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| Title     | Mode specificity in the OH + CHD <sub>3</sub> reaction: Reduced-dimensional quantum and quasi-classical studies on an ab initio based full-dimensional potential energy surface  |
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# Mode specificity in the OH + CHD<sub>3</sub> reaction: Reduced-dimensional quantum and quasi-classical studies on an *ab initio* based full-dimensional potential energy surface

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An initial state selected time-dependent wave packet method is applied to study the dynamics of the OH + CHD<sub>3</sub> reaction with a six-dimensional model on a newly developed full-dimensional *ab initio* potential energy surface (PES). This quantum dynamical (QD) study is complemented by full-dimensional quasi-classical trajectory (QCT) calculations on the same PES. The QD results indicate that both translational energy and the excitation of the CH stretching mode significantly promote the reaction while the excitation of the umbrella mode has a negligible effect on the reactivity. For this early barrier reaction, interestingly, the CH stretching mode is more effective than translational energy in promoting the reaction except at very low collision energies. These QD observations are supported by QCT results. The higher efficacy of the CH stretching model in promoting this early barrier reaction is inconsistent with the prediction of the naively extended Polanyi's rules, but can be rationalized by the recently proposed sudden vector projection model. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4947252>]

## I. INTRODUCTION

Until very recently, direct comparison between experimental and quantum mechanical studies of bimolecular reactions has mostly been done for atom-diatom reactions.<sup>1–5</sup> Thanks to the rapid rise of computing power and new techniques for constructing multi-dimensional potential energy surfaces (PESs), quantum studies of reaction dynamics are being extended from triatomic reactions to polyatomic reactions.<sup>6,7</sup> The involvement of more than three atoms presents the opportunity to investigate dynamics in more complicated potential landscapes, which has led to a better understanding of important dynamical behaviors, such as mode specificity and bond selectivity.<sup>8–10</sup>

The hydrogen abstraction reaction between hydroxyl radical and methane to form water and methyl radical (OH + CH<sub>4</sub> → H<sub>2</sub>O + CH<sub>3</sub>) is a key step in hydrocarbon combustion.<sup>11</sup> In the atmosphere, it also represents the major mechanism for the removal of the greenhouse gas methane in the troposphere.<sup>12</sup> As a result, experimental measurements of its rate coefficients have been reported over a wide range of temperatures (see Ref. 13 and references therein). This reaction has also served as a prototype for studying dynamics of reactions involving polyatomic atomic molecules. For example, Liu and co-workers have carried out crossed

molecular beam experiments on the OH + CD<sub>4</sub> reaction and its isotopologues, and reported the product pair mode correlation, translational energy dependence, and isotope effects.<sup>14–16</sup> In addition, Lester and co-workers have measured the vibrational spectroscopy and decay dynamics of a CH<sub>4</sub>–OH complex.<sup>17,18</sup>

Much of the past theoretical attention has been paid to the stationary points along the reaction path, particularly the transition state which determines the rate coefficients and kinetic isotope effects.<sup>19–27</sup> As shown in Fig. 1(a), this exothermic reaction has an early barrier, featuring a reactant-like transition state.<sup>28</sup> The early dynamical calculations of Nyman and co-workers have involved only a few (2–3) degrees of freedom and suffered from the lack of accurate PESs for this system.<sup>29–31</sup> In 2000, Espinosa-García and Corchado built the first global analytical PES (PES-2000).<sup>32</sup> Using this PES, quantum scattering calculations have been carried out by Yu using a five-dimensional model<sup>33</sup> and by some of the current authors using six-dimensional (6D) and seven-dimensional models<sup>34,35</sup> in which the vibrational and rotational mode specificities were investigated. This PES has also been used to compute the rate coefficients using a variety of techniques.<sup>36,37</sup> A refined PES (PES-2014) was later constructed by Espinosa-García and Corchado<sup>38</sup> and calculations were performed to explore the kinetics and dynamics on this PES.<sup>38–41</sup> The comparison with available experimental data has all been quite satisfactory, but the relatively simple form used to represent the PES remains as a source of uncertainty. Very recently,

