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Fully converged integral cross sections of collision induced dissociation, four-center, and single exchange reactions, and accuracy of the centrifugal sudden approximation in $\text{H}_2 + \text{D}_2$ reaction

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The initial state selected time-dependent wave packet method was employed to calculate the integral cross sections for the $\text{H}_2 + \text{D}_2$ reaction with and without the centrifugal sudden (CS) approximation by including all important K (the projection of the total angular momentum on the body-fixed axis) blocks. With a full-dimensional model, the first fully converged coupled-channel (CC) cross sections for different competitive processes from the ground rotational state were obtained: collision induced dissociation (CID), four-center (4C) reaction and single exchange (SE) reaction. The effect of the total angular momentum J on the reaction dynamics of $\text{H}_2 + \text{D}_2$ and the accuracy of the CS approximation have also been studied. It was found that the CID and SE processes occur in a wide range of J values while the 4C process can only take place in a narrow window of J values. For this reason, the CC cross section for the 4C channel is merely comparable to the SE channel. A comparison of the integral cross sections from CC and CS calculations showed that the CS approximation works well for the CID process but not for the 4C and SE processes, and the discrepancy between the CC and CS cross sections grows larger as the translational energy and/or the vibrational energy increase(s).

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I. INTRODUCTION

Quantum dynamical studies on chemical reactions of tetra-atomic and polyatomic systems have been carried out extensively, driven by the development of quantum scattering theory, advances in constructing potential energy surfaces (PESs), and the rise in computational power.^{1–11} Quantum scattering calculations provide a complete description of the dynamics of a chemical reaction, and thus serve as the ultimate benchmarks for assessing various approximate theories and testing the accuracy of PESs for chemical reactions.^{12,13} Since the benchmark, full-dimensional (six-dimensional) wave packet calculations of the total reaction probabilities for the reaction $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ with total angular momentum $J = 0$,^{14,15} much progress has been made in the area of accurate quantum-dynamics simulations of four-atom reactions.^{16–19} The study of four-atom bimolecular reaction dynamics is of relevance to combustion, radical chemistry and astrochemistry, and theoretically serves as a bridge between triatomic reactions and polyatomic reactions of five or more atoms.^{20,21}

Being the simplest neutral molecule-molecule reaction, the $\text{H}_2\text{--H}_2$ system has long been considered as a benchmark candidate for quantum dynamics studies of molecule-molecule collisions. Detailed information on the kinetics and

the dynamics of the four-atom $\text{H}_2 + \text{H}_2$ system is of key relevance in modeling several gas phase non-equilibrium complex technological processes, such as combustion,^{22,23} spacecraft re-entry,²⁴ and negative ion production from plasmas.²⁵ From the viewpoint of quantum chemistry, the four-electron system is ideal for high level *ab initio* calculations. Two global six-dimensional H_4 PESs have been reported: one by Aguado *et al.* (ASP) (Ref. 26) and another by Boothroyd *et al.* (BMKP).²⁷ Recently, Hinde²⁸ reported a full-dimensional PES for the $\text{H}_2\text{--H}_2$ system that includes an accurate description of the van der Waals interaction region. However, the PES of Hinde is designed to describe accurately the bound and quasibound states of the dimers $(\text{H}_2)_2$, $(\text{D}_2)_2$, and $\text{H}_2\text{--D}_2$ and thus not suitable for the current dynamical study of the $\text{H}_2 + \text{D}_2$ reaction.

For sufficiently high collision energies or high reactant internal excitation, several kinds of processes occur during the collision of hydrogen molecules. In addition to nonreactive elastic and inelastic processes, four-center (4C) reaction (exchange reaction) which involves cleavage of two bonds, $\text{AB} + \text{CD} \rightarrow \text{AC} + \text{BD}$, $\text{AD} + \text{BC}$, collision induced dissociation (CID) (nonreactive dissociation), $\text{AB} + \text{CD} \rightarrow \text{A} + \text{B} + \text{CD}$, $\text{AB} + \text{C} + \text{D}$, which is known to be very important at the high energies where 4C reaction happens, or single exchange (SE) reaction (reactive dissociation), $\text{AB} + \text{CD} \rightarrow \text{AC} + \text{B} + \text{D}$, $\text{AD} + \text{B} + \text{C}$, $\text{BC} + \text{A} + \text{D}$, $\text{BD} + \text{A} + \text{C}$, can take place. In contrast to three-center reactions where only one bond is broken and formed during the reaction process, 4C reactions involve simultaneous cleavage and formation

