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Energy efficiency in surmounting central energy barrier: quantum dynamics study of the OH + CH_3 → O + CH_4 reaction

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Abstract

The present quantum dynamics study of the OH + CH_3 shows, for this "central" (slightly early) barrier reaction, it is the vibrational energy of the reactant OH that is more effective in promoting the reactivity than the translational energy; while previous studies show that, for its forward reaction O + CH_4 also with a "central" (slightly late) barrier, it is the translational energy that is more effective in surmounting the energy barrier than the vibrational energy. Since both barriers only slightly deviate from the center of the potential energy surface, these findings indicate that for these two reactions with more-or-less central barriers, a small change of the barrier location can greatly affect which energy form determines the reaction reactivity. This study also shows both the rotational excitation states of OH and CH_3 hinder the reactivity.

Introduction

Energy efficiency in surmounting an energy barrier is one of fundamental aspects of chemical reaction dynamics. For atom + diatom reactions, based on experimental studies using the IR "chemiluminescence depletion" method as well as theoretical calculations using quasi-classical trajectory(QCT) method, Polanyi draws a conclusion[1] that for the exoergic reaction with an early barrier(in the entrance valley) the translational degree of freedom is favored for barrier crossing, whereas the vibrational energy is more effective for barrier crossing for the endoergic reaction with a later barrier. However, the Polanyi rules are formulated for the substantially exoergic (early barrier) and substantially endoergic (late barrier) reactions; in addition, Polanyi rules do not cover the reactions with slightly exoergic and endoergic reactions, namely approximate central barriers for atom-diatom reactions, not to mention poly-atomic reactions. Investigations of the energy requirement on reactivity for polyatomic reactions Cl, F, and O with methane[2-35] show that the Polanyi rules can not be simply extended to the polyatomic cases. It is especially interesting to see what the energy efficient roles are in surmounting the central-energy-barrier reactions which are not discussed by the Polanyi rules even in the atom-diatom cases.

The Cl + CH_4 hydrogen abstraction reaction is an endoergic late barrier reaction. In 2007, the crossed molecular beam experiment by Liu's group for the Cl + CHD_3 reaction[2] found that the translational energy is more effective on the reactivity than the vibrational excitation of the CH stretching mode, which doesn't support the Polanyi rules for the late barrier case. Later, a QCT study[15] by Czakó and Bowman on

their own constructing full dimensional potential energy surface(PES)[20] found that, for the same amount of total energy, only at low total energy, the translational energy is more effective than the vibrational energy for the reactivity. Then in 2012, two reduced quantum dynamics studies, one for the Cl + CH_4 in six degree of freedom (DOF)[13] by Wang's group and the other a seven DOF study[14] for the Cl + CHD_3 reaction from Zhang's group on the same PES[20] reveal that the Polanyi rules still hold except at very low scattering energy. Because of the difference between the theoretical calculations and experimental measurements, Liu's group did the experiment[3] again, this time they probed all the rotational channels of the $CD_3(v = 0)$ products, and found experimental results in consistent with theoretical calculations that basically the Polanyi rules still can be applied to the Cl + methane reaction except at very low energies.

For the F + CH_4 reaction, the PES for this reaction is quite complex, which has an early barrier and a van der Waals valley in the entrance, also has a relatively deep vdW minimum in the product channel. The experiment study on the F + CHD_3 reaction[6] by Liu and co-workers shows that the first excitation state of CH stretch mode of CHD_3 hinders the reaction rates and favors the DF + CHD_2 product. This observation has been confirmed by a QCT calculation[16, 17]. A 4DOF quantum dynamics on the F + CH_4 reaction[18] shows that the translational energy is more effective than the vibrational energy in enhancing the reactivity when the energy is below 0.38 eV; however, above 0.38 eV, the vibrational energy is more effective instead. Therefore, although this reaction has an early barrier, the energy requirement

in surmounting the energy barrier is more complicated to decide which energy form is the driving force for the reactivity. The Polanyi rules here can not be simply extended to this reaction Similar to the F + CH_4 reaction, the exoergic F + H_2O reaction[36] also has an early barrier, the study by Guo's group[36] shows that all the vibrational DOFs of the reactant H_2O have larger efficiency in enhancing the reactivity than the translational DOF. Thus Polanyi rules cannot simply be applied to this polyatomic reaction either.

The O + CH_4 reaction is slightly endoergic[37, 38] with a slightly late barrier. The crossed-beam experimental studies by Liu's group on the reactions of O with the isotopic variants find that the vibrational excitations of the C-H/C-D bond in the variants of methane reactant enhance the reactivity, but the translational energy is more efficient[10, 11]; the bending excitation in CD_4 for the O + CD_4 reaction slightly suppresses the reaction[8]. Later, Czakó and Bowman developed a full-dimensional *ab initio* PES[31] and performed QCT calculations on O(^{3}P) with the isotopic variant reactions[31, 32]. Their results show that different stretching motions of CH_4/CD_4/CHD_3 promote the reactions while the bending excitation only slightly enhances the reactivity; however, the translational is more effective than all the vibrational motions in surmounting the energy barrier. Recently, an 8DOF quantum dynamics calculation[30] also on this PES was reported for the O + CHD_3 reaction: the calculated ground-state integral cross section(ICS) agrees well with the experimental one; the translational energy is also more efficient in promoting the reaction than the vibrational energy, and the stretching excitations have a greater impact than bending

and umbrella excitations. Last year, we reported a 6DOF quantum dynamics calculation[29] on the O + CHD_3/CD_4 → OH/OD + CD_3 reaction. Our calculated ICS function of the ground state for O + CHD_3 is consistent with the QCT[31] results, and the C-H stretch-excited functions agree with that of the experiment[10]. Furthermore, for O + CD_4, all the vibrational excitations of the reactant CD_4 enhance reactivity, which is in agreement with QCT results[32] but contradicts with experimental findings[8] that the CD_4 bending excitation hinders the reaction. Although this reaction has a slightly late barrier reaction, it's the translational energy more effective in promoting the reactivity than the vibrational energy.