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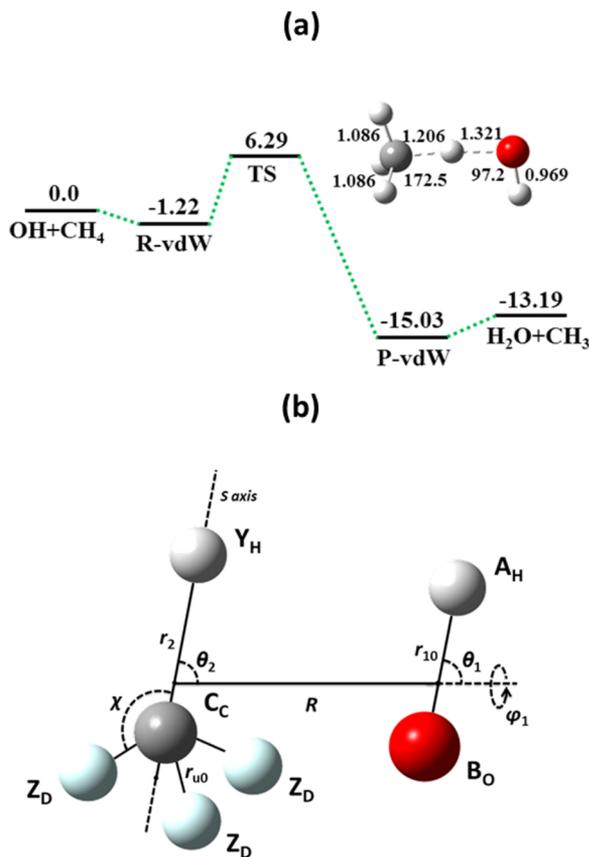


FIG. 1. (a) Schematic illustration of the reaction pathway for the  $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$  reaction with configuration at the transition state. All energies are given in kcal/mol and relative to the  $\text{OH} + \text{CH}_4$  asymptote, calculated at the level of UCCSD(T)-F12a/AVTZ; (b) the six-dimensional Jacobi coordinates for  $\text{AB} + \text{YCZ}_3$  system in the reactant frame. The  $s$  axis denotes the  $\text{C}_{3v}$  symmetry axis of  $\text{YCZ}_3$ .

two of the current authors developed a new global PES using the permutation invariant polynomial-neural network (PIP-NN) approach<sup>42,43</sup> based on  $\sim 135\,000$  high-level *ab initio* points.<sup>28</sup> This PES is considered globally accurate with a total root mean square fitting error of 3.9 meV. Preliminary calculations on this PES indicated that the calculated rate coefficients and cross sections agree well with experimental results.<sup>28</sup>

In this publication, we report a reduced-dimensional quantum dynamical (QD) study of the title reaction. As in our recent work,<sup>34,35</sup> the model Hamiltonian developed by Palma and Clary<sup>44</sup> was extended to describe the  $\text{OH} + \text{CHD}_3$  system in which the non-reactive methyl group is assumed to maintain the  $\text{C}_{3v}$  symmetry during the reaction. The model is further simplified by fixing the CD stretching coordinates in the  $\text{CD}_3$  moiety, the  $\text{CD}_3$  rotation, and the OH vibration,<sup>34,35</sup> which is similar in spirit to the rotating bond umbrella model proposed by Yu and Nyman.<sup>45</sup> This reduced-dimensional model is employed here to investigate the mode specificity in the  $\text{OH} + \text{CHD}_3$  reaction on the recently developed PIP-NN PES<sup>28</sup> using the initial state selected wave packet method.<sup>46</sup> In addition, the mode specificity is also studied using the quasi-classical trajectory (QCT) method with full dimensionality. This paper is organized as follows. Section II outlines the theoretical methodology of both the reduced-dimensional

initial state selected wave packet and QCT methods and the results and discussion are presented in Section III. We conclude in Section IV.

