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Time-dependent wave packet state-to-state dynamics of H/D + HCl/DCI reactions

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The H/D + HCl/DCI ($v_0 = 0, j_0 = 0$) reactions were investigated in the gas phase using the reactant coordinate based time-dependent wave packet method on the BW2 PES [W. Bian and H.-J. Werner, *J. Chem. Phys.* **112**, 220 (2000)]. The total and state-to-state integral and differential cross sections of both the abstraction and the exchange channels were reported over the energy range from threshold to 2.0 eV. The theoretical total exchange integral cross sections agree well with Volpp's experimental measurements but differ from Polanyi's experimental results for H + DCI reaction. The theoretical total abstraction integral cross sections are more than twice as large as the experimental results from the two groups for the H + HCl/DCI reactions. For the four isotope combinations, the total exchange integral cross sections increase monotonically with collisional energy while the abstraction integral cross sections start to decrease at relatively high collision energies. And the abstraction products are predominantly backward and sideways scattered while the exchange products are almost backward scattered. For the two channels, the D + HCl reaction presents the highest reactivity, the H + DCI reaction presents the lowest reactivity, and the H + HCl and D + DCI reactions are in between with the H + HCl reaction having a slightly larger reactivity. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4790116>]

I. INTRODUCTION

The gas-phase reaction of hydrogen atoms with hydrogen chloride and the corresponding reverse reaction and their isotopic variants have been the subject of numerous experimental and theoretical studies.^{1–14} They represent important steps in the $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ reaction, in which a chain mechanism is established with Cl atoms acting as chain carriers. During the collision of H and HCl, there exist two reaction channels: abstraction reaction, $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$, and exchange reaction, $\text{H} + \text{HCl} \rightarrow \text{HCl} + \text{H}$.

Much experimental attention has been paid to study the dynamics of the H + HCl/DCI reactions. Using coherent anti-Stokes Raman scattering spectroscopy, Aker *et al.*^{15,16} obtained the product rotational and vibrational state distributions for the H + HCl reaction at 1.6 eV. Then, Polanyi's group¹⁷ measured the cross sections of the H + DCI reaction by resonant enhanced multiphoton ionization technique with the translational energy ranging from 1.0 to 2.4 eV. The abstraction cross section was found to remain constant at $0.16 \pm 0.06 \text{ \AA}^2$, but the exchange cross section exhibited a moderate decrease with increasing collision energy. Using the laser photolysis/vacuum-UV laser-induced fluorescence “pump-and-probe” technique, Volpp's group^{18–20} investigated the collision energy dependence of the reaction cross

sections of the $\text{H} + \text{HCl/DCI} \rightarrow \text{H}_2/\text{HD} + \text{Cl}$ reactions for collision energy $E_{\text{col}} \geq 1.0 \text{ eV}$. Their experimental results revealed the increasing importance of the nonadiabatic abstraction reaction channel with increasing collision energy. Recently, the same group studied the exchange process of the H + DCI reaction.²¹ The experimental excitation function exhibited a monotonic increase from the threshold to 1.4 eV. It was in marked contrast to previous experimental results which showed a moderate decline.¹⁷

At the forefront of theoretical studies, much work has been carried out to construct global PESs for the H_2Cl system. The SPK PES²² was found to be the most successful one among the 11 PESs available at that time by Tucker *et al.*²³ Starting with the SPK PES, Schwenke *et al.*²⁴ constructed two new PESs (denoted by GQ and GQQ) by adding a localized three-center term. Then a new PES (called G3) was developed by Truhlar and co-workers²⁵ by incorporating an improved bending potential. Meanwhile, Bian and Werner²⁶ constructed two new global PESs (called BW1 and BW2) generated by fitting about 1200 *ab initio* energies based on internally contracted multireference configuration interaction calculations using a very large basis set. The BW2 PES, being computed by scaling the correlation energies at all geometries with a constant factor, was considered to be more reasonable. Furthermore, coupled PESs including the spin-orbit coupling for the reverse reaction: $\text{Cl} + \text{H}_2$ reaction^{10,11} were published and used to perform quantum scattering calculations. Excellent agreement between molecular beam experiments and theoretical calculations were obtained.^{12,13}

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Considerable efforts have also been made to validate the accuracy of the G3 and BW2 PESs by performing reaction dynamics calculations using quasi-classical trajectory (QCT)^{17,27} or quantum methods.^{28,29} On the G3 PES, Aoiz *et al.*^{30,31} carried out a QCT investigation of the pendular orientation effects in the H + DCI reaction. They concluded that rotational excitation has a minor effect on reactivity while vibrational excitation lowers the threshold and increases the cross section. In order to explain the experimental results, Volpp's group¹⁹⁻²¹ also carried out a series of QCT calculations of the H + HCl/DCI reactions on the G3, BW1, and BW2 PESs. They found that the theoretical abstraction cross sections on the G3 PES are in reasonably good agreement with the experimental results while the calculations on the BW1 and BW2 PESs yielded too large abstraction cross sections in comparison with the experimental data.^{19,20} However, the exchange cross sections on the BW2 PES can accurately reproduce the experimental results while the G3 cross sections are significantly smaller in absolute value for collision energies above ca. 0.9 eV.