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of two bonds, and they usually present very high barriers, comparable to or higher than a covalent bond energy.²⁹

The coexistence of several processes and the higher energy required to surmount the barrier pose a challenge to the exact full-dimensional quantum studies of the reaction dynamics. Therefore, most theoretical dynamics studies have been performed using reduced dimensional or full-dimensional classical or quasi-classical trajectories (QCT) (Refs. 30–38) and reduced dimensional quantum mechanical (QM) methods.^{29,39–44} Lu *et al.*⁴⁵ carried out the first accurate full-dimensional QM calculations of the $\text{H}_2 + \text{H}_2$ reaction using the time-dependent wave packet method. In their study, initial state selected total reaction probabilities for the three competitive processes were reported with total angular momentum $J = 0$, and the effect of reagent vibration on reactions was examined on the ASP PES. Another area of interest in the study of the H_4 system are the calculation of nonreactive vibrational de-excitation cross sections using full-dimensional QM methods of both time-independent^{46–49} and time-dependent type.^{50,51}

Recently, we performed full-dimensional time-dependent wave packet calculations of the $\text{H}_2 + \text{D}_2$ reaction and its isotopic variants on the ASP and BMKP PESs with $J = 0$.⁵² The role of both vibrationally and rotationally excited reagents was examined. We found that vibrational excitation of the hot diatom has an enhancement effect on the CID process while vibrational excitation of the cold diatom has an inhibition effect. The vibrational excitation of the cold diatom obviously enhances the SE process but inhibits the 4C process. The rotational excitation of both reagents has a significant effect on the reaction process. The 4C and SE reaction probabilities are at least one order of magnitude smaller than the CID probabilities over the energy range considered, and at high translational energies the 4C reaction probabilities are much larger than the SE probabilities for the ground rotational state. Furthermore, although the three isotope combinations ($\text{H}_2 + \text{H}_2$, $\text{H}_2 + \text{HD}$ and $\text{H}_2 + \text{D}_2$) have similar energy threshold behavior and probability profiles, they present remarkable isotope substitution effect. All these conclusions are, however, drawn from the non-measurable total reaction probabilities of $J = 0$. Thus, the study is of limited conclusiveness on observables (cross sections or rate constants).

The centrifugal sudden (CS) approximation^{53–55} provides tremendous conceptual simplicity and computational advantage over the coupled-channel (CC) theory and has been commonly used to calculate integral cross sections and rate constants for tetra-atomic and polyatomic reactions in the body-fixed (BF) frame.^{3,56–59} Some tests were performed to investigate the accuracy of the CS approximation in different four-atom reactions, such as $\text{H}_2 + \text{OH}$, $\text{H}_2 + \text{CN}$, $\text{OH} + \text{HCl}$ and $\text{H} + \text{H}_2\text{O}$.^{57–59} It has been shown that for the $\text{H}_2 + \text{OH}$ and $\text{OH} + \text{HCl}$ reactions the CS approximation does not have a major effect. The CS cross sections are smaller than the CC cross sections in the low energy region, and larger than the CC ones in the high energy region for the $\text{H}_2 + \text{CN}$ reaction. In strong contrast to what has been found in the above three diatom-diatom reactions, the CS approximation does not work well for both abstraction and exchange processes in the $\text{H} + \text{H}_2\text{O}$ reaction. All of these calculations are focused only

FIG. 1. The six-dimensional Jacobi coordinates for $\text{AB} + \text{CD}$ system in the reactant channel. R is the distance between the center-of-mass of molecule and CD , r_1 is the bond distance of AB , r_2 is the bond distance of CD , θ_1 is the angle between R and r_1 , θ_2 is the angle between R and r_2 and Φ is the out-of-plane torsional angle.

on reactions involving cleavage of one old bond. For the reactions with simultaneous cleavage of two bonds, the accuracy of CS approximation has never been tested. Thus, it is of practical value to carry out tests to address the accuracy of the CS approximation for the title reaction, especially for the 4C and SE processes.