## II. THEORY

### A. Six-dimensional quantum model

The Palma-Clary model<sup>44</sup> for the  $\text{B} + \text{YCZ}_3$  system has been widely used to provide a reduced-dimensional framework to understand dynamics of such six-atom reactions.<sup>47–55</sup> This model has been extended to the  $\text{AB} + \text{YCZ}_3$  system,<sup>34,35</sup> as shown in Fig. 1(b). Specifically, the A–B bond length  $r_1$  is fixed at equilibrium O–H distance:  $r_{10} = 1.834 a_0$ , and the C–Z distance ( $r_u$ ) is also fixed at its equilibrium position:  $r_{u0} = 2.0556 a_0$ . The resulting six-dimensional (6D) model has the following Hamiltonian ( $\hbar = 1$  hereafter):

$$\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_{r_2}} \frac{\partial^2}{\partial r_2^2} + \frac{(\hat{J} - \hat{j}_{12})^2}{2\mu_R R^2} + \frac{\hat{j}_1^2}{2\mu_{r_1} r_{10}^2} + \frac{\hat{j}_2^2}{2I_{\text{YCZ}_3}} + \hat{K}_{\text{CZ}_3}^{\text{vib}} + V(R, r_2, \chi, \theta_1, \theta_2, \varphi), \quad (1)$$

where

$$I_{\text{YCZ}_3} = \mu_{r_2} r_2^2 + \frac{3}{2} m_Z r_{u0}^2 \sin^2 \chi + \frac{3m_C m_Z}{m_C + 3m_Z} r_{u0}^2 \cos^2 \chi. \quad (2)$$

In Eq. (1),  $R$  is the distance between the center of masses (COM) of  $\text{AB}$  and  $\text{Y-CZ}_3$ , and  $r_2$  is the distance between the COM of  $\text{CZ}_3$  and  $\text{Y}$ . The reduced mass corresponding to the three radial coordinates is denoted as  $\mu_R$ ,  $\mu_{r_1}$ , and  $\mu_{r_2}$ , respectively.  $\hat{J}$  is the total angular momentum operator of the system, which is conserved.  $\hat{j}_1$  is the rotational angular momentum operator of  $\text{AB}$ , and  $\hat{j}_2$  is the rotational angular momentum operator of  $\text{YCZ}_3$ , which couples with each other to give rise to  $\hat{j}_{12}$ . The vibrational kinetic operator of  $\text{CZ}_3$ ,  $\hat{K}_{\text{CZ}_3}^{\text{vib}}$ , is defined as

$$\hat{K}_{\text{CZ}_3}^{\text{vib}} = -\frac{1}{2r_{u0}^2} \left( \frac{\cos^2 \chi}{\mu_x} + \frac{\sin^2 \chi}{\mu_s} \right) \frac{\partial^2}{\partial \chi^2} - \frac{1}{r_{u0}^2} \left( \frac{1}{\mu_s} - \frac{1}{\mu_x} \right) \sin \chi \cos \chi \frac{\partial}{\partial \chi}, \quad (3)$$

where  $\mu_x = 3m_Z$  and  $\mu_s = 3m_C m_Z / (m_C + m_Z)$ . Since the bond length of C–Z is fixed, the above kinetic energy operator describes only the umbrella motion of  $\text{CZ}_3$ . Since the Palma-Clary model treats the reactive and non-reactive hydrogen in methane differently, it is more suitable to study reactions involving  $\text{CHD}_3$  or  $\text{CDH}_3$ , rather than  $\text{CH}_4/\text{CD}_4$  or  $\text{CH}_2\text{D}_2$ , as the permutation symmetry in the latter cannot be maintained in this model.<sup>55</sup> As a result, we will mostly focus in this work on the  $\text{OH} + \text{CHD}_3$  reaction.

