

ARTICLE

Barrier Height Effect on Cl+H₂(D₂) Reaction

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Three-dimensional time-dependent quantum wave packet calculation was performed to study the reaction dynamics of Cl+H₂(D₂) on two potential energy surfaces (CW PESs). The first CW PES is with spin-orbit correction; the second is without spin-orbit correction. The integral cross-section and reaction probability as a function of collision energy are calculated in the collision energy range of 0.1 eV to 1.4 eV. For reaction of Cl with D₂, the reaction section with spin-orbit correction has a shift toward the high energy because the barrier height increases. As for the reaction of Cl with H₂ at low collision energy, it is more reactive on the PES with spin-orbit correction than on the low barrier height PES without spin-orbit correction, due to the tunnel effect for the reaction of the Cl with H₂. When the collision energy is higher than 0.7 eV, the reactivity on the low barrier height PES is larger than that on the high barrier height PES. It is believed that the barrier height plays a very important role in the reactivity of Cl with (H₂, D₂). For the Cl+H₂ reaction the barrier width is also very important because of the tunneling effect.

Key words: Barrier height, Time-dependent wave packet, Cl+H₂(D₂) reaction

I. INTRODUCTION

The Cl+H₂ reaction as well as its two isotopic variants Cl+HD/D₂ has attracted much attention for a long time, due to the important role it plays in the development of gas-phase reaction dynamics. Such a reaction has been considered a prototypical three-atom reaction system in the field of molecular reaction dynamics and serves as a case study for bimolecular reaction rate theory, particularly for transition state theory [1-11]. Recent experimental measurement has found that the spin-orbit excited state of atomic chlorine is much more reactive than its spin-orbit ground state, in addition, there is a large isotope effect [12,13]. Such an unexpected result has stimulated many experimenters and theorists to study the system again.

On the experimental side, many dynamic studies of the Cl+D₂ reaction have been performed. Kumaran *et al.* reported the rate constant for the Cl+H₂ and Cl+D₂ reactions by the laser photolysis-resonance absorption (LP-RA) technique [14]. Alagia *et al.*, by high-resolution crossed molecular beam experiments, provided angular distributions and time-of-flight spectra for the Cl+D₂ reaction at collision energies of 24.5, 26.3 and 26.7 kJ/mol [15]. Balucani and co-worker also studied the dynamics of the Cl+D₂ reaction at collision energy of 20.5 and 26.3 kJ/mol using the crossed molecular beam technique [16]. Skouteris *et al.* reported the differential cross section for the reactions of Cl+D₂ and Cl+H₂ by using the crossed molecular beam method with mass spectrometric detection [17]. At the same time, by exploiting two different Cl-beam sources and

concurrently monitoring the concentrations of the two reagents (Cl(²P_{3/2}) and Cl*(²P_{1/2})) and the H atom and D atom product, Liu *et al.* found the reactivity of spin-orbit excited Cl*(²P_{1/2}) is much more larger than the ground state Cl(²P_{3/2}) reactant for the reaction of Cl+D₂ [13]. This surprising experimental result has led to the theoretical interest.

From a theoretical point of view, the calculation of an accurate potential energy surface (PES) is very critical for studying a reaction system. In 1936 a PES called an LEP-type surface of this reaction was proposed by Ryring *et al.* [18]. In 1996, impressive progress was made in constructing a PES for the Cl+H₂ reaction system when Allison *et al.* fitted a new PES (called G3) for the chemical reaction Cl+H₂→HCl+H based on the previous potential surface GQQ [19]. This PES incorporates an improved bending potential that is fit to the *ab initio* data. The G3 PES is a significant step forward in quantitative modeling of the Cl+H₂ reaction and has been used in a number of dynamical studies including quantum mechanical reactive scattering calculations [7,19,20]. The results obtained from exact quantum calculations on the G3 surface for the Cl+H₂ and Cl+D₂ reactions are in good agreement with the experimental rate constant, but the branching ratio for the reaction Cl+DH obtained on G3 surface strongly differs from the experimental measurements [21]. Allison *et al.* has ascribed this to the probably too thin collinear barrier existing in the G3 PES and to the more pronounced tunneling effect that allows [19].

In 2000, Bian *et al.* presented a new [22], fully *ab initio* PES called BW2 for the H₂+Cl reaction system. Accurate quantum calculation has been performed by Manthe *et al.* to investigate the thermal rate constant on the BW2 surface [23]. Excellent agreement with experimental measurement was obtained. In contrast to

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the G3 PES [21], the exact QM reactive scattering calculations for Cl+HD on the BW2 PES correctly predicted a large DCl/HCl branching ratio at low collision energies, which is in rather good agreement with the recent crossed molecule beam experiment measurements.

