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Communication: Full dimensional quantum mechanical calculations of the reaction probability of the H+CH₄ reaction based on a mixed Jacobi and Radau description

Zhaojun Zhang¹, Fabien Gatti^{2, a)} and Dong H. Zhang^{1, b)}

¹*State Key Laboratory of Molecular Reaction Dynamics and Center for Theoretical and Computational Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R. China;*

²*ISMO, Institut des Sciences Moléculaires d'Orsay - UMR 8214 CNRS/Université Paris-Saclay, F-91405 Orsay, France*

A full-dimensional time-dependent wavepacket study using mixed polyspherical Jacobi and Radau coordinates for the title reaction has been reported. The non-reactive moiety CH₃ has been described using three Radau vectors whereas two Jacobi vectors have been used for the bond breaking/formation process. A potential-optimized discrete variable representation basis has been employed to describe the vibrational coordinates of the reagent CH₄. About one hundred billion basis functions have been necessary to achieve converged results. The reaction probabilities for some initial vibrational states are given. A comparison between the present approach and other methods, including reduced and full dimensional ones, is also presented.

^{a)}E-mail: fabien.gatti@u-psud.fr

^{b)}E-mail: zhangdh@dicp.ac.cn

A comprehensive description of elementary chemical reactions is of utmost relevance in fields such as combustion and interstellar chemistry. Ideally, an accurate understanding at a quantum level of theory is required. However, the computational effort of such calculations increases exponentially with the number of atoms. More relevantly, considering state-to-state reaction probabilities, triatomic and a few tetra-atomic reactive systems could be studied until now^{1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73,74,75,76,77,78,79,80,81,82,83,84,85,86,87,88,89,90,91,92,93,94,95,96,97,98,99,100}. Interestingly, several models and methods have been recently proposed to treat reactive systems with more than four atoms.

In this context, the six-atom system $\text{H}+\text{CH}_4 \rightarrow \text{H}_2+\text{CH}_3$ has served as a benchmark for both theoretical and experimental studies in quantum reaction scattering studies. Owing to its importance in industry, in the last twenty years different simulation approaches, ranging from 3 to 12 active nuclear degrees of freedoms, have been developed for its study. Takayanagi was the first to report a three dimensional study in which $\text{H}+\text{CH}_4$ was considered as a collinear four-atomic system.¹ Yu and Nyman added the umbrella mode of nonreacting CH_3 in a four-dimensional model including a rotating bond approximation (RBA).² Wang and Bowman carried out a six-dimensional (6D) time-dependent wave packet study by treating the three hydrogen atoms in CH_3 as a pseudo-atom.³ Zhang et.al. developed a semi-rigid vibrating rotor target (SVRT) model in which the CH_3 moiety is treated as a semi-rigid vibrating rotor.^{4,5}

In 2000, Clary and Palma proposed an eight-dimensional (8D) model for the reaction of the type $\text{X}+\text{YZZ}_3 \rightarrow \text{XY}+\text{CZ}_3$ in which the non-reactive CZ_3 group is restricted to a C_{3v} symmetry.⁶ Then Yang *et al.* carried out seven-dimensional calculations on the $\text{H}+\text{CH}_4$ reaction using that model with time-dependent wave packet method (TDWP).⁷ Subsequently, also using this model, Zhang and Yang carried a number of wave packet dynamics studies like $\text{H}+\text{CH}_4 \rightarrow \text{H}_2+\text{CH}_3$ ^{8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73,74,75,76,77,78,79,80,81,82,83,84,85,86,87,88,89,90,91,92,93,94,95,96,97,98,99,100}, $\text{H}+\text{CD}_4 \rightarrow \text{HD}+\text{CD}_3$ ⁹, $\text{H}+\text{CHD}_3 \rightarrow \text{H}_2+\text{CD}_3$ ¹⁰, $\text{O}+\text{CH}_4 \rightarrow \text{OH}+\text{CH}_3$ ¹¹, $\text{Cl}+\text{CHD}_3 \rightarrow \text{HCl}+\text{CD}_3$ ¹² and $\text{F}+\text{CH}_4 \rightarrow \text{HF}+\text{CH}_3$ ¹³. Surprisingly, even if in all these reactions the non-reactive methyl group is treated like a one- or two-dimensional C_{3v} rotor, the model provides results that quantitatively agree with the experimental results. For instance, Zhang and Zhou *et al.* used the 7D model to study the $\text{H}+\text{CD}_4 \rightarrow \text{HD}+\text{CD}_3$ reaction, leading to integral cross sections (ICS) in good agreement with experience.¹⁴ Wang *et al.* reported an interesting experimental result about the vibrational enhancement factor in the $\text{Cl}+\text{CHD}_3 \rightarrow \text{HCl}+\text{CD}_3$ reaction¹⁵ that agreed reasonably well with the 7D quantum dynamics calculation.¹⁶ Despite these exciting agreements between the low-dimensional models and experience, it is still unknown whether these reduced-dimensional models introduce significant differences with full dimensional simulations.