In this paper, we report the time dependent wavepacket state-to-state dynamics studies for H/D + HCl/DCI reactions on the BW2 PES at the collision energy up to 2.0 eV. The aims of this work are two-fold: (1) to provide detailed accounts for the isotopic substitution effects of the H + HCl ($v = 0, j = 0$) reaction dynamics, especially on the integral/differential cross sections, product state distributions, and branching ratios for the abstraction and exchange channels; and (2) to compare our theoretical results with the available experimental or other theoretical results when it is possible, and hopefully to clarify some doubts in the literature on this system. Although the accuracy of the BW2 PES for describing the abstraction channel is possibly questionable in the high energy region, it should have a minor and negligible effect on isotopic substitution effects which we are interested in here. The use of the BW2 PES also means the spin-orbit (SO) coupling and the non-adiabatic effects were not included in our calculations. The calculations are based on the coordinate transformation reactant coordinate based (RCB) wave packet method.³² The same method has been applied to state-to-state quantum dynamics studies of the H + HD, Cl + H₂, H + HCl, and H + O₂ by Sun *et al.*^{33,34} The paper is organized as follows: In Sec. II, the theoretical methodology of the RCB method is outlined. Section III presents the results and discussions. A summary is given in Sec. IV.

II. THEORY

The RCB wave packet method employed in the present study is almost the same as in the study on the H + O₂ reaction.³⁴ Here, we only briefly outline the theoretical aspects of the RCB approach.

For an atom-diatom reaction A + BC to produce products AB + C and/or AC + B, three sets of body-fixed (BF) Jacobi coordinates are used to represent the wave functions for different arrangements, in which the greek letter α denotes the A + BC reactant channel, β the AB + C product channel, and γ the AC + B product channel. The coordinates are written as $(R_\nu, r_\nu, \theta_\nu; \tilde{\Omega}_\nu)$, where ν is α, β , or γ . For $\nu = \alpha$ (β, γ), r_ν is

the bond distance of BC (AB, AC), R_ν is the distance from A (C, B) to the center of mass of BC (AB, AC), θ_ν is the angle between R_ν and r_ν , and $\tilde{\Omega}_\nu$ denotes the Euler angles orienting $\tilde{R}_\nu$ in the space-fixed (SF) frame. The Hamiltonian in the BF Jacobi coordinates for a given total angular momentum J can be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu_{R_\alpha}} \frac{\partial^2}{\partial R_\alpha^2} - \frac{\hbar^2}{2\mu_{r_\alpha}} \frac{\partial^2}{\partial r_\alpha^2} + \frac{(\hat{J} - \hat{j})^2}{2\mu_{R_\alpha} R_\alpha^2} + \frac{\hat{j}^2}{2\mu_{r_\alpha} r_\alpha^2} + \hat{V}, \quad (1)$$

where $\hat{J}$ is the total angular momentum operator and $\hat{j}$ is the rotational angular momentum operator of BC.

The wave function in the BF frame can be expressed as

$$\Psi^{JM\epsilon}(\tilde{R}_\alpha, \tilde{r}_\alpha) = \sum_{K_\alpha} \bar{D}_{MK_\alpha}^{J\epsilon*}(\tilde{\Omega}_\alpha) \psi_\alpha(R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}; K_\alpha), \quad (2)$$

where $\bar{D}_{MK_\alpha}^{J\epsilon*}(\tilde{\Omega}_\alpha)$ is the parity-adapted normalized rotation matrix, depending only on the Euler angles $\tilde{\Omega}_\alpha$,

$$\begin{aligned} \bar{D}_{MK_\alpha}^{J\epsilon*}(\tilde{\Omega}_\alpha) = & \sqrt{\frac{2J+1}{8\pi(1+\delta_{K_\alpha 0})}} [D_{MK_\alpha}^{J*}(\tilde{\Omega}_\alpha) \\ & + \epsilon(-1)^{J+K_\alpha} D_{M-K_\alpha}^{J*}(\tilde{\Omega}_\alpha)], \end{aligned} \quad (3)$$

where $\epsilon = (-1)^{j+l}$ is the parity of the system with l being the orbital angular momentum quantum number, K_α is the projection of the total angular momentum J on the BF z axis, and $D_{MK_\alpha}^J(\tilde{\Omega}_\alpha)$ is the Wigner rotation matrix. The wave function $\psi_\alpha(R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}; K_\alpha)$, only depending on the internal coordinates $(R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha})$ and K_α , can be expanded as

$$\psi_\alpha(R_\alpha, r_\alpha, \theta_\alpha^{K_\alpha}; K_\alpha) = \sum_{n,m,j} F_{nmj}^{K_\alpha} u_n(R_\alpha) \phi_m(r_\alpha) y_{jK_\alpha}(\theta_\alpha), \quad (4)$$

where n and m are the radial basis labels, and y_{jK_α} are spherical harmonics.