As we know, Polanyi rules do not cover the reactions with slightly exoergic and endoergic reactions, namely slightly late and slightly early barrier reactions. So far, for the O + $CH_4/CHD_3/CD_4$ → OH/OD + CD_3 reaction with an approximate central barrier, it is the translational energy that is more effective in promoting the reactivity in this slightly late barrier reaction. Since Polanyi rules do not provide guidances on the reactions with slightly exoergic and endoergic reactions, it is essential to investigate the more-or-less central-barrier reactions to see what rules govern these types of reactions. Thus here, we study the energy efficiency on the reverse reaction of O + CH_4. Since OH + CH_3 → O + CH_4 is the reverse reaction of O + CH_4 → OH + CH_3, it is a slightly exoergic reaction with a slightly early barrier. The barrier is only slightly deviated from the center of the PES reaction channel to the reactant side while the forward reaction to the product side(See Figure 1). A recent study by Guo's group, using a Sudden Vector Projection model[34] predicts that the OH vibrational excitation

enhances the reaction more effectively than the translational motion for the title reaction. Therefore, it is interesting to see, as the barrier slightly "moves" from the product side to the reactant side around the PES center, how does the reversion of this reaction change the relative efficiency of various types of reagent energy: Is the energy efficiency sensitive to the slight change of the barrier location? Is the correlation of the energy efficiency in terms of the translational and vibrational energy for the reverse reaction just the opposite of the forward reaction? What rules here, according to the barrier location, determine the energy efficiency in promoting the approximate center-barrier reactions?

So in this article, we carry out a reduced dimensional, 6DOF, time-dependent quantum scattering method for the OH + CH_3 reaction to study the energy efficiency. The initial-state-selected integral cross sections of the rotational and vibrational states of the reactants are computed to investigate the ro-vibrational effects on the reactivity, and the ratios of the excited OH vibrational state versus the ground state are calculated in terms of the equal amount of total energy to determine the relative efficiency of the various types of reactant energies. Then we can make a conclusion, based on the results for both the forward and reverse reactions, which degree of freedoms is the favorite in surmounting the barriers for these two slightly endoergic and exoergic reactions.

Theoretical method

We performed a time-dependent wave-packet, reduced-dimensional quantum dynamics study on the reverse reaction, OH + CH_3 → O +CH_4 on the Czakó and

Bowman[31] PES of $O(^3P) + CH_4$ reaction system. Here the three nonreactive H atoms in CH_3 were treated as one pseudo-atom, X, located at the center of mass of the three H atoms. Thus the title reaction became a pseudo 6DOF, diatom-diatom reaction[39], OH + CX → O + HCX. The pseudo-atom X moves towards or away to the C atom in phase to open or close the umbrella cone with the three C-H distances fixed at the equilibrium at asymptotic region, while they were fixed at the transition state distances during reaction.

The 6DOF Hamiltonian for the reaction system in the reactant Jacobi coordinates (see in Fig. 2) is given by,

$$H = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{(\mathbf{J}-\mathbf{j}_1-\mathbf{j}_2)^2}{2\mu R^2} + h_r(r) + h_\rho(\rho) + \frac{\mathbf{j}_1^2}{2\mu_r r^2} + \frac{\mathbf{j}_2^2}{2\mu_\rho \rho^2} + V_{6D}(R, r, \rho, \theta_1, \theta_2, \phi) \quad (1)$$

Where μ is the reduced mass of the whole reaction system; R is the distance between the center of mass of CX to OH, r and ρ are the bond lengths of OH and CX respectively; $\mathbf{J}$ is the total angular momentum operator, $\mathbf{j}_1$ and $\mathbf{j}_2$ are the rotational angular momentum operator for OH and pseudo-diatom CX, respectively; μ_r and μ_ρ are the reduced mass of OH and CX, respectively; V_{6D} is the interaction potential; θ_1 and θ_2 are the Jacobi angles formed by ρ and R, r and R, ϕ is the torsion angle labeled in Fig. 2. The vibrational reference Hamiltonians $h_r(r)$ and $h_\rho(\rho)$ are defined as,

$$h_r(r) = -\frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} + V(r) \quad (2a)$$

$$h_\rho(\rho) = -\frac{\hbar^2}{2\mu_\rho}\frac{\partial^2}{\partial \rho^2} + V(\rho) \quad (2b)$$

Where $V(r)$ and $V(\rho)$ are the one-dimensional reference potentials for r and ρ, respectively. These potentials are obtained in the corresponding coordinates by putting

the reaction system in the reaction channel when other coordinates are fixed at the equilibrium geometries.

The split-operator method[40] is employed here to propagate the wave-packet on the PES. The time-dependent wave-function can be expanded in terms of the body-fixed (BF) rovibrational eigenfunctions in terms of the reactant Jacobi coordinates[41].

