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Mode specific dynamics of the $\text{H}_2 + \text{CH}_3 \rightarrow \text{H} + \text{CH}_4$ reaction studied using quasi-classical trajectory and eight-dimensional quantum dynamics methods

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An eight-dimensional quantum dynamical model is proposed and applied to the title reaction. The reaction probabilities and integral cross sections have been determined for both the ground and excited vibrational states of the two reactants. The results indicate that the H_2 stretching and CH_3 umbrella modes, along with the translational energy, strongly promote the reactivity, while the CH_3 symmetric stretching mode has a negligible effect. The observed mode specificity is confirmed by full-dimensional quasi-classical trajectory calculations. The mode specificity can be interpreted by the recently proposed sudden vector projection model, which attributes the enhancement effects of the reactant modes to their strong couplings with the reaction coordinate at the transition state. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4933240>]

I. INTRODUCTION

The $\text{H} + \text{CH}_4 \leftrightarrow \text{H}_2 + \text{CH}_3$ reaction serves as a prototype for chemical reactions involving polyatomic molecules.^{1,2} It plays an important role in combustion³ and the chemistry of hydrocarbons in the atmosphere of Titan.⁴ As a result, it has been extensively studied both experimentally and theoretically. There have been many measurements of the forward rate coefficients^{5–10} and consensus recommendations exist.¹¹ Theoretical calculations of the rate coefficients range from transition-state theory calculations with semi-classical corrections of tunneling to full-dimensional quantum dynamical studies.^{12–29} In addition, the forward reaction has been extensively studied as a prototype for understanding reaction dynamics, mode specificity, and bond selectivity.^{19,30–56} Since this reaction involves six atoms, a full-dimensional characterization requires twelve degrees of freedom. Although several full-dimensional potential energy surfaces (PESs) have been developed based on *ab initio* data,^{13,47,57–62} the only full-dimensional quantum dynamics (QD) studies have been performed with the multi-configuration time-dependent Hartree (MCTDH) method.^{14–16,20,22,25–28,51,53,55,56} The conventional quantum dynamics studies of this reaction have been in reduced dimensionality,^{19,31–37,43,45–50,52,54} many with the Palma-Clary model.⁶³ However, comparison with the MCTDH results suggested that these reduced-dimensional

models are capable of producing quantitatively correct total reaction probabilities,²⁷ at least for ground vibrational state.⁵⁶

Comparing with the forward reaction, much less is known about the reverse reaction. Although the rate coefficients have been determined experimentally^{7,9,11,64} and theoretically,^{12,18,65–67} only a few dynamics studies have been reported.^{68–70} In particular, Chapman and Bunker studied vibrational mode specificity with a model PES.⁶⁸ More recently, Wang reported six-dimensional (6D) time-dependent quantum studies of the reaction and the isotopic reactions $\text{HD} + \text{CH}_3$ and $\text{D}_2 + \text{CH}_3$, treating the CH_3 moiety as a pseudodiatom in which the internal degree of freedom is the umbrella bend.^{69,70} He found that the excitation of the $\text{H}_2(\text{HD}, \text{D}_2)$ vibration substantially enhances the reactivity, whereas the excitation of the umbrella motion of CH_3 has the opposite effects. So far, no experimental studies have been reported.

In this work, we report an extensive investigation of the reaction dynamics of the $\text{H}_2 + \text{CH}_3 \rightarrow \text{CH}_4 + \text{H}$ reaction. Since both reactants in this reaction are molecules with vibrational modes, it provides an ideal testing case to examine the mode specificity. In the studies detailed below, the QD is characterized by a new eight-dimensional (8D) Hamiltonian based on the Palma-Clary model, which assumes that the CH_3 moiety maintains its C_{3v} symmetry during the reaction. The QD calculations were performed on the analytical PES of Corchado, Bravo, and Espinosa-García (PES2008).⁶¹ The QD calculations are complemented by quasi-classical trajectory (QCT) studies on the same PES, and the results are in good overall agreement. The calculated rate coefficients are found to agree with the experiment. These calculations indicated that