During the past two decades, possibly only the group of Manthe were able to carry out full-dimensional quantum dynamic simulations on the title system. They used the (multi-layer^{???}) multi-configurational time-dependent Hartree (ML-MCTDH) approach^{???} to perform many different types of calculations including the computation of reaction rate constants[?], initial state-selected reaction probabilities, state-to-state reaction probabilities, etc. always within the quantum transition state framework^{??????????}. In these simulations, these authors used a description based on Jacobi and Radau coordinates as we do in the present work^{??}.

In contrast, in our method we use a different definition of the coordinates (purely polyspherical[?]). This results in a less complicated Kinetic Energy Operator (KEO). Note that the idea to combine Jacobi and Radau coordinates was already introduced in spectroscopy by Bramley and Carrington for CH₂O in 1993[?].

In this communication, we present full dimensional quantum calculations on the H+CH₄ → H₂+CH₃ abstraction reaction using a time-dependent wave packet method. The KEO for the system is straightforwardly derived from the polyspherical formulation[?] based on mixed coordinates containing two Jacobi vectors and three Radau vectors. Since they are parameterized in terms of spherical coordinates and there are several vectors, these belong to a particular case of the so-called family of polyspherical coordinates[?]. In addition, this approach easily permits the introduction of subsystems. In other words, it is possible to define a body-fixed (BF) frame for specific groups of atoms in the molecular system and to introduce the spherical coordinates inside this body-fixed frame^{??} as in the formulation for van der Waals dimers[?]. The mixed coordinates of the system with the structure of X+YCZ_{1,2,3} are depicted in the Fig. 1. Here, we have one BF for the whole system, one subsystem for YCZ_{1,2,3}, and one subsystem for CZ_{1,2,3}. This allows us to separate easily the intramolecular motions of the CZ_{1,2,3} moiety from the rest. **This is a key aspect when considering the dynamics after the reaction.** Additionally, the YCZ_{1,2,3} moiety is also separated from the colliding X atom, which is very important prior to the reaction. This kind of strategy can be seen as a generalization of the formulation for van der Waals dimers[?] combined with polyspherical coordinates. More precisely, the global BF is defined such as its z axis is parallel to \vec{R} of Fig. 1 and such as the third Euler angle of the BF is the first Euler angle of the BF frame for YCZ_{1,2,3}. The BF of the subsystem YCZ_{1,2,3} is defined such as its z axis is parallel to \vec{r} of Fig. 1 and its third Euler angle is the first Euler angle of the BF of the CZ_{1,2,3} subsystem. The BF of the subsystem CZ_{1,2,3} is defined such as its z axis is parallel to \vec{R}_3 of Fig. 1 and its third Euler angle is defined such as \vec{R}_2 of Fig. 1 lies parallel to the $((x, z); x > 0)$ half-plan. The definition

of the BF frame for $CZ_{1,2,3}$ breaks the explicit symmetry of the three C-Z bonds. This has the advantage of keeping the structure of the polyspherical coordinates^{??} and its advantages with respect to the use of orthogonal coordinates, where the number of terms is rather well controlled. In terms of coordinates, we have to add the distance R to the ones necessary for the rotational description of $YCZ_{1,2,3}$ (12D including 3 Euler angles). Since we do not consider any overall rotation in the present work, only the last two Euler angles of $YCZ_{1,2,3}$ have to be kept. This leads to a problem in 11 dimensions plus R , i.e. 12 dimensions. Recently, this strategy using polyspherical coordinates with subsystems been successfully utilised in the study of the five-atomic scattering process of $H+NH_3$ [?]. In this system, the non-reactive group NH_2 of the reagent NH_3 was described by two Radau vectors while two Jacobi vectors were used for the bond breaking and formation. At this point, it should be noted that the use of subsystem coordinates, allows a direct product of potential-optimized discrete variable representation^{??} (PODVR) functions for the corresponding degrees of freedom which, in turn, reduces the size of the basis functions. As already shown, the combination of these mixed coordinates and the PODVR method can lead to a high efficiency. Therefore, such strategy can be extended to some elementary reactions involving six atoms in which the non-reactive moieties keep some symmetry and remain rather rigid. Note also that the flexibility provided by the combination of subsystems and polyspherical coordinates[?] is such that extensions to different structures with even more flexibility in the $CZ_{1,2,3}$ moiety would be possible without a qualitative change in the strategy. In particular, only new terms, similar to those already implemented in the present code, might be added to the KEO.