In order to obtain the initial-state-selected ICS, first, the partial-wave reaction probabilities of different initial total angular momentum **J** were computed. Then the initial-state-selected ICS, $\sigma_{\upsilon_0 j_0}(E)$ is obtained by summing over all the initial-state-selected reaction probability $P^J_{\upsilon_0 j_0 K_0}(E)$ for all partial waves

$$\sigma_{\upsilon_0 j_0}(E) = \frac{1}{2j_0+1}\frac{\pi}{k^2}\sum_J (2J+1) P^J_{\upsilon_0 j_0 K_0}(E) \tag{3}$$

here $k = (2\mu E)^{1/2}$ is the wave number and E is the translational energy; υ_0 denotes the initial vibrational quantum number of the reactants, and j_0 for the initial rotational quantum number; K_0 is the projection of **J** on to the BF z axis of the diatom-diatom system.

For the above numerical calculation, 135 sine basis functions are chosen to expand the wave-function for the translational coordinate R in the range of 3.5-12.0 bohrs, 75 to expand the wave-function in the interaction region among these functions; 30 OH potential-optimized vibrational discrete variable representation (DVR) points[42] for r coordinates and 8 CX potential-optimized vibrational DVR points for ρ coordinates are sufficient for convergence; 15 spherical harmonic rotational functions for θ_1 and 24 for θ_2 are coupled to give 2720 parity adapted total angular momentum basis. The wave packet was propagated with a time step of 15 a.u. for a total time of about 9000

a.u. time. The above numerical parameters are enough to make the calculations converge for the current 6DOF reduced-dimensional dynamic calculation of the OH + CH_3 systems.

Results and discussion

Integral cross sections and energy efficiency on reactivity

1. OH(v_1, j_1 = 0) + CX(v_2 = j_2 = 0) and OH(v_1 = j_1 = 0) + CX(v_2, j_2 = 0)

In order to obtain the ICS, we need to calculate all the partial wave reaction probabilities for the total angular momentum *J*. In the collision energy range of 4.6 ~ 23.0 kcal mol^{-1}, 150 partial waves were needed to get converged for the ground state ICS. Here we calculated the different *J* partial wave probabilities with a *J* step of 5, and all the other values of *J* partial waves were obtained using the J-shifting approximation[43]. In Fig. 3, we show eight different partial waves for *J* = 0, 20, 40, 60, 80, 100, 120, and 140 of the ground ro-vibrational state of the reactants OH + CX.

The ICS for the reactant ground ro-vibrational state was plotted as a function of translational energy in Figure 4. This plot shows the ground state ICS has a reaction threshold at about 8.2 kcal mol^{-1}, while the ground-state adiabatic barrier height on the PES is ~8.9 kcal mol^{-1}, indicating a tunneling effect in the reaction. Furthermore, the ICS increases rapidly in the post-threshold region as the translational energy increases. This behavior is typical for reactions with an energy threshold.

Fig. 5A shows the ICS comparison among the first four vibrational excitation states of OH(v_1, j_1 = 0) with CX at ground state (v_2 = j_2 = 0) as a function of translational

energy. Here 180, 195 and 209 partial-wave reaction probabilities were needed to converge the three excited state ICSs(v_1 = 1, 2, 3), respectively. As seen from Figure 5A, on one hand, the vibrational excitations of OH(v_1 = 1, 2, 3, j_1 = 0) raise the reactivity substantially by lowing the reaction thresholds; on the other hand, these OH excitation states have much larger amplitudes than that of the ground vibrational state. For example, the ICS of OH(v_1 = 1) has a much lower threshold at 1.8 kcal mol^{-1} comparing to the ground state at 8.2 kcal mol^{-1} and the amplitude of the ICS for OH(v_1 = 1) is about 6.4 times bigger than that of the ground state at 16.0 kcal mol^{-1}. The comparison here demonstrates that the vibrational excitations of the OH tremendously promote the reactivity for this reaction. The ICSs of the three excited states are flat from 12.0 kcal mol^{-1} to 23.0 kcal mol^{-1}. This suggests that, at high collision energy larger than 12.0 kcal mol^{-1}, increasing the OH translational energy will not increase the reaction reactivity at all. Moreover, the ICS behavior of the v_1 = 3 OH vibrational excitation state is much different from the other ICSs(v_1 =0, 1, 2). It has a broad, prominent resonance peak showing up at total energy of 40.04 kcal/mol(Fig 5B), which corresponding to a ro-vibrational energy of 37.36 kcal/mol. The cross section at the peak position is 16.64 bohr^2, which is about 45.0 and 3.5 times bigger than the v_1 = 1, 2 states' at the same translational energy, respectively. This resonance makes the vibrational energy much more efficient in surmounting the barrier than the translational energy. In addition, for the OH(v_1 = 3, j_1 = 0) + CX (v_2=j_2 = 0) initial reactant state, the vibrational energy of OH(v_1 = 3, j_1 = 0) is 34.76 kcal/mol, and that of CX (v_2= j_2 = 0) is 2.56 kcal/mol, which gives a total vibrational

energy of 37.32 kcal/mol, which happens to be where the peak position is. We think this is not a coincidence: the OH(v_1 = 3) + CX(v_2 = 0) initial reaction vibrational states couples with the meta-stable states of the transition complex to give rise of the resonance peak at 37.36 kcal/mol in the ICS. This transition state resonance phenomena has also been observed in both the experimental and theoretical studies of the F and Cl + CH_4 reaction.[5, 13, 18, 44]

The ICSs of the first three vibrational excitations of CX(v_2, j_2 = 0) against the ground vibrational state are plotted in Fig. 6 as a function of translational energy. Contrary to the vibrational excitations of OH, except at low translational energy, the ICSs of vibrational excitation of CX(v_2 = 1, 2, 3, j_2 = 0) are smaller than that of the ground state, which is not surprising due to the fact that CX mainly functions as a receiver in this reaction whose vibrations add difficulty for H atom in OH to approach the C atom in CH_3. In general, the vibration of C-X hinders the reaction reactivity.

