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The reaction probability and the reaction cross-section of the $N(^4S)+O_2(X^3\Sigma_g^-) \rightarrow NO(X^2\Pi)+O(^3P)$ reaction

Jianfeng He*

Department of Physics, School of Science, Beijing Institute of Technology, Beijing 100081, People's Republic of China
E-mail: hjf1919@yahoo.com.cn

Jing Li

Key Laboratory for Supermolecular Structure and Materials of Ministry of Education, Jilin University, Changchun 130012, People's Republic of China

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We have presented the reaction probability and the reaction cross-section of the $N(^4S)+O_2(X^3\Sigma_g^-)\rightarrow NO(X^2\Pi)+O(^3P)$ reaction by the quasi-classical trajectory (QCT) method with the fourth-order explicit symplectic algorithm (S4), based on a new ground potential energy surface. The variation of the reaction probability with the impact parameter has been analyzed in detail. And the effect of the relative translational energy, the vibrational and rotational level of O_2 molecule in the reaction cross-section of the reaction has been discussed. It has been documented by the comparison that the reaction probability and the reaction cross-section of the reaction determined in this work are more reasonable than those reported by Gilibert et al. because of employing the new ground potential energy surface and the S4 in the QCT calculation of this work.

KEY WORDS: quasi-classical trajectory method, fourth-order explicit symplectic algorithm, reaction probability, reaction cross-section

1. Introduction

The elementary atmospheric reaction

$$N(^4S) + O_2(X^3\Sigma_g^-) \rightarrow NO(X^2\Pi) + O(^3P), \quad \Delta_r H_{0K}^0 = -32.09\, kcal/mol \quad (1)$$

has been widely investigated in the Earth's atmospheric chemistry, infrared chemiluminescence and combustion chemistry [1–3]. The experimental study related to reaction (1) focuses mainly on the measurements of both thermal rate

*Corresponding author.

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constants and the vibrational distribution of product molecules, and the abundant experimental data about the atmospheric reaction has been accumulated. Theoretically, many *ab initio* studies have been carried out about the ground ($^2A'$) state of NO_2 [4–6], where the complete active space self-consistent field theory, the multi-reference contracted configuration interaction calculation and the density functional theory have often been employed. Based on these data of *ab initio* calculation, some analytical fits of the ground potential energy surface (PES) of reaction (1) have been constructed by means of the many-body expansion formalism [7]. However, these analytical PESs cannot accurately describe the dynamical character of the reaction system because of their localizations and disadvantage. In order to better explain the exoergicity of reaction (1) and the corresponding experimental rate constant at 300 K, Sayós et al. [8] recently constructed a new ground PES on the basis of their accurate *ab initio* calculation and some experimental data. Their new analytical ground PES exhibits several stationary points that have not been introduced in the previous analytical surfaces, and depicts accurately the $NO_2(X^2A_1)$ deep chemical well. Furthermore, the analytical PES not only describes accurately the C_s regions of the NOO system but also the ONO C_{2v} or near C_{2v} regions. Apparently, the dynamical research of the reaction on basis of the new analytical PES is necessary. The kinetics and dynamics study of reaction (1) have the quasi-classical trajectory method (QCT), the variational transition state theory and the quantum dynamics method, and QCT is the routine method in the study of the chemical reaction dynamics [9].

The calculation for QCT of reaction (1), where the new ground PES reported by Sayós et al. [8] has been employed, has been performed in our previous work by means of both the fourth-order explicit symplectic algorithm (S4) and the fourth-order Runge–Kutta scheme (RK4) [10]. The fact has been documented that RK4 cannot rightly reflect the collision mode and the reaction mode of the trajectories, and cannot preserve the amplitudes of vibration of the reactant molecule and the product molecule during the numerical integration. However, S4 maintains these characteristics and can actually describe the circumstance of the reaction system. Based on the new ground PES provided by Sayós et al. [8], we have performed the reaction probability and the reaction cross-section of reaction (1) by the QCT method with the S4. The paper is organized as follows: section 2 gives a brief introduction about the calculation of the reaction probability and reaction cross-section by the QCT method. In section 3, both the reaction probability and the reaction cross-section of reaction (1) have been determined at several initial conditions, and these results in this work have been compared with those of Gilibert et al. Finally, some remarks toward the main results of this work have been draw in section 4.