As already mentioned, the mixed coordinates of the system with the structure of $X+YCZ_{1,2,3}$ are depicted in the Fig. 1. The full dimensional Hamiltonian for such a system, defined in Jacobi and Radau mixed coordinates, can be written as

$$\begin{aligned}
\hat{H} = & -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} + \frac{(\vec{J}_{tot}^\dagger - \vec{L}_{YCZ_{1,2,3}}^\dagger) \cdot (\vec{J}_{tot} - \vec{L}_{YCZ_{1,2,3}})}{2\mu_R R^2} \\
& -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} + \frac{(\vec{L}_{YCZ_{1,2,3}}^\dagger - \vec{L}_{CZ_{1,2,3}}^\dagger) \cdot (\vec{L}_{YCZ_{1,2,3}} - \vec{L}_{CZ_{1,2,3}})}{2\mu_r r^2} \\
& + \hat{T}_{CZ_{1,2,3}} \\
& + V(R, \beta_Y, \alpha_s, r, \beta_s, \gamma_s, R_1, R_2, R_3, \theta_1, \theta_2, \varphi_1),
\end{aligned} \tag{1}$$

where

$$\mu_R = \frac{m_X m_{YCZ_{1,2,3}}}{m_X + m_Y + m_C + m_{Z_1} + m_{Z_2} + m_{Z_3}}, \quad (2)$$

$$\mu_r = \frac{m_Y m_{CZ_{1,2,3}}}{m_Y + m_C + m_{Z_1} + m_{Z_2} + m_{Z_3}}, \quad (3)$$

\vec{J}_{tot} is the total angular momentum operator of the system, $\vec{L}_{YCZ_{1,2,3}}$ and $\vec{L}_{CZ_{1,2,3}}$ are the rotational angular momentum operator of the $YCZ_{1,2,3}$ and $CZ_{1,2,3}$, respectively. V denotes the potential energy surface[?]. With respect to the kinetic energy operator $\hat{T}_{CZ_{1,2,3}}$, its purely vibrational part is given in the appendix of Ref.[?] and the additional rotational part is given in Eq. 5 of Ref.[?]. The excellent agreement between the rovibrational eigenvalues for different penta-atomic molecules obtained with our code and those from different approaches[?] proves that the KEO has been correctly implemented. We additionally define $u_1 = \cos \theta_1$, $u_2 = \cos \theta_2$ and $u_{\beta_s} = \cos \beta_s$ so that the integral volume element reads:

$$dV = dR_1 dR_2 dR_3 du_1 du_2 d\varphi_1 d\alpha_s du_{\beta_s} d\gamma_s dr \sin \beta_Y d\beta_Y dR, \quad (4)$$

using the convention for the coordinates of Ref.[?].

Concerning the time-dependent wave packet method, we have followed the approach used for the X+YNZ_{1,2} system by replacing the nonreactive group NZ_{1,2} by the CZ_{1,2,3} moiety. The potential energy surface used here was fitted using the permutation invariant polynomial-neural network method by Li *et al*.[?] **I FIND THAT SOME DESCRIPTION OF THE PIP-NN PARAMETERS AND CONVERGENCE SHOULD BE GIVEN HERE**

The main goal of this communication is to show the efficiency of our method, hence only the abstraction channel $H^+CH_4 \rightarrow H^+H+CH_3$ will be presented and the exchange channel $H^+CH_4 \rightarrow H+H^+CH_3$ will not be considered. An L-shaped wave function expansion scheme was used to reduced the size of the basis set. A total of 72 **sinus** basis functions was used for R range in a range of [2.0,15.0] **a.u. whereas 22 grid points were used in the interaction region**. For the breaking bond r , a total of 30 vibrational basis functions was used and 5 vibrational basis functions were used in the asymptotic region. For the three Radau radial degree of freedoms R_1 , R_2 and R_3 , three vibrational basis functions were used for each of them. For the three angular degrees of freedoms θ_1 , θ_2 and φ_1 in CH_3 , 5, 5 and 15 PODVR functions were used, respectively. For the two angular coordinates β_s and γ_s , we used 8 PODVR functions. The rotational basis is controlled by $L_{max}=24$ and $k_{max}=3$, resulting in a total of 163 functions for $J_{tot} = 0$, J_{tot} being the quantum number for the total angular momentum. **Consequently, the total number of the basis functions** reaches