To analyze which energy form is more effective in surmounting the energy barrier, we investigate the ICS ratio, $\sigma(v_1 = 1)/\sigma(v = 0)$, of the first vibrational state of OH over the ground vibrational state based on the equal amount of total energy as shown in Fig. 7. This Figure tells us that, only at very low total energy, less than 21.3 kcal mol^{-1}, the ICS ratio of OH is smaller than 1, which means the translational energy is more effective to promote the reaction than the vibrational energy. However, for the most part of the equal amount of total energy, ratios of the ICS for OH are considerably larger than 1 for total energy larger than 21.3 kcal mol^{-1}, and reach to the peak value of ~ 4.2 at 24.6 kcal mol^{-1}, then they come to a slowly drop. This indicates

basically that, the vibrational energy, not the translational energy, is the driving force for surmounting the barrier in this reverse reaction. Indeed, in a recent paper, Guo's group has made predictions[34] on the vibrational efficiencies for the title reaction using a Sudden Vector Projection model, suggesting the vibrational mode is much more strongly coupled with the reaction coordinate than the translational mode, thus enhancing the reaction more effectively. As we recall, the forward reaction $O + CH_4 \rightarrow OH + CH_3$ is slightly endoergic by ~ 1.7 kcal mol^{-1} on the PES[31], therefore it has a more-or-less central barrier and slightly toward to the product channel (As seen in Figure 1, the r(O-H) represents the incoming reactant channel, and r(C-H) the outgoing product channel); however, the theoretical calculations[29, 30-32] show that the translational motion is more efficient on surmounting the barrier than the vibrational motion even though it has a slightly late barrier. For the reverse reaction $OH + CH_3 \rightarrow O + CH_4$, it is slightly exoergic by ~ 1.7 kcal mol^{-1} with a slightly early barrier in the entrance channel (also see Figure 1, here the r(C-H) becomes the reactant channel and r(O-H) product channel). The Polanyi rules are for substantially exoergic and endoergic reactions with distinguished early and late barriers; note, here these two reactions have so-called "central" barrier, both reactions show clearly feature of one energy form is more dominant than the other in surmounting the energy barrier with a small change of the respective barrier location. Thus, the studies on both the forward reaction of $O + CH_4$ and the reverse reaction of $OH + CH_3$ show that even a small change of the barrier location can greatly affect the energy efficiency on barrier-crossing for these approximate central barrier reactions. Furthermore, more

interestingly, here for the slightly endoergic and exoergic reaction, it is the "late" barrier that has the translational energy more efficient in enhancing the reaction role, and the "early" barrier has vice-versa role.

2. OH($v_1 = 0, j_1$) + CX($v_2 = j_2 = 0$) and OH($v_1 = j_1 = 0$) + CX($v_2 = 0, j_2$)

Fig. 8 presents ICSs of the rotational excitations for the OH($v_1 = 0, j_1$) with CX($v_2 = j_2 = 0$) at ground state for j_1 up to 5 as a function of translational energy. It shows the ICS amplitudes decrease with the increase of the value of j_1, so the excited rotational states of OH restrain the reaction. This phenomena are understandable because the rotational wave function of OH($j_1 = 0$) is isotropic in every direction, thus allows H in OH to access C-X from more direction than the higher j_1 excited states, so $j_1 = 0$ state has the largest reactivity. Similar to Fig. 8, Figure 9 provides the first four ICSs of rotational excitations of the C-X($v_2 = 0, j_2$) with OH ($v_1 = j_1 = 0$) at the ground state. It is shown that the overall excitations of CX rotation mode greatly suppress the reactivity. This because that, as a receiver, the faster rotation of CX will further add difficult for H atom to be accepted by CH_3 during the reaction process.

Interestingly, recent QCT studies on the forward reactions O + CHD_3[33] and Cl + CHD_3[35] found that rotational excitations can substantially enhance their reactivity; however, a 7DOF quantum dynamics study on H + CHD_3[45] found that initial rotational excitation up to $J_{rot} = 2$ has no effect on the reactivity. These studies for the polyatomic rotational excitations show various effects on their reactions' reactivity. These concepts are beyond the scope of the well-known Polanyi rules. More studies

from both theoretical and experimental investigations are needed to provide the insight on whether the rotational efficiency on reactivity also depends on the location of the transition state on the PES.

Conclusions

A 6DOF time-dependent，quantum wave-packet propagation approach is employed to study the energy efficiency in surmounting the approximate central barrier reaction: $OH + CH_3 \rightarrow O + CH_4$ system. Here we study the ro-vibrational effects on the reactivity and energy requirement in surmounting the central barrier for this reaction system.

The vibrational-excitation ICSs show that the vibrational excitations of the reactant OH enhance the reactivity, while those of the reactant CH_3 hinder the reactivity. At the equal amount of total energy, the vibrational ICS ratios of OH display that, in general, the OH vibrational energy is much more effective in promoting the reaction than the translational energy for this slight early barrier. This situation is just reversed for its forward reaction $O + CH_4$ which has a slightly late barrier. These two reactions have so called more-or-less central barriers with the barrier location only slightly deviated from the center of the PES: one slightly deviates into the reactant side, the other slightly into product side; however, the slightly change of the barrier location totally inverses the vibrational and translational roles on the reactivity.

