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Full-Dimensional Quantum Dynamical Studies of the Cl + HOD → HCl/DCI + OD/OH Reaction: Bond Selectivity and Isotopic Branching Ratio

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ABSTRACT: Full-dimensional quantum dynamical calculations are carried out to study the mode specificity, bond selectivity, and isotopic branching ratio of the Cl + HOD reaction on an accurate global potential energy surface. Total reaction cross sections have been computed for several low-lying vibrational states of HOD. Our results confirm the experimentally observed vibrationally promoted bond cleavage, in which the breaking of the OH(OD) bond is strongly enhanced by the OH(OD) excitation. These results are rationalized by the recently proposed sudden vector projection model. In addition, the OH/OD branching ratio as a function of energy is investigated and rationalized by a reorientation effect.

I. INTRODUCTION

The $X + H_2O \leftrightarrow HX + OH$ ($X = H, F, Cl, O(^3P)$) reactions have become an important proving ground for understanding fundamental issues in chemical dynamics, such as mode specificity, bond selectivity, product energy disposal, and stereodynamics.¹ These reactions have the advantage that the size of the reactive system is sufficiently small for a full-dimensional quantum dynamical (QD) treatment on an accurate global potential energy surface (PES), but in the meantime the dynamics is much more complex than atom-diatom reactions. In the past few years, many authors including us have reported several accurate global PESs for these reactions and carried out extensive and systematic dynamical calculations on these PESs. Detailed comparisons with available experimental results have been performed. These studies have advanced our understanding of reaction dynamics of bimolecular reactions in the gas phase.

Mode specific reactivity sheds valuable light on the reaction dynamics.² In the case of the $F + H_2O$ reaction, for example, interesting and surprising findings have been reported. For this reaction with a decidedly early barrier, a naïve extension of the Polanyi rules³ would predict that translational energy is more effective in promoting the reaction than the same amount of vibrational energy. However, our dynamical calculations on an accurate PES indicated that excitations in the three vibrational modes of the water reactant promote the reaction more effectively than the same amount of translational energy.⁴ Although stretching excitations in H_2O do promote its late-barrier reaction with Cl,⁵ on the contrary, the HCl vibrational excitation was found to promote the reverse $HCl + OH$

reaction,⁶ which also has an early barrier. These apparent inconsistencies with the extended Polanyi rules have motivated us to search for more sophisticated rules of thumb to rationalize the new phenomena, which culminated with a new model for understanding the mode specificity. This so-called sudden vector projection (SVP) model relies on the coupling of reactant mode with the reaction coordinate at the transition state to predict the dependence of reactivity on reactant modes,^{7,8} and it has successfully explained these surprising observations.⁹

A related issue is the bond selectivity, in which the ability to cleave a selected chemical bond in the reactant is of concern.¹⁰ Crim, Zare, and their co-workers have experimentally studied the OH vs OD bond cleavage in reactions between H/Cl and HOD.^{11–18} The bond selective reaction dynamics has also been investigated theoretically,^{19–25} including our recent work on the $F + HOD$ ²⁶ and $Cl + HOD$ reactions.²⁷ In the latter work,²⁷ the focus was placed on highly excited O–H modes and comparison with experimental data. Here, we present a detailed full-dimensional quantum dynamics study of the title reaction, extending our earlier work²⁷ to include the other vibrational modes. Special attention was also paid to the OH/OD branching ratio in various scenarios. The paper is organized as follows. Section II details the theoretical method and their

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implementation. The results are presented and discussed in section III. Finally, conclusions are given in section IV.

II. THEORY

For a tetra-atomic system, the six-dimensional Hamiltonian for a given total angular momentum J in the atom-triatom Jacobi

Figure 1. Reactant Jacobi coordinates for the A + BCD system used in the QD calculations.

coordinates, as shown in Figure 1, can be written as ($\hbar = 1$ thereafter):²⁸

$$\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} + \hat{h}_1(r_1) + \hat{h}_2(r_2) + \frac{(\hat{J} - \hat{j}_{12})^2}{2\mu_R R^2} + \frac{\hat{l}_1^2}{2\mu_1 r_1^2} + \frac{\hat{j}_2^2}{2\mu_2 r_2^2} + \hat{V}(R, r_1, r_2, \theta_1, \theta_2, \varphi_1) - V_1^{\text{ref}}(r_1) - V_2^{\text{ref}}(r_2) \quad (1)$$