In this paper, we use the time-dependent wave packet method to calculate integral cross sections for the $\text{H}_2 + \text{D}_2$ reaction by including all important K (the projection of the total angular momentum on the body-fixed axis) blocks within a full-dimensional model. As the cross sections reported are well converged with respect to the further increase of K blocks, they can be considered as the fully CC results for the reaction. We present the first fully converged integral cross sections for the ground rotational state of the $\text{H}_2 + \text{D}_2$ reaction on the BMKP PES. The effect of the total angular momentum on the dynamics of the $\text{H}_2 + \text{D}_2$ reaction and the accuracy of the CS approximation for the three different processes are also studied. The paper is organized as follows: In Sec. II, the theoretical methodology of the initial state selected wave packet (ISSWP) method is outlined. Section III presents the results and discussions. A summary is given in Sec. IV.

II. THEORY

The ISSWP method employed in the present study is mainly based on the earlier time-dependent wave packet studies of diatom-diatom reactions¹⁴ with an application to the $\text{H}_2 + \text{D}_2$ reaction.⁵² Here, we only briefly outline the theoretical aspects of the time-dependent wave packet approach.

The full-dimensional Hamiltonian in the BF reactant Jacobi coordinates shown in Fig. 1 for a given total angular momentum J can be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial r_2^2} + \frac{(\hat{J} - \hat{j}_{12})^2}{2\mu R^2} + \frac{\hat{j}_1^2}{2\mu_1 r_1^2} + \frac{\hat{j}_2^2}{2\mu_2 r_2^2} + \hat{V}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2), \quad (1)$$

where $\hat{J}$ is the total angular momentum operator, and $\hat{j}_1$ and $\hat{j}_2$ are the rotational angular momentum operators of AB and CD which are coupled to $\hat{j}_{12}$.

The time-dependent wave function is expanded in terms of the BF rovibrational eigenfunctions as

$$\begin{aligned} \psi_{v_0 j_0 K_0}^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, t) = & \sum_{n, v, j, K} F_{nvjK, v_0 j_0 K_0}^{JM\epsilon}(t) u_n^{v_2}(R) \\ & \times \phi_{v_1}(r_1) \phi_{v_2}(r_2) Y_{jK}^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2), \end{aligned} \quad (2)$$

where n is the translational basis label, v denotes (v_1, v_2) , j denotes (j_1, j_2, j_{12}) , (v_0, j_0) denotes the initial rovibrational state. The $Y_{jK}^{JM\epsilon}$ in Eq. (2) is the coupled BF total angular momentum eigenfunctions which can be written as

$$\begin{aligned} Y_{jK}^{JM\epsilon} = & (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} \\ & \times [D_{K,M}^J Y_{j_1 j_2}^{j_{12} K} + \epsilon(-1)^{j_1+j_2+j_{12}} D_{-K,M}^J Y_{j_1 j_2}^{j_{12}-K}], \end{aligned} \quad (3)$$

where $D_{K,M}^J$ is the Wigner rotation matrix, ϵ is the total parity of the system defined as $\epsilon_0(-1)^J$ with ϵ_0 being the parity of the system, $0 \leq K \leq \min(J, j_{12})$ is the projection of total angular momentum on the BF axis, and $Y_{j_1 j_2}^{j_{12} K}$ is the angular momentum eigenfunction of $\hat{j}_{12}$ defined as

$$\begin{aligned} Y_{j_1 j_2}^{j_{12} K} = & \sum_{m_1} \langle j_1 m_1 j_2 K - m_1 | j_{12} K \rangle y_{j_1 m_1}(\theta_1, 0) \\ & \times y_{j_2 K-m_1}(\theta_2, \Phi), \end{aligned} \quad (4)$$

where y_{jm} are spherical harmonics. Note that in Eq. (3), the restriction $\epsilon(-1)^{j_1+j_2+j_{12}} = 1$ for $K = 0$ partitions the whole rotational basis set into even and odd parities. Thus, a $K = 0$ initial state can only appear in one of the two parity blocks. For $K > 0$, however, there is no such a restriction, and the basis set is the same for even and odd parities, but slightly different for different K blocks because of the restriction $j_{12} \geq K$.