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the excitations in the H₂ stretching and CH₃ umbrella modes, along with translational energy, strongly promote the reaction, while the CH₃ symmetric stretching excitation has little effect. The strong mode specificity of this reaction is rationalized by the recently proposed sudden vector projection (SVP) model.^{71–73} The remainder of the publication is organized as follows. In Sections II and III, the theoretical methods are introduced. The results and discussion are presented in Section IV and a brief conclusion is given in Section V.

II. QUANTUM DYNAMICS

A. The coordinate system

The eight-dimensional model is similar to that of its reverse reaction H + CH₄ → H₂ + CH₃⁴⁹ and is described in the coordinate system shown in Figure 1. Here, R is the distance from the center of mass (COM) of the CH₃ molecule to the COM of the H₂ molecule and r is the bond length of the H₂ molecule. The CH₃ group, which is assumed to maintain its C_{3v} symmetry throughout the reaction,⁶³ could be defined with either polar coordinates (ρ, χ)⁴³ or Cartesian coordinates (x, s).⁶³ Here, ρ is the C–H bond length and χ is the angle between a CH bond and vector $\vec{S}$ which is the symmetry axis of CH₃; x denotes the distance from a H atom to the symmetry axis $\vec{S}$ and s the distance between atom C and the center of three H atoms. In this work, the polar coordinates (q, γ) are employed to simplify the Hamiltonian.⁴⁹ θ_1 is the bending angle between vectors $\vec{R}$ and $\vec{r}$ and φ_1 is the azimuthal angle for the rotation of H₂ around R ; θ_2 is the bending angle between vectors $\vec{R}$ and $\vec{S}$; and φ_2 is the azimuthal angle for the rotation of CH₃ around its C_{3v} axis $\vec{S}$.

B. The model Hamiltonian

The Hamiltonian in the aforementioned coordinates is written as ($\hbar = 1$),^{49,63}

FIG. 1. (a) Jacobi coordinates for the eight-dimensional model for the H₂ + CH₃ reaction; (b) Cartesian and polar coordinates of the CH₃ group.

$$\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \frac{(\hat{J} - \hat{j}_{12})^2}{2\mu_R R^2} + \frac{\hat{j}_1^2}{2\mu_r r^2} + \hat{K}_{\text{CH}_3}^{\text{vib}} + \hat{K}_{\text{CH}_3}^{\text{rot}} + V(R, r, q, \gamma, \theta_1, \varphi_1, \theta_2, \varphi_2). \quad (1)$$

Here, μ_R is the H₂–CH₃ reduced mass and μ_r is the H₂ reduced mass. The first two terms represent the kinetic energy operators for R and r , respectively. $\hat{J}$ is the total angular momentum operator of the system and $\hat{j}_{12} = \hat{j}_1 + \hat{j}_2$, where $\hat{j}_1$ and $\hat{j}_2$ are the angular momentum operators for the molecules H₂ and CH₃, respectively. The third term of the Hamiltonian is the centrifugal potential and the fourth term is the rotational kinetic energy operator of H₂. $\hat{K}_{\text{CH}_3}^{\text{vib}}$ and $\hat{K}_{\text{CH}_3}^{\text{rot}}$ are the vibrational and rotational kinetic operators of CH₃, respectively. The last term $V(R, r, q, \gamma, \theta_1, \varphi_1, \theta_2, \varphi_2)$ in the Hamiltonian is the potential energy operator. In this work, the PES of Corchado *et al.*⁶¹ was used.