where R , r_1 , and r_2 are the distance from A to the center of mass (COM) of BCD, the distance from B to the COM of CD, and the bond distance of CD, respectively, with μ_R , μ_1 , and μ_2 as their corresponding reduced masses. $\hat{j}_2$ is the rotational angular momentum operator of CD and $\hat{l}_1$ is the orbital angular momentum operator of B with respect to CD, which are coupled to $\hat{j}_{12}$. $\hat{J}$ represents the total angular momentum operator. The one-dimensional (1D) reference Hamiltonians are defined as

$$\hat{h}_i(r_i) = -\frac{1}{2\mu_i} \frac{\partial^2}{\partial r_i^2} + V^{\text{ref}}(r_i) \quad i = 1, 2 \quad (2)$$

where $V^{\text{ref}}(r_i)$ are the corresponding 1D reference potentials along the coordinates r_i where other coordinates are fixed at the equilibrium geometry for the triatomic BCD molecule far away from the atom A.

The global PES used in the calculations is the one reported in our recent work.²⁷ Specifically, *ab initio* points at the Davidson corrected multireference configuration interaction level²⁹ with the correlation consistent aug-cc-pVTZ (MRCI + Q/AVTZ) basis set³⁰ were generated³¹ and fitted²⁷ with the permutation-invariant polynomial neural network (PIP-NN) method.^{32,33} The high-fidelity fit has a root-mean-square error (RMSE) of 8.4 meV. This PIP-NN PES has been used in our recent studies of the title reaction and its reverse,^{5,6,27,34} and the agreement with available experimental data has been quite satisfactory.

The parity (ϵ) adapted wave function is expanded in terms of the body-fixed (BF) ro-vibrational basis functions:

$$\Psi^{JMe}(\vec{R}, \vec{r}_1, \vec{r}_2) = \sum_{n, \nu_1, \nu_2, j, K} C_{n\nu_1\nu_2jK}^{JMe} u_n^{\nu_1\nu_2}(R) \phi_{\nu_1}(r_1) \phi_{\nu_2}(r_2) \Phi_{jK}^{JMe}(\hat{R}, \hat{r}_1, \hat{r}_2) \quad (3)$$

where n labels the translational basis functions, ν_1 and ν_2 are the basis indices for r_1 and r_2 , and the composite index j denotes (l_1, j_2, j_{12}) . The translational basis function, $u_n^{\nu_1\nu_2}$, is dependent on ν_1 and ν_2 due to the use of an L-shaped grid.³⁵ Φ_{jK}^{JMe} in eq 3 is the parity-adapted coupled BF total angular momentum eigenfunction, which can be written as³⁶

$$\Phi_{jK}^{JMe} = (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} [D_{K,M}^{J*} Y_{l_{j_2}}^{j_{12}K} + \epsilon(-1)^{l_1+j_2+j_{12}+J} D_{-K,M}^{J*} Y_{l_{j_2}}^{j_{12}-K}] \quad (4)$$

where $D_{K,M}^J$ is the Wigner rotation matrix.³⁷ M is the projection of J on the z axis in the space-fixed (SF) frame, and K is its projection on the BF z axis that coincides with R . $Y_{l_{j_2}}^{j_{12}K}$ is defined as

$$Y_{l_{j_2}}^{j_{12}K} = \sum_m D_{Km}^{j_{12}*}(0, \theta_1, \varphi_1) \sqrt{\frac{2l_1+1}{4\pi}} \sum_m \langle j_2 m l_1 0 | j_{12} m \rangle y_{j_2 m}(\theta_2, 0) \quad (5)$$

and y_{jm} denotes the spherical harmonics. Note the restriction that $\epsilon(-1)^{l_1+j_2+j_{12}+J} = 0$ for $K = 0$ in eq 4.

Under the coupled-state or centrifugal-sudden (CS) approximation,^{38,39} namely, neglecting the coupling between different K blocks, the centrifugal term, i.e., $(\hat{J} - \hat{j}_{12})^2$ in the Hamiltonian is approximately given by

$$\langle \Phi_{jK}^{JMe} | (\hat{J} - \hat{j}_{12})^2 | \Phi_{j'K'}^{JMe} \rangle \approx \delta_{jj'} \delta_{KK'} [J(J+1) + j_{12}(j_{12}+1) - 2K^2] \quad (6)$$

Because the CS approximation has been extensively tested and shown to work well for activated reactions,^{40–43} the scattering calculations reported here were performed using this approximation.

