

Time-dependent wave packet study for D + DCN reaction with SVRT model

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Received 13 April 2005; in final form 4 July 2005

Available online 15 August 2005

Abstract

Time-dependent wave packet calculation for the D + DCN reaction is carried out employing TSH3 potential energy surface [M.A. terHorst, G.C. schatz, L.B. Harting, J. Chem. Phys. 105 (1996) 558] with the semirigid vibrating rotor target (SVRT) model [J.Z.H. Zhang, J. Chem. Phys. 111 (1999) 3929]. We calculated the total reaction probabilities from the initial ground ro-vibrational state for various values of total angular momentum J . The reaction cross sections and rate constants are also calculated and compared with the previous results for the isotopic reaction H + HCN on the same potential energy surface.

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1. Introduction

Much effort has been devoted to the development of accurate quantum dynamics methods to perform reaction scattering calculation for elementary chemical reactions. At present, time-dependent (TD) quantum wave packet approach [1,2] has emerged as a powerful computational tool for studying quantum reaction dynamics of triatomic [3–8] and tetraatomic [2,9–13] systems. The main attraction of solving the time-dependent, as opposed to the time-independent, Schrödinger equation stems from its favorable computational scaling with the number of basis functions. This makes the TD wavepacket approach an attractive choice for studying reaction dynamics of large molecular systems. In addition, the TD wavepacket approach is conceptually simple and provides a classical-like interpretation of the numerical results through time propagation of the wavepacket.

As mentioned above, many triatomic and tetraatomic reaction systems ($A + BC$ and $AB + CD$) have been

studied with TD wavepacket approach, but there is no other accurate TD wavepacket approach calculated results for $A + BCD$ reaction except $H + H(D)_2O$ reaction [14]. In order to carry out quantitatively accurate quantum dynamics study for vast majority of chemical reactions that are of chemical or biological interest, recently, Zhang [15] proposed a semirigid vibrating rotor (SVRT) model to treat reactive scattering involving polyatomic molecules. Here, we study the reaction



with TD wavepacket approach with the SVRT model to investigate the isotopic effect by comparing the current results with the previous calculation for the H + HCN system on the same potential energy surface.

The H + HCN reaction is a prototypical example and the inverse reaction was the subject of the first quantum reactive scattering calculations on the four-atom reaction [16–18]. Its improved global potential energy surface has been reported by Horst, Schatz and Harding (denoted as TSH3) [19]. This PES used many body expansion as its functional form whose parameters are fitted to an extensive set of calculated high quality (MRCI) ab initio points with very large basis sets

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(cc-pvqz). The distributed version of this PES (TSH3) has a linear transition state, which is consistent with ab initio calculation by Bar and Dunning [20] and the experimental results of Lambert et al. [21] and Johnston and Bersohn [22]. The reaction (R1) is endothermic by 21.3 kcal/mol with a total barrier of 24.5 kcal/mol. Both the experimental and theoretical results suggest that in the H + HCN reaction the CN bond is unaffected during the reactive encounter, CN bond acted as a spectator. In the previous paper, we have calculated the reaction probabilities, the reaction cross sections and the rate constants for the H + HCN reaction [23] by using the SVRT model [15]. In the present Letter, SVRT model is now used to study the D + DCN reaction.

The Letter is organized as follows: Section 2 presents the time-dependent quantum dynamical formulation to treat the atom–triatom (linear) reaction for the SVRT model. Section 3 presents the results of our calculation including the total reaction probabilities, cross sections, and rate constants. Comparisons with other theoretical calculations are given and discussions are provided. Section 4 gives a summary of the present work.

2. Theory

In SVRT model [15] the letter T is used to denote the target (reacting) molecule and its associated quantities. For D + DCN reaction system as depicted in Fig. 1, T denotes the DCN molecule and the target molecule T is composed of two fragments B and C. Here, B and C denote the D atom and CN atomic group, respectively. The target molecule DCN is a linear molecule.