The time-dependent wave packet is expanded in terms of the body-fixed (BF) ro-vibrational eigenfunctions as

$$\psi_{v_0 j_0 K_0}^{JM\epsilon}(\vec{R}, \vec{r}_1, \vec{r}_2, \chi, t) = \sum_{m j K} F_{n v_0 j_0 K_0}^{JM\epsilon}(t) u_n^{v_2}(R) \phi_{v_2}(r_2) \phi_{v_\chi}(\chi) Y_{jK}^{JM\epsilon}(\hat{R}, \hat{r}_1, \hat{r}_2), \quad (4)$$

where  $n$  labels the translational basis,  $v$  denotes  $(v_2, v_\chi)$ ,  $j$  denotes  $(j_1, j_2, j_{12})$ ,  $(v_0, j_0)$  represents the initial ro-vibrational states of the reactants, and  $\varepsilon$  is the total parity of the system.

The angular basis function  $Y_{jK}^{JM\varepsilon}$  in Eq. (4) are the coupled BF total angular momentum eigenfunctions, which can be written as

$$Y_{jK}^{JM\varepsilon} = (1 + \delta_{K0})^{-1/2} \sqrt{\frac{2J+1}{8\pi}} [D_{K,M}^{J*} Y_{j_1 j_2}^{j_1 j_2 K} + \varepsilon (-1)^{j_1+j_2+j_{12}} D_{-K,M}^{J*} Y_{j_1 j_2}^{j_1 j_2 -K}], \quad (5)$$

where  $D_{K,M}^J$  is the Wigner rotation matrix.  $M$  is the projection of total angular momentum  $J$  on the space-fixed  $z$  axis and  $K$  is the projection on the body-fixed  $z$  axis.  $Y_{j_1 j_2}^{j_1 j_2 K}$  are the angular momentum eigenfunctions of  $\hat{j}_{12}$  defined as

$$Y_{j_1 j_2}^{j_1 j_2 K} = \sum_{m_1} \langle j_1 m_1 j_2 K - m_1 | j_{12} K \rangle y_{j_1 m_1}(\theta_1, 0) y_{j_2 K - m_1}(\theta_1, \varphi) \quad (6)$$

and  $y_{jm}$  are spherical harmonics. Note that the restriction  $\varepsilon(-1)^{j_1+j_2+j_{12}} = 1$  for  $K = 0$ .

The centrifugal term in the kinetic energy operator, i.e.,  $(\hat{J} - \hat{j}_{12})^2$ , under the centrifugal sudden (CS) approximation<sup>56,57</sup> is given by

$$\langle Y_{jK}^{JM\varepsilon} | (\hat{J} - \hat{j}_{12})^2 | Y_{jK}^{JM\varepsilon} \rangle \approx \delta_{j'j} \{ \delta_{KK'} [J(J+1) + j_{12}(j_{12}+1) - 2K^2] \}. \quad (7)$$

Hence,  $K$  becomes a good quantum number and is conserved under this approximation. All results reported below have been obtained using the CS approximation.

In our calculations, the initial wave packet is constructed by a direct product of a localized Gaussian wave packet along the scattering coordinate and specific ro-vibrational states of both reactants. It is then propagated in time using the second-order split operator method<sup>58</sup> and the reaction probabilities  $P_{v_2 v_\chi j_1 j_2 j_{12} K}^{J\varepsilon}(E)$  are calculated from the time-independent scattering wave function,  $\psi_i^+(E)$ , on the dividing surface  $S[r_2 = r_2^F]$ .

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

$$\sigma_{v_0 j_0}(E) = \frac{1}{(2j_1+1)(2j_2+1)} \times \sum_{j_{12} K \varepsilon} \left\{ \frac{\pi}{k^2} \sum_{J \geq K} (2J+1) P_{v_2 v_\chi j_1 j_2 j_{12} K}^{J\varepsilon}(E) \right\}, \quad (8)$$

where  $k = \sqrt{2\mu_R E}$ . In this study, we focus on the dynamics from the ground rotational states, i.e.,  $j_1 = j_2 = 0$ . Thus, we will drop the indices  $\varepsilon$ ,  $j_1, j_2$ , and  $j_{12}$  from now on.

