

# **Ab initio potential energy surface and quantum dynamics for the $H + CH_4 \rightarrow H_2 + CH_3$ reaction**

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A new full-dimensional potential energy surface for the title reaction has been constructed using the modified Shepard interpolation scheme. Energies and derivatives were calculated using the UCCSD(T) method with aug-cc-pVTZ and 6-311++G(3df,2pd) basis sets, respectively. A total number of 30 000 data points were selected from a huge number of molecular configurations sampled by trajectory method. Quantum dynamical calculations showed that the potential energy surface is well converged for the number of data points for collision energy up to 2.5 eV. Total reaction probabilities and integral cross sections were calculated on the present surface, as well as on the ZBB3 and EG-2008 surfaces for the title reaction. Satisfactory agreements were achieved between the present and the ZBB3 potential energy surfaces, indicating we are approaching the final stage to obtain a global potential energy surface of quantitative accuracy for this benchmark polyatomic system. Our calculations also showed that the EG-2008 surface is less accurate than the present and ZBB3 surfaces, particularly in high energy region. © 2011 American Institute of Physics. [doi:10.1063/1.3552088]

## I. INTRODUCTION

The  $H + CH_4 \rightarrow H_2 + CH_3$  reaction and its reverse, play important roles in  $CH_4/O_2$  combustion chemistry,<sup>1</sup> and have therefore been the subject of both experimental<sup>2-5</sup> and theoretical<sup>6-52</sup> interest for many years. Because five of the six atoms involved are hydrogens, it is an ideal candidate for high quality *ab initio* quantum chemistry calculations of the potential energy surface and quantum dynamics studies. As a result, this reaction has become a benchmark for developing and testing various theoretical methods for accurate studies of polyatomic chemical reactions.<sup>8,10,11,13,21,22,26,30,35,39,41,46,48-50</sup>

Due to the quantum nature of the reactive scattering problem, it is extremely difficult at present to treat such a six-atom reaction exactly in full dimension although significant progress has been made by Manthe and co-workers on the direction.<sup>12,14,48-50,53</sup> Various reduced dimensionality approaches, such as the rotating bond approximation,<sup>54-57</sup> the semirigid vibrating rotor target (SVRT) model,<sup>10,20,58,59</sup> and the atom-triatom model<sup>13</sup> have been applied to study the reaction. This group has been employing an eight-dimensional model for the time-dependent wave packet studies. The model was originally proposed by Palma and Clary,<sup>60</sup> by restricting the nonreacting  $CH_3$  group in a  $C_{3V}$  symmetry. Since the assumption holds very well in reality, the model has a quantitative level of accuracy.

Dynamical results not only depend on the dynamical method, but also depend on the quality of the potential energy surface (PES) used in a calculation. Although direct quantum dynamics<sup>15</sup> or direct quasiclassical trajectory method,<sup>61-63</sup>

which obtain potential energies or/and forces directly from quantum chemistry calculations on the fly, do not require an explicit form of PES, their capability is very limited at present. Consequently, substantial effort has been devoted to the PES construction for the title reaction over the past decades.<sup>40</sup> Jordan and Gilbert developed the first symmetric potential surface (JG PES) in term of the valence-bond molecular mechanics (VM-MM) type functions,<sup>64</sup> by treating the four hydrogen atoms in methane identically.<sup>6</sup> The surface, together with its various modified versions, have been widely used to test dynamics methods since then.<sup>10,11,14,22,48-50</sup> Following that, Espinosa-García and Corchado,<sup>7</sup> taking into account more recent *ab initio* and experimental data, recalibrated the JG PES and published the PES-1996 PES. Yu<sup>9</sup> also reparameterized the JG PES and carried out related time-independent scattering calculations. As a result of modifications, both PES-1996 PES and Yu's PES have the barrier heights close to accurate *ab initio* result. In 2002, Espinosa-García developed the EG-2002 PES by using a fully symmetric function form with respect to exchange of the four hydrogen atoms in methane.<sup>18</sup> Most recently, that group published a new version of PES for the reaction (EG-2008 PES),<sup>44</sup> with careful calibration of all parameters using exclusively high-level electronic structure results, and applied the PES in kinetics and dynamics studies.<sup>45</sup>

Bowman and co-workers have carried out *ab initio* calculations for a large number of configuration points at the RCCSD(T)/aug-cc-pVTZ level, and successively constructed three versions of global PES for the system, i.e., ZBB[1-3], using the invariant polynomial method.<sup>65,66</sup> These surfaces, of full permutation symmetry for all the five hydrogen atoms involved, are substantially more accurate than all the preceding

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surfaces. Quasiclassical trajectory calculations performed on these surface for the H + CH<sub>4</sub> and H + CD<sub>4</sub> reactions produced very interesting results.<sup>32,34,65,66</sup>

The modified Shepard interpolation method, developed by Collins and co-workers,<sup>67–70</sup> has been used to construct PESs for the system over the years. Collins and co-workers tested the method on the JG PES first,<sup>71</sup> and found that about 1000–1300 data points were sufficient to reproduce the JG PES. Later, Manthe and co-workers used the scheme to construct a full-dimensional PES based on high level *ab initio* calculations. Full-dimensional multiconfigurational time-dependent Hartree (MCTDH) studies on the PES yielded thermal rate constants comparable to (or even exceeding) experimental precision for the H + CH<sub>4</sub> → H<sub>2</sub> + CH<sub>3</sub> reaction.<sup>26,30,33</sup> Unfortunately, the PES is limited to the vicinity of abstraction saddle, therefore cannot be used for global dynamical studies.

