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Time-dependent quantum dynamics study for reaction of D+CH_4 →CH_3+HD*

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The semirigid vibrating rotor target (SVRT) model has been applied to the study of the reaction of D+CH_4 → CH_3+HD using a time-dependent wave packet method. The energy dependence of the calculated reaction probability shows oscillatory structures similar to those observed in the abstraction reaction of H+H_2, H+CH_4 etc. We have also studied the influence of rotational and vibrational excitation of the reacting molecule (CH_4) on reaction probability. The excitation of the H–CH_3 stretching vibration gives significant enhancement of reaction probability, which rises significantly with the enhancement of rotational quantum number j. Finally, we have compared the cross section and the rate constant of the D+CH_4 system with that of the H+CH_4 system.

Keywords: SVRT model, reaction probability, time-dependent wave packet
PACC: 3450, 3480B

1. Introduction

Currently, a major challenge in the field of quantum reaction dynamics [1–3] is to develop quantitatively accurate methods for practical computational study of chemical reactions involving polyatomic molecules. For reactions beyond tetra-atomic systems,[4] it is essential for one to reduce the number of mathematical degree of freedoms (DOF) in polyatomic quantum dynamics calculations. Recently, a number of reduced dimensionality approaches have been proposed to treat polyatomic systems,[5–13] and some good results have been obtained using these methods. We note, in particular, that reduced dimensionality quantum scattering calculations have been reported for the reaction of H+CH_4 →H_2+CH_3 by Takayanagi [6] and most recently by Yu and Nyman.[7] In the study of Takayanagi, the H+CH_4 system was treated as a linear pseudo-four-atom chemical reaction involving three degrees of freedom. Yu and Nyman employed a RBU (rotating bond umbrella) model in which the reagent CH_4 was treated as a pseudolinear triatomic molecule, but they introduced a bending mode to obtain a four-dimensional model.

The semirigid vibrating rotor target (SVRT) model [14] was proposed to treat reactive scattering of polyatomic molecules. The SVRT model is a reduced dimensionality model that is generally used for studying reaction dynamics of polyatomic systems. In the SVRT model, the reacting (target) polyatomic molecule is treated as a semirigid vibrating rotor whose spatial motion is described accurately. As a result of accurate treatment of spatial rotation, the SVRT model preserves the correct stereodynamics of the reaction system, which is very important for polyatomic reactions. The SVRT method has recently been applied to a number of chemical reactions including H+HOH(D),[15,16] H+CH_4,[17] H+CD_4 [18] and O+CH_4.[19] In this paper, we use the SVRT method to study the six-atom reaction: D+CH_4 →CH_3+HD. This reaction, being a hydrogen abstraction reaction, is a prototype of atom–polyatom reaction. We calculate the reaction probabilities depending on translational energy on a recent *ab initio* potential energy surface (PES) of Jordan and Gilbert [20] and investigate the influence of vibrational and rotational excitations on the reaction probabilities. Because the reaction D+CH_4 →CH_3+HD is an isotopic reaction

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of $H+CH_4$,[17] we compare the initial ground state reaction probability, the cross section and the rate constant of the former reaction with those of the latter. The time-dependent wave packet (TDWP) method [21] is employed as a computational tool to obtain reaction probabilities.

This paper is organized as follows: Section 2 gives a brief presentation of the mathematical treatment of the SVRT model for atom–polyatomic reactions with specific application to the $D+CH_4 \rightarrow CH_3+HD$ reaction. The results of numerical calculation and the comparison with the $H+CH_4$ results are given in Sec.3, and in Sect.4, a summary is given.

2. The basic SVRT model for $D+CH_4$ reaction

2.1. Hamiltonian

In the basic SVRT model for atom–polyatom reactions, the Hamiltonian for reactive collision between the atomic projectile A (D) and the SVRT molecule T (CH_4) takes the form [14]