The vibrational and rotational kinetic operators for CH₃ defined in the (q, γ) coordinate system are written as

$$\hat{K}_{\text{CH}_3}^{\text{vib}} = -\frac{1}{2\mu_x} \left(\frac{\partial^2}{\partial q^2} + \frac{1}{q^2} \frac{\partial^2}{\partial \gamma^2} + \frac{1}{4q^2} \right), \quad (2)$$

with $\mu_x = 3m_H$ and the integral element as $\partial q \partial \gamma$, and

$$\hat{K}_{\text{CH}_3}^{\text{rot}} = \frac{1}{2I_A} \hat{j}_2^2 + \left(\frac{1}{2I_C} - \frac{1}{2I_A} \right) \hat{j}_{2z}^2, \quad (3)$$

where $\hat{j}_2$ is the rotational angular momentum operator of CH₃ and $\hat{j}_{2z}$ is its z -component. The moments of inertia I_A and I_C are defined as⁶³

$$I_A = \frac{3}{2} m_H \left[\left(x^2 + \frac{2m_C}{m_C + 3m_H} s^2 \right) \right], \quad (4)$$

$$I_C = 3m_H x^2, \quad (5)$$

with $x = q \sin \gamma$ and $s = \sqrt{(m_C + 3m_H)/m_C} q \cos \gamma$. The parity-adapted rotational basis set for the H₂ + CH₃ system is defined as

$$\begin{aligned} \Phi_{j_1 j_2 j_3 k_2}^{JMK\varepsilon}(\hat{R}, \hat{r}, \hat{s}) &= \sqrt{\frac{1}{2(1 + \delta_{\bar{K}0} \delta_{k_2 0})}} \left[\Phi_{j_1 j_2 j_3 k_2}^{JMK}(\hat{R}, \hat{r}, \hat{s}) \right. \\ &\quad \left. + \varepsilon(-1)^{J+j_1+j_2+j_3+k_2} \Phi_{j_1 j_2 j_3 -k_2}^{J-\bar{M}\bar{K}}(\hat{R}, \hat{r}, \hat{s}) \right], \end{aligned} \quad (6)$$

here

$$\Phi_{j_1 j_2 j_3 k_2}^{JMK}(\hat{R}, \hat{r}, \hat{s}) = \bar{D}_{MK}^J(\hat{R}) Y_{j_1 j_2 k_2}^{J12K}(\hat{r}, \hat{s}), \quad (7)$$

and

$$Y_{j_1 j_2 k_2}^{J12K}(\hat{r}, \hat{s}) = \sum_m \langle j_1 m j_2 K - m | j_{12} K \rangle Y_{j_1 m}(\hat{r}) \bar{D}_{K-m, k_2}^{j_2}(\hat{s}), \quad (8)$$

with the spherical harmonics and Wigner rotational matrix defined as⁷⁴

$$Y_{j_1, m}(\hat{r}) = Y_{j_1, m}(\theta_1, \phi_1), \quad (9)$$

$$\bar{D}_{K-m, k_2}^{j_2}(\hat{s}) = \sqrt{\frac{2j_2 + 1}{4\pi}} D_{K-m, k_2}^{*j_2}(0, \theta_2, \phi_2), \quad (10)$$

where $\bar{K} = |K|$ and ε is the parity of wavefunction under space-inverse operation.

The time-dependent wavefunction is thus expanded in the parity-adapted rotational basis functions as

$$\Psi^{JM\epsilon} = \sum_{n_R, n_r, n_q, n_\gamma} \sum_{K j_{12} j_1 j_2 k_2} c_{n_R n_r n_q n_\gamma j_{12} j_1 j_2 k_2}^{JM\epsilon}(t) G_{n_R}(R) \times F_{n_r}(r) Q_{n_q}(q) H_{n_\gamma}(\gamma) \Phi_{j_{12} j_1 j_2 k_2}^{JM\epsilon}(\hat{R}, \hat{r}, \hat{S}), \quad (11)$$