Recently, we constructed a new *ab initio* full-dimensional PES for the system using the modified Shepard interpolation method based on extensive high level of *ab initio* calculations. Seven-dimensional quantum dynamics calculations carried out on the PES for the H + CD<sub>4</sub> → HD + CD<sub>3</sub> reaction produced an integral cross section (ICS) in good agreement with the experimental results,<sup>52</sup> and with that obtained on the ZBB3 PES. Since these two PESs were constructed by using two totally different methods, the good agreement on the ICS obtained from these two PESs indicates that PES for this benchmark six-atom reaction is approaching a quantitative level of accuracy. In this paper, we report in detail the construction of the PES, and compare it with the EG-2008 PES and ZBB3 PES by carrying out seven-dimensional time-dependent wave packet (TDWP) calculations.

The paper is structured as follows. In Sec. II we present the method used in PES construction as well as that in TDWP calculation. Results and discussions are showed in Sec. III. The conclusions are given in Sec. IV.

## II. THEORY

### A. The PES interpolation scheme

In the modified Shepard interpolation method, interpolation is given by a weighted sum of Taylor polynomials. For an  $N$ -atom reaction system, the nuclei geometry can be defined by  $3N - 6$  ( $3N - 5$  for collinear geometry) internal coordinates (inverse distances here). The potential energy at a configuration,  $\mathbf{Z}$ , in the vicinity of a data point  $\mathbf{Z}(i)$  can be expanded as a Taylor series  $T_i$ :

$$T_i(\mathbf{Z}) = V[\mathbf{Z}(i)] + \sum_{k=1}^{3N-6} [Z_k - Z_k(i)] \left. \frac{\partial V}{\partial Z_k} \right|_{\mathbf{Z}=\mathbf{Z}(i)} + \frac{1}{2!} \sum_{k=1}^{3N-6} \sum_{j=1}^{3N-6} [Z_k - Z_k(i)] \times [Z_j - Z_j(i)] \left. \frac{\partial^2 V}{\partial Z_k \partial Z_j} \right|_{\mathbf{Z}=\mathbf{Z}(i)} + \dots, \quad (1)$$

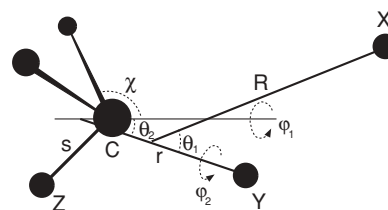


FIG. 1. The eight-dimensional Jacobi coordinates for the X + YCZ<sub>3</sub> system.

where  $V[\mathbf{Z}(i)]$  is the value of the potential at  $\mathbf{Z}(i)$ , the derivatives are taken with respect to inverse distances at  $\mathbf{Z}(i)$ .

Suppose that the energy and derivatives are calculated at a number,  $N_d$ , of nuclei configurations, total potential energy at any configuration  $\mathbf{Z}$  is given as a weighted average of the Taylor series about all  $N_d$  data points and their symmetry equivalents:

$$V(\mathbf{Z}) = \sum_{g \in G} \sum_{i=1}^{N_d} w_{g \circ i}(\mathbf{Z}) T_{g \circ i}(\mathbf{Z}), \quad (2)$$

where

$$w_i(\mathbf{Z}) = \frac{v_i(\mathbf{Z})}{\sum_{g \in G} \sum_{k=1}^{N_d} v_{g \circ k}(\mathbf{Z})}. \quad (3)$$

The normalized weight function,  $w_i$ , represents how close is the data point to the configuration  $\mathbf{Z}$ , and data points nearer to  $\mathbf{Z}$  will have larger weights than those at large distances. The un-normalized weight function,  $v_i$  is defined as

$$v_i(\mathbf{Z}) = \left\{ \left[ \frac{\|\mathbf{Z} - \mathbf{Z}(i)\|}{\text{rad}(i)} \right]^{2q} + \left[ \frac{\|\mathbf{Z} - \mathbf{Z}(i)\|}{\text{rad}(i)} \right]^{2p} \right\}^{-1}, \quad (4)$$

where  $\text{rad}(i)$  plays the role of a confidence radius.<sup>69</sup> Note that in Eq. (3) the summation is taken over the appropriate symmetry group  $G$ , which roots in the nature that any permutation performed onto the six hydrogen atoms will not influence the potential value. With all subgroups of  $G$  taken into consideration, the dataset is symmetrized, thus the PES of Eq. (3) exhibits the full molecular symmetry.