2. Computational method

If the potential energy surface of the reaction system has been evaluated, the reaction probability and reaction cross-section can be estimated by the QCT method [11]. In the center-of-mass coordinates, the Hamiltonian function of the three-atom reaction system A+BC has the following form

$$H = \frac{1}{2\mu_{\mathrm{B,C}}} \sum_{j=1}^{3} P_j^2 + \frac{1}{2\mu_{\mathrm{A,BC}}} \sum_{j=4}^{6} P_j^2 + V(Q_1, Q_2, \ldots, Q_6), \tag{2}$$

where $Q_j (j = 1, 2, \ldots, 6)$ represents the generalized Cartesian coordinate, $P_j (j = 1, 2, \ldots, 6)$ is the momentum conjugate to the Q_j, $V(Q_1, Q_2, \ldots, Q_6)$ is the potential energy function of the three-atom reaction system. If the masses of atom A, B, and C denote $m_{\mathrm{A}}, m_{\mathrm{B}}$, and m_{C}, $\mu_{\mathrm{B,C}} = m_{\mathrm{B}} m_{\mathrm{C}}/(m_{\mathrm{B}} + m_{\mathrm{C}})$ and $\mu_{\mathrm{A,BC}} = m_{\mathrm{A}}(m_{\mathrm{B}} + m_{\mathrm{C}})/(m_{\mathrm{A}} + m_{\mathrm{B}} + m_{\mathrm{C}})$ are the reduced masses of the reaction system. In this case, A is the nitrogen atom (N), B is the first oxygen atom (O), and C is the second oxygen atom (O), respectively.

Canonical equations of the reaction system are

$$\dot{Q}_j = \frac{\partial H}{\partial P_j}, \quad \dot{P}_j = -\frac{\partial H}{\partial Q_j} = -\frac{\partial V}{\partial Q_j}, \quad (j = 1, 2, \ldots, 6). \tag{3}$$

After a large number of initial conditions are randomly selected by the Monte–Carlo sampling, we can obtain a lot of QCT by the integrating of equation (3). The reaction probability of reaction (1) can be evaluated from the following equation

$$Pb(b; v, J, E_t) = \lim_{N \to \infty} (N_{\mathrm{r}}(b; v, J, E_{\mathrm{t}})/N(b; v, J, E_{\mathrm{t}})), \tag{4}$$

where b is the impact parameter, v and J is the vibrational and rotational level of O_2 molecule, E_t is the relative translational energy, $N_r(b; v, J, E_t)$ and $N(b; v, J, E_t)$ are the numbers of reactive collisions and total collisions, respectively. At the fixed initial condition set$(b; v, J, E_t)$ with the values of other variables selected by the Monte–Carlo random sampling procedure, batches of 5,000 trajectories are run to compute the corresponding reaction probability of reaction (1). The reaction cross-section of reaction (1) can be determined by

$$S_{\mathrm{r}}(v, J, E_t) = \pi b_{\max}^2(v, J, E_{\mathrm{t}})[N_{\mathrm{r}}(v, J, E_{\mathrm{t}})/N(v, J, E_{\mathrm{t}})], \tag{5}$$

where $b_{\max}(v, J, E_{\mathrm{t}})$ is the maximal impact parameter, $N_{\mathrm{r}}(v, J, E_{\mathrm{t}})$ and $N(v, J, E_{\mathrm{t}})$ are the numbers of reactive collisions and the total number of the computed trajectories, respectively. To ensure a statistical error less than 5%, a total of 10,000 trajectories have been integrated to evaluate the reaction cross-section at each set of initial conditions.

In fact, both the RK4 and the sixth-order predictor–corrector scheme by Gear have reflected worse conservation of the total energy and the total angular momentum of the reaction system, which has been assessed in the previous works [10,12,13]. Thus, we adopt the S4 provided by Qin et al. [14] that can conserve not only the symplectic structure of Hamilton system but also the total energy of the reaction system. In calculations, all trajectories are started from a N–O_2 distance of 20 Å, and ended when the product species are formed and found at least 20 Å away from each other. The time step size selected in all calculations is 1.0×10^{-16}s.

3. Results and discussion

Figure 1 has displayed the variation of the reaction probability with the impact parameter at the ($v = 0$, $J = 8$, $E_t = 0.40$, and 1.50 eV) initial condition. The reaction probability of reaction (1) has indicated a descending trend when the impact parameter increases from 0 to its maximum with an increment of 0.15Å. According to the qualitative explain of the angle dependent line-of-centers (ADLOC) model [15], the energy along the line-of-centers help to the reaction decreases while the impact parameter enhances, therefore the reaction probability will reduce with the impact parameter increasing. The variational curves of the reaction probability with the impact parameter seem to be similar for other initial condition sets (v, J, E_t) considered in this work. By comparison with figure 4 of Ref. [16], it is obvious that there are two main differences between the results determined in this work about the dependence of the reaction probability on the impact parameter and the ones carried out by Gilibert et al. One is that the phenomenon of a slight increase of the reaction probability followed by the descending trend like figure 4 in Ref. [16] does not exhibited in the figure 1 of this work at the ($E_t = 0.40$ eV) lower relative translational energy. Another is that the maximal impact parameters in this work are greatly larger than the ones in figure 4 of Ref. [16] at the same initial conditions, especially at the low relative translational energy. We consider that the enhancement of the results in this work is mainly attributed to the adoption of the new ground PES in the QCT study, and that the S4 which preserve the sympletic structure of Hamilton system and the total energy of the reaction system also has an important contribution.