The initial wave packet $|\chi_i\rangle$ is prepared by the direct product of a localized Gaussian wave packet in the scattering coordinate and a specific rovibrational state of HOD in the BF representation:

$$|\chi_i\rangle = \left(\frac{1}{\pi \delta^2} \right)^{1/4} e^{-(R-R_0)^2/2\delta^2} e^{-ik_i R} |v_0 j_0 \tau; j \epsilon\rangle \quad (7)$$

where R_0 and δ are the mean position and width of the Gaussian function and k_i is the mean momentum given by E_i via $k_i = (2\mu_R E_i)^{1/2}$, where v_0 , j_0 , and τ denote the initial vibrational quantum number, the initial angular momentum quantum number, and the parity of the reactant BCD, respectively. The initial ro-vibrational wave function of the reactant HOD was obtained by diagonalizing its three-dimensional Hamiltonian. The second-order split-operator method⁴⁴ was employed to propagate the wave packet. Transformations between the discrete variable representation (DVR) and the finite basis representation (FBR)⁴⁵ were used in applying the Hamiltonian onto the wave packet at each propagation step. To impose outgoing boundary conditions, the negative imaginary absorbing potentials D are applied at the grid edges:

$$D(x) = -i\alpha \left(\frac{x - x_a}{x_{\text{max}} - x_a} \right)^n \quad (8)$$

where $x = R$, r_1 and r_2 , x_a is the starting point of the absorbing potential.

From the propagation of the initial wave packet, the energy-dependent scattering wave function, $\Psi_i^+(E)$, can be obtained by

Fourier transforming the time-dependent wave function at the dividing surface. The total reaction probability, P_i^E , from a given initial state $|v_{0j_0}\tau\rangle$ is calculated at each J and E values using the flux formula:

$$P_i = \langle \psi_i^+(E) | \hat{F} | \psi_i^+(E) \rangle \quad (9)$$

where $\hat{F}$ is the flux operator defined on a dividing surface in a product channel.

The total reaction integral cross section (ICS) from a specific initial state at the collision energy E_c is calculated by summing the reaction probabilities over all relevant partial waves:

$$\sigma_{v_{0j_0}\tau}(E_c) = \frac{1}{(2j_0 + 1)} \frac{\pi}{2\mu_R E_c} \sum_{K_0} \sum_{J \geq K_0} (2J + 1) P_{v_{0j_0}\tau K_0}^E(E_c) \quad (10)$$

III. RESULTS

The vibrational state of HOD is represented by the three quantum numbers (n_1, n_2, n_3), which denote the excitations in the OD stretching, bending, and OH stretching modes, respectively. The fundamentals of the three vibrational modes, namely, (100), (010), and (001), have been computed in the reactant asymptote to be 2675.14, 1384.70, and 3655.35 cm^{-1} . These theoretical values are in good agreement with known experimental values of 2726.73, 1402.20, and 3707.47 cm^{-1} .⁴⁶ For simplicity, only the ground rotational state is studied in this work. In the QD calculations, the OH and OD bonds in the reactant HOD are treated on an equal footing; i.e., they are allowed to be broken simultaneously. Thus, the reaction probabilities for both channels from a specific initial state can be calculated by a single propagation. This model is more general than those assuming a nonreactive bond. However, it poses a bigger challenge to numerical calculations. Table 1 lists the numerical parameters employed in this study.

Table 1. Numerical Parameters Used in the Wave Packet Calculations^a

Cl + HOD $\rightarrow$ HCl/DCl + OD/OH	
grid/basis range and size:	$R \in [2.0, 18.0]$ $N_R^{\text{tot}} = 308, N_R^{\text{int}} = 100$ $N_{r_1}^{\text{int}} = 32, N_{r_1}^{\text{asy}} = 3$ $N_{r_2}^{\text{int}} = 35, N_{r_2}^{\text{asy}} = 3$ $j_{1\text{max}} = 46, j_{2\text{max}} = 42$
initial wave packet:	$R_0 = 15.5, \delta = 0.15, E_i = 1.0 \text{ eV}$
absorbing potential:	$R_a = 15.5, \alpha_R = 0.05, n_R = 1.5$ $R_{1a} = 3.5, \alpha_{r_1} = 0.05, n_{r_1} = 1.5$ $R_{2a} = 3.5, \alpha_{r_2} = 0.05, n_{r_2} = 1.5$
flux position:	$r_1^F = 3.5, r_2^F = 3.5$

^aAtomic units are used unless stated otherwise.