69, 711, 840, 000 in the interaction region and 26, 406, 000, 000 in the asymptotic region. The storage for the wavefunctions necessitates more than 716 GB. We have used combined shared memory parallelization using OpenMP and distributed memory parallelization using message passing interface (MPI). The convergence with respect to the number of DVR points for all the degrees of freedom has been tested very carefully. These tests are presented in the supplementary material.

To carry out the scattering calculations, we first computed vibrational energies of some initial states of CH_4 using the aforementioned parameters. Table I displays the calculated fundamental and excited energy levels for the four vibrational modes of the methane molecular together with their experimental counterparts. In previous papers^{2,3}, we have calculated the vibrational and rotational energy levels for some isotopic derivatives of methane and CH_3F and **these results have been thoroughly compared to experimental data and to other theoretical methods^{2,3,4,5}**. We have shown that the strategy with one Jacobi vectors and three Radau vectors (1+3) along with the PODVR approach leads to very accurate results, proving the reliability of our method, in particular the correct implementation of the complicated KEO to prepare the studies of reactions of the type $\text{X}+\text{YCZ}_{1,2,3}$.

Fig. 2 depicts the reaction probabilities for $J_{tot}=0$ and the initial ground state CH_4 as a function of translational energy. **obtained with the present full-dimensional, together with reduced-dimensional models (7D and 8D) as well as the results of the MCTDH method in full dimensionality (12D), respectively.** These MCTDH results have taken from Ref.². By visual inspection of Fig. 2, we can notice that the probability increases very fast from around translational energy 0.4 to 0.6 eV. Then the curve goes down slightly. From the energy of 0.66 eV to 1.0 eV, the probability rises very slowly and reaches a maximum of about 0.0036 at 1.0 eV. Overall, the probability for the (0000) initial state is very small for the abstraction reaction and is relatively smooth. As a comparison, the reaction probabilities of the seven- and eight-dimensional method based on the C_{3v} models are also given. In the 7D model, the non-reactive CH_3 model includes only one vibrational degree of freedom, the so-called umbrella angle, and the stretching motion of three C-H bonds is included in the 8D model. Importantly, the shapes of the probabilities of the reduced-dimensional methods are very similar to the present full-dimensional method except in a tiny shift in translational energy. The probabilities for the reduced-dimensional methods also increase very fast in the low energy region whereas in the high energy region the positions of the oscillating structures are almost the same again with a very small shift. The full dimensional probability of the MCTDH method is almost identical to the present 12D results in the low energy region thus

showing that both approaches are **in an excellent agreement**. However, the MCTDH probability drops down when the energy is larger than about 0.62 eV. Even though the PESs of the MCTDH method is slightly different from our present PES, we **firmly** believe that such difference cannot be caused by this difference. Indeed, as shown in our previous studies^{2, 3, 4}, the differences of probabilities among those different PESs for the $\text{H}+\text{CH}_4 \rightarrow \text{H}_2+\text{CH}_3$ reactions are very small: the PES² used for the MCTDH calculations is refitted based on the PES of Ref.² On the one hand, the transition state for the abstraction channel has a C_{3v} symmetry and the reaction system always keeps it along the minimal reaction path. On the other hand, we have obtained results with the 7D model, which were in very good agreement with the experimental results.^{2, 3, 4} **I FIND THAT THE 7D MODEL SHOULD BE RECALLED HERE** With those results in mind, we are confident that the results of the present full-dimensional method are reliable, thus confirming that the 7D reduced-dimensional model is sufficient to predict the reaction probability starting from (0000). Moreover, we believe that the calculations with MCTDH there is probably a lack of convergence in the high-energy region.