### B. The time-dependent wave packet method

The time-dependent quantum wave packet calculations used the eight-dimensional (8D) model for the X + YCZ<sub>3</sub> reaction by restricting the nonreacting CZ<sub>3</sub> group in a C<sub>3v</sub> symmetry.<sup>22,37,39,61</sup> The 8D Hamiltonian in the Jacobi coordinates ( $R, r, s, \chi, \theta_1, \phi_1, \theta_2, \phi_2$ ) shown in Fig. 1 can be written as

$$\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \frac{(\hat{J}_{\text{tot}} - \hat{J})^2}{2\mu_R R^2} + \frac{\hat{l}^2}{2\mu_r r^2} + \hat{K}_{\text{CZ}}^{\text{vib}} + \hat{K}_{\text{CZ}}^{\text{rot}} + V(R, r, s, \chi, \theta_1, \phi_1, \theta_2, \phi_2), \quad (5)$$

where  $\mu_R$  is the reduced mass of X and YCZ<sub>3</sub>,  $\mu_r$  is the reduced mass of Y and CZ<sub>3</sub>,  $R$  is the distance between X and the center of mass (COM) of YCZ<sub>3</sub>,  $r$  is the distance between Y and the COM of the CZ<sub>3</sub> group,  $s$  is the bond length of CZ,  $\chi$  is the angle between the CZ bond and the C<sub>3v</sub> symmetry axis, vector  $\mathbf{s}$ , of the CZ<sub>3</sub> group,  $\hat{J}_{\text{tot}}$  is the total angular

momentum operator of the system,  $\hat{J}$  is the rotational angular momentum operator of YCZ<sub>3</sub>, and  $\hat{l}$  is the orbital angular momentum operator of atom Y with respect to CZ<sub>3</sub>. The last term  $V(R, r, s, \chi, \theta_1, \varphi_1, \theta_2, \varphi_2)$  is the potential energy.

In the present study, we fixed the CH bond length in the nonreacting CH<sub>3</sub> group based on the fact that it essentially does not change during the reaction, to reduce the degree of freedom from 8 to 7. As a result, the vibrational kinetic energy operator in Eq. (5) can simply be given as,<sup>22,37</sup>

$$\hat{K}_{CZ}^{\text{vib}} = -\frac{1}{2s^2} \left( \frac{\cos^2 \chi}{\mu_x} + \frac{\sin^2 \chi}{\mu_s} \right) \frac{\partial^2}{\partial \chi^2} + \frac{1}{s^2} \left[ \frac{1}{\mu_x} - \frac{1}{\mu_s} \right] \sin \chi \cos \chi \frac{\partial}{\partial \chi}, \quad (6)$$

where  $\mu_x$  and  $\mu_s$  are related to the mass of atoms C and Z,  $\mu_x = 3m_z$  and  $\mu_s = 3m_c m_z / (m_c + 3m_z)$ . The rotational kinetic energy operators of CZ<sub>3</sub>  $\hat{K}_{CZ}^{\text{rot}}$  can be written as,

$$\hat{K}_{CZ}^{\text{rot}} = \frac{1}{2I_A} \hat{j}^2 + \left( \frac{1}{2I_C} - \frac{1}{2I_A} \right) \hat{j}_z^2, \quad (7)$$

where  $I_A$  and  $I_C$  are the rotational inertia of CZ<sub>3</sub>, defined as

$$I_A = \frac{3}{2} m_z s^2 \left( \sin^2 \chi + \frac{2m_c}{m_c + 3m_z} \cos^2 \chi \right) \quad (8)$$

and

$$I_C = 3m_z s^2 \sin^2 \chi, \quad (9)$$

$\hat{j}$  is the rotational angular momentum of CZ<sub>3</sub> and  $\hat{j}_z$  is its z-component.

The seven-dimensional (7D) time-dependent wave function is expanded in terms of basis functions of  $R, r, \chi$ , and the body-fixed (BF) total angular momentum eigenfunctions as

$$\Psi^{J_{\text{tot}} M K \varepsilon} = \sum_{n, v_r, v_\chi} \sum_{K J l j k} C_{n v_r v_\chi J l j k}^{J_{\text{tot}} M K \varepsilon}(t) F_n^{v_r}(R) \phi_{v_r}(r) \phi_{v_\chi}(\chi) \times \Phi_{J l j k}^{J_{\text{tot}} M K \varepsilon}(\hat{R}, \hat{r}, \hat{s}), \quad (10)$$

where  $n, v_r$ , and  $v_\chi$  are labels for the basis functions in  $R, r$ , and  $\chi$  coordinates, respectively,  $F_n^{v_r}$  are sine basis functions for  $R$  which are dependent on  $v_r$  for their spatial ranges to separate interaction region from asymptotic region,<sup>72</sup> and  $\phi_{v_r}(r)$  and  $\phi_{v_\chi}(\chi)$  are basis functions for  $r$  and  $\chi$ , respectively.

The BF total angular momentum basis functions  $\Phi_{J l j k}^{J_{\text{tot}} M K \varepsilon}(\hat{R}, \hat{r}, \hat{s})$  are defined as

$$\Phi_{J l j k}^{J_{\text{tot}} M K \varepsilon}(\hat{R}, \hat{r}, \hat{s}) = \sqrt{\frac{1}{2(1 + \delta_{K0} \delta_{k0})}} \left[ \bar{D}_{MK}^{J_{\text{tot}}}(\hat{R}) Y_{j l k}^{J K}(\hat{r}, \hat{s}) + \varepsilon (-1)^{J_{\text{tot}} + J + l + j + k} \bar{D}_{M-K}^{J_{\text{tot}}}(\hat{R}) Y_{j l -k}^{J -K}(\hat{r}, \hat{s}) \right], \quad (11)$$

where  $\varepsilon$  is the parity of the system and  $\bar{D}_{MK}^{J_{\text{tot}}}(\hat{R})$  are the Wigner rotation matrices with three Euler angles which rotate the space-fixed frame onto the body-fixed frame<sup>37</sup> and are