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{\hat{L}^2}{2\mu R^2} + \hat{H}_{\rm T} + V \\ &= -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{\hat{L}^2}{2\mu R^2} + \frac{1}{2}\sum_{ij}\hat{\prod}_i G_{ij}\hat{\prod}_j \\ &\quad - \frac{\hbar^2}{2\mu_{\rm T}}\frac{\partial^2}{\partial r^2} + V_{\rm T}(r) + V, \end{aligned} \tag{1}$$

where

$$\mu = \frac{M_{\rm D}M_{\rm CH_4}}{M_{\rm D}+M_{\rm CH_4}}$$

is the reduced translational mass,

$$\mu_{\rm T} = \frac{M_{\rm H}M_{\rm CH_3}}{M_{\rm H}+M_{\rm CH_3}}$$

is the reduced mass between H and CH_3 fragments of molecule T, R is the relative radial distance between the CMS (centre-of–mass) of CH_4 and D, r is the radial distance between the CMS of CH_3 and H, $\hat{L}$ is the orbital angular momentum operator, $\hat{\prod}_i$ is the projection of the angular momentum operator for molecule CH_4 along the body-fixed (BF) axis I ($I = x, y, z$), $V_{\rm T}(r)$ is the interaction potential between CH_3 fragments and H, and V is the interaction potential between CH_4 and D depending on four internal coordinates (R, r, θ, χ). The SVRT Jacobi coordinates (R, r, θ, χ) for the $D+CH_4$ system are shown in Fig.1.

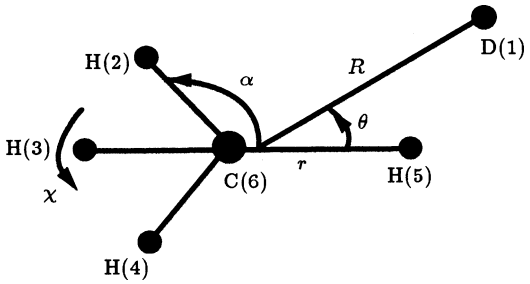


Fig.1. SVRT model applied to the reaction $D+CH_4$.

2.2. TD wave packet propagation

In the TDWP approach, one solves the TD Schrödinger equation,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(t) = H\,\Psi(t), \tag{2}$$

with the Hamiltonian defined in Eq.(1). With an appropriate choice of basis set, the expansion of $\Psi(t)$ can take the form [21]

$$\Psi(t) = \sum_{pvjKn} U_p^v(R) Z^{\rm JM}_{jK(n)}(\Omega,\theta,\chi)\phi_v(r) C_{pvjKn}(t), \tag{3}$$

where $U_p^v(R)$ is the translational basis function whose definition is given in Ref.[21], $\phi_v(r)$ is the vibrational basis function and $Z^{\rm JM}_{jK(n)}(\Omega,\theta,\chi)$ is the body-fixed (BF) total angular momentum eigenfunction, which takes the form [21]

$$Z^{\rm JM}_{jK(n)}(\Omega,\theta,\chi) = \bar{D}^{j^*}_{\rm MK}(\Omega)\bar{d}^{j^*}_{Kn}(\theta)\frac{1}{\sqrt{2\pi}}\mathrm{e}^{\mathrm{i}n\chi}. \tag{4}$$

The TD wavefunction is propagated by employing the split-operator method,[22]

$$\Psi(t+\Delta) = \mathrm{e}^{-\mathrm{i}\hat{H}_0\Delta/2}\mathrm{e}^{-\mathrm{i}\hat{U}\Delta}\mathrm{e}^{-\mathrm{i}\hat{H}_0\Delta/2}\,\Psi(t), \tag{5}$$

where the operator $\hat{H}_0$ can be defined as

$$\hat{H}_0 = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu_{\rm T}}\frac{\partial^2}{\partial r^2} + V_{\rm T}(r). \tag{6}$$

The generalized potential operator U is defined as

$$\hat{U} = \hat{H}_{\rm rot} + \hat{V} = \frac{\hat{L}^2}{2\mu R^2} + \frac{1}{2}\sum_{ij}\hat{\Pi}_i G_{ij}\hat{\Pi}_j + \hat{V}. \tag{7}$$

2.3. Rovibrational eigenfunction

The exact rovibrational eigenfunction of the SVRT molecule T, denoted by $\psi_v^{jKn}(\Omega_{\rm T}, r)$ with three Euler angles $\Omega_{\rm T}$ and vibrational coordinate r, satisfies the Schrödinger equation

$$\left[\frac{1}{2}\sum_{ij}\hat{\Pi}_i G_{ij}\hat{\Pi}_j - \frac{\hbar^2}{2\mu_{\rm T}}\frac{\partial^2}{\partial r^2} + V_{\rm T}(r)\right]\psi_v^{jKn} = E_{vjn}\psi_v^{jKn}. \tag{8}$$

Here j and K are, respectively, quantum numbers of the angular momentum of CH_4 and its projection on the body-fixed R-axis, n is the projection on the H–CH_3 molecular axis and v is the label for vibrational state.