An  $L$ -shaped grid associated with the radical coordinates  $R$  and  $r_2$  is employed in the numerical calculations. The numerical parameters have been well tested to give converged results. A total of 120 sine discrete variable representation<sup>59</sup> (DVR) basis/points were used for the translational coordinate  $R$  in the range from 3.5 to 12  $a_0$  and 40 sine DVR basis/points in the interaction region. For the dissociating CH bond  $r_2$ , 26 potential optimized discrete variable representation<sup>59</sup> (PODVR) basis/points were used in the interaction region and

3 PODVR basis/points in the asymptotic region. 15 PODVR basis/points were constructed in a range from  $\pi/3$  to  $5\pi/6$  to represent the umbrella motion. The angular basis is 54 for  $j_{1 \max}$  and 55 for  $j_{2 \max}$ . The center of the initial wave packet is located at 11.0  $a_0$  and the propagation time is around 12 000 a.u. with a time step of 15 a.u. The flux is taken at  $r_2^F = 3.5$  a.u. To impose outgoing boundary conditions, negative imaginary absorbing potentials are applied at the grid edges of  $R$  and  $r_2$ .

## B. Quasi-classical trajectory

The standard QCT method, implemented in VENUS,<sup>60</sup> was also employed to calculate the total reactive ICS for the title reaction. The ICS was computed according to the following formula:

$$\sigma_r(E_c) = \pi b_{\max}^2(E_c) P_r(E_c), \quad (9)$$

in which the reaction probability at the specified collision energy  $E_c$  is calculated by the ratio between the number of reactive trajectories  $N_r$  and total trajectories  $N_t$ ,

$$P_r(E_c) = N_r/N_t. \quad (10)$$

The standard error is given by  $\Delta = \sqrt{(N_t - N_r)/N_t/N_r}$ . The trajectories were initiated with a reactant separation of 10.0 Å and terminated when products reached a separation of 8.0 Å, or when reactants were separated by 8.0 Å for non-reactive trajectories. The central-difference algorithm was employed to calculate numerically the gradient of the PES. The propagation time step was selected to be 0.05 fs, which conserves the energy better than  $10^{-2}$  kcal/mol for almost all the trajectories. Batches of trajectories (40 000-100 000) have been sampled at selected collision energies (from 0.1 to 1.0 eV) to make the statistical errors all within 5%. A few trajectories which failed to converge energy to 0.05 kcal/mol or were nonreactive after 10.0 ps, less than 0.05%, were discarded. The trajectories were analyzed without a zero-point energy (ZPE) constraint. The maximal impact parameter ( $b_{\max}$ ) was determined using small batches of trajectories with trial values and taken as 3.0 Å.

## III. RESULTS

### A. Mode specificity

Figure 2(a) shows the calculated QD reaction probabilities for the OH + CHD<sub>3</sub> reaction from the reactant ground ro-vibrational state for several selected partial waves. For  $J = 0$ , as the figure shows, the reaction energy threshold is around 0.2 eV. Since the classical (adiabatic) barrier height for this reaction is 0.2728 (0.1998) eV,<sup>28</sup> the quantum tunneling effect is apparently present. This is not entirely surprising as the reaction involves the transfer of light atoms (H) over a significant barrier. Above the reaction threshold, the reaction probability increases monotonically with translational energy, which is a common feature for activated reactions. Interestingly, the reaction probabilities for higher partial waves have similar profiles, and the energy threshold shift for higher partial waves is almost proportional to the value of  $J(J+1)$ .