The dependence of the reaction cross-section of reaction (1) on the relative translational energy and the comparison with that determined by Gilibert et al. [16] have been described in the plot of figure 2 at the ($v=0$, $J=0$) rovibrational level of O_2 molecule. Obviously, the reaction cross-section rapidly increases with the relative translational energy above the energy threshold ($\sim$0.35 eV) predicted in this work. Although the function of $S_r(v, J, E_t)$ versus E_t begins to become smooth at the higher relative translational energy, they do not immediately reach

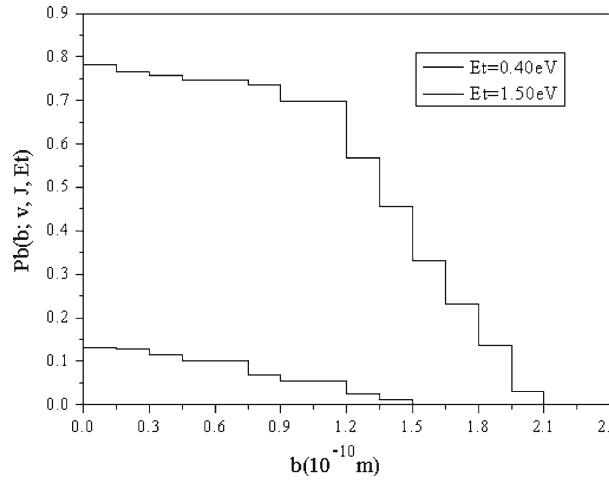

Figure 1. Variation of the reaction probability with the impact parameter at $v=0$ and $J=8$.

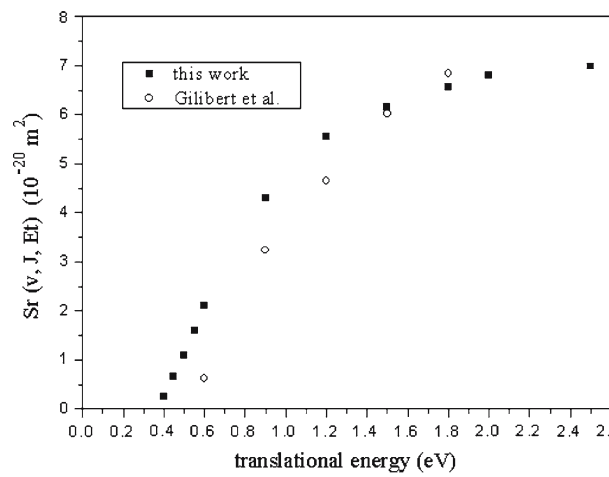

Figure 2. Function of the reaction cross-section versus the relative translational energy compared with that of Gilibert et al. [16] at $v = 0$ and $J = 0$.

to saturation, which is consistent with that of the reaction system with an early energy barrier. From the plot of figure 2, it is revealed that the energy threshold determined in this work on the basis of the new ground PES constructed by Sayós et al. [8] is much lower than the one predicted by Gilibert et al. [16] The plot of figure 2 also suggested that the reaction cross-sections of reaction (1) in this work have a systematical enhancement than those carried out by Gilibert et al. [16] at all relative translational energies considered, especially at the low relative translational energy. These discrepancies are owing to the fact that the energy barrier of the new ground PES employed in this work ($\sim$0.30 eV) is much

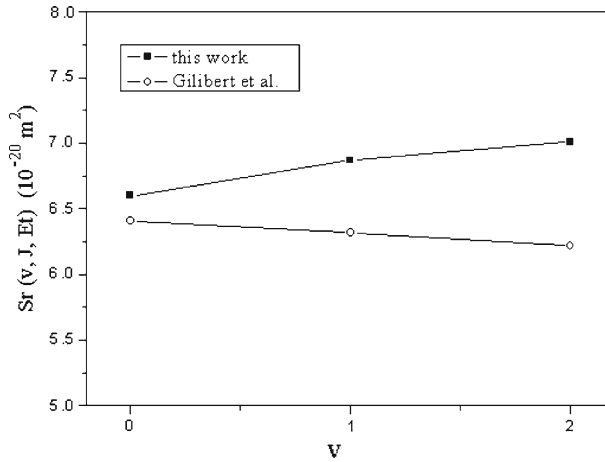

Figure 3. Dependence of the reaction cross-section on the vibrational level of O_2 molecule compared with that of Gilibert et al. [16] at $J = 8$ and $E_t = 1.80$ eV.

lower than the value of the ground PES adopted by Gilibert et al. (~ 0.55 eV) [16]. In addition, the S4 is also benefited to the accurate prediction of the energy threshold and the enhancement of the reaction cross-section of reaction (1).