In the 7D model, the bond length of the non-reactive CH_3 group is fixed, so that the stretching mode will be localized at the broken bond C-H. In contrast, the three bond lengths of the non-reactive CH_3 group can change simultaneously in the 8D model. **As a consequence, there will exist one symmetry stretching mode and one asymmetrical stretching mode. In the full dimensional model, there are four stretching modes including a symmetric one and a triply-degenerate asymmetric one.** Similarly, as in the reaction $\text{H}+\text{NH}_3$ ², the four bonds in the reagent CH_4 do not possess explicit permutation symmetry in our 12D model due to the fact that we use one Radau vector to define the z BF axis of the BF of CH_3 . The three asymmetrical stretching modes are thus not perfectly degenerate. For the asymmetrical stretching vibrational state (0010), the reaction probability is obtained by averaging over the three (0010) probabilities. In Fig. 3, the comparison for the present 12D results and 7D and 8D reduced dimensional results is provided. The reaction probabilities of (1000) and (0010) states are almost exactly the same and both rise smoothly as translational energy increases. The probabilities for the two stretching states are much larger **than those of the ground state** and reach about 0.01 at 1.0 eV. In order to further compare the results of our present 12D calculations with the 7D and 8D models, we also give the sums of the probabilities of the stretching vibrational states for both 8D and 12D methods. It is observed that from the threshold energy region to about 0.5 eV, the agreement of the probabilities of the three methods is very good. This indicates that the C_{3v} model can work very well for low energies and

that the reaction happens around the minimal reaction path. However, as the energy increases, the C_{3v} model fails to describe the reaction: this is one important result of our new calculations. The behavior with increasing energy of the three curves is rather different: the probability in the 12D model is the largest whereas the 7D probability is the smallest.

In Fig 4, we depict the comparison of the probabilities of the present full dimensional method and the calculations with the MCTDH method for the reactant CH_4 (1000) and (0010) initial states. When plotted as a function of total energy, which includes the excitation energy, a very tiny difference between the probabilities of the symmetrical and asymmetrical vibrational states in our simulations can be observed. In the low energy region, our results with the results obtained with MCTDH agree very well. However, the reaction probabilities with MCTDH are higher than our 12D result as the total energy increases.

In summary, a full dimensional time dependent wave packet method for the $H+CH_4$ reaction system based on a model combining Jacobi and Radau coordinates along with a PODVR approach has been presented. Since the CH_3 moiety does not change dramatically during the whole reaction process, three Radau vectors and PODVR functions can be used to describe very effectively CH_3 thus substantially reducing the number of basis functions needed. This opens up the path to full quantum studies of the title reactions. About one hundred billion functions were needed to converge our results in our energy domain. The reaction probabilities for the ground and stretching excited vibrational states have been calculated. A detailed comparison of the present 12D simulations and reduced-dimensional 7D and 8D models has also been given. This has proven the reliability of the C_{3v} model in the low energy region. Our results seem to indicate that the convergence of the former MCTDH simulations needs to be further improved in the high energy region.

Data Availability Statement The data that support the findings of this study are available from the corresponding author upon reasonable request.

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TABLE I. Vibrational energies (in cm^{-1}) of CH_4 for $L_0 = 0$ (no rotation). Second column: calculated values with the potential energy surface constructed by Li and Chen *et al.*; third column: experimental values. Our present zero-point energy is equal to 9689.43 cm^{-1}

State	This work	Expt.
(0001) F_2	1309.19	1310.76
	1309.83	
	1310.33	
(0100) E	1530.40	1533.33
	1530.83	
(1000) A_1	2912.89	2916.48
(0010) F_2	3014.60	3019.49
	3015.13	
	3015.51	

