

The Reaction Probability and the Reaction Cross-section of $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$ Reaction Computed by the 6th-order Explicit Symplectic Algorithm

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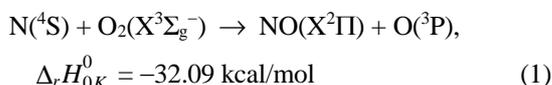
Received April 17, 2006

We have calculated the reaction probability and the reaction cross-section of the $\text{N}(^4\text{S}) + \text{O}_2(\text{X}^3\Sigma_g^-) \rightarrow \text{NO}(\text{X}^2\Pi) + \text{O}(^3\text{P})$ reaction by the quasiclassical trajectory method with the 6th-order explicit symplectic algorithm, based on a new ground potential energy surface. The advantage of the 6th-order explicit symplectic algorithm, conserving both the total energy and the total angular momentum of the reaction system during the numerical integration of canonical equations, has firstly analyzed in this work, which make the calculation of the reaction probability more reliable. The variation of the reaction probability with the impact parameter and the influence of the relative translational energy on the reaction cross-section of the reaction have been discussed in detail. And the fact is found by the comparison that the reaction probability and the reaction cross-section of the reaction estimated in this work are more reasonable than the theoretical ones determined by Gilibert *et al.*

Key Words : Quasiclassical trajectory method, 6th-order explicit symplectic algorithm, Reaction probability, Reaction cross-section

Introduction

The elementary atmospheric reaction



has been widely investigated in the Earth's atmospheric chemistry, infrared chemiluminescence and combustion chemistry.¹⁻³ From the theoretical point of view, many ab initio studies have been carried out about the ground energy surface (PES) of reaction (1),⁴⁻⁶ where the complete active space self-consistent field calculation, 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 of reaction (1) have been constructed by means of the many-body expansion formalism.⁷ The kinetics and dynamics study of reaction (1) have the quasiclassical trajectory (QCT) method, the variational transition state theory (VTST) and the quantum dynamics (QD) method. Since the accurate full-dimension quantum dynamics calculation is computationally expensive for the large number of opening channels, QCT is the routine method in the dynamics study of reaction (1).⁸

The improvement of the calculated dynamical results for a reaction system depends primarily on the constructing of the more accurate PES. However, numerical integration methods, especially those preserving constancies of the reaction system, are also advantageous in the QCT study.⁹ Since Hamilton system has the symplectic structure, Feng¹⁰ and

Ruth¹¹ have respectively advanced the symplectic algorithm, for which each integral step is a symplectic transform. And some reliable symplectic algorithms of 4th, 6th and higher order, whose significance in the QCT calculation has been assessed,¹² are provided by Qin *et al.*,¹³ Yoshida,¹⁴ Schlier and Seiter.¹⁵ Both the 4th-order Runge-Kutta scheme and the 6th-order predictor-corrector scheme by Gear, which have often been used in the QCT study, have reflected worse conservation of energy and angular momentum of the reaction system.^{16,17} The fact is going to influence the correctitude of the reaction dynamical attributes determined by the QCT calculations.¹⁶ Therefore, it is necessary to use the symplectic algorithm,¹⁵ which can conserve not only the symplectic structure of Hamilton system but also the total energy and the total angular momentum, in the QCT calculation of the chemical reaction.

In this work, we have carried out a QCT study with the 6th-order explicit symplectic algorithm for reaction (1) by employing the new ground PES which has been fitted on the basis of the data of the accurate ab initio calculation and some valid experimental values.¹⁸ The paper is organized as follows: Section 2 gives a brief introduction about the evaluation of the reaction probability and reaction cross-section of the reaction (1) by the QCT method. In Sec. 3, the advantage of the 6th-order explicit symplectic algorithm in the QCT study of the reaction (1) has been analyzed, and then the reaction probabilities and the reaction cross-sections in the some given initial conditions are provided and compared with those of Gilibert *et al.*¹⁹ Finally, some remarks about the main results of this work have been deduced in Sec. 4.

Computational Method

After the ground PES of reaction (1) has been constructed, the reaction probability and the reaction cross-section can be estimated by the QCT method.⁹ In the center-of-mass coordinates, the Hamiltonian function of the three-atom reaction system $A+BC$ has the following form

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

Where Q_j ($j = 1, 2, \dots, 6$) represents the generalized Cartesian coordinate P_j ($j = 1, 2, \dots, 6$) is the momentum conjugate to the Q_j , $V(Q_1, Q_2, \dots, Q_6)$, is the potential energy function of the three-atom reaction system. If the masses of atom A , B and C denote m_A , m_B and m_C , the reduced masses are

$$\mu_{B,C} = \frac{m_B m_C}{m_B + m_C} \quad \text{and} \quad \mu_{A,BC} = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C}$$