An L -shaped scheme³⁵ is employed in the numerical calculations, in which the configuration space is divided into two regions, the interaction region and the asymptotic region. Therefore, one can truncate basis functions in the asymptotic region. For the scattering coordinate R , 308 sine discrete variable representation (DVR) basis/points are used in the whole range from 2.0 to 18.0 a_0 and 100 sine DVR basis/points are used in the interaction region. For the coordinate r_1 , 32 potential optimized discrete variable representation (PODVR) basis/points are used in the interaction region, and 3 PODVR

basis/points are used in the asymptotic region. A total of 35 PODVR basis/points in the interaction region and 3 PODVR basis/points in the asymptotic region are used for the coordinate r_2 . These parameters were well tested to give converged results. The total angular momentum J is taken from 0 to 180 with uneven intervals, i.e., 0, 2, 5, 10, 20, 30, 40, 60, 80, 100, 140, and 180, for the ground vibrational state and more partial waves are included for higher vibrational state to converge the integral cross sections over the whole energy range studied. The interpolation scheme is applied to obtain the reaction probabilities for other J within the range. The propagation was around 3000 steps with a time step of 10 au and the number of propagation steps decreases with the increasing total angular momentum.

A. Mode Specificity. We first examine the Cl + HOD(n_1, n_2, n_3) $\rightarrow$ HCl + OD reaction, in which the H–O bond of the HOD reactant is cleaved. The calculated ICSs are plotted in Figure 2 as a function of total energy, which is

Figure 2. ICSs for the Cl + HOD $\rightarrow$ HCl + OD reaction from four different vibrational states of HOD as a function of total energy. The inset provides a close-up view of the reaction thresholds.

measured from the reactant asymptote. A more detailed depiction of the energy threshold region is given in the inset. The ICS from the ground state of HOD is extremely small, consistent with previous work.^{5,27,34} It is clear from the figure that the excitation of the OH stretching mode of HOD significantly promotes the reaction, whereas the excitation of the bending mode or the OD stretching mode only slightly enhances the reactivity. In addition, it can be readily seen from the inset that the excitation of the OD stretching mode is a little more efficient than the excitation of the bending mode in enhancing the reaction over the energy range. Furthermore, the vibrational energy initially deposited in any of the three modes of HOD promotes the reaction more than translational energy of the same amount.

The situation is quite similar for the Cl + HOD(n_1, n_2, n_3) $\rightarrow$ DCl + OH reaction, in which the O–D bond is broken. Figure 3 shows the corresponding ICSs, which indicate that the excitation in the O–D stretching mode is highly effective in promoting this reaction, whereas the excitation of the bending mode or the OH stretching mode only slightly enhances the reactivity. Similarly to the HCl + OD channel modes, all three

Figure 3. ICSs for the $\text{Cl} + \text{HOD} \rightarrow \text{DCl} + \text{OH}$ reaction from four different vibrational states of HOD as a function of total energy. The inset provides a close-up view of the reaction thresholds.

vibrational modes of HOD promote the reaction more effectively than translational energy.

The clear bond selective nature of the reactions discussed above is consistent with the experimental evidence that excitation of the local stretching mode of HOD greatly enhances the cleavage of the corresponding bond in the $\text{H}/\text{Cl} + \text{HOD}$ reactions.^{11–18}

To rationalize the strong mode specificity, we rely on the recently proposed SVP model,^{7–9} which attributes the reactant mode efficacy in enhancing a reaction to its projection onto the reaction coordinate at the transition state. This model is reasonable as the collision time is sufficiently short compared with the IVR rate in the reactant molecule. Practically, the normal mode vector of the reactant is projected onto the reaction coordinate at the transition state, and the projection value is used to measure the coupling strength. Figure 4 shows the reactant vibrational mode vectors of HOD and the reaction

Figure 4. Comparison of the reactant vibrational mode vectors and the reaction coordinate vectors in the two transition states and the alignment of the reactant/product vectors with the reaction coordinate vector. The H, D, O, and Cl atoms are color coded as white, yellow, red, and green.

coordinate vectors for the transition states leading to the two reaction channels. The alignments of the vectors are also given in the bottom of the figure. For completeness, the alignments for the reverse reactions are also plotted. The corresponding SVP values are also listed in Table 2.

