I. INTRODUCTION

Understanding mode-specific dynamics of elementary chemical reactions is highly desirable in the field of molecular reaction dynamics [1–4]. Since the mode specificity can be used to control the related chemical reaction and, ideally, to improve the efficiency in industrial chemical processes [5–8]. It has been long realized that the reactivity will generally be enhanced significantly by vibrationally exciting the reactant mode along the reaction coordinate, especially for the late-barrier reactions [9]. Recently, it was found that the reactivity will be changed remarkably in some polyatomic reactions by rotationally exciting the reactants as the excitation alters the initial orientation of reactants [10]. The time-dependent quantum wave packet method combined with a seven-dimensional reduced model is employed to calculate the reaction probability on an accurate potential energy surface. The obtained reaction probability depends on the values of both $K$ and $K_{\text{tot}}$, with $P_{K_{\text{tot}}=K=0}>P_{K_{\text{tot}}=K=J}>P_{K_{\text{tot}}=J,K=0}=P_{K_{\text{tot}}=0,K=J}$. This observation can be well rationalized by the reactant alignment pictures. Rotational excitations of CHD$_3$ up to the angular momentum quantum number $J=4$ have a very weak enhancement effect on the reaction except for the state ($J=4$, $K=0$). In addition, the rotationally excited states of CHD$_3$ with $K=0$ promote the reaction more than those with $K=J$. The quantum dynamics calculations indicate that the $K=0$ enhancements are mainly caused by the contributions from the components with $K=K_{\text{tot}}=0$. The components correspond to the tumbling rotation of CHD$_3$, which enlarges the range of the reactive initial attack angles.

Key words: Polyatomic reaction, Rotational excitation, Time-dependent wave packet
dimensional quantum scattering methods [37, 38, 41, 43, 44, 60–64]. The number of degrees of freedom included in the quantum scattering model was ranging from 3 to 8. These calculations were mainly concerned with the ground state and/or vibrationally excited states of CH$_4$/CHD and the calculated excitation function for the ground state of CH$_4$ agreed well with experiment. Furthermore, some investigations on the dynamics of the O(1D)+CH$_4$/CHD$_3$/CD$_4$ reactions have been performed as well [65–69].

In this work, the effect of CHD$_3$ rotation on the dynamics of the O(3P)+CHD$_3$→OH+CD$_3$ reaction will be studied using a reduced seven-dimensional (7D) quantum scattering model. The potential energy surface (PES) developed by Czaékó and Bowman was employed in the calculations, which was fitted to 17212 accurate ab initio points using a permutationally invariant polynomial method [58]. The O(3P)+CHD$_3$→OH+CD$_3$ reaction has a classical (adiabatic) barrier height of ~14 (10) kcal/mol. Although Czaékó has carried out QCT calculations on the rotational mode specificity of the O(3P)+CHD$_3$→OH+CD$_3$ reaction [59], the quantum effects, such as tunneling and zero-point energy, are expected to be significant in the reaction.

II. THEORY

The reduced 7D Palma-Clary model and the initial state-selected time-dependent wave packet method both have been detailed in the literature. Here, we only describe briefly the theoretical aspects relevant to this work [16, 43, 60, 70]. In the 7D Palma-Clary model for the X+CYZ$_3$ system, the CZ$_3$ moiety is assumed to maintain its C$_{3v}$ symmetry in the reaction process. The Jacobi coordinates are shown in FIG. 1, in which $\mathbf{R}$ is the vector from the center of mass (COM) of CYZ$_3$ to X, $\mathbf{r}$ is the vector from the COM of CZ$_3$ to Y, q is the bond length of CZ and fixed at its equilibrium value of 2.067 a.u. for CHD bond length of CZ and fixed at its equilibrium value of 1.067 a.u. for CHD. $\mathbf{R}$ has been detailed in the literature. Here, we only state-selected time-dependent wave packet method both