Note both the forward $O + CH_4$ and reverse reaction $OH + CH_3$ have 12DOF, however, the above conclusions were made based on our 6DOF reduced-dimensional

quantum dynamics calculations. Nonetheless, for the similar type reaction H + CH_4, Schiffel and Manthe compared their full 12DOF quantum dynamics results[46] with the 6DOF results by Wang and Bowman[47] and 7DOF results by Zhou and Zhang[46]: for the ground state reactants, the 6DOF gives almost the same reaction probability as the 7DOF; and more importantly, the full dimensional results agree quite well with the results of the two reduced-dimensional calculations with only a small shift of about 0.01eV [See Figure 1 in Ref. 46]; furthermore, the comparison of the cumulative reaction probabilities between the 6DOF results[47] and full 12DOF results[48] agree with each other very well too[See Figure 7 in Ref. 47]. Therefore, since we adopted the same 6DOF models for the OH + CH_3 and O + CH_4 reactions, we believe that the conclusions we drew here in terms of the energy efficiencies are rational based on our 6DOF models. However, the models are limited to 6DOF, only the freedoms related to bond-breaking and bond-forming are included in the 6DOF modes, if one wants to investigate the energy efficiency on other degrees of freedoms which are not included in the 6DOF modes, then more degrees of freedom need to be covered in the quantum dynamics calculations.

In summary, because the Polanyi rules don't cover the slightly endo- and exo- ergic reactions, we think more studies including both experimental and theoretical approaches are needed to generalize the central barrier reaction situation. Nonetheless, for these two reactions with more-or-less central barriers, it's the vibrational motion that is more effective to the reactivity for the "early" barrier reaction, while the translational motion more effective to the "late" barrier case.

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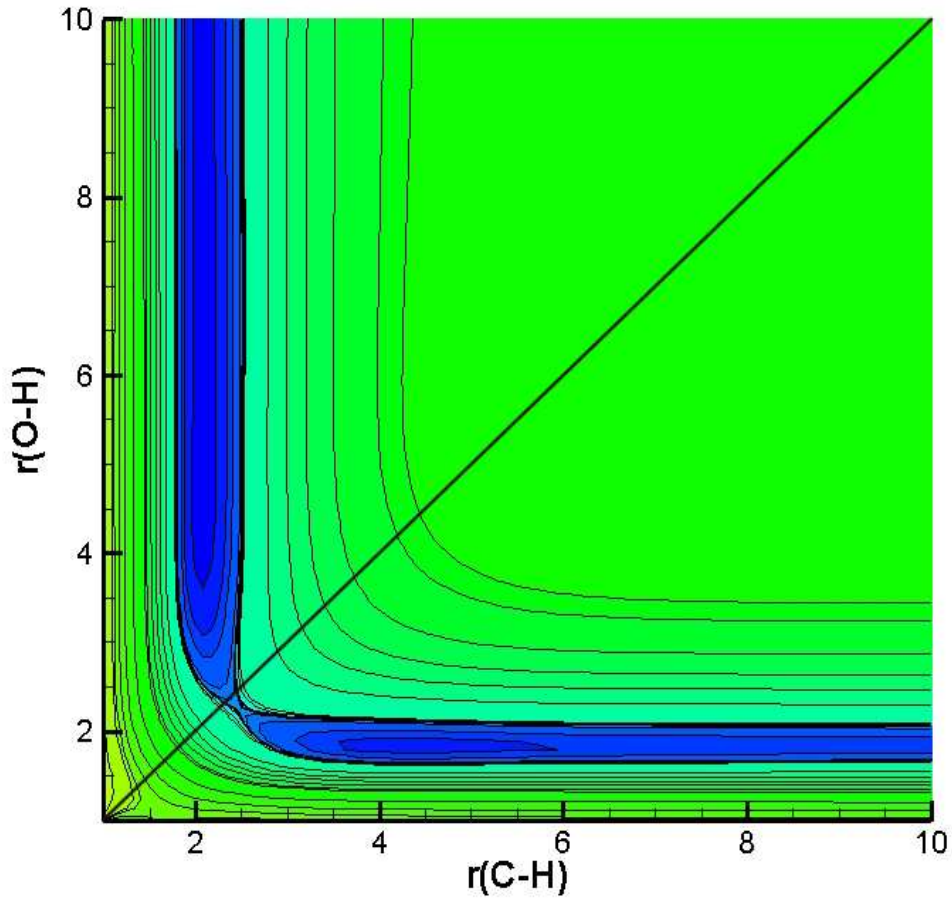

Fig. 1 Contour plot of the PES in terms of r(C-H) (the distance from C atom in CH_3 to the H atom in OH) and r(O-H) (the distance from O atom to the H atom in OH). All other degrees of freedom are fixed at transition state geometry. The distances are in bohr.