3. Results for D+CH_4 reaction

As shown in Fig.1, the reaction molecule H–CH_3 is treated as a semirigid vibrating rotor consisting of a H atom and a CH_3 fragment. Because the H–CH_3 fragment preserves the C_{3v} symmetry throughout the reaction process, all the geometric parameters are chosen accordingly to maintain the symmetry. A total of 30 vibrational basis functions are used in the expansion for the r-dependence of the wavefunction. The maximum rotational quantum state of the CH_4 molecule included in the basis expansion is j=35, which is sufficient to give a converged result. A total of 90 sine basis functions spanning from 3.0 to 13.5 Bohr in translational coordinate R are used in the wavefunction expansion. The initial wave packet is located at R=10.0 Bohr. Since the hydrogen atom in CH_4 is treated as indistinguishable, the reaction probability from the dynamics calculation is multiplied by a factor of 4 to account for the contribution to reaction probability from all the hydrogen atoms in CH_4.

3.1. Reaction probability

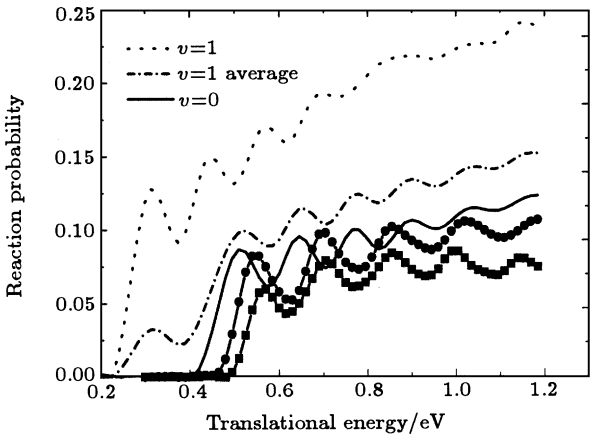


Fig.2. Reaction probability as a function of translation energy of the initial rovibrational state j=0, v=0,1, and v=1 average. The line-circle curve denotes the ground state (v=j=0) reaction probability of H+CH_4 (Ref.[17]). The line-square curve denotes the ground state (v=j=0) reaction probability of H+CD_4 (Ref.[18]).

We have calculated the reaction probability from the ground state of the reactive molecule CH_4. As indicated in Fig.2, the reaction probability for D+CH_4 →CH_3+HD from the initial ground state as a function of translational energy, shows oscillatory structures, similar to those observed in the H+H_2,[23] H+CH_4,[17] and H+CD_4 [18] reactions. But the reaction threshold, about 0.42eV, is much lower than that of H+CH_4 (about 0.46eV) and that of H+CD_4 (about 0.49eV). A comparison of reaction probabilities among D+CH_4, H+CH_4 and H+CD_4 shows that the tunnelling at low energies is greatly enhanced in D+CH_4. The isotopic and the zero-point-energy shift effects can account for the results.

3.2. Effect of vibrational excitation

We have calculated the reaction probabilities for reaction D+CH_4 →CH_3+HD of vibrational quantum number v=0,1, and their averaged result with its rotational state fixed at j=0. Here the vibrational quantum number v denotes the pseudo-vibrational mode between the reacting hydrogen atom and the CH_3 group. The averaged result is the reaction probability for v=1, which consists of one quarter of reaction probability of v=1 and three quarters of reaction probability of v=0. We consider the fact that CH_4 is in its first vibration excitation to mean that only one C–H bond is in its excitation state and the other three C–H bonds are in their ground states. So we think that the averaged result is valid to account for the fact. From Fig.2, we can draw the conclusions that (1) reaction probability is enhanced significantly when v increases from 0 to 1, and (2) reaction threshold is reduced by 0.19eV when H–CH_3 stretching vibration is excited from v=0 to v=1 state.