The initial wave packet $\Psi_{v_0 j_0 l_0}^{JM\epsilon}$ is constructed as the product of a total angular momentum eigenfunction, a rovibrational eigenfunction of molecule BC and a Gaussian wave packet in the SF frame. In order to propagate it in the BF frame, we transform it to the BF frame and then propagate it using the second-order split operator method.³⁵ During the propagation, the fast Fourier transform method is employed to calculate the radial kinetic energy operator acting on the wave packet in an L -shaped grid.³⁶ The generalized discrete variable representation³⁷ is used to evaluate the action of the potential energy operator, in which the wave packet is converted from the angular finite basis representation to a grid representation. A damping function that has the same form as in Ref. 33 is employed to prevent the wave packet from reflecting back from the boundaries.

The coordinate transformation RCB method is used to extract the state-to-state S-matrix for both product channels. The coordinate transformation approach³² is based on the fact that the product wave function has only two degrees of freedom, r_ν and θ_ν , as R_ν is fixed at the projection plane R_{v_0} . To implement the RCB method, an "intermediate" coordinate system, in which R_ν is combined with either $(R_\alpha, \theta_\alpha)$ or

$(r_\alpha, \theta_\alpha)$, is chosen to provide a convenient platform for projection. The two-dimensional product internal eigenfunctions are transformed and stored in the reactant grid before propagation. In each propagation step, the wave packet is transformed to the same grid by two one-dimensional transformations, facilitating the calculation of the overlaps. The computational costs are equivalent to those required for evaluating a norm. Finally, the BF frame needs to be rotated into the corresponding new reference axis.

The obtained BF scattering time-independent wave function from an initial state (v_0, j_0, l_0) is transformed into the SF frame by an orthogonal transformation matrix as

$$\Phi_{v_v j_v l_v \leftarrow v_0 j_0 l_0}^{J\epsilon}(E) = \sum_{K_v} C_{l_v K_v}^{J j_v \epsilon} \Phi_{v_v j_v K_v \leftarrow v_0 j_0 l_0}^{J\epsilon}(E). \quad (5)$$

The state-to-state scattering matrix $S_{v_v j_v l_v \leftarrow v_0 j_0 l_0}^{J\epsilon}(E)$ ($v = \beta, \gamma$) in the SF frame can then be obtained by imposing the asymptotic boundary conditions,

$$\begin{aligned} \Phi_{v_v j_v l_v \leftarrow v_0 j_0 l_0}^{J\epsilon}(E; R_{v_0}) &= -\mathcal{A}(E) \left(\frac{2\pi \hbar^2 k_{v_v j_v}}{\mu R_v} \right)^{1/2} \\ &\times S_{v_v j_v l_v \leftarrow v_0 j_0 l_0}^{J\epsilon}(E) \tilde{\mathcal{H}}_{l_v}(k_{v_v j_v} R_{v_0}), \end{aligned} \quad (6)$$

where $\mathcal{A}(E)$ is defined as

$$\mathcal{A}(E) = \left(\frac{\mu R_\alpha}{2\pi \hbar^2 k_{v_0 j_0}} \right)^{1/2} \int \tilde{\mathcal{H}}_{l_0}(k_{v_0 j_0} R_\alpha) G(R_\alpha) dR_\alpha, \quad (7)$$

where $\tilde{\mathcal{H}}$ is an outgoing Riccati-Hankel function.

Finally, the scattering matrix $S_{v_v j_v l_v \leftarrow v_0 j_0 l_0}^{J\epsilon}(E)$ in the SF frame is transformed into the helicity representation by the standard transformation,^{38,39}

$$\begin{aligned} S_{v' j' K' \leftarrow v j K}^J &= \sum_{l'l'} i^{l-l'} \sqrt{\frac{2l'+1}{2J+1}} \langle j' K' l' 0 | J K' \rangle \\ &\times S_{v' j' l' \leftarrow v j l}^J \sqrt{\frac{2l+1}{2J+1}} \langle j K l 0 | J K \rangle. \end{aligned} \quad (8)$$