the eigenfunctions of  $\hat{J}_{\text{tot}}^2$ . The spherical harmonics  $Y_{j l k}^{J K}(\hat{r}, \hat{s})$  are given by

$$Y_{j l k}^{J K}(\hat{r}, \hat{s}) = \sum_m \bar{D}_{K m}^J(\hat{r}) \sqrt{\frac{2l+1}{2J+1}} \langle j m l 0 | J m \rangle \bar{D}_{m k}^j(\hat{s}), \quad (12)$$

where  $\bar{D}_{K m}^J(\hat{r})$  depend on Euler angles which rotate the XYZ<sub>3</sub> body-fixed frame onto the YCZ<sub>3</sub>-fixed frame, and  $\bar{D}_{m k}^j(\hat{s})$  depend on Euler angles which rotate the YCZ<sub>3</sub>-fixed frame onto the CZ<sub>3</sub>-fixed frame.

The initial state wave function is constructed as the direct product of a standard Gaussian function

$$G^0(R) = (\pi \delta^2)^{-1/4} \exp\left(-\frac{(R - R_0)^2}{2\delta^2}\right) \exp(-ik_0 R) \quad (13)$$

and the rovibrational eigenfunction of YCZ<sub>3</sub>,  $\psi_{n_0 J_0 K_0 P_0}^{J_{\text{tot}} M \varepsilon}$ , which satisfies the following asymptotic Hamiltonian

$$\hat{H}_{\text{YCZ}_3} = -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \frac{\hat{l}^2}{2\mu_r r^2} + \hat{K}_{CZ}^{\text{vib}} + \hat{K}_{CZ}^{\text{rot}} + V(R \rightarrow \infty, r, \chi, \theta_1, \theta_2, \varphi_1, \varphi_2). \quad (14)$$

The wave function is propagated using the split-operator method and the total reaction probabilities for a specific initial state are calculated from the time-independent wave function at a dividing surface  $r = r_s$ ,

$$P_i(E) = \frac{\hbar}{\mu_r} \text{Im}(\langle \psi_{iE} | \psi'_{iE} \rangle) |_{r=r_s}, \quad (15)$$

where

$$|\psi_{iE}\rangle = \frac{1}{a_i(E)} \int_0^\infty e^{i(E-H)t/\hbar} |\Psi_i(0)\rangle dt, \quad (16)$$

with  $a_i(E) = \langle \phi_{iE} | \Psi_i(0) \rangle$  being the overlap between the initial wave packet  $\Psi_i(0)$  and the energy-normalized asymptotic scattering function  $\phi_{iE}$ .

### III. RESULTS

We used the unrestricted coupled cluster method with single and double excitations including a perturbative treatment of the triple excitations [UCCSD(T)] for the *ab initio* calculations, since it has been showed that a single-reference calculation is sufficient to describe the electronic correlation for the system.<sup>33</sup> As we did for the OH<sub>3</sub> system,<sup>73</sup> the gradients and Hessians for all the data points were calculated using the 6-311++G(3df,2pd) basis sets, while the energies were calculated with the aug-cc-pVTZ basis set to improve the accuracy of the PES. The sampled configurations were obtained from the paths of classical trajectories in the usual way.<sup>71</sup>

Quantum wave packet calculations were carried out repeatedly to check the convergence of PES with respect to the number of data points as shown in Fig. 2. It can be seen that a dataset with 5000 points is sufficient to converge the total reaction probability in the low collision energy region, partially due to the fact that our ‘‘growing’’ procedure started by sampling the region near the minimum energy path. However, to achieve a good convergence on the total reaction probability

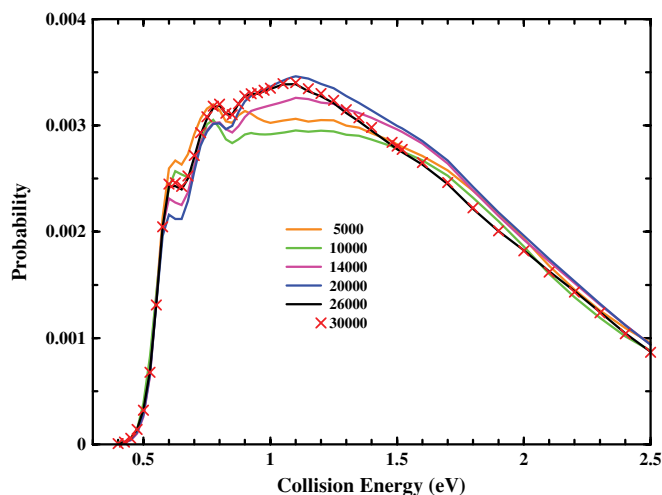


FIG. 2. Convergence of PES with respect to the number of data points for the total angular momentum  $J_{\text{total}} = 0$ .

for the collision energy up to 2.5 eV, one needs to use 30 000 data points to construct the PES. This number is much larger than the one once predicted by Collins and co-workers of the order of 1000,<sup>71</sup> mainly because we use quantum dynamical method instead of quasiclassical trajectory method (QCT) to gauge the convergence. In fact, the maximum error for all the reaction probabilities shown in Fig. 2 is about 10%, which is comparable to the statistical error in most QCT calculations.