3.3. Effect of rotational excitation

Figure 3 shows the calculated reaction probabilities from initial rotational states j=0–4 at J=0. From Fig.3 we can see that reaction probability is increased by more than a factor of 2 when the rotational quantum number j increases from 0 to 1. There is a more significant increase of reaction probability when j increases from 1 to 2 and to 3. However, there is no further increase of reaction probability when j increases to 4, as shown in Fig.3. Furthermore, the increase of reaction probability is at relatively low collision energies and near the threshold. At j=3 or 4, the reaction probability actually drops at high collision energies. The reaction probability of j=4 is equal to that of j=0

at 1.2eV. Obviously, the initial j-dependant of reaction probability can be explained by orientation effect. Next, we examine rotational states K=0,1,2 and j=4, n=0. We see in Fig.4 that the reaction probability decreases drastically from near-threshold energy to a higher energy. The same trend of reaction probability is found as the quantum number K increases. Figure 5 shows the calculated reaction probabilities from initial rotational states j=4 K=1 and n=0–3. From Fig.5 we can see that reaction probability drastically decreases as the projection quantum number n increases. But for the case of n=0, it has the largest probability near the threshold energy and the probability drastically decreases as the translational energy increases. However, the probability for the case of $K = n$ has the largest value when the translational energy arrives at its higher value.

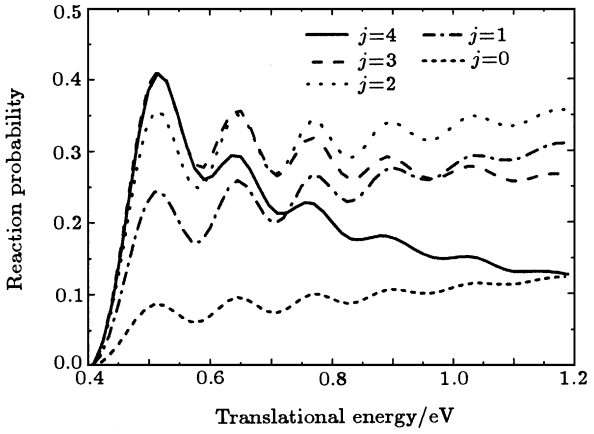


Fig.3. Reaction probabilities for initial rotational states j=0–4 and $K = n = 0$.

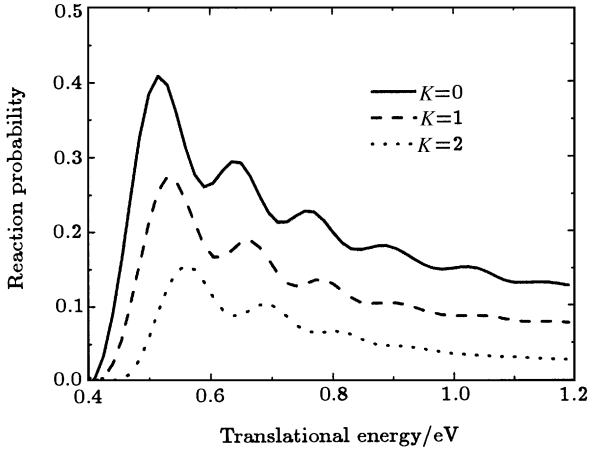


Fig.4. Reaction probabilities for initial rotational states K=0–2 and j=4, n=0.

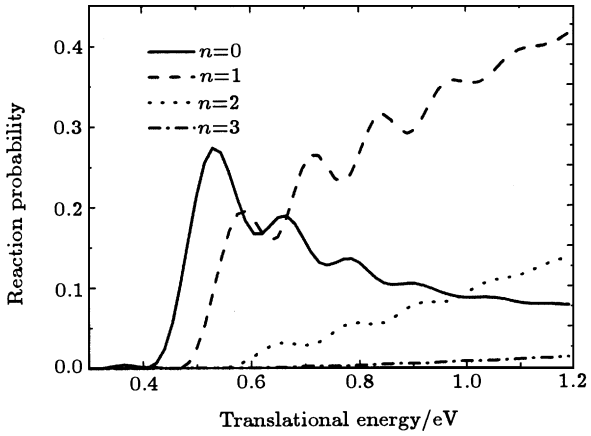


Fig.5. Reaction probabilities for initial rotational states j=4 and K=1, n=0–3.