Canonical equations of the three-atom reaction system are

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

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

$$Pb(b; \nu, J, Et) = \lim_{N \rightarrow \infty} (Nr(b; \nu, J, Et)/N(b; \nu, J, Et)) \quad (4)$$

where b is the impact parameter, ν and J is the vibrational and rotational level of O_2 molecule, Et is the relative translational energy, $Nr(b; \nu, J, Et)$ and $N(b; \nu, J, Et)$ are the numbers of reactive collisions and total collisions, respectively. At the fixed initial condition set $(b; \nu, J, Et)$ 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 the equation,

$$Sr(\nu, J, Et) = \pi b_{\max}^2(\nu, J, Et) [Nr(\nu, J, Et)/N(\nu, J, Et)], \quad (5)$$

where $b_{\max}(\nu, J, Et)$ is the maximal impact parameter, $Nr(\nu, J, Et)$ and $N(\nu, J, Et)$ are the numbers of reactive collisions and the total number of the computed trajectories at the initial condition set (ν, J, Et) , respectively. $b_{\max}(\nu, J, Et)$ is the value of b such that $Pb(b; \nu, J, Et)$ is zero for $b \geq b_{\max}(\nu, J, Et)$. 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 the present case, A is taken to be the nitrogen atom (N), B is the first oxygen atom (O) and C is the second oxygen atom (O). 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 the calculations is 1.0×10^{-16} s. In order to rapidly evaluate the reaction probability and the reaction cross-section of reaction (1), a homemade parallel program has run in the massive parallel computer cluster during the QCT calculation of this work.

Results and Discussion

In order to analyse the superiority of the 6th-order explicit symplectic algorithm (SL6) with respect to the 4th-order Runge-Kutta scheme (RK4) in the QCT study of reaction (1), the reaction probabilities at several impact parameters have been determined by both SL6 and RK4 on the same initial conditions, respectively. There are some discrepancies between the values of the reaction probabilities at the several impact parameters computed by SL6 and the ones of RK4 at the rovibrational level of O_2 molecule and the relative translational energy ($\nu = 0, J = 8$ and $Et = 1.50$ eV), as shown by the plot of Figure 1. The reaction probabilities at the lower relative translational energy ($Et = 0.40$ eV is considered here) for reaction (1) have also been estimated by both SL6 and RK4 with the O_2 molecule at the ($\nu = 0, J = 8$) rovibrational level, and we can observe some similar discrepancies by the comparison of two kinds of results.

Figure 2 has displayed the total energies of the reaction system, which are carried out by SL6 and RK4 at the ($\nu = 0, J = 8$ and $Et = 0.40$ eV) initial condition, evolving with the integrating time. It is obvious that the total energy of the reaction system decreases rapidly with the integrating time increasing while RK4 is employed during the numerical integration of canonical equations of reaction (1). Therefore, the conclusion has been suggested in the plot of Figure 2 that the total energy of the reaction system will have a larger dissipation if the integrating time is longer. We consider that

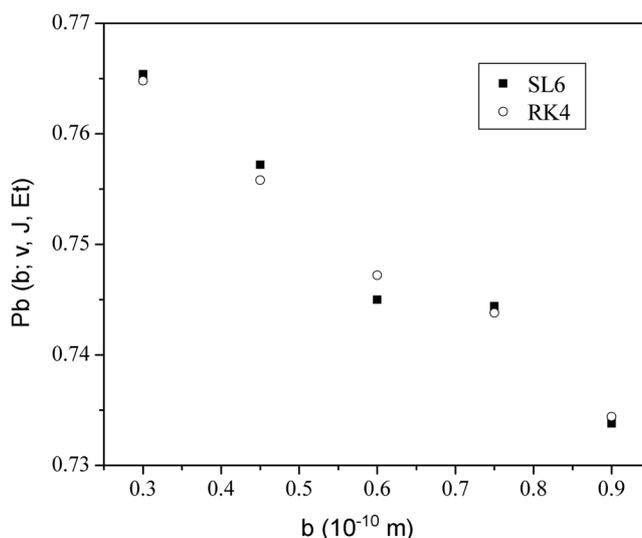


Figure 1. Comparison of the reaction probabilities at several impact parameters computed by SL6 and RK4 with the ($\nu = 0, J = 8$ and $Et = 1.50$ eV) initial condition.