By substituting the scattering matrix $S_{v_v j_v K_v \leftarrow v_0 j_0 K_0}^{J\epsilon}(E)$ in the helicity representation into the standard formulas, we ob-

tain the state-to-state integral cross sections,

$$\begin{aligned} \sigma_{v_v j_v \leftarrow v_0 j_0} &= \frac{\pi}{(2j_0 + 1) k_{v_0 j_0}^2} \\ &\times \sum_{K_v} \sum_{K_0} \sum_J (2J + 1) |S_{v_v j_v K_v \leftarrow v_0 j_0 K_0}^J|^2, \end{aligned} \quad (9)$$

and the state-to-state differential cross sections,

$$\begin{aligned} \frac{d\sigma_{v_v j_v \leftarrow v_0 j_0}(\vartheta, E)}{d\Omega} &= \frac{1}{2j_0 + 1} \sum_{K_v} \sum_{K_0} \left| \frac{1}{2i k_{v_0 j_0}^2} \right. \\ &\times \left. \sum_J (2J + 1) d_{K_v K_0}^J(\vartheta) S_{v_v j_v K_v \leftarrow v_0 j_0 K_0}^J \right|^2 \end{aligned} \quad (10)$$

in which ϑ is the scattering angle between the incoming A + BC reactants and the scattered AC + B/AB + C products. In this paper, we will restrict our study to reactions with the reagent HCl (or DCl) in its initial ground rovibrational state, i.e., $v_0 = j_0 = 0$.

III. RESULTS

The numerical parameters used in the calculations on an *L*-shaped grid are summarized in Table I. The range of the total angular momentum is taken as $0 \leq J \leq 80$ for the H + HCl/DCI reaction, $0 \leq J \leq 110$ for the D + DCI reaction, and $0 \leq J \leq 120$ for the D + HCl reactions. The number of *K* blocks used in our calculations is $\min(25, J + 1)$ (i.e., from 0 to $\min(25, J + 1) - 1$) for the H + HCl reaction and $\min(31, J + 1)$ for the other three isotopic variants.

Figure 1 shows the schematic reaction profiles of the abstraction and exchange channels on the BW2 PES.²⁶ Both reaction channels are thermo neutral or nearly thermo neutral reaction processes. For the abstraction channel, the barrier height is 0.218 eV, and there exists a collinear well with a depth of 0.02 eV in the entrance valley and a T-shaped well with a depth of 0.022 eV in the exit channel. For the exchange channel, the barrier height is 0.776 eV, and there exists a collinear well with a depth of 0.013 eV in both the entrance

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

	H+HCl	H+DCI/D+HCl/D+DCI
Grid/basis range and size:	$R \in [0.8, 16.0]$, $N_R^{tot} = 129$, $N_R^{int} = 127$ $r_2 \in [1.2, 16.0]$, $N_r^{tot} = 127$, $N_r^{asy} = 29$ $j_{min} = 0$, $j_{max} = 140$	$R \in [0.8, 16.0]$, $N_R^{tot} = 181$, $N_R^{int} = 179$ $r_2 \in [1.2, 16.0]$, $N_r^{tot} = 179$, $N_r^{asy} = 41$ $j_{min} = 0$, $j_{max} = 196$
Initial wave packet: ^a	$R_0 = 11.0$, $\delta = 0.16$, $E_0 = 1.3$ eV	$R_0 = 11.0$, $\delta = 0.16$, $E_0 = 1.2$ eV
Absorbing potential: ^b	$C' = 0.07$, $n' = n = 2$, $R_a = 12.0$ $C_a = 0.05$, $C_b = 0.2$, $r_a = 12.0$, $r_b = 13.0$	$C' = 0.07$, $n' = n = 2$, $R_a = 12.0$ $C_a = 0.05$, $C_b = 0.2$, $r_a = 12.0$, $r_b = 13.0$
Matching plane:	$R_0^A = 9.0$, $R_0^E = 10.0$	$R_0^A = 9.0$, $R_0^E = 10.0$
Total propagation time:	2000 iterations with $\Delta_t = 10.0$	2000 iterations with $\Delta_t = 10.0$

^a $\varphi_{k_0}(R) = (\frac{1}{\pi \delta^2})^{1/4} e^{-(R-R_0)^2/2\delta^2} e^{-ik_0 R}$, $k_0 = \sqrt{2\mu_R E_0}$.

^b $F_{abs}(r) = \begin{cases} \exp[-\Delta_t \cdot C_a \cdot (\frac{r-r_a}{r_b-r_a})^n], & r_a \leq r \leq r_b, \\ \exp[-\Delta_t \cdot C_b \cdot (\frac{r-r_b}{r_{end}-r_b})^n] + \exp[-\Delta_t \cdot C_a], & r_b < r \leq r_{end}. \end{cases}$

^c $F_{abs}(R) = \exp[-\Delta_t \cdot C' \cdot (\frac{R-R_0}{R_{end}-R_0})^{n'}]$, $R_a \leq R \leq R_{end}$.

FIG. 1. Schematic reaction profiles with geometries and energies (in eV) of the stationary points on the BW2 PES.

valley and the exit valley. In addition, both of the two reaction channels present a collinear transition state.