The variation of reaction cross-sections with the vibrational level of O_2 molecule at $E_t = 1.80$eV and $J = 8$ has been displayed in the plot of figure 3. The reaction cross-sections of reaction (1) in this work have a linear variation with the vibrational level of O_2 molecule ranging from 0 to 2, which implies that the vibrational level of O_2 molecule contributes modestly to the enhancement of the reaction cross-section at the rotational level of O_2 molecule and relative translational energy considered. The moderate effect of the vibrational level of O_2 molecule on the reaction cross-sections is due to the new ground PES with an early barrier, for which the vibrational energy of the reactant molecule essentially influences the relative motion perpendicular to the coordinate leading over the barrier to reaction. Therefore, the enhancement of the vibrational level of O_2 molecule is beneficial to the increase of the reaction cross-section of reaction (1). However, the reaction cross-sections of reaction (1) determined by Qin et al. [14] show a little fall with the vibrational level of O_2 molecule increasing, which suggests that the reaction cross-sections of reaction (1) in this work are more reliable than the ones of Gilibert et al. [16].

In the plot of figure 4, the effect of the rotational level of O_2 molecule on the reaction cross-sections of reaction (1) at $E_t = 1.50$ eV and $v = 0$ has been analyzed. From figure 4, the rotational level of O_2 molecule plays the minor role in enhancing the reaction cross-sections of reaction (1) at the given vibrational level of O_2 molecule and relative translational energy. Apparently, the reaction cross-sections of reaction (1) are not very sensitive to the rotational level of O_2

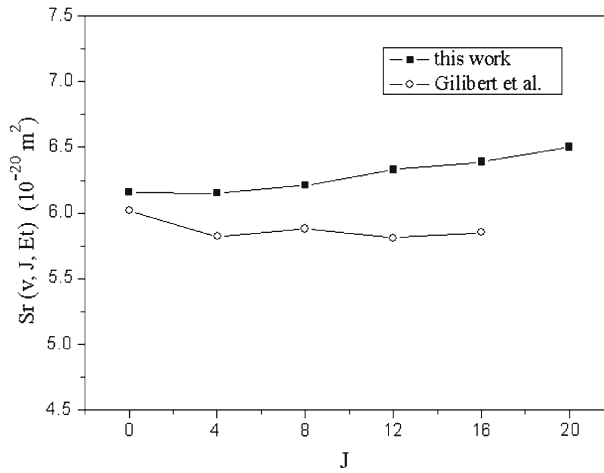

Figure 4. Dependence of the reaction cross-section on the rotational level of O_2 molecule compared with that of Gilibert et al. [16] at $v = 0$ and $E_t = 1.50$ eV.

molecule, which is attributed to that the O_2 molecule is almost rotationally frozen at the low rotational level of O_2 molecule and relative translational energy. However, the reaction cross-sections of reaction (1) carried out by Gilibert et al. [16] exhibits a slight downtrend because of the competing orientation and energy effects, which seem consistent to the general behavior of the reaction system with an energy barrier. Nevertheless, the results determined in this work are also rational as the orientation effect unfavorable to the reaction has compensated by the anisotropic character of the new PES and the reaction system comes back to the preferable orientation.

4. Conclusions

In this work, the reaction probability and the reaction cross-section of reaction (1) have been calculated by the QCT method, based on the new ground PES reported by Sayós et al. [8]. The reaction probability of reaction (1) determined in this work has revealed a declining trend with the impact parameter increasing, and the slight increase like figure 4 in Ref. [16] at the lower relative translational energy do not exhibit because of the adoption of the S4. The reaction cross-section of reaction (1) rapidly increases with the relative translational energy above the energy threshold. The vibrational level of O_2 molecule has the modest contribution to the reaction cross-section of reaction (1), and the rotational level of O_2 molecule plays the minor role in the enhancement of the reaction cross-section of reaction (1). Since we employed a new ground PES of reaction (1) and the S4 in the QCT calculation, the energy thresholds predicted in this work are much lower than those predicted by Gilibert et al. [16] at the rovibrational

levels of O_2 molecule considered, and the reaction cross-sections determined in this work also have a systematical enhancement than those carried out by Gilibert et al. [16] at the same initial conditions.

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