The interaction potential matrix in the angular momentum basis $Y_{jK}^{JM\epsilon}$, which is diagonal in K , can be calculated as⁶⁰

$$\langle Y_{jK}^{JM\epsilon} | V | Y_{j'K'}^{JM\epsilon} \rangle = 2\pi \delta_{KK'} \langle Y_{j_{12} K}^{j_{12} K} | V | Y_{j_{12}' K'}^{j_{12}' K'} \rangle. \quad (5)$$

Thus, we can see the potential matrix for even parity is identical to that for odd parity for $K > 0$.

The centrifugal potential, i.e., the $(J - j_{12})^2$ term in the Hamiltonian, which gives rise to the coupling between different K blocks in the BF representation, is given by⁶⁰

$$\begin{aligned} \langle Y_{jK}^{JM\epsilon} | (J - j_{12})^2 | Y_{j'K'}^{JM\epsilon} \rangle = & \delta_{j'j'} \{ \delta_{KK'} [J(J+1) \\ & + j_{12}(j_{12}+1) - 2K^2] \\ & - \delta_{K+1, K'} \lambda_{JK}^+ \lambda_{j_{12}K}^+ (1 + \delta_{K0})^{1/2} \\ & - \delta_{K-1, K'} \lambda_{JK}^- \lambda_{j_{12}K}^- (1 + \delta_{K1})^{1/2} \} \end{aligned} \quad (6)$$

and the quantity λ is defined as

$$\lambda_{AB}^{\pm} = [A(A+1) - B(B \pm 1)]^{1/2}. \quad (7)$$

In the CS approximation, we neglect the coupling between different K blocks in Eq. (6), thus K becomes a good quantum number and is conserved in reaction. For $K > 0$ both the interaction potential matrix in Eq. (5) and the centrifugal potential

FIG. 2. Grid ranges for the Jacobi coordinates r_1 , r_2 , and R . The interaction and asymptotic grid ranges in R are defined by $(R_2 - R_1)$ and $(R_3 - R_1)$, respectively. The three planes $S[R^F]$, $S[r_1^F]$ and $S[r_2^F]$ form the dividing surface for projecting the scattering wave function, while r_1^D and r_2^D denote the boundaries for the r_1 and r_2 coordinates, respectively.

matrix in Eq. (6) are not dependent on the total parity of the system, thus $\epsilon = \pm 1$ yield the same reaction probabilities. But in the CC calculations, they are expected to be different because the $K = 0$ block only exists in one parity.

As in Refs. 14 and 52, we construct Gaussian wave packets and propagate them using the split-operator method.⁶¹ In order to obtain the reaction probabilities $P_{v_1 v_2 j_1 j_2 j_{12} K}^{J\epsilon}(E)$ for different competitive processes, we calculate the time-independent wave function (TIDWF), $\psi_i^+(E)$, on one dividing surface which comprises three planes denoted by $S[R^F]$, $S[r_1^F]$, $S[r_2^F]$, as shown in Fig. 2.

The integral cross section from a specific initial state is obtained by summing the reaction probabilities over all the partial waves (total angular momentum J),

$$\begin{aligned} \sigma_{v_1 v_2 j_1 j_2}(E) = & \frac{1}{(2j_1+1)(2j_2+1)} \\ & \times \sum_{j_{12} K \epsilon} \left\{ \frac{\pi}{k^2} \sum_{J \geq K} (2J+1) P_{v_1 v_2 j_1 j_2 j_{12} K}^{J\epsilon}(E) \right\} \\ = & \frac{1}{(2j_1+1)(2j_2+1)} \sum_{j_{12} K \epsilon} \sigma_{v_1 v_2 j_1 j_2}^{j_{12} K \epsilon}(E), \end{aligned} \quad (8)$$

where $\sigma_{v_1 v_2 j_1 j_2}^{j_{12} K \epsilon}(E)$ is defined as the j_{12} , K , and ϵ specified cross section. In this study, we will restrict ourselves to the reactions with the H_2 and D_2 reagents in their initial ground rotational states, i.e., $j_1 = j_2 = 0$, for which the indexes j_{12} , K , and ϵ can only be 0, 0, and +1, respectively. Hence, we drop them from now on.