Table 2. SVP Values ($\eta_i = \vec{Q}_i \cdot \vec{Q}_{RC}$) for the $\text{Cl} + \text{HOD} \rightarrow \text{HCl}/\text{DCl} + \text{OD}/\text{OH}$ Reaction

HOD mode	SVP	
	$\text{Cl} + \text{HOD} \rightarrow \text{HCl} + \text{OD}$	$\text{Cl} + \text{HOD} \rightarrow \text{DCl} + \text{OH}$
ν_{OH}	0.99	0.07
ν_{OD}	0.09	0.99
ν_{b}	0.06	0.05
trans	0.07	0.08

As can be seen from the second column of Table 2, the projection of the OH stretching mode in the reactant HOD to the reaction coordinate at the $\text{Cl}\cdots\text{HOD}$ transition state is 0.99, which indicates that the OH vibrational coordinate is practically the reaction coordinate. The vibrational energy initially deposited in the OH stretching mode flows virtually all into the reaction coordinate to promote the reactivity for the O–H bond cleavage. Thus, excitation of the OH stretching mode leads to very strong enhancement of this reactive channel. On the contrary, the bending and OD stretching modes have comparable SVP values with the translational mode and are all much smaller than that of the OH stretching mode. Thus, their efficacies for promoting this reaction channel is quite small. Analogously, the OD stretching mode vector is well aligned with the reaction coordinate at the $\text{Cl}\cdots\text{DOH}$ transition state and this mode greatly promotes the $\text{Cl} + \text{HOD} \rightarrow \text{DCl} + \text{OH}$ reaction, whereas the bending, OH stretching, and translational modes are much less effective for this channel. All these predictions agree well with the QD results.

B. Isotopic Branching Ratio. Now we focus on the branching ratio between the two channels. This issue has been extensively discussed for triatomic reactions: $\text{X} + \text{HD} \rightarrow \text{XD} + \text{H}/\text{XH} + \text{D}$ ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{O}, \text{and S}$).^{47–51} It was argued on the basis of these studies on triatomic reactions that abstraction reactions generally have an XH/XD ratio less than 1 whereas insertion reactions have an XH/XD ratio greater than 1. The bias was attributed to the mass asymmetry that results in a biased cone of acceptance and the reorientation effect.^{48,52,53} In contrast, recent studies on tetra-atomic reactions, such as $\text{H} + \text{HOD}$ and $\text{F} + \text{HOD}$, showed the OD channel is more favored than the OH channel.^{25,26} The $\text{Cl} + \text{HOD}$ reaction resembles the late-barrier $\text{H} + \text{HOD}$ reaction and is expected to have isotopic branching ratios similar to those of the $\text{H} + \text{HOD}$ reaction.

The QD ICSs for the two channels of the title reaction are shown in Figure 5 as a function of translational energy with the reactant HOD in its ground ro-vibrational state. Obviously, the OH channel is more favorable than the OD channel at collision energies higher than the reaction threshold although the two channels present almost the same energy threshold. This is quite different from the findings in the $\text{H}/\text{F} + \text{HOD}$ reactions,^{25,26} in which the OH bond cleavage is preferred.

To gain mechanistic insights of the reaction dynamics, standard quasi-classical trajectory (QCT) calculations implemented in VENUS⁵⁴ were carried out at the collision energy of 1.5 eV. A total of 6×10^6 trajectories were propagated, and the error of the reactive integral cross section is within 8%. There

Figure 5. Excitation functions for the $\text{Cl} + \text{HOD} \rightarrow \text{HCl} + \text{OD}/\text{DCI} + \text{OH}$ reaction with the reactant HOD in its ground ro-vibrational state. The QCT ICSs with $E_c = 1.5$ eV are also given for comparison.

exist 163 reactive trajectories for the $\text{HCl} + \text{OD}$ channel and 214 reactive trajectories for the $\text{DCI} + \text{OH}$ channel. The corresponding cross sections are shown in Figure 5. Clearly, the QCT results confirm the preference of the $\text{DCI} + \text{OH}$ channel over the $\text{HCl} + \text{OD}$ channel, although their amplitudes are larger than their quantum counterparts. The discrepancy is possibly caused by the ZPE leakage of the trajectories, an intrinsic defect in the QCT methodology, or by the CS approximation employed in the QM calculations.