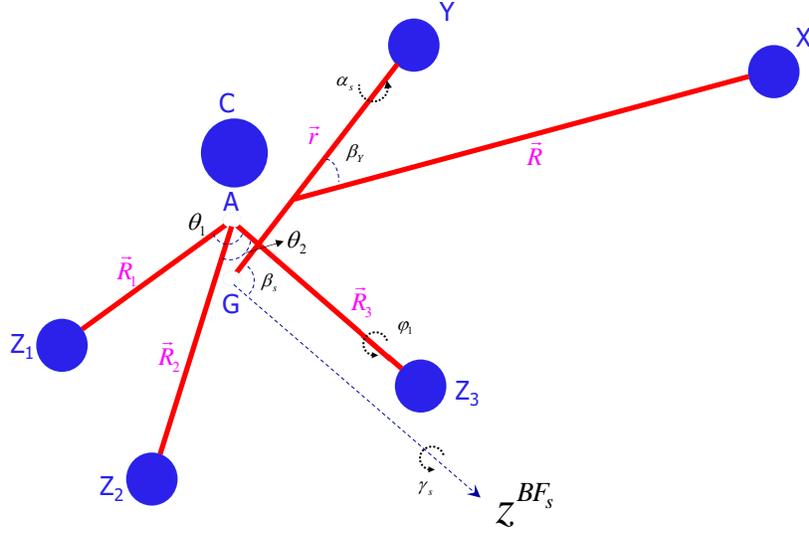


FIG. 1. The Jacobi and Radau mixed coordinates for the $X+YCZ_{1,2,3}$ system. A denotes the “canonical” point of $CZ_{1,2,3}$, G is the center mass of the $CZ_{1,2,3}$. \vec{R}_1 , \vec{R}_2 and \vec{R}_3 are the Radau vectors. \vec{R} and \vec{r} are the Jacobi vectors: \vec{r} from G to Y, \vec{R} from the center of mass of $YCZ_{1,2,3}$ to X.

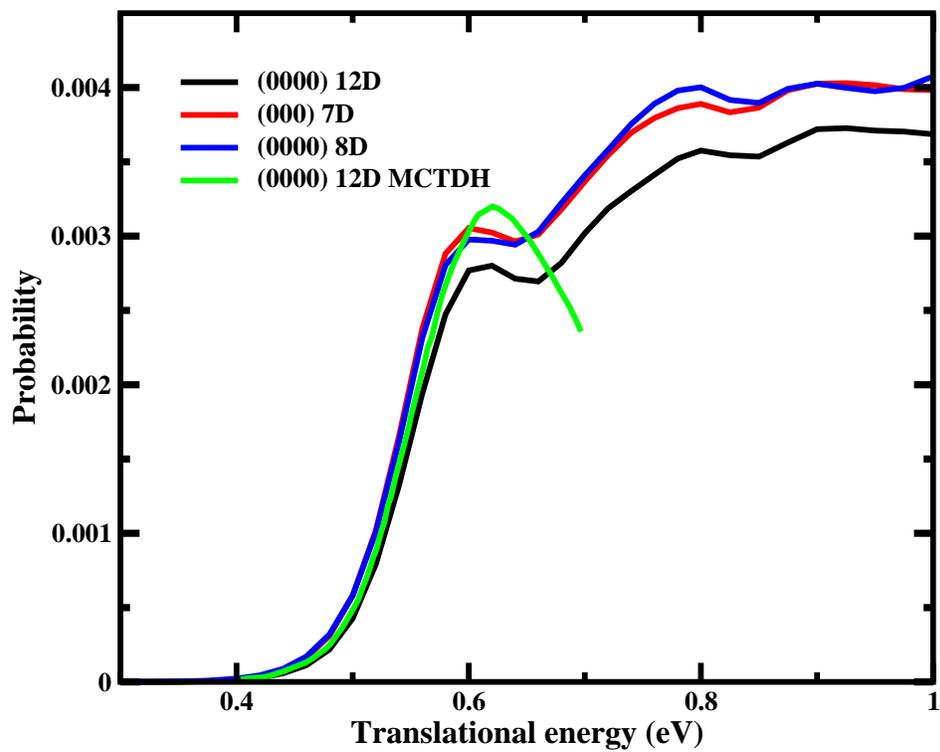


FIG. 2. The calculated $J_{tot} = 0$ reaction probabilities for the $\text{H}+\text{CH}_4(0000) \rightarrow \text{H}_2+\text{CH}_3$ as a function of translational energy for different kinds of methods: in black our new 12D calculations, in red model with 7 dimensions, in blue with 8 dimensions, in green calculations with MCTDH with a slightly different PES.