III. RESULTS

The numerical parameters used in the wave packet calculations on an L -shaped grid are summarized in Table I, which

TABLE I. Numerical parameters used in the wave packet calculations. (Atomic units are used unless stated otherwise.)

$\text{H}_2 + \text{D}_2$	
Grid/basis range and size:	$R \in [0.0, 12.0], N_R^{\text{tot}} = 83, N_R^{\text{int}} = 54$ $r_1 \in [0.5, 12.0], N_{r_1}^{\text{tot}} = 75$ $r_2 \in [0.5, 7.5], N_{r_2}^{\text{tot}} = 61, N_{r_2}^{\text{asy}} = 12$ $j_{1\text{max}} = 54, j_{2\text{max}} = 52$
Initial wave packet:	$\varphi_{k_0}(R) = \left(\frac{1}{\pi\delta^2}\right)^{1/4} e^{-(R-R_0)^2/2\delta^2} e^{-ik_0 R}$ $R_0 = 10.0, \delta = 0.4$
Absorbing potential:	$F_{\text{abs}} = \exp[-\Delta_t \alpha (\frac{x-x_a}{x_{\text{max}}-x_a})^n], \text{ for } x_a \leq x \leq x_{\text{max}}$ $R_a = 10.0, \alpha_R = 0.05, n_R = 1.5$ $r_{1a} = 10.5, \alpha_{r_1} = 0.05, n_{r_1} = 1.5$ $r_{2a} = 6.5, \alpha_{r_2} = 0.05, n_{r_2} = 1.5$
Flux position:	$R^F = 7.5, r_1^F = 10.0, r_2^F = 5.5$
Total propagation time:	600 iterations with $\Delta_t = 10.0$

are similar to those employed in Ref. 52. The exchange symmetry of H/D atom in the H_2/D_2 molecule has been considered in the calculation. The center momentum of the wave packet, k_0 , was chosen according to the initial state to cover the interesting energy range. We calculated the reaction probabilities with total angular momentum J from 0 to 50 (60) with an interval of 5 for the initial vibrational state $v_1 = 10$ (11) due to the extremely huge computational cost. The interpolation algorithm was applied to obtain reaction probabilities for other J within the range. The number of K blocks used in our calculations is $\min(3, J+1)$ (i.e., from 0 to $\min(3, J+1) - 1$). As a convergence test, we have calculated the reaction probabilities for the three processes with $J = 15$ by increasing the number of K blocks from 3 to 5. The relative error (the probability difference between 3 K and 5 K blocks divided by the probability for the 5 K blocks) is no more than 1% for the CID process and less than 5% for the 4C and SE processes.

It is not straightforward to separate the reactive flux of different channels based on diatomic-diatom reactant Jacobi coordinates. While the calculation of CID probability is quite straightforward since the corresponding reactive flux is well localized, the separation of the 4C flux from the SE channel is complicated and challenging. A “binning” procedure is employed in the calculations. Briefly, the TIDWF is first transferred from a function of the reactant Jacobi coordinates to a double variable function. Then, according to the distribution of the wave function in the new double variable plane, we are able to know statistically in which area the TIDWF falls for 4C and SE processes. It should be noted that the “binning” method will unavoidably introduce some errors for the separation of 4C and SE probabilities. However, we believe that the errors are negligible. More details are given in Ref. 52.

A. Reaction probabilities

The CS approximation can reduce the complexity of calculations and is shown to be justified for the scattering problems where the main contribution comes from the small J region.⁵³ Although the accuracy of the CS approximation has been extensively studied in the diatom-diatom and atom-triatom reactions in which only one old bond is broken, it has never been tested in reactions involving simultaneous cleav-

age of two bonds. In the 4C and SE processes of the $\text{H}_2 + \text{D}_2$ reaction, two old bonds are broken. One new bond is formed for the SE process and two new bonds are formed for the 4C process. Thus, it is an ideal candidate to study the accuracy of the CS approximation for the scattering problems including cleavage of one and/or two bond(s).