A lot of dynamic calculations on the BW2 surface indicated that the BW2 surface is very successful [24-27], but these do not include the spin-orbit coupling of the Cl atom because of the open-shell character of the Cl atom. In 2002, Alexander *et al.* fitted a new potential energy surface for the Cl+H₂ (named CW), which includes four potential energy surfaces and two spin-orbit interaction matrix elements. This PES was fitted to the accurate *ab initio* calculations using the least-squares method, and the dynamic calculation was carried out using an exact quantum, time-independent method. The results are strongly different from experimental data [28].

In this work, we aim to study the isotope effects of the spin-orbit coupling by employing the time-dependent wave packet (TDWP) method for the Cl+H₂(D₂) reaction on the two PESs developed by Capecchi and Werner, one which includes spin-orbit coupling and the other without spin-orbit coupling. The reaction probability and integral cross section at collision translation energy range of 0.1-1.4 eV are obtained.

II. THEORETICAL METHOD

In this work, we solve the time-dependent Schrödinger equation by the time-dependent wave packet (TDWP) method. We just briefly describe the TDWP method in this section; for more detail, the reader can refer to Ref.[29,30] and the references therein. The total Hamiltonian expressed in the reactant Jacobin coordinates for the Cl(²P_{3/2}, ²P_{1/2})+H₂(D₂) can be written as (in atomic units)

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

where μ_R is the reduced mass between atom and diatom, μ_r is the reduced mass of D₂, and \mathbf{L} is the orbital angular momentum operator of the atom around the center of mass of the diatomic. $h(r)$ is the diatomic reference Hamiltonian and defined as

$$h(r) = -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + V_r(r) \quad (2)$$

where $V_r(r)$ is the diatomic reference potential.

The expansive basis functions of the time-dependent wave function are written as

$$\Psi_{v_0, j_0, K_0}^{JM\varepsilon} = \sum_{n, v, j, K} F_{nvjK, v_0 j_0 K_0}^{JM\varepsilon} u_n^v(R) \phi_v(r) Y_{jK}^{JM\varepsilon}(\hat{R}, \hat{r}) \quad (3)$$

where $u_n^v(R)$ is the translational basis function

$$u_p^v = \begin{cases} \sqrt{\frac{2}{R_4 - R_1}} \sin\left(\frac{P\pi R}{R_4 - R_1}\right), & V_1 \leq V_{\text{asy}} \\ \sqrt{\frac{2}{R_2 - R_1}} \sin\left(\frac{P\pi R}{R_2 - R_1}\right), & V_1 > V_{\text{asy}} \end{cases} \quad (4)$$

where R_1 is inception value of radial coordinate R , R_2 and R_4 define the interaction and asymptotic grid respectively, and V_{asy} is the number of energetically open vibrational states plus a few closed vibrational states of the H₂(D₂). In Eq.(3), $\phi_v(r)$ is the vibrational basis, $Y_{jK}^{JM\varepsilon}(\hat{R}, \hat{r})$ is the spherical harmonic, J is the total angular momentum, and M is the projection of J along the space-frame z axis. K is the projection of J along the vector R . The definitions of various basis functions can be found elsewhere [29,30].

The split-operator method is employed to carry out the wave packet propagation [31]. The time-dependent wave function is absorbed at the edges of the grid to avoid boundary reflection [32]. The reaction probabilities are obtained through the flux calculation [29,30,33]

$$P_i^R(E) = \frac{\hbar}{\mu_r} \text{Im} \left(\langle \Psi_{iE}^+ | \delta(r - r_0) \frac{\partial}{\partial r} | \Psi_{iE}^+ \rangle \right) \quad (5)$$

where r is vibrational coordinate and μ_r is the reduced mass of D₂. The integral cross section can be obtained by summing the corresponding reaction probabilities over all the partial waves

$$\sigma_{v_0, j_0}(E) = \frac{\pi}{k_{v_0 j_0}^2} \sum_J (2J+1) P_{v_0 j_0}^J(E) \quad (6)$$

where $k = \sqrt{2\mu E}$, E is the collision energy, J is the total angular momentum, v_0 and j_0 denotes the initial vibration state and rotation state respectively, and $P_{v_0 j_0}^J$ is the reaction probability.

III. RESULTS AND DISCUSSION

We put an initial packet at $12a_0$, and then propagate it. The numerical parameters during the wave packet propagation are as follows: a total number of 190 sine functions are employed for the translational coordinate R from $1.0a_0$ to $20.0a_0$, and 60 vibrational bases are used for r in the range of $0.5a_0$ to $8.5a_0$ in the interaction region. For the rotational basis $j_{\text{max}}=40$ is used. The width of the initial wave packet is $0.16a_0$ in the R coordinate in order to cover a sufficient energy range of 0.1-1.4 eV. A propagation time of 16000 a.u. (a time step-size of 10 a.u. is used) can get convergent reaction calculations.