The energy and geometry of the saddle point are given in Table I, in comparison with the corresponding values obtained from some PESs published recently. The barrier heights for these PESs all agree rather well. It is 15.03 kcal/mol for the present PES, very close to the result predicted by the CCSD(T)/aug-cc-pvqz calculation of 14.87 kcal/mol.<sup>33</sup> This difference may lead to a relative error of 24% in thermal rate constant at the room temperature, estimated by the Arrhenius formula. For the geometry of saddle point, the present PES gives nearly the same structure as the ZBB3 PES and the Wu's PES. But some small differences exist between the present PES and the EG-2008 PES, in particular for the umbrella H-C-H' angle of the methane molecule. Table II lists the harmonic frequencies of the reactant, saddle point, and products for those PESs. In general, the agreement is very good.

Table III lists the eigenenergies of the lowest five initial bound states for the zero angular momentum of CH<sub>4</sub> with the nonreacting CH<sub>3</sub> group restricted on the C<sub>3v</sub> geometry (four dimension with CH bond length fixed) calculated on the EG-2008, ZBB3, and the present PES. The state assignment labels ( $v_u, v_b, v_s$ ) represent, respectively, the umbrella excitation of the CH<sub>3</sub> group, the bending excitation of the reactive CH bond, and the stretching excitation of the reactive CH bond. We can see that all of the three PESs give results in good agreement with each other with the maximum of discrepancies of 0.01 eV, indicating these three PESs describe the asymptotic reaction region equally well.

The time-dependent wave packet calculations were carried out on the ZBB3, EG-2008, and the present PES, to compare these PESs beyond the stationary properties. An L-shaped wave function expansion for  $R$  and  $r$  was used to reduce the size of the basis set.<sup>72</sup> A total number of 100 sine basis functions in the range of  $[3.0, 15.0]a_0$  were used for translational coordinate  $R$  including 30 for the interaction region. For the reactive CH bond( $r$ ), 5 and 40 vibrational basis functions in the range of  $[1.0, 5.0]a_0$  were used for the asymptotic and interaction regions, respectively. The CH bond length in the nonreacting CH<sub>3</sub> group was frozen at  $2.06 a_0$  based on the fact that it essentially does not change during the reaction. For the umbrella motion, 5 basis functions were used. The size of rotational basis functions is controlled by the parameters,  $J_{\text{max}} = 53$ ,  $l_{\text{max}} = 35$ ,  $j_{\text{max}} = 18$ , and  $k_{\text{max}} = 18$ , corresponding, respectively, to the rotational angular momentum of CH<sub>4</sub>, the orbital angular momentum of H<sub>Y</sub> with respect to the CH<sub>3</sub> group, and the rotational angular momentum of CH<sub>3</sub> and its  $z$ -component. The size of the rotational basis functions is 44 460 and the number of grid points for the integration of the rotational basis set is 493 506, with parity and C<sub>3v</sub> symmetry of the nonreacting CH<sub>3</sub> group considered.

Figure 3 shows the total reaction probabilities for the total angular momentum  $J_{\text{total}} = 0$  on the ZBB3, EG-2008, and our new PES, together with that obtained earlier on the JG PES.<sup>6</sup> Note that since the basis set used here is slightly larger than that used in potential convergence check, one may notice that total reaction probability shown in Fig. 3 differs slightly from that shown in Fig. 2. It can be seen that the reaction threshold for the present PES agrees very well with that for the ZBB3 PES of about 0.4 eV, but is about 0.02 eV lower than that for the EG-2008 PES, in according with the fact that the barrier

TABLE I. Comparison of CH<sub>5</sub> saddle point geometries and energies.

	Zhang <i>et al.</i> <sup>a</sup>	Wu <i>et al.</i> <sup>b</sup>	Corchado <i>et al.</i> <sup>c</sup>	Present <sup>d</sup>
Energy <sup>e</sup> (kcal/mol)	14.8	14.93	15.1	15.03
$R_{\text{CH}}$ (Å)	1.0861	1.085	1.0901	1.085
$R_{\text{CH}'}$ (Å)	1.3965	1.401	1.3903	1.399
$R_{\text{H}'\text{H}''}$ (Å)	0.8988	0.895	0.9728	0.895
$\angle \text{H} - \text{C} - \text{H}'$ (°)	102.80	103.1	106.82	103.11
$\angle \text{C} - \text{H}' - \text{H}''$ (°)	180.0	180.0	180.0	180.0

<sup>a</sup>RCCSD(T)/aug-cc-pVTZ (Ref. 32).

<sup>b</sup>CCSD(T)/scaled-cc-pVTZ (Ref. 33).

<sup>c</sup>CCSD(T)/cc-pVTZ (Ref. 44).

<sup>d</sup>UCCSD(T)/aug-cc-pVTZ.

<sup>e</sup>Relative to the energy of H + CH<sub>4</sub>.



TABLE II. Comparison of normal mode frequencies (cm<sup>-1</sup>).