$\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \left(\hat{J}_{\text{tot}} - \hat{j}\right)^2 + \frac{\hat{l}^2}{2\mu_r r^2} + \hat{K}^{\text{vib}}_{\text{CZ}_3} + \hat{K}^{\text{rot}}_{\text{CZ}_3} + V(R, r, \theta_1, \phi_1, \theta_2, \phi_2) \tag{1}

$\hat{K}^{\text{vib}}_{\text{CZ}_3} = -\frac{1}{2q^2} \left(\frac{\cos^2 \chi}{\mu_x} + \frac{\sin^2 \chi}{\mu_x}\right) \frac{\partial^2}{\partial \chi^2} - \frac{1}{q^2} \left(\frac{1}{\mu_x} - \frac{1}{\mu_z}\right) \sin \chi \cos \chi \frac{\partial}{\partial \chi} \tag{2}$

$\hat{K}^{\text{rot}}_{\text{CZ}_3} = \frac{1}{2I_A} \hat{j}_z^2 + \left(\frac{1}{2I_C} - \frac{1}{2I_A}\right) \hat{j}_z^2 \tag{3}$

in which $\hat{j}$ is the rotational angular momentum with respect to CZ$_3$, $\hat{J}_{\text{tot}}$ and $\hat{j}_z$ is its z-component. $\mu_x=3m_Z$ and $\mu_z=3m_cm_z/(m_C+3m_Z)$. $I_A$ and $I_C$ are the rotational inertia, which are defined as

$I_A = \frac{3}{2} m_Z q^2 \left(\sin^2 \chi + \frac{2mc}{m_C + 3m_Z} \cos^2 \chi\right) \tag{4}$

$I_C = 3m_Z q^2 \sin^2 \chi \tag{5}$

The vibration-rotation coupling is neglected in the model due to the constraint of the C$_{3v}$ symmetry.

The time-dependent wavefunction is expanded in terms of the rovibrational eigenfunctions as

$\psi_{J\mu_1M_1\epsilon}(t) = \sum_{n_R, n_r, n_n, K_{\text{tot}}, \ell_{jk}} \sum \left(c_{J\mu_1M_1K_{\text{tot}}\ell_{jk}}(t)G_{n_R}(R) \cdot F_{n_R}(r)H_{n_n}(\chi)\Phi_{J\mu_1M_1K_{\text{tot}}\ell_{jk}}(\tilde{R}, \tilde{r}, \tilde{s})\right) \tag{6}$

where $c_{J\mu_1M_1K_{\text{tot}}\ell_{jk}}(t)$ are time-dependent coefficients. $n_R$ is the translational basis label along $R$ and the associated basis functions $G_{n_R}(R)$ are defined [71] as

$G_{n_R}(R) = \sqrt{\frac{2}{R_{\text{max}} - R_{\text{min}}}} \sin \frac{n_R \pi (R - R_{\text{min}})}{R_{\text{max}} - R_{\text{min}}} \tag{7}$

$n_r$ and $n_\chi$ are the vibrational basis labels along $r$ and $\chi$, respectively. The associated basis functions $F_{n_r}(r)$ and $H_{n_\chi}(\chi)$ in Eq.(6) are obtained by solving one-dimensional reference Hamiltonians, which are defined as follows

$\hat{h}_r(r) = -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + v^{\text{ref}}(r) \tag{8}$
\[ \hat{a}_u(\chi) = \hat{K}^{\text{ vib}}_{CZ_2} + v_u^{\text{ ref}}(\chi) \]  

where \( v_u^{\text{ ref}}(r) \) and \( v_u^{\text{ ref}}(\chi) \) are the corresponding one-dimensional reference potentials. 

\[ \Phi_{Jljk}^{M_{\text{tot}},K_{\text{tot}}}^{\epsilon_{\text{tot}}}(\hat{R},\hat{r},\hat{s}) \]

\[ = \frac{1}{\sqrt{2(1 + \delta_{J\epsilon_0})}} \left[ \Phi_{Jljk}^{M_{\text{tot}},K_{\text{tot}}}^{\epsilon_{\text{tot}}}(\hat{R},\hat{r},\hat{s}) + \varepsilon(-1)^{J_{\text{tot}}+J+1} \Phi_{Jljk}^{M_{\text{tot}}-K_{\text{tot}}}^{\epsilon_{\text{tot}}}(\hat{R},\hat{r},\hat{s}) \right] \]  

where \( M_{\text{tot}} \) and \( K_{\text{tot}} \) are the projections of total angular momentum \( J_{\text{tot}} \) on space-fixed (SF) and body-fixed (BF) \( \hat{z} \)-axes, respectively, and \( K_{\text{tot}} \) denotes the absolute value of \( K_{\text{tot}} \). 