According to the SVRT model, we treat the target molecule T as a semirigid rotor composed of two rigid parts. Here, the bond length of CN is fixed. Then, for a fixed total angular momentum J , the Hamiltonian of D + DCN system can be expressed in terms of the Jacobi coordinates of reactant arrangement A + BC ($T = BC$),

$$H = H_0 + U, \quad (1)$$

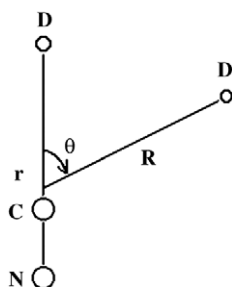


Fig. 1. The D + DCN coordinate system, R is the distance between D and the center of mass of the DCN molecule, r is the distance between D and the center of mass of CN, and θ is the angle formed by R and r .

where H_0 and U are defined as

$$H_0 = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} + h(r), \quad (2)$$

$$U = \frac{(\mathbf{J} - \mathbf{j})^2}{2\mu_R R^2} + \frac{\mathbf{j}^2}{2I} + V(\mathbf{R}, \mathbf{r}), \quad (3)$$

where \mathbf{r} and \mathbf{R} are the vibrational and the translational vectors, while μ_R is the reduced mass between the center-of-mass of BC and A; I , the moment of inertia of BC (DCN), is function of r , i.e., R_{CN} fixed at $2.197a_0$; \mathbf{j} is the rotational angular momentum operator of BC; $h(r)$ is the triatomic (DCN) reference Hamiltonian given by

$$h(r) = -\frac{\hbar^2}{2\mu_T} \frac{\partial^2}{\partial r^2} + V_T(r), \quad (4)$$

where μ_T is the reduced mass between the center-of-mass of B and C (D atom and CN atomic group), $V_T(r)$ is a triatomic reference potential.

The time-dependent wave function can be expanded in terms of the body-fixed (BF) translational–vibrational–rotational basis defined using the reactant Jacobi coordinates [3]

$$\Psi_{v_0, j_0, K_0}^{JM\varepsilon}(\mathbf{R}, \mathbf{r}, t) = \sum_{n, v, j, K} F_{nvjK, v_0, j_0, K_0}^{JM\varepsilon}(t) u_n^v(R) \phi_v(r) Y_{jK}^{JM\varepsilon}(\hat{R}, \hat{r}), \quad (5)$$

where n is the translational basis label, M and K are the projection quantum numbers of J on the space-fixed (SF) z-axis and (BF) z-axis, respectively, (v_0, j_0, K_0) denotes the initial rovibrational state, and ε is the parity of the system defined as $\varepsilon = (-1)^{j+L}$ with L being the orbital angular momentum quantum number. The definitions of various basis functions can be found elsewhere [3]. The split-operator method [24] is employed to carry out the wavepacket propagation

$$\Psi^{JM\varepsilon}(\mathbf{R}, \mathbf{r}, t + \Delta) = e^{-iH_0\Delta/2} e^{-iU\Delta} e^{-iH_0\Delta/2} \Psi^{JM\varepsilon}(\mathbf{R}, \mathbf{r}, t). \quad (6)$$

The matrix version of Eq. (6) for the expansion coefficient vector \mathbf{F} is then given by

$$\mathbf{F}(t + \Delta) = e^{-iH_0\Delta/2} e^{-iU\Delta/2} e^{-iH_0\Delta/2} \mathbf{F}(t). \quad (7)$$

The total (final state-summed) reaction probabilities $P_{v_0, j_0}^J(E)$ is obtained by evaluating the reactive flux as described in [3,9]. Here, the standard CS (centrifugal sudden) approximate method was used. Then we can evaluate the reaction cross section for a specific initial state by simply summing the reaction probabilities over all the partial waves (total angular momentum J),

$$\sigma_{v_0, j_0}(E) = \frac{\pi}{k_{v_0, j_0}^2} \sum_J (2J + 1) P_{v_0, j_0}^J(E), \quad (8)$$

where $k_{v_0, j_0} = \sqrt{2\mu_R E}/\hbar$ is the initial translational wave-number corresponding to the initial state at fixed collision energy E , and $P_{v_0, j_0}^J(E)$ is given by

$$P_{v_0 j_0}^J(E) = \frac{1}{2j_0 + 1} \sum_{K_0} P_{v_0 j_0 K_0}^J(E), \quad (9)$$

The rate constant is calculated using uniform J -shifting approach in [25].