where $c_{n_R n_r n_q n_\gamma j_{12} j_1 j_2 k_2}^{JM\epsilon}(t)$ are time-dependent coefficients. n_R , n_r , n_q , and n_γ are the labels for basis functions of R , r , q , and γ , respectively. $G_{n_R}(R)$ are sine basis functions⁷⁵ and the basis functions $F_{n_r}(r)$, $Q_{n_q}(q)$, and $H_{n_\gamma}(\gamma)$ are the eigenfunctions of one-dimensional reference Hamiltonians defined as follows:

$$\hat{h}_r(r) = -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + v_r^{\text{ref}}(r), \quad (12)$$

$$\hat{h}_q(q) = -\frac{1}{2\mu_x} \frac{\partial^2}{\partial q^2} + v_q^{\text{ref}}(q), \quad (13)$$

and

$$\hat{h}_\gamma(\gamma, q_{\text{ref}}) = -\left(\frac{\partial^2}{\partial \gamma^2} + \frac{1}{4}\right) + 2\mu_x q_{\text{ref}}^2 v_\gamma^{\text{ref}}(\gamma), \quad (14)$$

where $v_r^{\text{ref}}(r)$, $v_q^{\text{ref}}(q)$, and $v_\gamma^{\text{ref}}(\gamma, q_{\text{ref}})$ are the corresponding reference potentials and q_{ref} is a reference value of q to define $h_\gamma(\gamma, q_{\text{ref}})$.

We note in passing that Wang and coworkers have recently studied the OH + CH₃ reaction by proposing another reduced-dimensional model for AB + HCX type reactions,⁷⁶ but the coordinates used in their work address a different set of modes in such reactions. Furthermore, a recent full-dimensional QD study of the H + CH₄ reaction has examined the validity of the reduced dimensional models and found errors might be introduced when some degrees of freedom are not included.⁵⁶ However, the reduced dimensional Hamiltonian employed in that study is not of Palma-Clary form and as a result the error of our reduced dimensional model is still uncertain.

C. Propagation and projection

The wave packet is propagated using the split-operator propagator,⁷⁷

$$\Psi(t + \Delta) = e^{-i\hat{H}_0\Delta/2} e^{-iU\Delta} e^{-i\hat{H}_0\Delta/2} \Psi(t), \quad (15)$$

where the reference Hamiltonian $\hat{H}_0$ is defined as

$$\begin{aligned} \hat{H}_0 = & -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} + \hat{h}_r^{\text{ref}}(r) + \hat{h}_q^{\text{ref}}(q) \\ & + \frac{1}{2\mu_x q^2} \hat{h}_\gamma^{\text{ref}}(\gamma, q_{\text{ref}}) \end{aligned} \quad (16)$$

and the potential U is defined as

$$\begin{aligned} U = & \frac{(\hat{J} - \hat{j}_{12})}{2\mu_R R^2} + \frac{\hat{j}_1^2}{2\mu_r r^2} + \hat{K}_{CH_3}^{\text{rot}} \\ & + V(R, r, q, \gamma, \theta_1, \varphi_1, \theta_2, \varphi_2) \\ & - v_r^{\text{ref}}(r) - v_q^{\text{ref}}(q) - \frac{q_{\text{ref}}^2}{q^2} v_\gamma^{\text{ref}}(\gamma). \end{aligned} \quad (17)$$

The calculations of total reaction probabilities are exactly the same as in the previous works.^{35,43,47,78} For a specific initial

state, the reaction probability can be calculated at a dividing surface $r = r_s$,

$$P_i(E) = \frac{\hbar}{\mu_r} \text{Im}(\langle \psi_{iE} | \psi'_{iE} \rangle) |_{r=r_s}, \quad (18)$$

where ψ_{iE} and ψ'_{iE} are the time-independent wavefunction and its first derivative in r and they are determined by Fourier transforming the wave packet at the dividing surface.