CH <sub>5</sub> (TS)				CH <sub>4</sub> + H				CH <sub>3</sub> + H <sub>2</sub>		
Present	Zhang <i>et al.</i> <sup>a</sup>	Wu <i>et al.</i> <sup>b</sup>	Corchado <i>et al.</i> <sup>c</sup>	Present	Zhang <i>et al.</i> <sup>a</sup>	Wu <i>et al.</i> <sup>b</sup>	Corchado <i>et al.</i> <sup>c</sup>	Present	Zhang <i>et al.</i> <sup>a</sup>	Corchado <i>et al.</i> <sup>c</sup>
1467i	1352i	1414i	1488i							
522	364	534	542							
522	364	534	542							
1062	1007	1074	1085	1346	1331	1341	1384			
1115	1125	1125	1183	1346	1331	1341	1384			
1115	1125	1125	1183	1346	1331	1341	1384	499	399	496
1442	1420	1442	1443	1569	1580	1569	1551	1425	1425	1426
1442	1420	1442	1443	1569	1580	1569	1551	1425	1425	1426
1784	1673	1795	1833	3026	3054	3031	2994	3114	3094	3121
3073	3113	3076	3036	3148	3156	3151	3167	3297	3284	3300
3223	3309	3223	3173	3148	3156	3151	3167	3297	3284	3300
3223	3309	3223	3173	3148	3156	3151	3167	4404	4432	4414 <sup>d</sup>

<sup>a</sup>RCCSD(T)/aug-cc-pVTZ (Ref. 32).<sup>b</sup>CCSD(T)/scaled-cc-pVTZ (Ref. 33).<sup>c</sup>CCSD(T)/cc-pVTZ (Ref. 44).<sup>d</sup>This subrow related to the H<sub>2</sub> product.

height of EG-2008 PES is 0.013 eV higher than that of ZBB3 PES as listed in Table I.

Overall, the agreement between the present PES and the ZBB3 PES on the total reaction probability is satisfactory. Both PESs give very small reaction probability in the energy range studied, with the maximum of about 0.4%. Above the threshold, the total reaction probabilities obtained on both PESs first increase quickly with the collision energy, then decline with further increase of collision energy, similar to the H + CD<sub>4</sub> reaction.<sup>52</sup> Nevertheless, as one can see from the figure that the peak positions for the total reaction probabilities differ a little bit, and ZBB3 probabilities decrease slightly faster in high collision energy region than the present one. The EG-2008 reaction probability in low energy region is quite close to those from the ZBB3 and present PES. However, for collision energy higher than 0.7 eV, the EG-2008 PES gives a substantially larger probability. Finally, one can see that the JG probability is much larger than those obtained from the other three PESs (note the JG probability was divided by a factor of 5 before plotting). This clearly reveals that the JG PES is qualitatively inaccurate for the system despite the fact that it had been widely used for the developments of new theoretical methods for polyatomic reactions.<sup>10, 11, 14, 22, 48–50</sup>

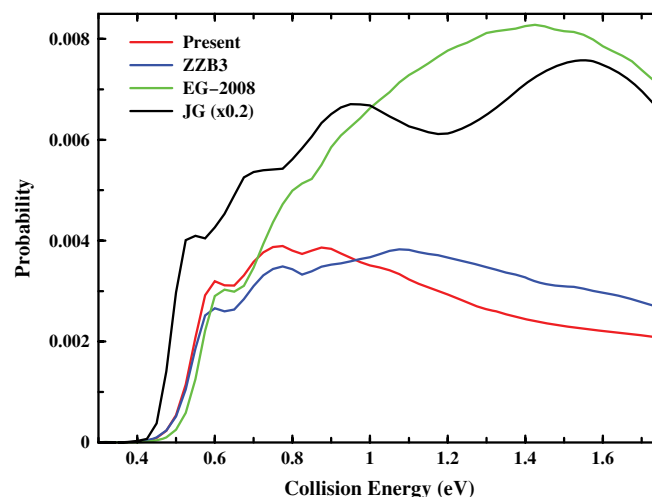
Figure 4 shows the ICSs for the title reaction obtained on three PESs by using the centrifugal sudden (CS) approximation. As expected, the ICSs from the ZBB3 PES and the

present PES agree rather well in the entire collision energy range considered, despite the fact that ICSs from these two PESs agreed even better for the H + CD<sub>4</sub> → HD + CD<sub>3</sub> reaction.<sup>52</sup> The ICS from EG-2008 PES is quite close to the present one in the low collision energy region, but is considerably higher in the high collision energy region. From Figs. 3 and 4, one can see that the accuracy of the potential energy surface is converging for this benchmark polyatomic system, but some differences still exist among these PESs.

The ZBB3 PES was constructed based on about 20 000 *ab initio* data points,<sup>32,34</sup> and the present PES contains 30 000 data points, so there are in total 50 000 *ab initio* data points available for the reaction system. All these data points had been chosen carefully to sample the molecular configuration well, so that they can be used as a good dataset to check the global accuracy of a PES. In Fig. 5, we show the distributions of potential energy error (the energy difference between the potential value from a PES and the *ab initio* value for a configuration) for the EG-2008, ZBB3, and the present PES. The

TABLE III. Comparison of eigenvalue of the initial bound states from three different PESs. All energy values in eV. See text for the definition of ( $v_u, v_b, v_s$ ) used in the state assignment.

Eigenstate index	ZBB3 PES	EG-2008 PES	Present	Assignment ( $v_u, v_b, v_s$ )
0	0.452	0.450	0.455	(0,0,0)
1	0.614	0.615	0.622	(1,0,0)
2	0.775	0.779	0.786	(2,0,0)
3	0.798	0.804	0.808	(0,2,0)
4	0.819	0.821	0.827	(0,0,1)

FIG. 3. Total reaction probabilities on the JG, ZBB3, EG-2008, and present PES for the total angular momentum  $J_{\text{total}} = 0$ .