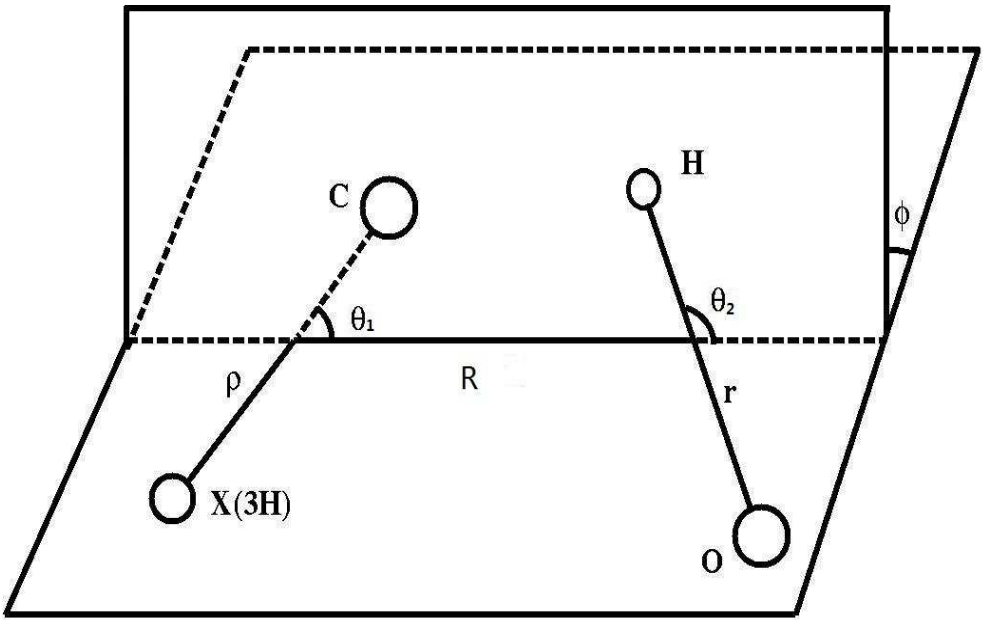

Fig. 2 Reactant Jacobi coordinates for the reactions $OH + CH_3 \rightarrow O + CH_4$.

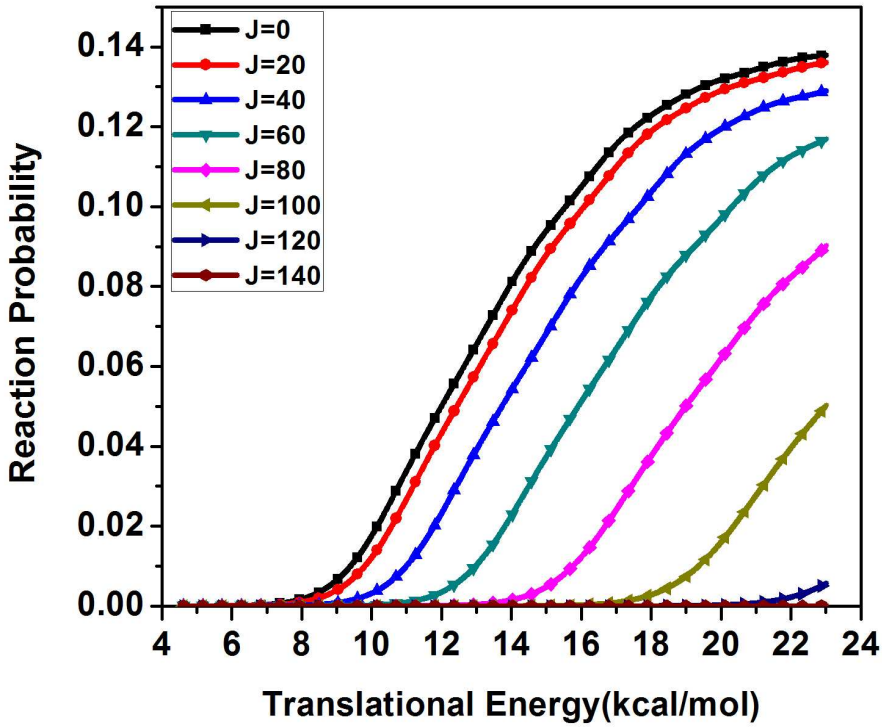

Fig. 3 The reaction probabilities of the OH($v_1 = j_1 = 0$) + CX($v_2 = j_2 = 0$) reaction for different partial waves J = 0, 20, 40, 60, 80, 100, 120, and 140 as a function of the translational energy.

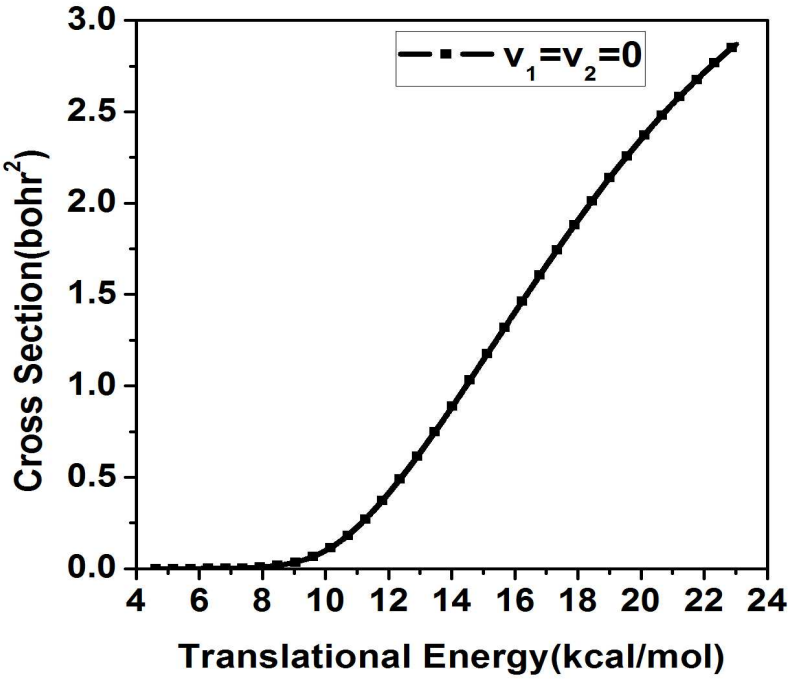

Fig. 4 The ICS of the ground state of the OH($v_1 = j_1 = 0$) + CX($v_2 = j_2 = 0$) reaction.