Figure 3(a) shows the six-dimensional (6D) CC and CS CID probabilities for the H_2 ($v_1 = 10, j_1 = 0$) + D_2 ($v_2 = 0$),

FIG. 3. The six-dimensional CC and CS collision induced dissociation, four-center and single exchange probabilities for the H_2 ($v_1 = 10, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction with total angular momentum $J = 0, 5, 10, 15$, and 25 as a function of translational energy.

$j_2 = 0$) reaction with total angular momentum $J = 5, 15$, and 25 as a function of translational energy. The CID probability for $J = 0$ is also presented for comparison. It can be seen that the 6D CC probability is almost identical to the 6D CS one over the energy range considered for $J = 5$. As J increases, the discrepancy between the CC and CS results becomes visible. The CS probability is smaller than the CC probability near the energy threshold. With the further increase of the collisional energy, the CS probability is slightly larger than the CC probability. Overall, the CS results agree with the CC ones quite well in the energy range studied and for the different total angular momentum J presented.

In Fig. 3(b), we present the CC and CS 4C reaction probabilities for the H_2 ($v_1 = 10, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction with $J = 5, 10$, and 15 as a function of translational energy, together with that for $J = 0$. As can be seen from the figure, the difference between the CC and CS probabilities increases with the increase of J , which is similar to the CID process. However, the relative error is much larger than that in the CID process for the same J . In the high energy region, the CC probability is about three times as large as the CS one for $J = 15$.

The CC and CS SE reaction probabilities with $J = 5, 15$, and 25 are plotted in Fig. 3(c). Clearly, the trend of the discrepancy between CC and CS results is the same as what we have found in the CID and 4C processes, i.e., it increases with J . This is consistent with the fact that the CS approximation is valid for scattering problems where the main contribution comes from the small J region, because the centrifugal coupling between different K blocks is proportional to J . It can also be noted that, for $J = 25$, the CS SE probability is at least one order of magnitude smaller than the CC probability in the high energy region.

The accuracy of the CS approximation is generally affected by two factors: the geometry and the reaction dynamics. Reactions which are quite similar in dynamics but with different mass combinations (i.e., different geometries) would result in different performance of the CS approximation. The distinct performance of the CS approximation in the $\text{H}_2 + \text{OH}$ and $\text{H} + \text{H}_2\text{O}$ reactions^{57,58} can be attributed to the different mass combinations. On the other hand, for different reaction processes (i.e., different dynamics), the accuracy of the CS approximation would be quite different even if they have same mass combinations. As we know, there is only one old bond broken in the CID process of $\text{H}_2 + \text{D}_2$, which is somewhat similar to the $\text{H}_2 + \text{OH}$, $\text{H}_2 + \text{CN}$ and $\text{OH} + \text{HCl}$ dissociative-associative reactions. For the three collinearly dominated diatom-diatom reactions, it has been found that the CS approximation works well.^{57,59} This is in accord with what we have found in the CID process of $\text{H}_2 + \text{D}_2$. In strong contrast to the CID process, the CS approximation does not work well for the 4C and SE processes involving cleavage of two bonds. The accuracy of the CS approximation also becomes worse from 4C to SE process. The poor performance of the CS approximation for the 4C and SE processes of $\text{H}_2 + \text{D}_2$ as compared to the CID process can be rationalized by the different dynamics of the three processes. It is shown below that the 4C process occurs in a narrow window of J ; thus the geometry should be dominant over the dynamics on the

FIG. 4. The six-dimensional CC collision induced dissociation probabilities for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction at several selected collision energies as a function of total angular momentum quantum number J . Note that different energies are selected for different initial states.

performance of the CS approximation for the 4C process of $\text{H}_2 + \text{D}_2$.