3.4. Cross section and rate constant

For calculations of cross sections and rate constants with total angular momentum $J > 0$, the CS (centrifugal sudden) approximation is employed and the calculation is carried out for J up to 64. These calculations yield the following total integral cross sections:

$$\sigma_v(E) = \frac{\pi}{K^2} \sum_J (2J+1) P_v^J(E). \qquad (9)$$

Figure 6 shows the integral cross sections as functions of translational energy for the reacting ground state. Comparison with the results in Refs.[17] and [18] shows that the calculated reaction cross section of D+CH_4 is larger than the results of H+CH_4 and H+CD_4 in the whole range of translational energy. The threshold energy of D+CH_4 is the smallest among the three reactions while H+CD_4 has the largest threshold energy.

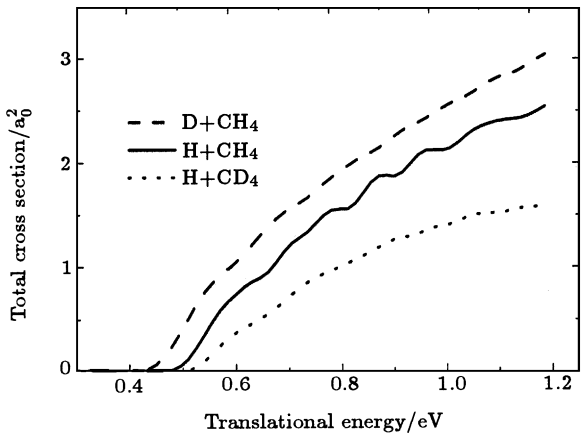


Fig.6. Total cross section as a function of translational energy from initial vibrational state v=0 at ground rotation j=0 for D+CH_4; the solid line is for H+CH_4, taken from Ref.[17]. The dotted line is for H+CD_4, taken from Ref.[18].

We also calculated the reaction rate constant at the initial ground rotational state by using the following formula:

$$K_v(T) = \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} (kT)^{-2} \int_0^\infty \mathrm{d}E_t E_t \times \exp(-E_t/kT)\sigma_v(E_t). \quad (10)$$

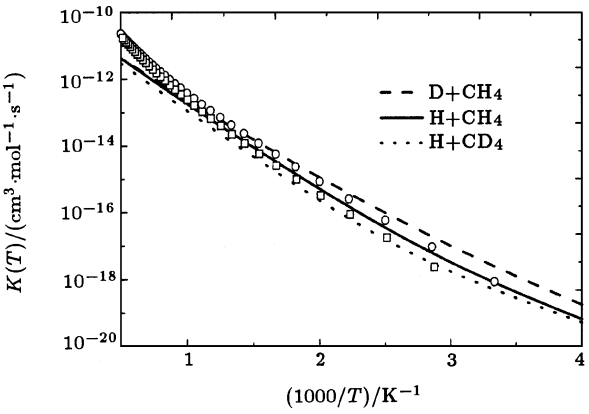


Fig.7. Rate constants with the other theoretical results for the reaction H+CH_4. Solid line is the result for the initial v=0 from Ref.[17] and the dashed line is for reaction D+CH_4 at v=0. The dotted line is for reaction H+CD_4 from Ref.[18]. Square and circle symbols are experimental results from Refs.[24] and [25], respectively.

Figure 7 shows the comparison of our calculated rate constant with the results in Ref.[17], Ref.[18] and the experimental results for H+CH_4. The rate constant of D+CH_4 is slightly larger than that of H+CH_4 over a wide range of temperatures in calculation, and is larger than that of H+CD_4 in the whole range of calculation temperatures. However, the rate constant of D+CH_4 is nearly the same as that of H+CH_4 in the temperature range of 1000–2000K. Compared with the experimental results from Refs.[24] and [25], our rate constant for D+CH_4 is larger than the experimental results at low temperatures, but at high temperatures, the rate constant for D+CH_4 is lower than the experimental data.

4. Conclusions

Similar to the reaction H+CH_4, the reaction probability of the ground state shows an oscillatory structure. These structures give a strong indication that dynamical resonances are present in this reaction. But the reaction barrier is much lower than the reaction H+CH_4. When the stretching vibrational quantum number v changes from 0 to 1 at j=0, the reaction probability enhances significantly, and the reaction threshold energy decreases by about 0.19eV. Reaction probability increases by more than a factor of 2 when the rotational quantum number j rises from 0 to 1 at v=0, J=0. However, this can be explained by an orientation effect. These results suggest that it is possible and perhaps useful to design relative orientations of reacting molecules to maximize or minimize the reaction probabilities. The addition of rotation motion in the SVRT model significantly enriches the study of steric effect in polyatomic reactions.

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