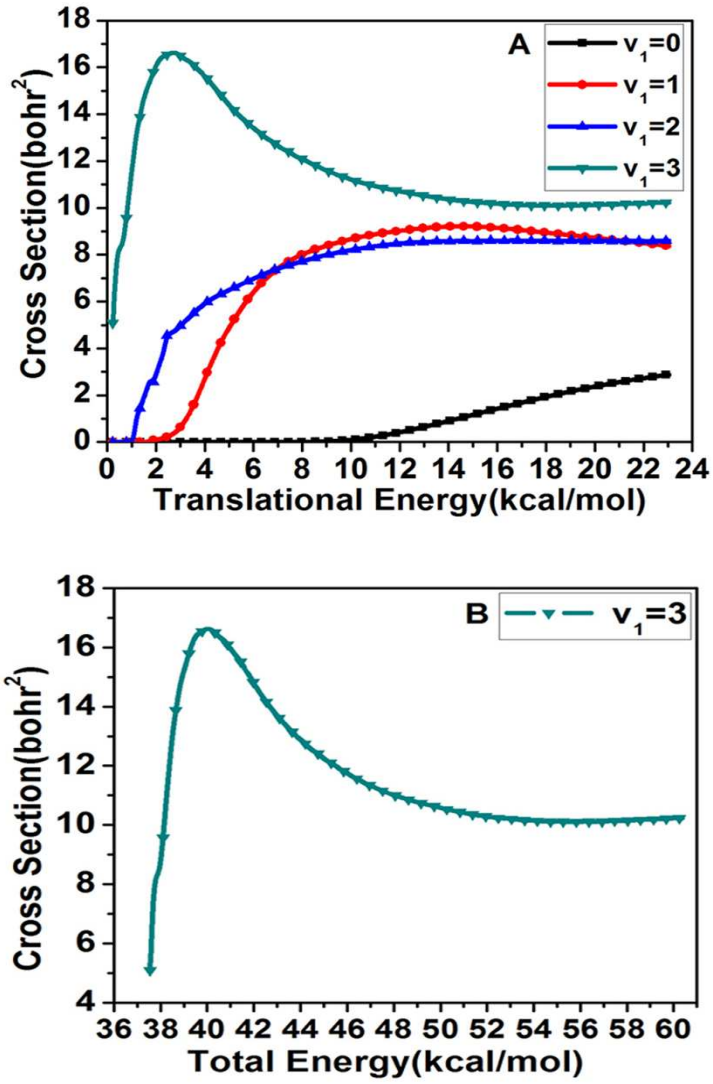

Fig. 5 (A,B): A. The integral cross section of the OH(v_1, j_1 = 0) with CH_3(v_2 = j_2 = 0) reaction for v_1 = 0, 1, 2, 3 as a function of the translational energy; B. for v_1 = 3 as a function of the total energy.

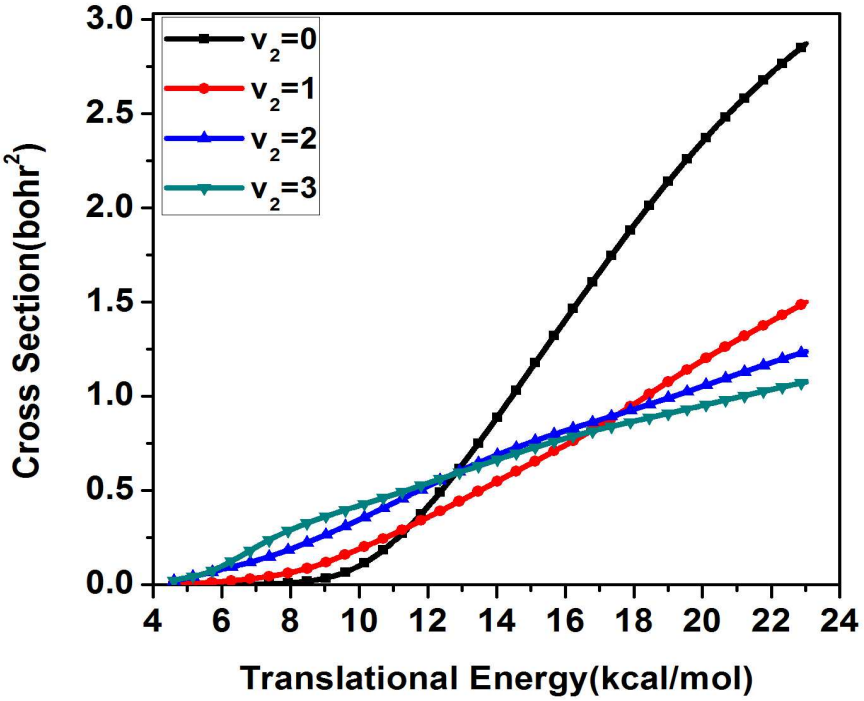

Fig. 6 The integral cross section of the reaction OH($v_1 = j_1 = 0$) + CH_3($v_2, j_2 = 0$) for v_2 = 0, 1, 2, 3 as a function of the translational energy.