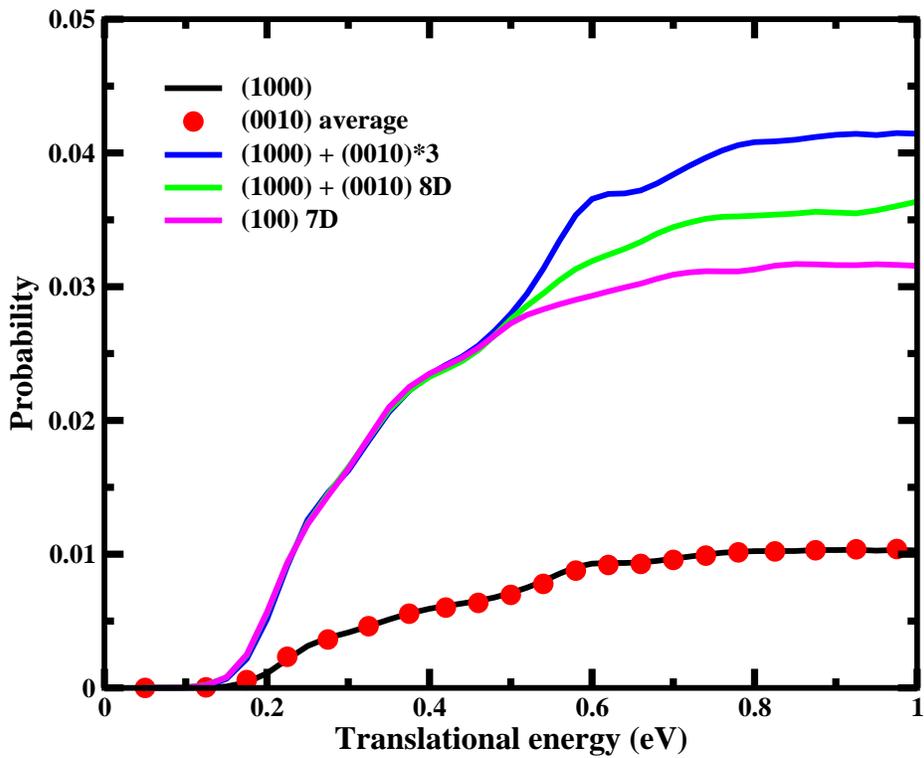


FIG. 3. The $J_{tot}=0$ reaction probability for the initial states (1000) and (0010) of CH_4 as a function of translational energy and comparison of the probabilities based on 7D, 8D and present method.

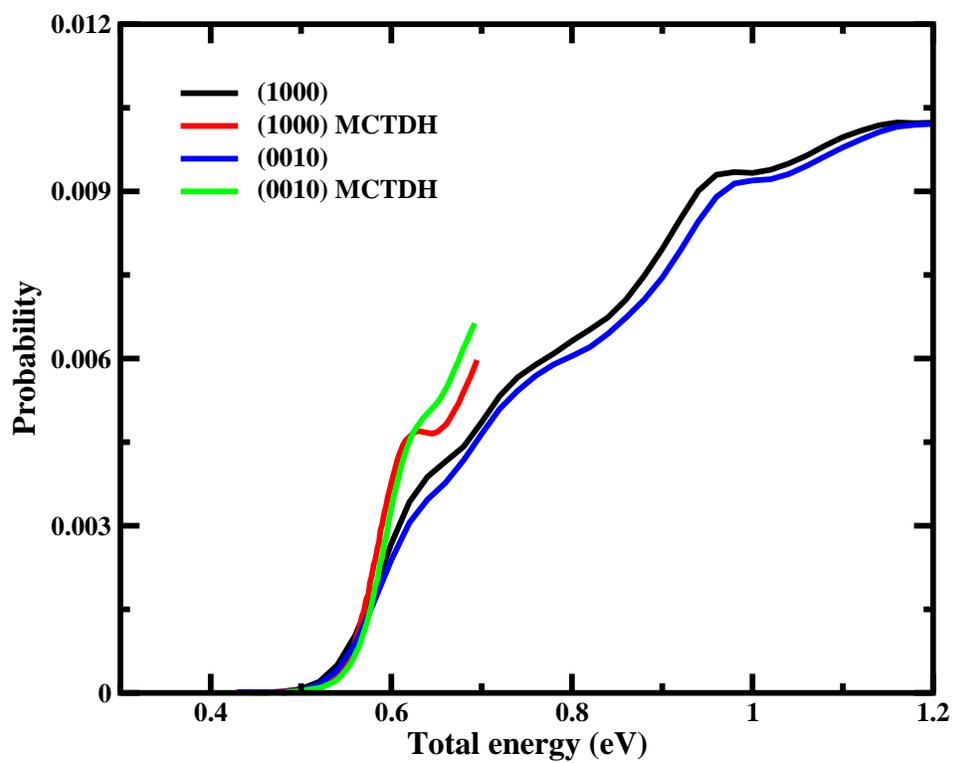


FIG. 4. Comparison of the (1000) and (0010) probabilities based on the present method and MCTDH method as a function of total energy.