3. Results and discussion

3.1. Numerical aspect

A typical initial wavepacket is chosen to be centered at $R_0 = 10.0a_0$ with a width of $0.20a_0$ and an average kinetic energy of 2.0 eV. We use 60 vibrational and 50 rotational basis functions in the expansion of wavefunction that is found sufficient to give converged total reaction probabilities. The total propagation time, time step, and the absorption parameters are also test with $J = 0$ partial wave for SVRT model.

3.2. Reaction probability, cross-section and rate constant

We calculated reaction probabilities for reaction (R1) with SVRT models. The results of $J = 0$ are plotted as function of the translational energy on the TSH3 [19] potential energy surface. Fig. 2 shows the total reaction probabilities corresponding to $j = 0, 1, 2, 10, 20$. From Fig. 2 we can see that all the total reaction probabilities are smaller than 0.10 in the energy region we considered. The results show that the title reaction is difficult to occur, which can easily be expected since the reaction has a late barrier and a high endothermicity. The reaction probabilities for $j = 1, 2, 10$ and 20 of DCN are all smaller than that for $j = 0$, so the higher excited rotational states can not promote reaction (R1). From Fig. 3 we can see that the reaction probability for the first excited vibrational state is much larger than that for the ground vibrational state, and so the excited vibrational state greatly increases the reaction.

In present work, the calculations of the collision energy dependence of the integral cross sections for initial

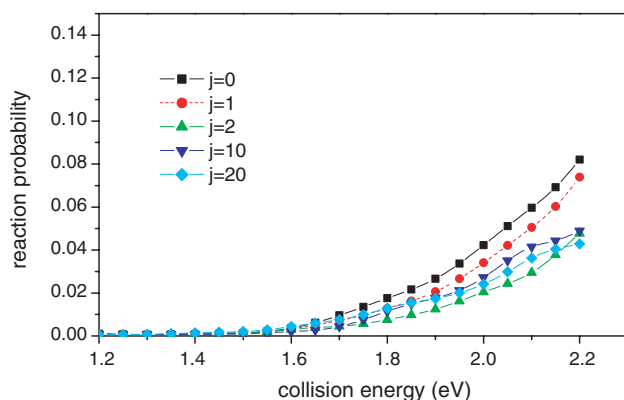


Fig. 2. Total reaction probabilities of $J = 0$ for $j = 0, 1, 2, 10, 20$ with SVRT model.

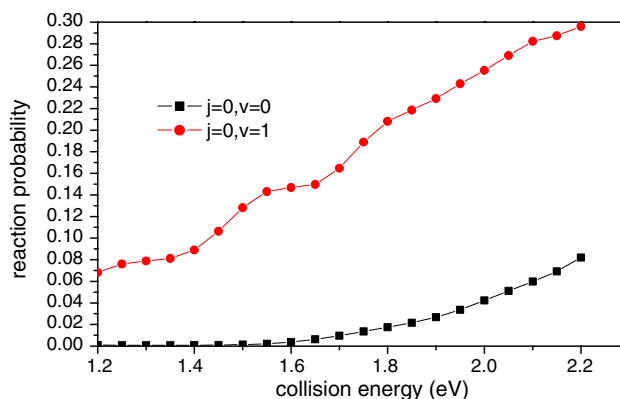


Fig. 3. Total reaction probabilities of $J = 0$ for $v = 0, 1$ with SVRT model.

rotational ground state have been performed. Fig. 4 depicts the comparison of our integral cross sections with those for $H + HCN$ reaction from [23] on the same potential energy surface. The reference reaction cross sections were also calculated using SVRT method. Fig. 4 shows that the cross sections for reaction (R1) are smaller than that for $H + HCN$ reaction. The isotope-effect is obvious.