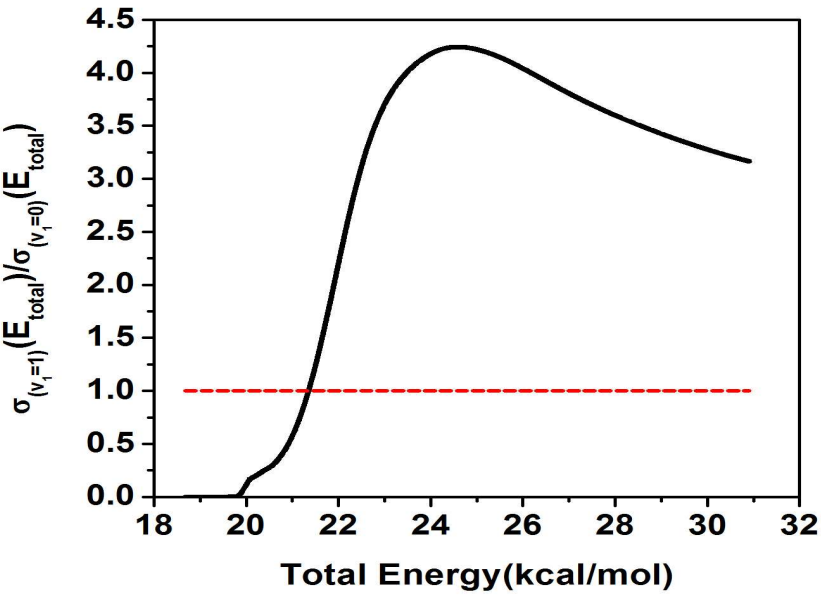

Fig. 7 The ratio of the ICS for $\sigma(v_1 = 1)/\sigma(v_1 = 0)$ in terms of the total energy on the basis of equivalent amount of the total energy.

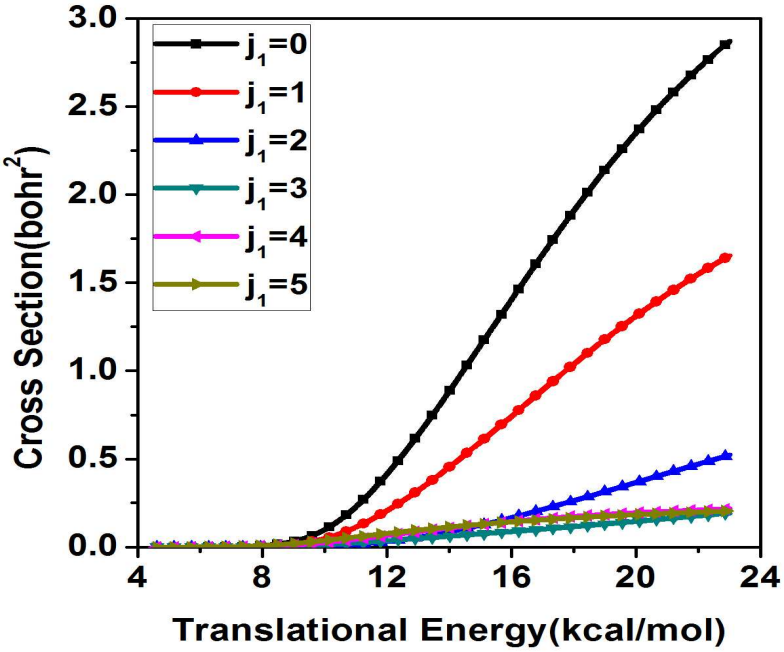

Fig. 8 The integral cross section of the reaction OH(v_1 = 0, j_1) + CH_3(v_2 = j_2 = 0) for j_1 = 0, 1, 2, 3, 4, 5 as a function of the translational energy.

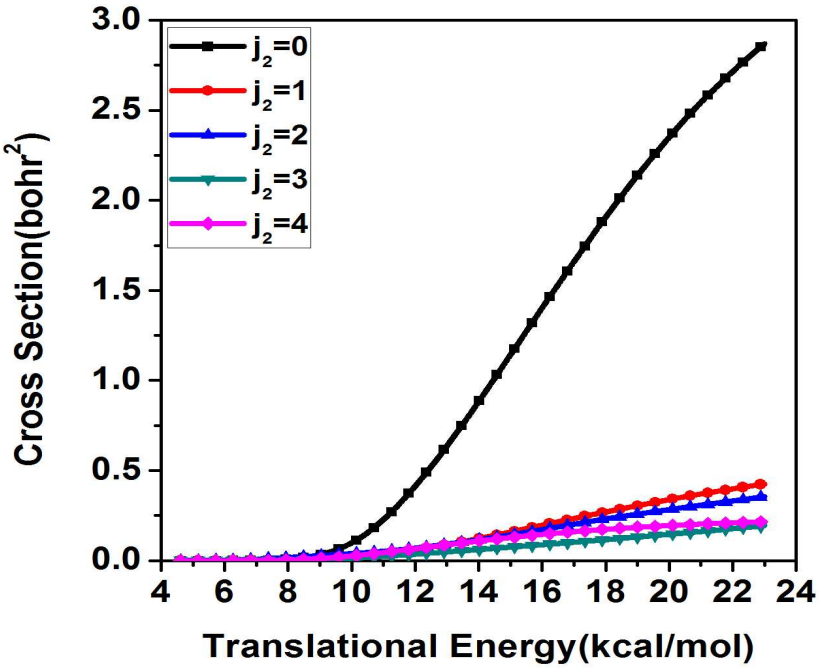

Fig. 9 The integral cross section of the reaction OH($v_1 = j_1 = 0$) + CH_3($v_2 = 0, j_2$) for j_2 = 0, 1, 2, 3, 4 as a function of the translational energy.