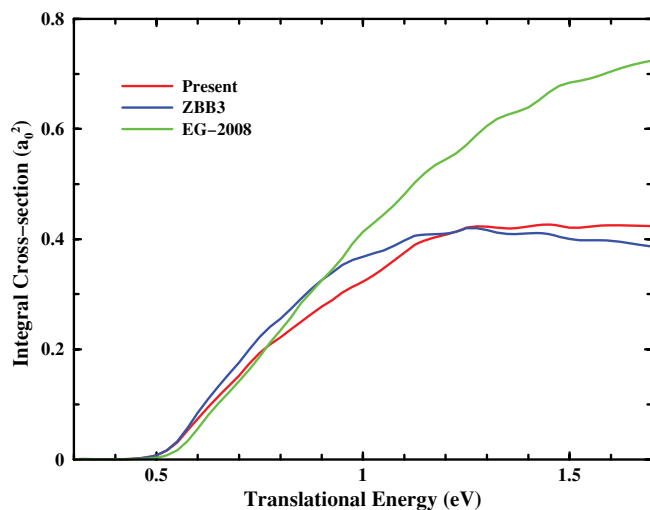


FIG. 4. Integral cross sections for the  $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$  reaction obtained on the ZBB3, EG-2008, and present PES.

error distributions in Figs. 5(a)–5(c) were obtained by using the 30 000 data points calculated in this work. For the present PES, a data point was removed from the dataset when the error on that data point was calculated. The error distribution in Fig. 5(d) was obtained by using the 20 000 data points for the ZBB3 PES. It can be seen that the EG-2008 PES has an error distribution with a width substantially larger than that of the

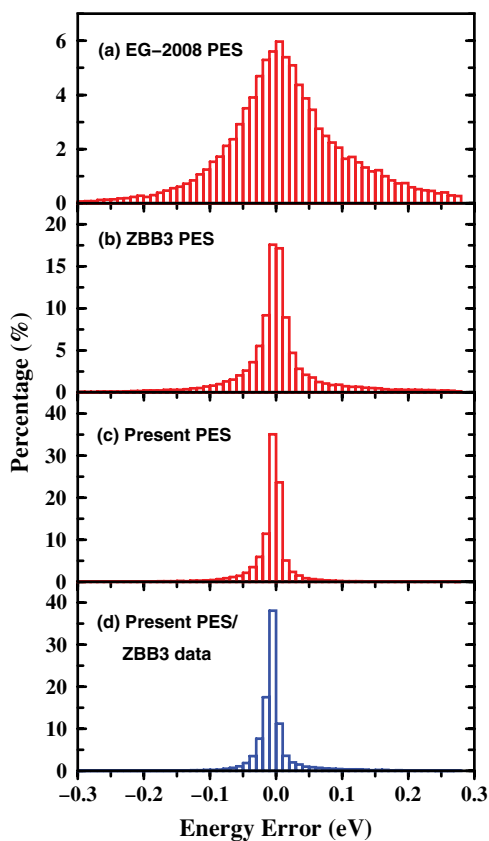


FIG. 5. Distributions of potential energy errors: (a–c) obtained by using the 30 000 data points calculated in this work; (d) obtained by using the 20 000 data points for the ZBB3 PES.

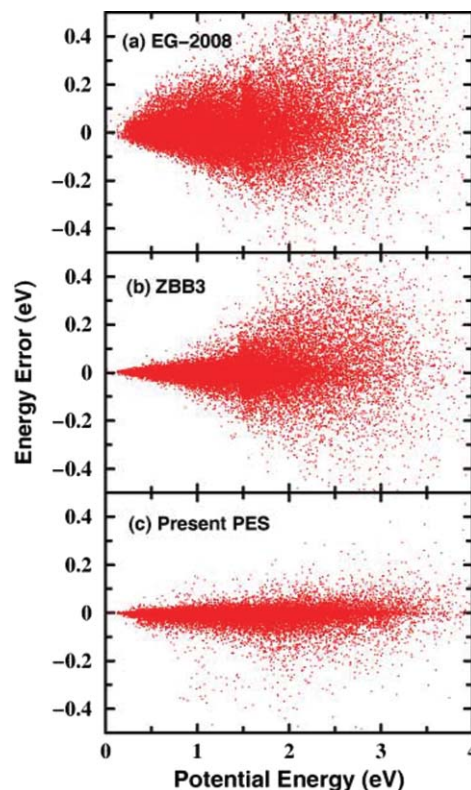


FIG. 6. Distributions of potential energy errors for the 30 000 data points calculated in this work on the EG-2008, ZBB3, and present PES, according to their *ab initio* values.

other two, while the present PES has a width slightly smaller than that of the ZBB3 PES. The percentages of data points with error smaller than 0.05 eV are 48%, 74%, 91%, and 88% for Figs. 5(a)–5(d), respectively. Thus it is quite reasonable to say that in general the EG-2008 PES is less accurate than the other two PESs, and the present PES is slightly more accurate than the ZBB3 PES.

Figure 6 shows the distributions of energy errors calculated for these 30 000 data points on the EG-2008, ZBB3, and present PES, according to their *ab initio* potential values. It can be seen that both the ZBB3 PES and EG-2008 PES describe the low energy region substantially better than the high energy region. In contrast, the present PES describes the entire energy region more equally well.