The total reaction probability, for the total angular momentum $J=0$, as a function of collision energy for the reaction of Cl with H₂(D₂) in its ground state are presented in Fig.1. As shown in Fig.1, the behavior of

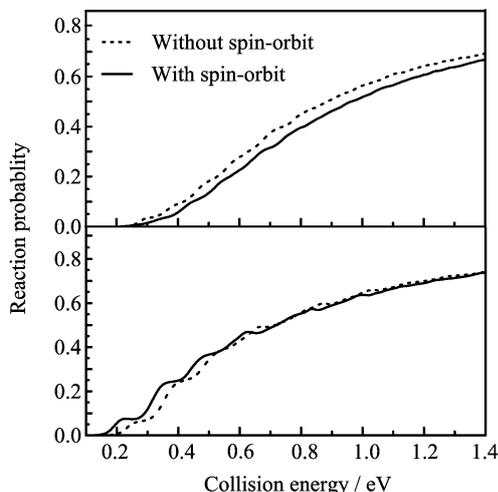


FIG. 1 Probabilities for the reaction of Cl+D₂ and Cl+H₂ ($v=0, j=0$) as a function of the collision energy for $J=0$ on CW PESs. The upper and lower panels correspond to the reaction of Cl+D₂ and Cl+H₂ respectively.

the reaction probability on the surface with spin-orbit correction and that without spin-orbit correction is different over the energy range of interest for the reaction of Cl+D₂ and Cl+H₂. It can be found that overall reaction probability without spin-orbit correction is higher than that with spin-orbit correction. Both reaction probabilities have the same shape, but there is a shift toward the high energy in the range of calculated energy when the spin-orbit coupling is included for the Cl+D₂ reaction. As for the collision of the Cl atom with H₂, in direct contrast to the Cl+D₂ reaction, it is more reactive while the spin-orbit coupling is included at low collision energy. At 0.3 eV, the reaction probability is 0.12 on the CW PES with spin-orbit correction, but only 0.07 without spin-orbit correction. As with the Cl+D₂ reaction, the Cl+H₂ reaction probability excluding spin-orbit coupling is larger than when including spin-orbit coupling at the high collision energy. These characteristics can also be found for the higher total angular momentum, for example, total angular momentum $J=20$ as illustrated in Fig.2.

Figure 3 shows the total reaction cross sections as a function of the translational energy, which are obtained by summing the corresponding reaction probabilities over all contributing J using Eq.(6). For the reaction of Cl with H₂ ($v=j=0$), the maximum value of J is 75, but it is 98 for the reaction of Cl with D₂ ($v=j=0$). As for the reaction probability, for the Cl+D₂ reaction, the reactivity obtained without spin-orbit correction is always larger than that with spin-orbit correction in the range of our calculated energy. As for the collision of the Cl atom with H₂, it is more reactive when the spin-orbit is included at the low collision energy; at the high collision energy, the reaction reactivity without spin-orbit correction is larger than that

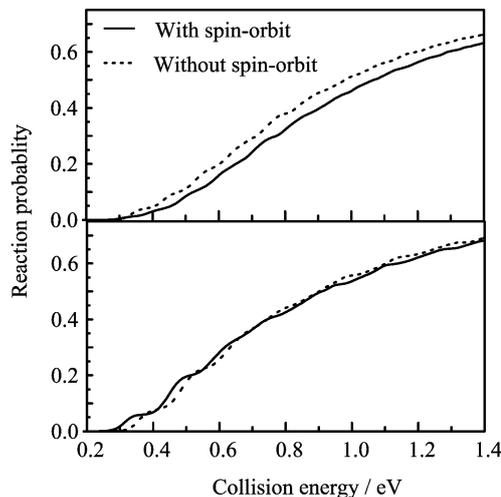


FIG. 2 Probabilities for the reaction of Cl+D₂ and Cl+H₂ ($v=0, j=0$) as a function of the collision energy for $J=20$ on CW PESs. The upper and lower panels correspond to the reaction of Cl+D₂ and Cl+H₂ respectively.

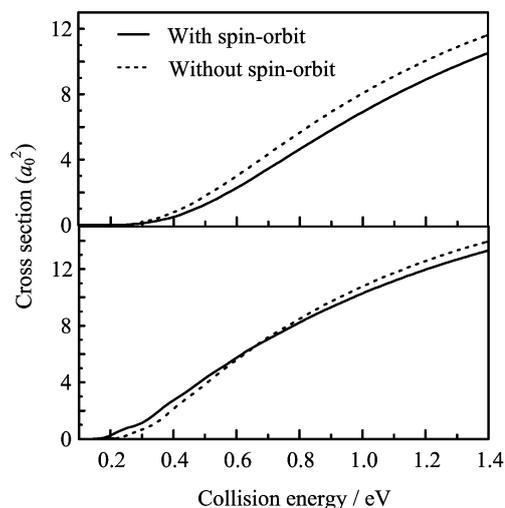


FIG. 3 The total integral cross sections for the reaction of Cl and D₂(H₂) with diatom in $v=0, j=0$ as a function of the collision energy on CW PESs. The upper and lower panels correspond to the reaction of Cl+D₂ and Cl+H₂ respectively.

with spin-orbit correction. The cross section with spin-orbit correction is $11.95a_0$ in comparison with $12.56a_0$ on the surface without spin-orbit correction at 1.2 eV.