The rotational basis functions \( \Phi_{Jljk}^{M_{\text{tot}},K_{\text{tot}}}^{\epsilon_{\text{tot}}} \) for the \( X + \text{CYZ}_3 \) system can be written as:

\[ \Phi_{Jljk}^{M_{\text{tot}},K_{\text{tot}}}^{\epsilon_{\text{tot}}}(\hat{R},\hat{r},\hat{s}) = D_{jlk}^{J_{\text{tot}}} M_{\text{tot}}^{K_{\text{tot}}} \phi_{Jljk}^{\epsilon_{\text{tot}}}(\hat{r},\hat{s}) \]  

where \( D_{jlk}^{J_{\text{tot}}} M_{\text{tot}}^{K_{\text{tot}}} \) is the Wigner rotational matrix [72]. The spherical harmonics are given by

\[ Y_{jlk}^{K_{\text{tot}}}(\hat{r},\hat{s}) = \sum_{K} D_{jlk}^{K} \Phi_{K_{\text{tot}}}^{\epsilon_{\text{tot}}}(\hat{r}) \sqrt{\frac{2J+1}{2J+1}} \langle jK_l|JK \rangle D_{K_{\text{tot}}}^{\epsilon_{\text{tot}}}(\hat{s}) \]  

The initial wave packet from a specific state \( (J_{\text{tot}}, K_{\text{tot}}, \epsilon) \) of the system is prepared by the direct product of a localized Gaussian wave packet \( G^0(R) \) in the scattering coordinate and a specific eigenfunction of CYZ\(_2\) \( (n_0, J_0, K_0, p_0) \), where \( n_0, J_0, K_0 \) and \( p_0 \) denote the initial vibrational state, the initial rotational state on the BF \( \hat{z} \)-axis, and the parity of CYZ\(_2\), respectively. Note that \( K_{\text{tot}} \) is a nonnegative integer (i.e., the absolute value of the projection of \( J_{\text{tot}} \) on the BF \( \hat{z} \)-axis) due to the calculations of the employment of the parity-adapted rotational basis functions. Thus, the calculated reaction probability from a specific state \( (J_{\text{tot}}, K_{\text{tot}}, \epsilon) \) of the system includes contributions from both the positive and negative projections of \( J_{\text{tot}} \) on the BF \( \hat{z} \)-axis.

The total reaction probability from a specific initial state can be calculated from the time-independent wavefunction at a dividing surface \( r = r_s \) by

\[ P_t(E) = \frac{1}{\mu_r} \text{Im}(\langle \psi_i|E|\psi_f\rangle)|_{r=r_s} \]  

where the time-independent wavefunction \( |\psi_f\rangle \) is obtained by Fourier transforming the time-dependent wavepacket as

\[ |\psi_f(t)\rangle = \frac{1}{\sqrt{\alpha(E)}} \int_{0}^{\infty} e^{iEt} |\psi(t)\rangle \, dt \]  

The coefficient \( \alpha(E) \) is the overlap between the initial wavepacket \( \Psi_i(0) \) and the energy-normalized asymptotic scattering function \( \varphi_{iE} \).