A. Reaction probabilities

For the sake of clarifying the J dependence of the total reaction probability, the state-to-state reaction probabilities are summed at different J values. The total abstraction reaction probabilities at several selected translational energies are shown in Fig. 2 as a function of total angular momentum. The four panels from (a) to (d) correspond to the H + HCl reaction, the H + DCl reaction, the D + HCl reaction, and the

D + DCl reaction (hereinafter the same for the other similar figures). As can be seen from this figure, the reaction takes place at relatively small J values and the probability maximum occurs at $J = 0$ at low collision energies. With the increase of translational energy, a marked shift of the probability maximum occurs towards larger J values except the H + DCl reaction (Fig. 2(b)) in which the probability maximum is always at $J = 0$. It is well known that the J dependence of the total reaction probability is an analogue of classical opacity function (i.e., the reaction probability as a function of the impact parameter). Thus, different J dependence means different impact parameter dependence. Two reaction mechanisms have been proposed for the abstraction process: a rebound mechanism referring to small impact parameter collisions and a stripping mechanism associated with relatively large impact parameter collisions. The rebound mechanism leads to the backward scattering while the stripping mechanism leads to the forward and sideways scattering. Hereafter, the forward direction is always along the incoming H (D) atom. From Fig. 2, we can expect that the backward scattering is predominant at low collision energies and the sideways and forward scatterings are prevailing at high collision energies.

The total exchange reaction probabilities are shown in Fig. 3. In sharp contrast to the abstraction reaction, the exchange reaction presents a monotonic dependence with respect to J in the whole energy range studied. Both the probability maximum and the preferred J values increase with translational energy. Two reaction mechanisms have been proposed for the exchange process: end-on and insertion mechanisms. The end-on mechanism results in the backward scattering while the insertion mechanism brings about the forward scattering. Since the exchange reaction occurs in a relatively

FIG. 2. Total abstraction reaction probabilities for the H/D + HCl/DCl reactions at selected translational energies of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 eV as a function of total angular momentum J .

FIG. 3. Total exchange reaction probabilities for the $\text{H/D} + \text{HCl/DCI}$ reactions at selected translational energies of 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 eV as a function of total angular momentum J .

small J region and the probability maximum is always located at $J = 0$, i.e., end-on collisions, we can expect that the exchange products are predominantly backward scattered.

Comparing the two channels with the same reagents, we find that the abstraction reaction occurs in a wider range of J values than the exchange reaction in the energy range investigated. However, the exchange probability maximum is about one order of magnitude larger than the abstraction maximum. Aoiz *et al.*^{30,31} investigated the $\text{H} + \text{HCl/DCI}$ reactions using the QCT method on the G3 PES for collision energies from threshold to 2.4 eV. They found that the maximum impact parameter b_{max} for the exchange channel is about 1.4 Å while it reaches about 2.5 Å for the abstraction channel, and the reaction probability for low b is up to two orders of magnitude larger in the exchange channel. They attributed the high reactivity of off-center collisions for the abstraction channel to the character of “peripheral” reaction.⁴⁰ Large- b collisions sampling the attractive potential (about the lighter and outer atom) are responsible for the observed forward scattering. These conclusions are generally consistent with our findings here.

B. Integral cross sections

Figure 4 shows the total integral cross sections (ICSs) of the abstraction and exchange channels for the $\text{H/D} + \text{HCl/DCI}$ reactions as a function of translational energy. Clearly, the four isotopic combinations present similar ICS profiles for the two channels. For the abstraction channel, the ICSs first increase, reach a maximum and then decrease as the translational energy increases. In contrast, the exchange ICSs increase monotonically with translation energy. The energy thresholds are close to each other for different combinations. Thus, the isotope substitutions have a minor effect on the

energy threshold and the ICS profiles. It is reasonable considering that the zero point energy difference is only 0.05 eV between the reagents HCl and DCI . In addition, for each of the four combinations, the abstraction energy threshold is much lower than the exchange threshold, whereas the exchange ICSs become much larger than the abstraction ones at higher collision energies. This can be understood from the reaction profiles as shown in Fig. 1 that the exchange reaction barrier is 0.558 eV higher than the abstraction reaction barrier.

The differences among different isotope combinations are actually more interesting. For both of the two channels over the energy range studied, the $\text{D} + \text{HCl}$ reaction presents the highest reactivity, the $\text{H} + \text{DCI}$ reaction presents the lowest reactivity, and the $\text{D} + \text{DCI}$ and $\text{H} + \text{HCl}$ reactions

FIG. 4. Total integral cross sections for the $\text{H/D} + \text{HCl/DCI}$ reactions as a function of translational energy. ‘A’ denotes the abstraction reaction and ‘E’ means the exchange reaction.

FIG. 5. State-to-state abstraction integral cross sections for the H/D + HCl/DCI reactions as a function of translational energy. The values in the bracket (v', j') denote the product vibrational and rotational quantum numbers.

are in between, and the ICS amplitudes of the H + HCl reaction are close to but a little larger than those of the D + DCI reaction. In order to clarify it, we look at the quantum opacity functions (Figs. 2 and 3). For the abstraction channel as shown in Fig. 2, we can see that the D + HCl reaction takes place in the widest region of J values while the H + DCI reaction occurs in the narrowest region, and the probability amplitudes of the four combinations are close to each other. This can explain at least in part the different reactivity of the abstraction channel for the four reactions. The different reactivity can also be explained by the model proposed by Zhang *et al.*^{41,42} in their study of the single barrier H + CD₄ reaction, the colliding H-atom moves so quickly that the heavier D-atom on CD₄ cannot concertededly keep up with it to form the HD product. For the exchange channel, it can be found from Fig. 3 that the D + HCl reaction has the largest probability amplitudes and the widest J region while the H + DCI reaction has the smallest amplitude and the narrowest J region. This will undoubtedly lead to the highest reactivity of the D + HCl reaction and the lowest reactivity of the H + DCI reaction.