Garcia *et al.* have investigated the effect of total angular momentum on the dynamics of the $\text{H}_2 + \text{H}_2$ reaction using the QCT method.³⁸ To further attest their conclusions in the QM frame, we here also study the efficiency of varying J on the various processes in $\text{H}_2 + \text{D}_2$. Figures 4–6 present the 6D CC CID, 4C, and SE probabilities for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction at several selected collision energies as a function of J . The upper panel is for the initial state $v_1 = 11$ and the lower panel for $v_1 = 10$. From the figures, we can see that the maximum of the necessary J (J_{max}) increases for all kinds of processes with both collision and vibrational energy. The increase in J_{max} with vibrational energy (from the bottom panel up at the same collision energy) is slightly larger than that with collision energy (from internal to external curves within the same panel) in the energy range studied (the excitation energy from $v_1 = 10$ to 11 is 0.215 eV). This trend is consistent with Garcia *et al.*'s result, whereas it is not as apparent as their plots, especially for the 4C and SE processes. It is because we only focus on the relatively low initial vibrational states ($v_1 = 10, 11$), while the initial vibrational state studied is as high as $v_1 = 14$ in Garcia's paper. Unfortunately, we are unable to reach those

FIG. 5. The six-dimensional CC four-center probabilities for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction at several selected collision energies as a function of total angular momentum quantum number J . Note that different energies are selected for different initial states.

high vibrational states within the quantum method due to excessively large basis/grid size required. On the other hand, what we have studied is the isotope substitution system, $\text{H}_2 + \text{D}_2$, and not $\text{H}_2 + \text{H}_2$. The mass difference and the quantum tunneling effects (not included in their study) are likely to have an effect on the J behavior. Furthermore, different collision energies are covered at different initial vibrational states to save computational cost.

Comparing the three figures within the same initial state, we can find that the CID process occurs in a wide range of J values. In contrast, the 4C process can only take place in a narrow window of J . The CID curve plotted in Fig. 4 presents a longer tail than the 4C curve in Fig. 5. These behaviors can be explained by a hard sphere model. As indicated by Garcia *et al.*,³⁸ the narrow window of J in the 4C process can be attributed to a locking radius, depending on the bond length at which the exchange occurs. In the CID process, the larger range of J can be associated with the radius of optimum vibration-translation energy exchange. For the SE process, two old bonds are broken and only one new bond is formed. It is subject to both the exchange and dissociative constraints. Thus the SE process, as shown in Fig. 6, occurs in a wide range of J while not presenting a long tail. The difference can also be rationalized by the fact the energy

FIG. 6. The six-dimensional CC single exchange probabilities for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction at several selected collision energies as a function of total angular momentum quantum number J . Note that different energies are selected for different initial states.

exchange takes place at longer range than mass exchange. All these findings are essentially in agreement with the QCT results.

B. Integral cross sections

Figures 7(a) and 7(b) show the 6D CC CID integral cross sections for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction together with the corresponding CS cross sections as a function of translational energy and total energy, respectively. Hereafter, energies are referred to the bottom of the $\text{H}_2 + \text{D}_2$ entrance valley. It is not surprising to see that the CC cross section is almost indistinguishable from the CS cross section for the CID process from the same initial state, as the CC total reaction probabilities agree well with the CS ones for different total angular momentum J . In the low energy region, the CC cross section is slightly larger than the CS cross section. While in the high energy region, the CC cross section is a little smaller than the CS cross section. This is similar to the observations of the $\text{H}_2 + \text{OH}$ and $\text{H}_2 + \text{CN}$ reactions from the ground rovibrational state reported by Zhang and Lee.⁵⁷ The 6D 4C and SE integral cross sections are plotted in Figs. 8 and 9, respectively. Obviously, for the 4C process, the CC cross

FIG. 7. The six-dimensional CC and CS collision induced dissociation integral cross sections for the $\text{H}_2(v_1 = 10, 11, j_1 = 0) + \text{D}_2(v_2 = 0, j_2 = 0)$ reaction as a function of (a) translational energy and (b) total energy. Energies are referred to the bottom of the $\text{H}_2 + \text{D}_2$ entrance valley.

section is larger than the corresponding CS cross section, and the discrepancy increases as the translational energy and/or the vibrational energy increase(s). The SE process is close to the 4C process except that it shows an even larger discrepancy between the CC and CS cross sections. In the SE process, the CC cross section is more than three times as large as the CS cross section. In brief, we can conclude that the CS approximation works well for the CID process but it does not work well for the 4C and SE processes for the ground rotational state. In the 4C and SE processes, the CC cross section is much larger than the CS cross section.

