enhancing integral cross sections. And the rotational excitation is also effective in enhancing the integral cross sections.

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1. Introduction

The $A + BC$ ($B, C = H, D$) type reactions like $F + H_2$, $Cl + H_2$, etc. have played important roles in studying elementary chemical reactions for the last decades [1–7]. As one of the benchmark $A + BC$ reactions, the $S(^1D, ^3P) + H_2$ reaction has been widely investigated both experimentally and theoretically by many groups because of its significant role in combustion [8] and atmosphere [9] chemistry. Among a series of studies, Lee and Liu [10] investigated the excitation functions and intriguing H/D isotope effect of $S(^1D) + H_2/D_2/HD$ using a crossed-beam apparatus, and found that the reagent rotation has significant effects on radical reactivity. Subsequently, Ho et al. [11] constructed a globally smooth potential energy surface (PES) for the $^1A'$ state of the $S(^1D) + H_2$ reaction, and carried out the quasi-classical trajectory (QCT) simulations. The comparison of the calculated results with the experimental data [10] indicated that this PES has more improvement than the earlier work [12]. Employing the DIFFREALWAVE code, Yang et al. [13] presented fully converged state-to-state integral and differential cross sections for $S(^1D) + HD$ reaction. Their results agree well with other theoretical results given by statistical and QCT calculations. To obtain the thermal rate constant for the $S(^1D) + H_2/D_2/HD$ reactions at room temperature, Song and Varandas [14] constructed a global PES of $H_2S(^1A')$, and performed the QCT calculation on it. The result is in reasonably good agreement with the experimental value [15]. Through adiabatic time-independent quantum mechanical calculations

and crossed-beam experiments, Lara et al. [16,17] investigated the integral cross sections for the $S(^1D) + H_2/HD$ reactions at low collision energies. They indicated that the integral cross sections observed are consistent with the theoretical calculations.

It is noted that most studies above focus mainly on $^1A'$ surface for $S(^1D) + H_2/D_2/HD$ reactions, and these efforts surely revealed the importance of the reaction $S + H_2$ and its isotopic variants. [18–24] However due to the spin-orbit coupling and intersystem crossing effects, the dynamics of the $S(^1D) + H_2$ reaction involves three PESs, i.e., $^3A'$, $^3A''$ and $^1A'$. From Fig. 1, it can be seen that the singlet $^1A'$ PES crosses the two lowest triplet ones ($^3A'$ and $^3A''$) in the reactant channel. In order to explore intersystem crossing effects on $S(^1D, ^3P) + H_2$ reaction, Maiti et al. [25] performed a QCT surface-hopping calculation in the $S(^3P)H_2$ and $S(^1D)H_2$ PESs, and found a remarkable effect of spin-orbit coupling close to the threshold on the $S(^3P) + H_2$ reaction. Based on two degenerate $^3A'$, a $^3A'$ [25], and a $^1A'$ [11] PESs, Chu et al. [26] presented a quantum nonadiabatic [7] study for the $S(^1D) + HD$ reaction using the time dependent wave packet (TDWP) method, and pointed that the important discrepancy of intramolecular isotope effects in simulation and experiment can be attributed to the significant nonadiabatic effects. In order to clearly reveal the dynamics mechanism of the $S(^3P) + H_2$ reaction, Lv et al. recently constructed new *ab initio* $^3A'$ [27] and $^3A''$ [28] PESs and calculated the reaction probabilities and integral cross sections with collision energies of 0.8–2.2 eV using TDWP method. Based on this $^3A''$ PES, Wang et al. [29] studied the stereodynamics of $S(^3P) + H_2$ reaction, and pointed out that this reaction is a direct reaction and the collision time becomes shorter with increasing collision energy. The integral cross sections

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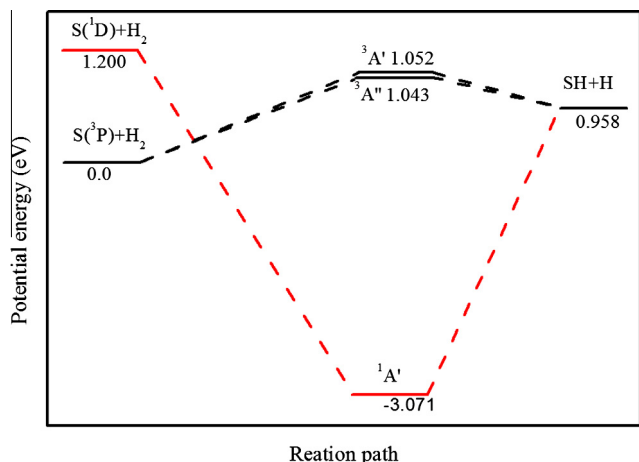


Fig. 1. Schematics of the reaction path for the $S(^1D)+H_2$ reaction and $S(^3P)+H_2$ reactions [25,27,28].

and thermal rate coefficients of $H+HS$ reaction on the $^3A''$ and $^3A'$ PESs were investigated by Duan et al. [30] employing QCT method [31]. The thermal rate coefficients given by the sum of both contributions from $^3A''$ and $^3A'$ PESs are in good agreement with the experimental results of Tiee et al. [32] For the adiabatic dynamics study, the $S(^3P)+D_2$ reaction involves two lowest triplets states, i.e., $^3A''$ and $^3A'$, and the integral cross sections can be obtained by summing the integral cross sections on this two states. However with the increase of the vibrational quantum number, the contribution from the two state is different. In this work we are dedicated to explore the dynamics mechanism of the vibrational excited for the $S(^3P)+D_2$ reaction on the adiabatic $^3A''$ [27] and $^3A'$ [28] PESs employing the TDWP [33] method. The emphasis is to be on the variation of effective potential barrier with the increase of vibrational quantum number and the influence of vibrational excitation on reactivity. The remainder of the paper is outlined as follows. Section 2 gives a brief description of the TDWP method to calculate the reaction probabilities and integral cross sections of the title reaction and the features of the $^3A''$ and $^3A'$ PESs. Section 3 presents the dynamical results and the detailed discussion on the reaction probabilities, integral cross sections, as well as the efficacies of vibrational excitation in promoting the reaction. The conclusions are summarized in Section 4.