D. Numerical parameters

In this work, an L -shaped grid⁷⁹ was used to reduce the size of basis set. A total of 130 sine basis functions were used for R ranging from 2.0 to 15.0 bohrs and 50 nodes were placed in the interaction region. This means that the reaction region is from 2.0 to 7.0 bohrs, and the asymptotic region is from 7.0 to 15.0 bohrs. 5 and 28 basis functions for r were employed in the asymptotic and interaction regions, respectively. The size of the rotational basis functions is controlled by the parameters, $j_{12} = 60$, $j_1 = 24$, $j_2 = 36$, and $k_2 = 6$. Considering parity and C_{3v} symmetry, the size of rotational basis functions is 22 878 and the number of nodes for the integration of the rotational basis set is 60 125. The size of the total basis functions is 1.44×10^9 and the number of nodes for potential energy calculation are 4.33×10^9 .

III. QUASI-CLASSICAL TRAJECTORY

Standard full-dimensional QCT calculations were performed using VENUS⁸⁰ The trajectories were initiated with a reactant separation of 8.0 Å and terminated when products reached a separation of 8.0 Å or when reactants are separated by 8.0 Å for non-reactive trajectories. The initial positions and momenta of the atoms were sampled from the vibrational normal modes.⁸¹ 10⁶ trajectories were calculated for each specific state to make the statistical errors $\leq 2.2\%$. The maximal impact parameter (b_{max}) was determined using small batches of trajectories with trial values, and they are between 1.7 and 2.0 Å, depending on energy. The other scattering parameters (impact parameter, vibrational phases, and spatial orientation of the initial reactants) were selected via a Monte Carlo approach.⁸¹ The propagation time step was selected to be 0.01 fs. Energy conservation of the trajectories was found to be excellent with the chosen time step. Almost all trajectories conserved energy to within a chosen criteria (0.04 kcal/mol).

The total integral cross section (ICS) for the title reaction was computed according to the following formula:

$$\sigma_i(E_c) = \pi b_{\text{max}}^2(E_c) P_r(E_c), \quad (19)$$

where the reaction probability $P_r(E_c)$ at the specified collision energy E_c is given by the ratio between the number of reactive trajectories (N_r) and total number of trajectories (N_{total}),

$$P_r(E_c) = N_r / N_{\text{total}}. \quad (20)$$

The standard error is given by $\Delta = \sqrt{(N_{\text{total}} - N_r) / N_{\text{total}} N_r}$.

IV. RESULTS AND DISCUSSION

A. QD total reaction probabilities

For the title reaction on PES2008, the classical barrier height is 15.1 kcal mol⁻¹ (0.65 eV) and the energy difference between the products and reactants is 2.89 kcal mol⁻¹ (0.13 eV). In the following presentation, three vibrational quantum numbers (n_1, n_2, n_3) are used to denote the H₂, CH₃ symmetric stretching, and CH₃ umbrella modes. Only the ground rotational states of the reactants are considered in this work. Eleven initial states are considered: (1) Both H₂ and CH₃ in their ground states, denoted as (0,0,0), with the zero point energies of H₂ and CH₃ of 2174.9 cm⁻¹ and 1825.7 cm⁻¹, respectively; (2) the first three excited states of the umbrella motion of CH₃, denoted as (0,0,1), (0,0,2), and (0,0,3), with excitation energies of 604.5 cm⁻¹ (0.075 eV), 1282.6 cm⁻¹ (0.159 eV), and 2021.7 cm⁻¹ (0.249 eV); (3) the symmetric stretching excited state of CH₃, denoted as (0,1,0), with an excitation energy of 3083.4 cm⁻¹ (0.382 eV); (4) the combined excited state of the symmetric stretching and umbrella mode of CH₃, denoted as (0,1,1), with an excitation energy of 3687.1 cm⁻¹ (0.457 eV); (5) H₂ on its first vibrational excited state, denoted as (1,0,0), with an excitation energy of 4157.2 cm⁻¹ (0.515 eV); and (6) the combined excited states of H₂ and CH₃, denoted as (1,0,1), (1,0,2), (1,1,0), and (1,1,1). These excitation energies are listed in Table I.