Now, let us focus on the CC results. From Fig. 7, we can see that, first, there exists a vibrational enhancement effect. The effect of initial vibrational excitation of H_2 is more than just using the entire energy initially deposited in it, it also promotes the CID process. Second, the cross section profiles become steeper as v_1 increases. The 4C and SE CC cross sections, as shown in Figs. 8 and 9, are about one order of magnitude smaller than the CID cross sections. Hence, the CID process is dominant over the energy range considered. These results are consistent with the conclusion reported in our earlier paper.⁵² In other words, for the CID process,

FIG. 8. The six-dimensional CC and CS four-center integral cross sections for the $\text{H}_2(v_1 = 10, 11, j_1 = 0) + \text{D}_2(v_2 = 0, j_2 = 0)$ reaction as a function of (a) translational energy and (b) total energy.

the conclusion drawn from the total reaction probability for $J = 0$ remains unchanged. From Figs. 8 and 9, it is also found that the magnitude of 4C CC cross section is comparable to the SE cross section for the same initial state, which is, however, quite different from the observation for $J = 0$ that the 4C reaction probability is much larger than the SE probability at high translational energy for the ground rotational state.⁵² This can be easily understood by comparing the opacity functions (total reaction probability as a function of total angular momentum J at a fixed energy) of 4C and SE processes, as plotted in Figs. 5 and 6. From Fig. 5, we can see that the opacity function is a monotonous decreasing function. As J increases, the 4C reaction probability constantly decreases at a specific translational energy and the 4C process exploits a narrow window of J value. However, for the SE process shown in Fig. 6, there is a shift of the maximum of the reaction probability. The SE probability first increases as J increases, then reaches an maximum, and decreases with the further increase of J . As mentioned above, the effective window of J value is also much wider than that of the 4C process. The different values of $J_{\max}$ (or the effective J window) and the factor $(2J + 1)$ in Eq. (8) weighing the terms of the sum of the partial probability terms significantly affect the resultant cross section and thus lead to the comparable 4C and SE cross sections.

FIG. 9. The six-dimensional CC and CS single exchange integral cross sections for the H_2 ($v_1 = 10, 11, j_1 = 0$) + D_2 ($v_2 = 0, j_2 = 0$) reaction as a function of (a) translational energy and (b) total energy.

IV. CONCLUSIONS

The initial state selected time-dependent wave packet method has been employed to calculate the integral cross sections for the diatom-diatom $\text{H}_2 + \text{D}_2$ reaction with and without the CS approximation. By including all important K blocks in the body-fixed frame, the obtained CID, 4C and SE integral cross sections can be treated as the first fully converged coupled-channel ones from the ground rotational state. Detailed studies have been carried out on the accuracy of the CS approximation for the three competitive processes in the $\text{H}_2 + \text{D}_2$ reaction.

It was found that the CC cross section is almost identical to the CS cross section for the CID process. In the low energy region, the CC cross section is slightly larger than the CS cross section. In the high energy region, the CC cross section is a little smaller than the CS cross section. Overall, the CS approximation works well for the CID process of $\text{H}_2 + \text{D}_2$. For the 4C and SE processes, the CC cross section is much larger than the CS cross section, which means that the CS approximation does not work well for the two processes. The discrepancy between the CC and CS cross sections increases as the translational energy and/or the vibrational energy increase(s).

From the CC cross sections, we validated that the conclusion drawn from the total reaction probability for $J = 0$

remains unchanged for the CID process. It is dominant over the energy range considered. And the 4C and SE CC cross sections are about one order of magnitude smaller than the CID cross section. In strong contrast to the observation for $J = 0$ that the 4C probability is much larger than the SE probability at high translational energy for the ground rotational state, the magnitude of the 4C CC cross section is only comparable to the SE cross section.

The effect of the total angular momentum J on the reaction dynamics of $\text{H}_2 + \text{D}_2$ has also been studied and compared with the QCT results of Garcia *et al.* for $\text{H}_2 + \text{H}_2$.³⁸ We found that the necessary J_{max} increases with both collision and vibrational energy for all the three processes. The CID process occurs in a wide range of J values and shows a long tail. In contrast, the 4C process can only take place in a narrow window of J . The SE process has features of both CID and 4C processes, which occurs in a wide range of J without a long tail. All these findings are essentially in agreement with the QCT results.

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