For clarity, the behaviors of the reactive trajectories were found to belong to two groups, “migratory” and “non-

migratory”. For the migration group, the chlorine atom reacts with the end of the HOD molecule opposite to the one initially attacked, whereas for the nonmigration group the chlorine atom reacts with the H/D atom in the molecule initially attacked. Figure 6 shows four typical trajectories as a function of Jacobi coordinates R and θ_1 to visualize the two different groups for each of the two isotopic channels. The upper two panels correspond to the $\text{HCl} + \text{OD}$ channel and the lower two panels refer to the $\text{DCI} + \text{OH}$ channel. In Figure 6a,c, the Cl atom reacts directly with the atom initially attacked and the trajectory just passes over the corresponding transition state. From Figure 6b,d, it can be seen that the Cl atom is pulled toward the other end opposite to the initially attacked through the reorientation of HOD and the trajectory crosses over the transition state. By analyzing all the reactive trajectories, it was found that for the $\text{DCI} + \text{OH}$ channel, 73 trajectories proceed via a nonmigration mechanism and 141 trajectories via a migration mechanism whereas for the $\text{HCl} + \text{OD}$ channel 151 trajectories take place with a nonmigration mechanism and 12 trajectories with a migration mechanism. Thus, it is clear that the bias to break the OD bond in the reactant HOD results from a reorientation effect. A large number of trajectories initially attacking the H end of HOD are reoriented toward the D end to produce the product DCI and OH . This feature is quite similar to those found in the $\text{F} + \text{HD}$ and $\text{Cl} + \text{HD}$ reactions,^{49,50} in which the preference of the DF/DCI product was partly attributed to the reorientation effect caused by the mass asymmetry. The reaction mechanism for the title reaction is much more complicated than the triatomic reactions and thus further works are still needed to gain an in-depth understanding.

Figure 6. Four typical trajectories along the Jacobi coordinates R and θ_1 defined in Figure 1 to illustrate the two classes, migratory and nonmigratory, in the two isotopic channels: (a) nonmigratory; (b) migratory; (c) nonmigratory; (d) migratory. The positions of the two transition states ($\text{Cl}\cdots\text{HOD}$ and $\text{Cl}\cdots\text{DOH}$) are also given as “+” in red and blue, respectively. The configuration of the system at the turning point is plotted, marked as purple solid circle, in the trajectory.

Figure 7 shows the translational energy dependence of the product branching ratio between the HCl + OD and DCl + OH

Figure 7. Product branching ratios for the $\text{Cl} + \text{HOD}(n_1, n_2, n_3) \rightarrow \text{HCl} + \text{OD}/\text{DCl} + \text{OH}$ reaction as a function of collision energy.

channels with the reactant HOD initially in different vibrational states. In the top panel, the OH/OD branching ratios for the reaction HOD initially in the ground and first excited bending states are plotted as a function of translational energy. As can be seen from this panel, the OH/OD branching ratio from the ground state is greater than 1 over the energy range studied and it increases monotonically with the collision energy. When the reactant HOD is excited to the fundamental of the bending mode, the profile of the branching ratio resembles that from the ground state. However, the ratio is smaller than 1 when the translational energy is lower than 0.95 eV. Thus, the OD channel is preferred to the OH channel at low collision energies when the bending mode of HOD is excited. In the middle panel, the reactant HOD is excited to the first excited OD stretching state. The OH/OD branching ratio first raises very sharply and then becomes more or less saturated around a value of ~ 23 . The ratio is apparently larger than those from the HOD ground and first excited bending states. The OD/OH ratio from the first excited OH stretching state is given in the bottom panel. In contrast to the profile in the middle panel, the ratio is much larger than 1 at low collision energies near the energy threshold and then drops steeply and finally becomes leveled off around a value of 30 with the increase of the collision energy. The behavior is similar to that found in the $\text{F} + \text{HOD}$ reaction, where the branching ratio has a weak energy dependence at high collision energies.²⁶

IV. CONCLUSIONS

The mode specificity, bond selectivity, and isotopic branching ratio of the $\text{Cl} + \text{HOD}$ reaction have been studied using a full-dimensional QD method on a recently developed global PES. On one hand, excitations in the OD stretching and bending and OH stretching modes enhance the reactivity for both channels and are all more effective than translational excitation in promoting the reaction. On the other hand, excitation in the local OH or OD stretching mode significantly facilitates the breaking of the corresponding bond and thus promotes the reactivity significantly. These dynamical features can be well explained by the coupling between the reactant vibrational mode vectors and the reaction coordinate vector in the SVP model. In addition, it was found that the $\text{Cl} + \text{HOD}$ reaction from the ground vibrational state prefers the $\text{DCl} + \text{OH}$ channel to the $\text{HCl} + \text{OD}$ channel. By analyzing the reactive trajectories, the preference was attributed to a reorientation effect of the HOD reactant.

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Notes

The authors declare no competing financial interest.

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