The state-to-state abstraction ICSs for the H/D + HCl/DCI reactions are presented in Fig. 5. The values (v', j') in the bracket denote the product vibrational and rotational quantum numbers. Considering that the amplitudes of the state-to-state ICSs corresponding to the vibrationally excited product molecule are relatively small, we only show the state-to-state ICSs for the product molecule being in the rotationally excited state ($j' \geq 0$) and in the ground vibrational state ($v' = 0$). It can be seen that, first, all of the state-to-state abstraction ICSs show a similar trend, i.e., they increase sharply, reach a maximum, and then decrease with the increase of collision energy. Second, the state-to-state ICSs present some kinks for rela-

tively low j' values ($j' = 0, 1$) in the energy range just above the reaction threshold. These kinks are possibly caused by the shallow wells in the entrance and exit channels. As the depth of the two wells is only around 0.02 eV, they have little effect on the reaction process in the high energy region. Third, there exist some shoulders in the energy range after the probability maximum except the H + DCI reaction (Fig. 5 (b)). These shoulders may result from the competition between the rebound mechanism and the stripping mechanism. Finally, the energy thresholds of the state-to-state ICSs with larger j' values are shifted to higher energies.

The state-to-state exchange ICSs, as plotted in Fig. 6, are quite different from those for abstraction. They initially increase and become more or less saturated with the increase of translational energy, and those with relatively higher j' values oscillate more. At first thought, it seems unreasonable to simply attribute the oscillations to the existence of the wells in both the entrance and exit channels as the depth of the wells is just 0.013 eV. However, we should note that these oscillations occur for the reaction process with very high product rotational state, which means that the products have relatively small translational energy. In this case, the shallow well in the exit channel should have an impact on the reaction process. In addition, the energy threshold is also shifted to higher energies as j increases.

Figure 7 shows the product rotational state distributions of the abstraction channel for the H/D + HCl/DCI reactions at several selected translational energies. Again, we only present the results for the product molecules in their ground vibrational state ($v' = 0$). Obviously, the ICS maximum shifts to higher j' values and the amplitude of the maximum decreases with the increase of collision energy. Comparing the four panels in this figure, we note that the D + DCI reaction has the

FIG. 6. State-to-state exchange integral cross sections for the H/D + HCl/DCI reactions as a function of translational energy. The values in the bracket (v', j') denote the product vibrational and rotational quantum numbers.

most product internal states excited (Fig. 7(d)) at a specified translational energy, while the least product internal states are excited for the H + HCl reaction (Fig. 7(a)). The other two, the H + DCI reaction (Fig. 7(b)) and the D + HCl reaction (Fig. 7(c)), are in between. This difference can be understood by considering the different densities of the internal states of the products H_2 , HD, and D_2 .

Figure 8 shows the product rotational state distributions of the exchange channel. It can be seen that the ICS maximum shifts to higher j' values as collision energy increases. The amplitude of the maximum first increases with collision energy, and then decreases at the translational energy of 2.0 eV except the D + HCl reaction. The increase of the amplitude of the maximum with collision energy means more

FIG. 7. State-to-state abstraction integral cross sections for the H/D + HCl/DCI reactions as a function of the product rotational quantum number at selected translational energies of 0.4, 0.8, 1.2, 1.6, and 2.0 eV with the product molecule in its ground vibrational state.

FIG. 8. State-to-state exchange integral cross sections for the H/D + HCl/DCI reactions as a function of the product rotational quantum number at selected translational energies of 0.8, 1.0, 1.2, 1.6, and 2.0 eV with the product molecule in its ground vibrational state.

rotational channels of products effectively open at higher collision energies. By comparing the four panels, one gathers that the products are excited to higher internal states for the D + HCl (Fig. 8(c)) and D + DCI (Fig. 8(d)) reactions than the other two reactions at a specified translation energy. This can also be rationalized by considering the different densities of the internal states of the product HCl and DCI.

C. Differential cross sections

The total abstraction differential cross sections (DCSs) for the H/D + HCl/DCI reactions at translational energies of 0.4, 0.8, 1.2, 1.6, and 2.0 eV are shown in Fig. 9. As apparent from this figure, the products (H_2 , HD, or D_2) are mainly backward scattered at low collision energies ($E_{trans} = 0.4$ and 0.8 eV) while they are predominantly forward and sideways

FIG. 9. Total abstraction differential cross sections for the H/D + HCl/DCI reactions at selected translational energies of 0.4, 0.8, 1.2, 1.6, and 2.0 eV.