2. Method

The TDWP method [33,34] is employed to study the $S+D_2$ reaction. For a given total angular momentum J , the Hamiltonian can be written in the reagents' Jacobi coordinates as

$$\hat{H} = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + \frac{(\hat{J}-\hat{j})^2}{2\mu_R R^2} + \frac{\hat{j}^2}{2\mu_r r^2} + V(R, r) + \hat{h}(r). \quad (1)$$

Here μ_R is the reduced mass of S and D_2 , R the distance between the center-of-mass of D_2 and S , r the vibrational coordinate of D_2 , \hat{J} the total angular momentum operator, and \hat{j} the rotational angular momentum operator of D_2 . The vibrational reference Hamiltonian $\hat{h}(r)$ is defined as

$$\hat{h}(r) = -\frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} + V(r), \quad (2)$$

where $V(r)$ is the reference potential of diatom D_2 . And the TD wave function can be written in terms of the body-fixed (BF) translational-vibrational-rotational basis as

$$\psi_{v_0 j_0 K_0}^{JMp}(R, r, t) = \sum_{n, v, j, K} F_{n v j K, v_0 j_0 K_0}^{JMp}(t) u_n^v(R) \varphi_{v j}(r) Y_{jK}^{JMp}(\hat{R}, \hat{r}), \quad (3)$$

where p stands for parity of the reaction system, n is the translational basis label, v and j are used to denote the initial rovibrational states of D_2 , and K is the projection of J on the BF z -axis. In the BF frame, the centrifugal term or the Coriolis coupling (CC) is off-diagonal in K states, so the CC calculation usually has a large matrix size, which makes the quantum calculations intractable to deal with. If these off-diagonal elements are neglected in the TDWP calculation, we can use centrifugal sudden (CS) approximation to decouple these K states and thus reduce the size of the matrix.

The split-operator scheme [35] is employed to propagate the wave packet. For a short time interval Δ , the wave packet $\psi(R, r, t + \Delta)$ at time $t + \Delta$ can be derived from $\psi(R, r, t)$,

$$\psi^{JMp}(R, r, t + \Delta) = e^{-i\hat{H}_0 \Delta / 2} e^{-i\hat{U} \Delta} e^{-i\hat{H}_0 \Delta / 2} \psi^{JMp}(R, r, t), \quad (4)$$

with the reference Hamiltonian \hat{H}_0 and effective potential operator \hat{U} being defined as

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} + V(r), \quad (5)$$

$$\hat{U} = \frac{(\hat{J}-\hat{j})^2}{2\mu_R R^2} + \frac{\hat{j}^2}{2\mu_r r^2} + V(R, r). \quad (6)$$

The product of a specific rovibrational eigenfunction and a localized translational wave packet is used as the initial wave function,

$$\psi(0) = u_{k_0}(R) \varphi_{v_0 j_0} Y_{j_0 K_0}^{JMp}(\hat{R}, \hat{r}), \quad (7)$$

where the wave packet $u_{k_0}(R)$ is chosen to be a standard Gaussian function

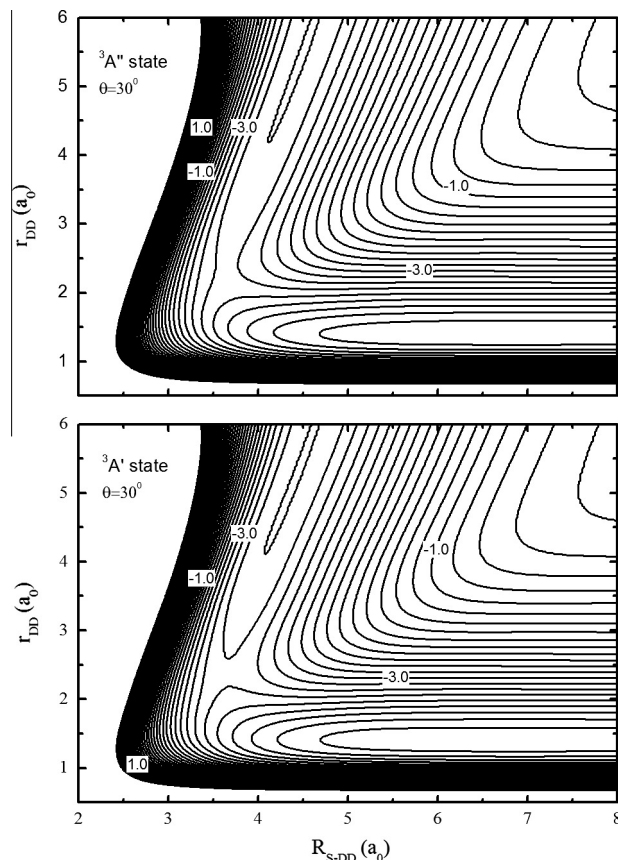


Fig. 2. The contours of the $^3A''$ and $^3A'$ PESs. Reactant Jacobi coordinates is used with a fixed Jacobi angle $\theta = 30^\circ$. The values indicated on the contour lines are in eV.

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