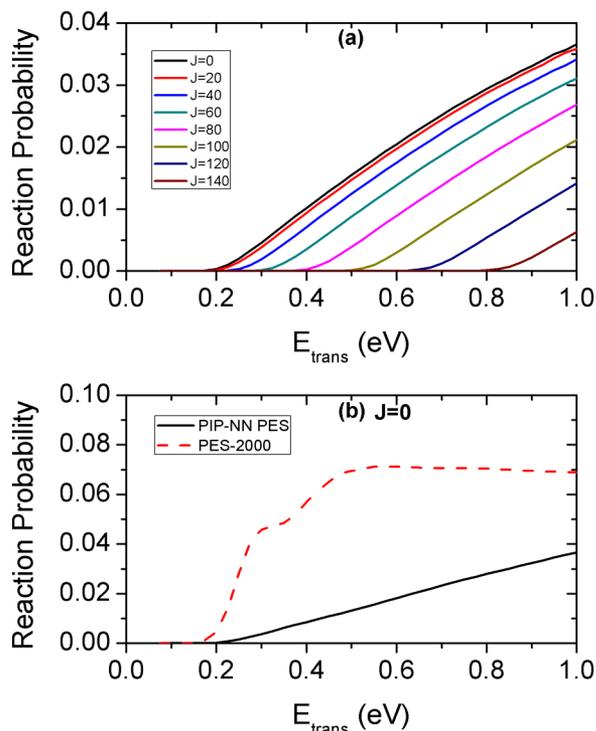


FIG. 2. (a) The calculated reaction probabilities for the OH+CHD<sub>3</sub> reaction from the ground state with the total angular momentum  $J_{\text{tot}} = 0, 20, 40, 60, 80, 100, 120, \text{ and } 140$ ; (b) comparison of reaction probabilities for the OH+CH<sub>4</sub> reaction on the PIP-NN PES and PES-2000 from the ground state with  $J_{\text{tot}} = 0$ .

Thus, we expect that the  $J$  shifting approximation<sup>61</sup> works well for this reaction.

In our previous reduced-dimensional QD study of the OH + CH<sub>4</sub> reaction on PES-2000,<sup>34</sup> in contrast, the reaction probability first increases sharply and then becomes more or less leveled off. These results are compared in Fig. 2(b) with that on the new PIP-NN PES. As shown in the figure, the  $J = 0$  reaction probability on the two PESs possess quite different profiles, although they have roughly the same reaction threshold. In addition, the reaction probability on the PES-2000 is several times larger than the counterpart on the PIP-NN PES over the entire energy range. This large difference in reactivity underscores the different topographies in the two PESs, despite the similar barrier heights in the two PESs. It is expected that the more recent PES-2014 will provide a better description of the reaction channel,<sup>38</sup> but no QD result is available on that PES.

The calculated QD integral cross sections for the OH + CHD<sub>3</sub> reaction for the reactant CHD<sub>3</sub> in the first several lowest excited vibrational states are shown in Fig. 3. The vibrational state of CHD<sub>3</sub> is denoted by  $(\nu_2, \nu_\chi)$  in which  $\nu_2$  represents the CH stretching mode and  $\nu_\chi$  refers to the CHD<sub>3</sub> umbrella mode. (The numbering scheme for the vibrational modes follows our coordinates, rather than the convention in vibrational spectroscopy.) In Fig. 3(a), the cross section is plotted as a function of translational energy. It can be seen that excitation of the umbrella mode has almost no effect on the reactivity, as the cross sections for CHD<sub>3</sub> in the fundamental and first overtone of the umbrella mode are almost indistinguishable from that of the ground state.