FIG. 10. Total exchange differential cross sections for the $\text{H/D} + \text{HCl/DCI}$ reactions at selected translational energies of 0.8, 1.0, 1.2, 1.6, and 2.0 eV.

scattered at high energies ($E_{\text{trans}} = 1.2, 1.6$, and 2.0 eV). This is consistent with our expectation from Fig. 2. As mentioned above, the backward scattering indicates a rebound mechanism and the forward and sideways scattering is associated with a stripping mechanism. The increase of forward and sideways scattering products is due to the participation of larger impact parameter collisions while the decrease of backward scattering products results from the depression of reactivity by collision energy at high collision energies. This is actually a feature of the mechanism proposed by Zhang *et al.*⁴¹ in which the DCSs in the backward direction decrease substantially or even vanish at collision energies far above the barrier height. We can also look at the reaction profile of the abstraction channel shown in Fig. 1. There exists a collinear transition state with a barrier of 0.218 eV. Thus, at relatively low collision energies, the reaction is mainly governed by the collinear transition state, which brings about head-on collisions and thus the backward scattering. However, the oblique collisions become more prevalent at high collision energies, in which the centrifugal potential plays an important role. The large centrifugal potential in the transition state area enhances the forward and sideways scattering and simultaneously inhibits the backward scattering. Comparing the four panels, we find that the DCS profile of the $\text{H} + \text{DCI}$ reaction (Fig. 9(b)) is slightly different from the other three reactions although they all present a similar trend along the scattering angle. On the one hand, the total DCSs for $\text{H} + \text{DCI}$ reaction oscillate more strongly than the other three reactions in the forward scattering direction at high collision energies, while, on the other hand, there does not exist a significant decline in the backward direction for high-energy collisions.

Figure 10 shows the total exchange DCSs for the $\text{H/D} + \text{HCl/DCI}$ reactions. In sharp contrast to the abstraction channel, the products (HCl or DCI) are almost exclusively

backward scattered with only minor components being forward scattered, which is in accord with our expectation from the quantum opacity functions. Here, the backward scattering is due to end-on collisions, whereas the forward scattering corresponds to an insertion of the H/D atom. The prevalence of the backward scattering in the whole energy range studied can be understood from the reaction profile of the exchange channel. In Fig. 1, it can be found that there is a collinear transition state with a barrier as high as 0.776 eV. Thus, at collision energies near the energy threshold or not far above it, the reaction is predominantly governed by the collinear transition state, i.e., end-on collisions. Undoubtedly, this kind of collisions results in the backward scattering. When the collision energy becomes far above the reaction barrier, the channel corresponding to the insertion mechanism opens and thus the forward scattering becomes visible. As a large part of the products are backward scattered, we conclude that the exchange process is mainly governed by the collinear transition state in the whole energy range studied, and from the four panels in Fig. 10, it can be seen that there does not exist obvious discrepancy in the exchange reaction mechanisms among the four isotope combinations.

In Fig. 11, we present the state-to-state abstraction DCSs for the $\text{H/D} + \text{HCl/DCI}$ reactions at the translational energy of 0.8 eV. From this figure, we find that the state-to-state DCSs generally follow the prevalence of backward and sideways scattering except that they oscillate much more strongly than the total DCSs at $E_{\text{trans}} = 0.8$ eV. And the products are almost excited to higher rotational states when they scatter increasingly into the sideways direction.

Figure 12 shows the state-to-state exchange DCSs for the $\text{H/D} + \text{HCl/DCI}$ reactions at the translational energy of 1.2 eV. Obviously, the products of different rotational states are almost backward scattered. For the product molecules

FIG. 11. State-to-state abstraction differential cross sections for the H/D + HCl/DCI reactions at the translational energy of 0.8 eV. The values in the bracket ($v' j'$) denote the product vibrational and rotational quantum numbers.

with low j' values, the DCS maximum occurs at 180° . For those with relatively high j' values, there exists a shift of the maximum of the state-to-state DCSs towards the sideways direction. Overall, they are still in the backward hemisphere. The shift of the DCS maximum can be easily understood in terms of classical billiard-ball collisions. For the collision between an atom A and a diatomic molecule BC,

supposing that the preferred approach geometry is collinear and it is a direct reaction, it is reasonable to expect that the AB product rebounds back with little rotational excitation for small impact parameters, whereas for relatively larger impact parameters, the AB product becomes more sideways scattered and is simultaneously excited to higher rotational states.⁴³

FIG. 12. State-to-state exchange differential cross sections for the H/D + HCl/DCI reactions at the translational energy of 1.2 eV. The values in the bracket ($v' j'$) denote the product vibrational and rotational quantum number.