Figure 2 shows the total $J = 0$ reaction probabilities for the title reaction as a function of collision energy with the eleven initial states. When both reactants are in their ground vibrational states, as denoted as the (0,0,0) state, the total reaction probability rises at about 0.53 eV and increases with the collision energy. All vibrationally excited reactant states have a lower reaction threshold than that of the (0,0,0) state, indicating that these vibrational excitations reduce the reaction threshold for the reaction. For the first vibrational excited state of H₂ (1,0,0), about 33% (0.168 eV) of the 0.515 eV excitation energy is used to reduce the reaction threshold. For the first CH₃ umbrella excited (0,0,1) state, almost all of the excitation energy (0.075 eV) is used to reduce the reaction threshold. For the (0,0,2) and (0,0,3) initial states, 75% and 62% of the excitation energies are used to reduce the threshold. However, for the (0,1,0) initial state, only about 6% of the excitation energy (0.382 eV) was used to reduce the threshold. For the (0,1,1) initial state, this proportion is 23%. For the (1,0,1), (1,0,2), (1,1,0), and (1,1,1) states, the proportions are 44%, 47%, 21%, and 29%, respectively.

TABLE I. Excitation energies of the eleven initial states.

State	cm ⁻¹	eV	State	cm ⁻¹	eV
(0,0,0) ^a	2179.0	0.226			
	1825.7	0.270			
(0,0,1)	604.5	0.075	(1,0,0)	4157.2	0.515
(0,0,2)	1282.6	0.159	(1,0,1)	4716.7	0.590
(0,0,3)	2021.7	0.249	(1,0,2)	5439.8	0.674
(0,1,0)	3083.4	0.382	(1,1,0)	7240.6	0.898
(0,1,1)	3687.1	0.457	(1,1,1)	7844.3	0.973

^aThe values of (0,0,0) represent the zero point energies of H₂ and CH₃, respectively.

FIG. 2. Total $J = 0$ reaction probabilities for the H₂+CH₃ reaction as a function of the collision energy.

In addition to reducing reaction threshold, all the vibrational excited reactant states enhance the reactivity. From Fig. 2, it is clear that the reaction probability for the (0,1,0) initial state follows that of the (0,0,0) state very closely, suggesting the excitation of the CH₃ symmetric stretching mode has little effect on the reactivity. However, excitations of other vibrational modes are shown to promote the reaction. Excitations of the H₂ vibration and/or the umbrella mode of CH₃ enhance the reactivity substantially. This is different from the previous results by Wang^{69,70} who found that excitation of the H₂ stretch enhances the reaction probability, whereas the excitation of the CH₃ umbrella mode has the opposite effect.

To compare the relative efficacy between vibrational and translational energies, the total $J = 0$ reaction probabilities for the eleven initial states are plotted in Figure 3 as a function of the total energy. As shown, the first CH₃ umbrella excited state, denoted as (0,0,1), has the highest reactivity in the entire energy range, followed by the ground state (0,0,0) and the higher umbrella excited states (0,0,2) and (0,0,3). This indicates that excitation of the CH₃ umbrella mode to its first excited state promotes the reaction more effectively than the translational energy. However, further excitation of the CH₃ umbrella mode does not improve the efficacy. This is a common trend in mode specificity in reactions.⁸² On the other hand, all other initial states have lower reactivity than that of the (0,0,0)

FIG. 3. Total $J = 0$ reaction probabilities for the H₂+CH₃ reaction as a function of the total energy.

state, suggesting their efficacies are lower than the translational energy in promoting the reaction.

B. QD integral cross sections

The QD ICS for a specific reactant state is obtained by summing the total reaction probabilities over all the partial waves,

$$\sigma_{v_1 j_1 v_2 j_2}(E_C) = \frac{1}{(2j_1 + 1)(2j_2 + 1)} \frac{\pi}{2\mu_R E_C} \times \sum_J (2J + 1) P_{v_1 j_1 v_2 j_2}^J(E_C), \quad (21)$$

where E_C represents the collision energy. In this work, the $J > 0$ partial waves were calculated with the centrifugal-sudden (CS) approximation.^{83,84} The maximum value of J needed to converge the ICS is 50.