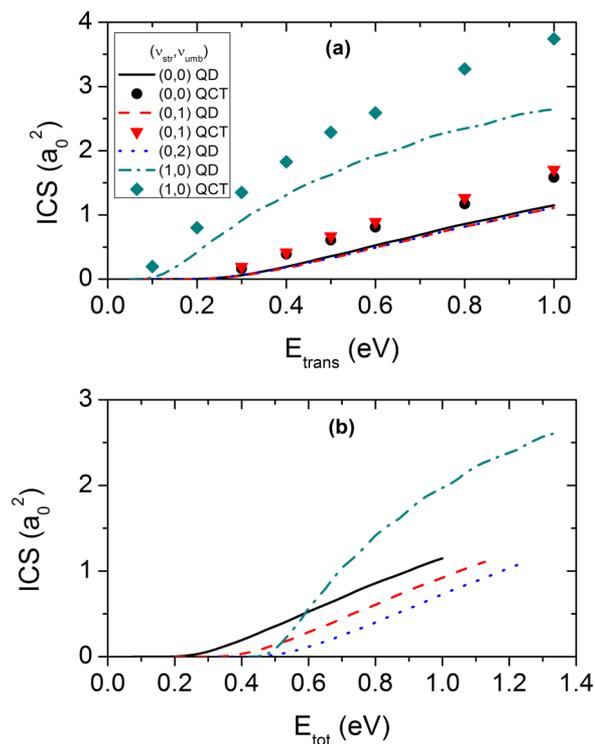


FIG. 3. The calculated integral cross sections for the OH+CHD<sub>3</sub> ( $\nu_2 = 0-1, \nu_\chi = 0-2$ )  $\rightarrow$  H<sub>2</sub>O+CD<sub>3</sub> reaction as a function of (a) translational energy and (b) total energy.

In contrast, excitation of the CH stretching mode enhances the reactivity remarkably, although the enhancement effect decreases with increasing translational energy. In the same figure, the QCT results are also included. The trends in the QD excitation functions are reasonably reproduced although the QCT cross sections are obviously larger than the QD results over the energy range studied. The discrepancy between them increases with the collision energy. This possibly caused by the zero point energy (ZPE) leakage, an intrinsic defect in the QCT methodology,<sup>62,63</sup> and the inaccuracy of the reduced-dimensional model used in the QD calculations.

To compare the relative efficacy of the reactant modes in promoting the reaction, the QD cross sections are plotted in Fig. 3(b) as a function of the total energy, which is defined as the sum of the initial ro-vibrational energy relative to the reactant ZPE and the translational energy. Clearly, the energy thresholds for the CHD<sub>3</sub> in the vibrationally excited states are all shifted to higher energies, suggesting that not all vibrational energies are used to overcome the barrier. At very low energies, translational energy promotes the reactivity more effectively than the reactant vibrational modes, which is understandable as translational energy is needed for all collisional processes. The dominance of translational energy at the low energy regimes is a common feature in bimolecular reactions.<sup>50,64,65</sup> However, at higher total energies, the situation is quite different. While the reactivity for excited umbrella states is consistently lower than that of the ground state counterpart, the cross section for the reactant CHD<sub>3</sub> in the first excited state of the CH stretching mode is significantly larger, which indicates that this mode has a higher efficacy in promoting the reaction than translational energy. This appears to be in conflict with the

prediction of the naively extended Polanyi rules for this early barrier reaction. However, as we argue below, this seemingly abnormal observation can be rationalized by the recently proposed Sudden Vector Projection (SVP) model.<sup>64</sup>

The SVP model assumes that the intramolecular vibrational energy redistribution (IVR) of reactants is much slower than the collision time. In the SVP model, the efficacy of a reactant mode in promoting the reaction is attributed to its coupling with the reaction coordinate at the transition state, which is quantified approximately by the projection of the reactant normal mode vector ( $\vec{Q}_i$ ) onto the reaction coordinate vector ( $\vec{Q}_{RC}$ ):  $\eta_i = \vec{Q}_i \cdot \vec{Q}_{RC} \in [0, 1]$ . The SVP model has been successfully applied to predict the mode specificity and bond selectivity in many polyatomic reactions.<sup>66,67</sup> For the OH + CHD<sub>3</sub> reaction, the calculated SVP values are 0.87, 0.12, and 0.44 for the CH stretching mode, CD<sub>3</sub> umbrella mode, and translational mode, respectively, with near zero values for the other modes. Clearly, the CH stretching mode has the largest projection on the reaction coordinate, which is followed by the translational mode and the umbrella mode. This is consistent with the large efficacy of the CH stretching mode and the fact that this mode is more effective than translational energy in promoting the reaction observed in the results presented above. This is quite interesting as the SVP model reaches a different conclusion from that of the naively extended Polanyi rules for this early barrier reaction. Similar violations of Polanyi rules have been reported in other reactive systems,<sup>68–70</sup> but the SVP model seems to be able to consistently predict the vibrational efficacy. On the other hand, the SVP model seems to overestimate the efficacy of the umbrella mode in enhancing the reaction. Such overestimations have been found before for low-frequency bending modes in other reactions.<sup>66</sup>