We calculated the reaction rate constant r_j for a series of initial rotational states ($j = 0-5$) of DCN by using the Uniform J -shift approach [25] with SVRT model. For calculating every r_j , three total J states were employed. Then, according to the thermal distribution of the rotational levels, the thermal rate constant of reaction (R1) at the temperature T can be expressed as

$$k(T) = \sum_{j=0} \frac{r_j}{Q_r} (2j+1) e^{-Bj(j+1)hc/kT},$$

in which Q_r is

$$Q_r = 1 + 3 e^{-2Bhc/kT} + 5 e^{-6Bhc/kT} + \dots$$

where B is the rotational constant of DCN, k is the Boltzmann constant, h the Planck's constant, and c the velocity of light in vacuum. Thermal rate constants

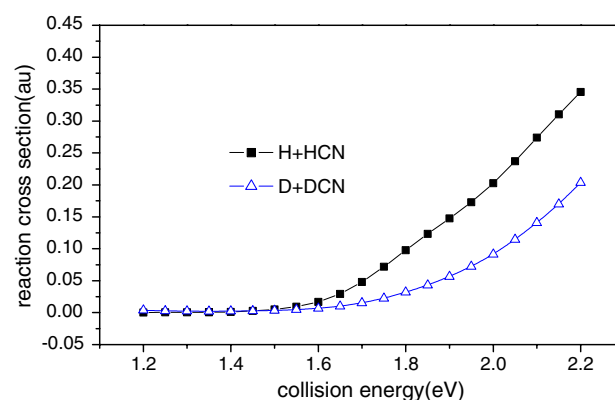


Fig. 4. Cross-sections for the ground state of reactant with SVRT model.

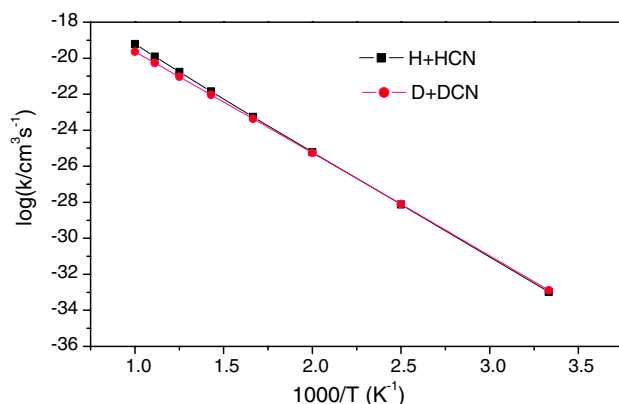


Fig. 5. The thermal rate constants for D + DCN reactions with SVRT model.

$k(T)$ obtained from 300 to 1000 K. Fig. 5 gives the results of our calculations and the reference results of [23]. It can be seen that the values of thermal rate constants of reaction (R1) rapidly increase with an increase of temperature, so high temperature is favorable for this reaction. The rate constants are smaller than those for H + HCN reaction [23], especially at high temperatures, which is consistent with reaction sections.

4. Conclusion

We reported detailed quantum dynamics studies for D + DCN reaction system using a time-dependent wavepacket approach with SVRT model. Initial state-selected total reaction probabilities, integral cross sections for total angular momentum J and the thermal rate constants are computed. The results show that the title reaction is difficult to occur, and high temperature is favorable for this reaction. By comparing with H + HCN reaction, we found that the isotope-effect is obvious at high temperature.

Acknowledgements

This work was supported by the Shandong Natural Science Foundation of China (No. Y2003B03 and Q2002B03) and the Shandong Doctoral Foundation of China (No. 2004BS04011).

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