Figure 4 shows the excitation function, namely, the ICSs as a function of the collision energy, for the eleven initial states. As we can see, the ICS curves are very similar to the reaction probability counterparts. In particular, the ICS of the (0,1,0) state is only marginally higher than that of the (0,0,0) state over the whole collision energy range. Similarly, the excitation functions of the (1,0,0) and (1,1,0) states also track each other closely. These observations confirm the spectator nature of the symmetric stretching mode of CH₃. On the other hand, the ICSs associated with vibrationally excited H₂ are much larger, indicating an enhancement effect. Excitations of the umbrella mode of CH₃ also promote the reaction.

Figure 5 shows the ICSs for the eleven initial states as a function of the total energy. Similar to Fig. 3, the (0,0,1) ICS is the highest in the entire energy range, suggesting a higher efficacy in promoting the reaction than the translational energy. This is followed by the ICSs for the (0,0,2), (0,0,3), and (0,0,0) states, although the latter rises slower with the energy than those of the former. In comparison with the translational energy, it is clear that the (0,0,1) excitation is more effective, the (0,0,2) excitation is roughly equally effective, and the (0,0,3) excitation is less effective in promoting the reaction. The efficacies of other vibrationally excited reactant states are lower than the translational energy in promoting the reaction. Recently, Zhang *et al.* also studied this reaction with seven- and eight-dimensional on

FIG. 4. Total integral cross sections for the H₂ + CH₃ reaction as a function of the collision energy.

FIG. 5. Total integral cross sections for the H₂ + CH₃ reaction as a function of the total energy.

their neural network potential energy surface, and they have drawn similar conclusion as that in this work (D. Zhang, private communication, 2015).

C. QCT results

To assess the reduced-dimensional QD treatment of the reaction dynamics, we have carried out full-dimensional QCT calculations for four initial states and the comparison is shown in Fig. 6. The QCT results are in excellent agreement with the reduced-dimensional QD results for all four initial states, although the former is somewhat larger than the QD ICSs except for (0,0,1). The slight overestimation is typical for QCT, presumably because of zero-point energy leakage. Importantly, the excitation functions obtained from the QCT calculations predicted the same mode specificity. In particular, the H₂ vibration enhances the reaction most, followed by the CH₃ umbrella excitation, while the CH₃ symmetric stretching has essentially no effect. These results provide supporting evidence that the reduced-dimensional QD treatment correctly captures the mode specific reaction dynamics.

D. Sudden vector projection model

The mode specificity observed in both QD and QCT calculations can be rationalized by the recently proposed SVP

FIG. 6. Comparison of the QD and QCT integral cross sections in collision energy for the (0,0,0), (0,0,1), (0,1,0), and (1,0,0) initial states of the H₂ + CH₃ reaction.