FIG. 13. Total abstraction integral cross sections as a function of translational energy for the $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ (upper panel) and $\text{H} + \text{DCI} \rightarrow \text{HD} + \text{Cl}$ (lower panel) reactions. In the upper panel, the solid circle denotes the experimental results of Ref. 18 while the open circles correspond to the experimental results of Ref. 19. In the lower panel, the solid squares are the experimental results of Ref. 17 while the open squares represent the experimental results of Ref. 20.

D. Comparison between theoretical and experimental results

The calculated total abstraction ICSs for the $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ (upper panel) and $\text{H} + \text{DCI} \rightarrow \text{HD} + \text{Cl}$ (lower panel) reactions from the ground rovibrational state, together with the experimental results from Polanyi's group¹⁷ and Volpp's group,^{18–20} are shown in Fig. 13. Aoiz *et al.*³¹ showed that the initial rotational excitation for all j values significantly populated at room temperature has a relatively small influence on the reactivity. Thus, it is meaningful to directly compare our initial state-selected ICSs ($v_0 = 0, j_0 = 0$) with experimental results. From this figure, we can see that our theoretical ICSs are more than twice as large as the experimental results for both reactions. And the discrepancy increases with collision energy. At high collision energies, the theoretical ICSs are more than five times as large as the experimental results. The large difference can be understood as follows. On the one hand, the nonadiabatic effects, which are important in the abstraction process and become pronounced as the collision energy increases, are not considered in the present calculations. The experimental measurements by Volpp's group^{19,20} revealed that the relative contribution

FIG. 14. Total exchange integral cross sections as a function of translational energy for the exchange $\text{H} + \text{DCI} \rightarrow \text{HCl} + \text{D}$ reaction. The solid triangles are the experimental results of Ref. 17 while the open triangles represent the experimental results of Ref. 21.

of the nonadiabatic abstraction reaction channel for the two reactions increases with increasing collision energy. This can explain why the discrepancy increases with collision energy. On the other hand, the SO coupling effects are not included in the BW2 PES employed here. The G3 PES, which includes the SO coupling effects, has been used to calculate the ICSs for the two reactions. Good agreement between experimental and theoretical results have been found.^{19,20,31} Thus, the SO coupling effects also play an important role in the abstraction reaction process.

Figure 14 shows the calculated total ICSs for the $\text{H} + \text{DCI} \rightarrow \text{HCl} + \text{D}$ reaction, together with the experimental results. The experimental cross sections reported by Polanyi's group¹⁷ (solid triangle) did not present a clear energy dependence. It seems that there exists a moderate decrease with increasing collision energy. In contrast, the recent experimental results from Volpp's group²¹ showed an obvious energy dependence, i.e., the reaction cross section increases monotonically with collision energy. Our theoretical ICSs agree with Volpp's experimental results quite well. They are well located within the experimental uncertainty. Good agreement has also been found by the QCT calculations on the BW2 PES.²¹ Volpp's group¹⁹ also performed the QCT calculations on the G3 and BW1 PESs. Although the two PESs both gave smaller cross sections than experimental results, they presented a clear monotonic increase. These findings are in contrast to Polanyi's experimental results as most of them are out of the error bar of Polanyi's experiment. Thus, we believe that Volpp's experimental results are more reliable, i.e., the exchange cross section is a monotonic increasing function above the energy threshold. Our calculations (Fig. 8) have already shown that the increase of collision energy results in exchange products excited to much higher rotational states with the simultaneous increase of the exchange ICS maximum. So, more product rotational channels are effectively opening at higher collision energies, which justifies the experimental observations on the monotonic increase of the exchange ICSs.

IV. CONCLUSIONS

The reactant coordinate based time-dependent wave packet method was employed to study the H/D + HCl/DCI ($v_0 = 0, j_0 = 0$) reactions on the BW2 PES. We presented the total and state-to-state integral cross sections and differential cross sections of both the abstraction and exchange channels at collision energies up to 2.0 eV.

The theoretical total exchange integral cross sections agree well with Volpp's experimental results for the H + DCI reaction. However, they are at variance with Polanyi's experimental results. We suggest that Volpp's experimental results are more reliable. The theoretical total abstraction integral cross sections are more than twice as large as the experimental results from the two groups for the H + HCl/DCI reactions, and the discrepancy increases with collision energy.

The total exchange integral cross sections for the H/D + HCl/DCI reactions increase monotonically with the translation energy while there exists a slight decline for the abstraction cross sections at high collision energies. The state-to-state abstraction integral cross sections with relatively low j' values oscillate more strongly than those with relatively high j' values, whereas the state-to-state exchange integral cross sections with relatively high j' values oscillate more wildly.

The abstraction products (H₂, HD, D₂) are predominantly backward scattered at low collision energies and forward and sideways scattered at high energies. In contrast, the exchange products (HCl, DCI) are almost exclusively backward scattered with only minor components being forward scattered.

For both the abstraction and exchange channels over the energy range studied, the D + HCl reaction presents the highest reactivity, the H + DCI reaction presents the lowest reactivity, and the H + HCl and D + DCI reactions are in between them with the former having a slightly larger reactivity.

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