As discussed by the Alexander and co-worker for the chemically similar F+H₂ reaction [34], at the entry channel, the energy with spin-orbit correction decreases by 3.5 kJ/mol. The spin-orbit element between the Π and Σ decreases when the Cl–H bond is formed. In the area near the barrier, the energy separation of the Π and Σ is very large, but the spin-orbit coupling element is small, so spin-orbit coupling almost has no effect in the barrier region. For the Cl+H₂ asymptoti-

cally, spin-orbit coupling lowers the energy by one-third of the Cl atom spin-orbit splitting, and the net result is an increase of the barrier height by 3.5 kJ/mol. The energies along reaction path with spin-orbit correction and without spin-orbit correction for the Cl+D₂ and Cl+H₂ reaction are presented in Fig.4.

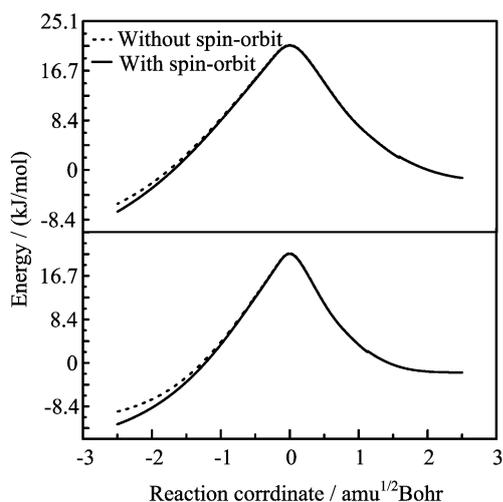


FIG. 4 The reaction path for the reaction of Cl and D₂(H₂). The upper and lower panels correspond to the reaction of Cl+D₂ and Cl+H₂ respectively.

From Fig.4, it can be found that another difference between the energy with spin-orbit correction and without spin-orbit correction is the barrier width. The barrier without spin-orbit correction is wider than that with spin-orbit correction. It is plausible that the relatively thinner barrier on the surface with spin-orbit correction enables easier barrier transmission by the Cl+H₂ than the barrier of the surface without spin-orbit correction, especially at the threshold. This indicates that the CW PES with spin-orbit correction has a thinner barrier, which might lead to more pronounced tunneling effects. At low collision energy, tunneling effects play a very important role, especially at collision energies lower than the barrier height 0.36 eV. The reactivity of the high barrier is larger than that of the low barrier because of tunnel transition. The cross section is $1.14a_0^2$ at 0.3 eV with spin-orbit correction compared to $0.66a_0^2$ without spin-orbit correction. The tunnel transition plays a minor role as the collision energy increases. The barrier height is the main factor when the collision energy is higher than 0.7 eV, and at this much higher collision energy, the tunnel transition has a negligible effect. The reactivity obtained on the high barrier PES with spin-orbit correction is smaller than that of the low barrier. The isotopic substitution of H₂ by D₂ causes the tunnel transition to be reduced because of the heavier deuterium molecule. For the reaction of Cl+D₂, the barrier height is important: the barrier height increases when the spin-orbit coupling is included. The reaction reactivity when excluding spin-

orbit coupling is larger than that when including spin-orbit coupling at a given translation energy.

IV. CONCLUSION

In this work, we have carried out time-dependent wave packet calculation on the CW (Capecchi and Werner) potential energy surfaces, with spin-orbit correction and without spin-orbit correction for the reaction of Cl+H₂($v=j=0$) and Cl+D₂($v=j=0$). The integral cross-sections and reaction probability of the reactions as a function of collision energy are calculated in the energy range of 0.1 eV to 1.4 eV. For the reaction of Cl with D₂, the reaction section has a shift toward the high energy because the spin-orbit coupling increases the barrier height. But for the reaction of Cl with H₂, at low collision energy, the tunneling effect plays a very important role. The reactivity with spin-orbit correction becomes large because the spin-orbit coupling makes the barrier width thin, making the tunneling effect large so it is more reactive. When the collision energy is higher than 0.7 eV, the barrier height plays a very important role compared to the tunnel effect. The reactivity on the surface with spin-orbit correction is smaller than that without spin-orbit correction.

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