The total reaction integral cross section (ICS) is computed by summing up all relevant partial waves:

\[ \sigma_{JK,K_{\text{tot}}}(E_c) = \frac{1}{2J+1} \sum_{\epsilon_{\text{tot}}=0}^{\infty} (2J+1) P_{JK,K_{\text{tot}}}^{\epsilon_{\text{tot}}}(E_c) \]  

Since the exact close-coupling calculation for \( J_{\text{tot}}>0 \) is too expensive, the centrifugal sudden (CS) approximation [73, 74] is employed to calculate the reaction probability for \( J_{\text{tot}}=K>0 \). The reaction probabilities for \( J_{\text{tot}}=K \) are computed by the \( J \)-shifting approximation [75, 76], i.e., \( P_{J_{\text{tot}}>K}(E)=P_{J_{\text{tot}}=K}(E-D\epsilon) \) with \( D\epsilon=B^\ast|J_{\text{tot}}(J_{\text{tot}}+1)-K(K-1)| \). The rotational constant \( B^\ast \) is obtained from the geometry of the saddle point of the PES [58], which is taken as 0.32 cm\(^{-1}\). In this work, we are only interested in the effect of reactive rotational excitation on the \( \Omega(3^P)+\text{CHD}_3\rightarrow\text{OH}+\text{CD}_3 \) reaction. The reactant CHD\(_3\) is constrained in the ground vibrational state and both the system and the reactant CHD\(_3\) are set to have the even parity. Hence, we will drop the indices \( (\epsilon, n_0, p_0) \) thereafter.

III. RESULTS AND DISCUSSION

The calculations are carried out on an \( L \)-shaped grid along the coordinates \( R \) and \( r \) to reduce the size of the basis set [77]. For the scattering coordinate \( R, 240 \) sine discrete variable representation (DVR) grid points/basis [78] are used in the whole region from 3.0 bohr to 15.0 bohr and 100 sine DVR grid points/basis in the interaction region. For the dissociating bond \( r, 5 \) and 25 potential optimized DVR (PODVR) grid points/basis [79] are used in the asymptotic and interaction regions, respectively. 12 PODVR grid points/basis are used for the umbrella motion. The parameters for the rotational basis functions are \( J_{\text{max}}=57, l_{\text{max}}=33, J_{\text{max}}=24 \) and \( k_{\text{max}}=9 \). The initial Gaussian wavepacket is launched from \( R_0=13.0 \) bohr with a full width at half maximum of \( \delta=0.08 \) bohr and the central energy is taken as \( E_0=0.5 \) eV.

The calculated reaction probabilities from different rotational states \( (J=0, 1) \) of CHD\(_3\) are plotted in FIG. 2 as a function of collision energy. The initial states in the figure are denoted by three quantum number \( (J, K, K_{\text{tot}}) \). The total angular momentum quantum number

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$J_{\text{tot}}$ of the system is set to equal to $K_{\text{tot}}$. As aforementioned, $K$ and $K_{\text{tot}}$ are the projections of the angular momentum $J$ of CHD$_3$ on the $C_3v$ symmetry axis $s$ and the BF $z$-axis, respectively. Thus, $K$ and $K_{\text{tot}}$ are both taken from 0 to $J$ for each specific value of $J$. It can be seen that the reaction probability from each initial state increases monotonically from an energy threshold of $\sim$8 kcal/mol with collision energy, satisfying the activation nature of the reaction. The reaction probability varies with not only the initial rotational state of CHD$_3$ but also the initial orientation of CHD$_3$ with respect to the scattering coordinate $R$. For $J=1$, the state (100) produces the largest reaction probability, followed by the state (111), and the reaction probabilities from the two states are much larger than from the ground state. In addition, the reaction is almost completely prohibited over the energy range studied when the system is initially excited to the states (101) and (110).

The reactant rotational excitation generally affects the reaction dynamics in two ways: one is the energy effect, for which the coupling between the reactant rotation and the reaction coordinate at the transition state leads to the initial rotational energy to flow into the reaction coordinate [15]; and the other one is the geometry effect, for which the coupling between the reactant rotational energy and the reaction coordinate at the transition state generates the initial orientation of the reactants from the ground state. The initial orientation of the reactants from the ground state.

FIG. 2 Reaction probabilities of the O($^3P$)+CHD$_3$ ($JK\rightarrow$ OH+CD$_3$) reaction from different rotational states ($J=0, 1$) of the reactant CHD$_3$ as a function of collision energy.