model.^{71,72} The SVP model assumes that the collision time for an activated reaction is much shorter than the time required for the intramolecular vibrational energy redistribution (IVR) in the reactants. As a result, the reaction can be treated in the sudden limit. This model further attributes the efficacy of a reactant mode for promoting the reaction to the coupling of this mode with the reaction coordinate at the transition state. Such coupling can then be quantified by the projection of the reactant normal mode vector ($\vec{Q}_i$) on to the reaction coordinate vector ($\vec{Q}_{RC}$): $P_i = \vec{Q}_i \cdot \vec{Q}_{RC} \in [0, 1]$. The simple and powerful model has been successfully applied to many gas phase and gas surface reactions,⁷³ including the $X + \text{CH}_4 \leftrightarrow \text{HX} + \text{CH}_3$ ($X = \text{H}, \text{F}, \text{Cl}, \text{O}(^3\text{P}),$ and OH) reactions.⁸⁵ For the $\text{H}_2 + \text{CH}_3$ reaction, the SVP model predicts that the reaction coordinate is strongly coupled with the CH_3 umbrella, H_2 vibration, and translational modes with the projection values of 0.33, 0.64, and 0.69, while its coupling with the symmetric stretching mode of CH_3 is rather weak ($P_i = 0.06$).⁸⁵ The reactivity enhancement by the CH_3 umbrella and H_2 vibrational excitations is indeed consistent with the results presented here, although the SVP model seems to underestimate the efficacy of the CH_3 umbrella model relative to the translational and the H_2 vibrational modes. Nevertheless, we note that the enhancement of reactivity by exciting the CH_3 umbrella mode would be very difficult to predict using the well-known Polanyi's rules,⁸⁶ as they were designed for atom-diatom reactions.

We emphasize that the QD and QCT results presented here are in strong contrast with the earlier reduced-dimensional QD results of Wang, who found the excitation of the CH_3 umbrella mode inhibits the reaction.^{69,70} It is still not clear the origin of the difference between the two calculations, but we note that the umbrella mode of CH_3 was treated as a one-dimensional model in which the H_3 moiety was treated as a pseudo-atom.

E. Thermal rate coefficients

The QD rate coefficients for the eleven initial states are calculated from the total reaction probabilities as

$$k_i(T) = \left(\frac{2\pi}{\mu_R k_B T} \right)^{1/2} \sum_J (2J+1) \times \int_0^\infty \exp(-E_C/k_B T) P_{v_1 j_1 v_2 j_2}^J(E_C) dE_C, \quad (22)$$

where k_B is the Boltzmann constant and μ_R is the reduced mass of the scattering coordinate. These rate coefficients are presented in Figure 7. For comparison purposes, the rate coefficients calculated using the canonical variational transition-state theory (CVT) method⁸⁷ on the same PES2008⁶¹ as well as experimental values^{7,9,11} are also showed in the figure. The 8D QD rate coefficients satisfactorily describe the rate constants in temperature range of 200–2000 K and are in good agreement with the experimental measurements and the results calculated with CVT method on EG-2008 PES.

To delineate the contributions of various reactant states to the thermal rate coefficient, we have plotted the Boltzmann weighted contributions in Fig. 8. As shown in the figure, the lowest three umbrella excited states make the largest

FIG. 7. The calculated thermal rate coefficients in comparison with previous theoretical and experimental rate coefficients^{7,9,11} for the $\text{H}_2 + \text{CH}_3$ reaction.

FIG. 8. Arrhenius plot of the initial state-selected rate constants obtained from reduced dimensional QD calculations.

contributions, along with the ground state reactants. This is consistent with the mode specificity observed in the ICS, as discussed above.

V. CONCLUSIONS

In this work, we present a new reduced-dimensional quantum dynamical model for characterizing the dynamics of the $\text{H}_2 + \text{CH}_3 \rightarrow \text{H} + \text{CH}_4$ reaction. Specifically, this eight-dimensional model allows the investigation of the influence of three vibrational modes in the two reactants, namely, the H_2 vibration, the CH_3 umbrella, and symmetric stretching vibrations, on the reactivity. It is shown that the H_2 stretching and CH_3 umbrella modes along with the translational energy strongly promote the reaction, while the CH_3 symmetric stretching mode has little effect. While agreeing on the promoting effect of the H_2 vibration, our results disagree with the conclusion reached by an earlier reduced-dimensional quantum dynamical calculations which predicted an inhibitory effect for the CH_3 umbrella excitation. The mode specificity observed in our reduced-dimensional quantum dynamical calculations is confirmed by full-dimensional quasi-classical trajectory results. The recently proposed SVP model provides rationalization of the mode specificity in terms of the coupling

strengths of reactant modes with the reaction coordinate at the transition state.

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