The EG-2008 PES was constructed by only sampling the configuration space with energy slightly above the barrier height,<sup>74</sup> so that it can predict the thermal rate constant quite well.<sup>45</sup> Although the VM-MM model is able to extrapolate reasonably the potential energy for the region not covered in fitting, the accuracy is very limited. In contrast, the data points used to construct the ZBB3 PES and the present PES sample a much wider energy range as shown in Fig. 7. As a result, these two PESs are more accurate than the EG-2008 PES, in particular in high energy region. From Fig. 7, one also can see that the present PES has substantially more data points in the energy range of [0.8, 2.5] eV, indicating the present PES should be more reliable than the ZBB3 PES in that energy region.

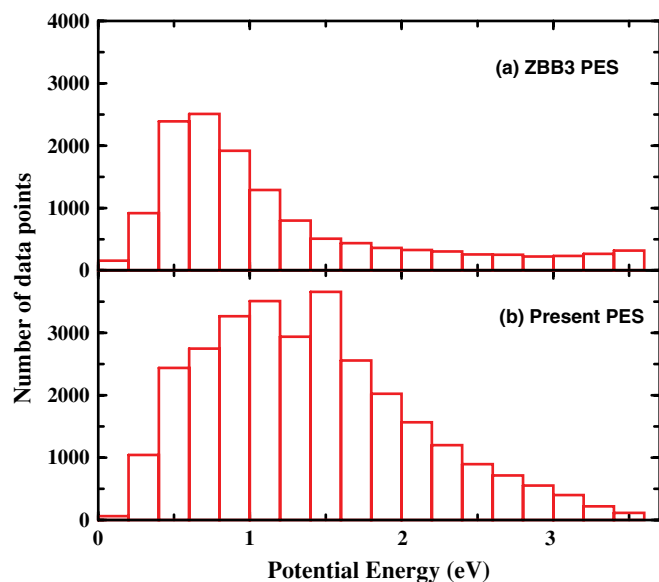


FIG. 7. Distributions of data points in energy domain for the ZBB3 and present PES.

However, it is worthwhile to point out that the ZBB3 PES is much faster than the present PES on evaluating the potential value for a given molecular configuration. In fact, the evaluations of potential values on a huge number of grid points used in seven- or eight-dimensional quantum wave packet calculations, rather than the *ab initio* calculations for all the data points, have substantially hindered the construction of the present PES. The *ab initio* calculations took about 600 days on a workstation with 8 CPU cores in total, while the evaluations of the potential values on all the grids for the title reaction took about 400 days despite the fact that we have developed many techniques to accelerate the evaluation speed (not like the *ab initio* calculation, the evaluation should be repeated for different grid sets). In contrast, it only took a few days to carry out the same evaluation for the ZBB3 PES. Obviously, more work should be done to speed up the evaluation further in order to make the PES more useful for QCT or quantum dynamics calculations.

#### IV. CONCLUSIONS

A full-dimensional global potential energy surface has been constructed for the title reaction by using the modified Shepard interpolation method. The first and second order derivatives for the data points were calculated at the UCCSD(T)/6-311++G(3df,2pd) level, while the energies were calculated at the UCCSD(T)/aug-cc-pVTZ level to improve the accuracy of the PES. Quantum wave packet calculations were used to gauge the convergence of the PES with respect to the number of data points. A total number of 30 000 nuclei configurations were selected as the final dataset for the PES, out of a huge number of configurations sampled by trajectories.

Seven-dimensional time-dependent wave packet calculations were carried out on the EG-2008, ZBB3, and present PES. Satisfactory agreements were achieved between the

ZBB3 and the present PES on the total reaction probabilities and integral cross sections for the collision energy up to 2.5 eV. The results on the EG-2008 PES agree reasonably with those from the other PESs in the low collision energy region, but substantially larger than the other two PESs in high collision energy region. Because the ZBB3 PES and the present PES were constructed using two totally different approaches, the satisfactory agreements on the ICS for the title reaction as well as for the  $\text{H} + \text{CD}_4 \rightarrow \text{HD} + \text{CD}_3$  reaction<sup>52</sup> on these two PESs indicate that we are approaching to the final stage for a quantitatively accurate PES for the benchmark polyatomic reaction.

Quantum dynamical calculations also showed that some differences still exist between the ZBB3 and the present PES. Detailed examinations of the three PESs by using the *ab initio* data points obtained in this work and in the work of the ZBB3 PES revealed that the present PES is slightly more accurate than the ZBB3 PES, in particular in high energy region, while the EG-2008 PES is substantially less accurate than the other two PESs. However, the ZBB3 PES is faster than the present PES on evaluating the potential values by about a factor of 40. Despite the fact that we have developed many techniques to accelerate the evaluation speed, it is still very expensive computationally to evaluate potential values for QCT or quantum dynamics calculations. More work should be done to speed up the evaluation further in order to make the PES more useful.

Finally, it is worthwhile to point out that the 30 000 data points included in the present PES actually cover the configuration space important for both abstraction and exchange reactions because they were selected from the paths of classical trajectories for both reactions. Quantum dynamical calculations will be carried out to test the convergence of PES with respect to the number of data points for the exchange reaction, although it will be even more expensive to evaluate potential values on all the grids for the reaction than that for the abstraction reaction.

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