FIG. 3 Schematic diagrams of the alignments of reactants corresponding to different initial rotational states.
case for $J=1$, the reaction is greatly enhanced by exciting the reactant CHD$_3$ to the rotational states ($J=2$, 4) with $K=K_{tot}=0$. The initial rotational states ($J=2$, 4) with $K=K_{tot}=J$ also promote the reaction but their efficiencies are not as high as the states with $K=K_{tot}=0$. The initial states with $K \neq K_{tot}$ have negligible reaction probabilities except for the state (401). The results can also be rationalized by the initial reactant alignment pictures.

FIG. 5(a) presents the calculated $K_{tot}$-averaged ICSs of the O($^3P$)+CHD$_3$→OH+CD$_3$ reaction. Interestingly, the ICSs from the rotationally excited states of CHD$_3$, except for the states (40), almost coincide with that from the ground state. The reaction is slightly enhanced by exciting the reactant CHD$_3$ to the state (40). The $JK$-dependence of the cross section ratios ($\sigma_{JK}/\sigma_{00}$) is plotted in FIG. 5(b) as a function of collision energy. On one hand, the ratios from all rotationally excited states decrease with the increase of collision energy and become more or less flat at high collision energies. The ratio between the states (40) and (00) have negligible reaction effect in the H+CHD$_3$→H$_2$+CD$_3$ reaction. Actually, according to the initial reactant orientations of different rotational states, the enlargement is mainly attributed to the component with $K=K_{tot}=0$.

The minimum energy path (MEP) of the O($^3P$)+CHD$_3$→OH+CD$_3$ reaction quite resembles the MEP of the H+CHD$_3$→H$_2$+CD$_3$ reaction. Both of them have a central barrier and the barrier height is ∼14 kcal/mol. It is expected that the rotational mode specificity found here is similar to the rotational effect in the H+CHD$_3$→H$_2$+CD$_3$ reaction. Zhang et al. studied the rotational mode specificity in the H+CHD$_3$→H$_2$+CD$_3$ reaction by the same reduced seven-dimensional quantum scattering model [20]. They found that the $K_{tot}=K$ initial states are much more reactive and the initial rotational excitation of CHD$_3$ up to $J=2$ does not have any effect on the total cross sections. These findings agree well with the results in the O($^3P$)+CHD$_3$→OH+CD$_3$ reaction.

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However, they emphasized that the coupled-channel cross sections are visibly larger than the corresponding CS results due to the strong Coriolis coupling in the H+CHD$_3$→H$_2$+CD$_3$ reaction [20]. So, further theoretical investigations based on more accurate quantum scattering model are very desired in the immediate future.

IV. CONCLUSION

The rotational mode specificity in the prototypical O($^3$P)+CHD$_3$→OH+CD$_3$ reaction has been studied using a reduced 7D quantum scattering model, in which the CD$_3$ moiety is assumed to maintain the C$_{3v}$ symmetry. It was found that, on one hand, the reaction probability depends sensitively on the relative orientation between the angular momentum J of the reactant CHD$_3$ and the scattering coordinate R. The reaction probability ranking follows $P_{K_{tot}=K=0}>P_{K_{tot}=K=J}>P_{K_{tot}=K=J=0}>P_{K_{tot}≠K}$ up to J=4, which can be rationalized by reactant alignment pictures. On the other hand, the $K_{tot}$-averaged integral cross section shows a very weak dependence on J and K up to J=4 except for the state (J=4, K=0). In addition, the cross section ratio ($\sigma_{J\rightarrow K}/\sigma_{0\rightarrow 0}$) first decreases and then becomes nearly flat with the increase of collision energy. The rotational excitation of CHD$_3$ with K=0 enhances the reactivity more than the excitation with K=J. According to the reactant alignment pictures, the stronger K=0 enhancements are mainly attributed to the components with K=$K_{tot}$=0, which enlarge the range of the reactive initial attack angles by the tumbling rotation.

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