## B. Comparison between theoretical and experimental cross sections

Zhang *et al.*<sup>15</sup> measured the relative cross section of the OH + CD<sub>4</sub> reaction using a crossed-beam experiment over

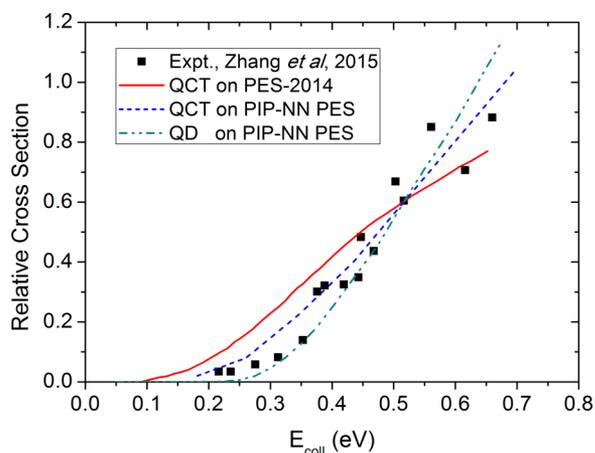


FIG. 4. Comparison of the theoretical and experimental relative cross sections for the OH + CD<sub>4</sub> reaction. The experimental values are adapted from Ref. 15 in which only the ground state product CD<sub>3</sub> was considered. The QCT results on the PES-2014 and the PIP-NN PES are adapted from Refs. 38 and 28, respectively.

the collision energies ranging from the reaction threshold to 0.7 eV. In Fig. 4, we compare the theoretical cross section with the experimental counterpart by normalizing the cross section at the collision energy of 12 kcal/mol. The reduced quantum dynamical cross section is well within the experimental error range. The cross sections obtained from quasi-classical trajectory (QCT) calculations on both the PES-2014 and PIP-NN PESs are also included in the comparison.<sup>28,38</sup> Clearly, the QCT cross sections on the PIP-NN PES and the PES-2014 agree well with the experimental values at relatively high collision energies. However, at collision energies just above the energy threshold, they both overestimate the cross section with the latter a little more. In contrast, the QD cross section appears to overestimate the cross section at very high collision energies, possibly resulting from the reduced-dimensional model employed in the QD calculations.

## IV. CONCLUSIONS

The mode specificity in the OH + CHD<sub>3</sub> reaction has been studied using a reduced six-dimensional time-dependent wave packet method on a newly developed *ab initio* based globally accurate PES. The model employed in the study is ideally suited for the study of the OH + CHD<sub>3</sub> reaction. It was found that the CH stretching mode enhances the reaction while the umbrella motion of CHD<sub>3</sub> has little effect on the reaction. Except for the low collision energies, the CH stretching mode promotes the reaction more than the translational mode, while the umbrella is the least effective in promoting the reaction. These observations are reproduced by full-dimensional QCT calculations on the same PES. The more efficacious CH mode excitation is a surprising finding as the naively extended Polanyi rules would predict that translational energy is more effective in promoting the reaction in this early barrier reaction. However, this surprising mode specificity can be explained by the SVP model, which attributes the relative efficacy of a reactant mode in promoting the reaction to the projection of its normal mode vector on to the reaction coordinate at the transition state.

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