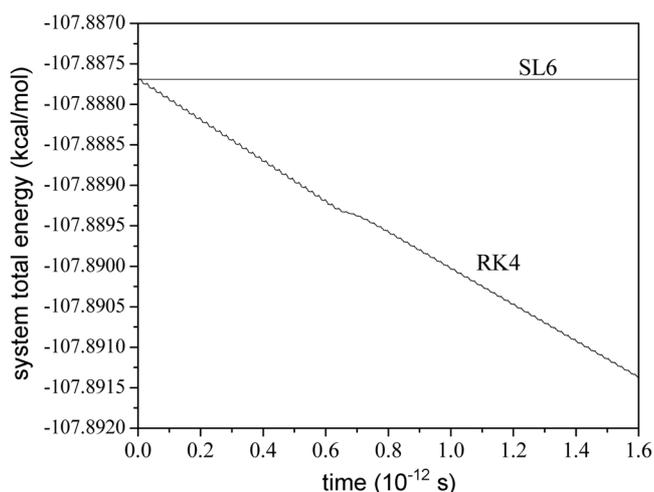


Figure 2. Comparison of the variation of the system total energy with the time computed by SL6 and RK4 at the ($v = 0$, $J = 8$ and $E_t = 0.40$ eV) initial condition.

the computed error contains the round error and the truncation error. Since the truncation error of RK4 has a continuously unilateral accumulation during the numerical integration of canonical equations of reaction (1), the loss of the total energy of the reaction system increases with the integrating time. However, as depicted by the plot of Figure 2, the total energy of the reaction system can be conserved very well by SL6 because of no unilateral accumulation of the truncation error of the total energy.

Since the total angular momentum of the reaction system is a vector, we only present the variation of the total angular momentum component on the X-axis with the integrating time at the ($v = 0$, $J = 8$ and $E_t = 0.40$ eV) initial condition in Figure 3. The angular momentum component on the axis X of the reaction system determined by SL6 keep always invariable with the integrating time, as displayed in the plot of Figure 3, which indicates that SL6 can strictly conserve the total angular momentum of the reaction system. Figure 3

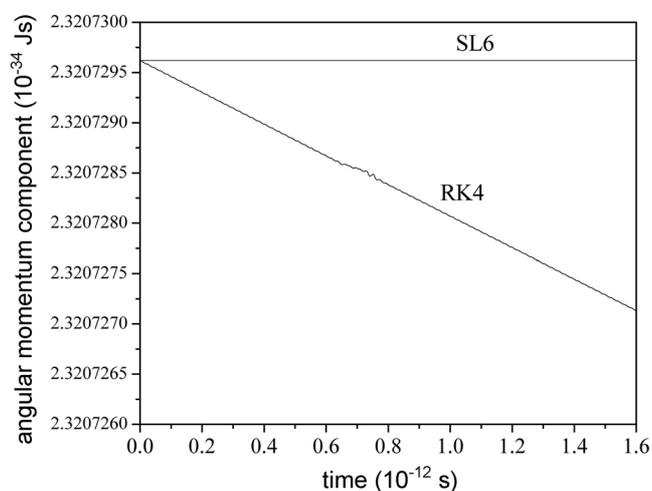


Figure 3. Comparison of the variation of the total angular momentum component on the X-axis with the time computed by SL6 and RK4 at the ($v = 0$, $J = 8$ and $E_t = 0.40$ eV) initial condition.

has also revealed the fact that the total angular momentum component on the X-axis of the reaction system obtained by RK4 dissipates gradually with the integrating time. And the identical conclusion can be drawn for the total angular momentum components on the Y-axis axis and Z-axis of the reaction system. From these discussion above, it has been found out that SL6, but not RK4, can conserve both the total energy and the total angular momentum of the reaction system during the integrating of canonical equations, therefore the reaction probabilities of reaction (1) computed by SL6 is more reasonable relative to those calculated by RK4 at the same initial condition in Figure 1.

The dependence of the reaction probability $P_b(b, v, J, E_t)$ on the impact parameter b at the ($v = 0$, $J = 8$, $E_t = 0.55, 1.80$ eV) initial condition has been shown in Figure 4. The reaction probability of reaction (1) has exhibited a declining trend while the impact parameter increases from 0 to its maximum with an increment of 0.15 \AA . According to the qualitative explain of the angle dependent line-of-centers (ADLOC) model,²⁰ it is attributed to the fact that the energy along the line-of-centers available for reaction (1) decreases with the impact parameter increasing. Except that both maximal impact parameters $b_{\max}(v, J, E_t)$ and the areas under the curves of $P_b(b, v, J, E_t)$ versus b have associated to the relative translational energy, the variation 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 the Figure 4 of Ref. [19] carried out by Gilbert *et al.*, however, it is easily found that there are some differences between the function of the reaction probability versus the impact parameter determined in this work and the one carried out by Gilbert *et al.* Firstly, the maximal reaction probability at $E_t = 1.80$ eV are about 0.80, however the value in the Figure 4 of Ref. [19] are up to 1.0, which can be interpreted in terms of a steric requirement of reaction (1). Since the reaction probability at the zero-impact-parameter still connects with the angle between the coordinate of N atom relative to the center of mass of O_2 molecule and O_2 molecule axis, some angle selected here

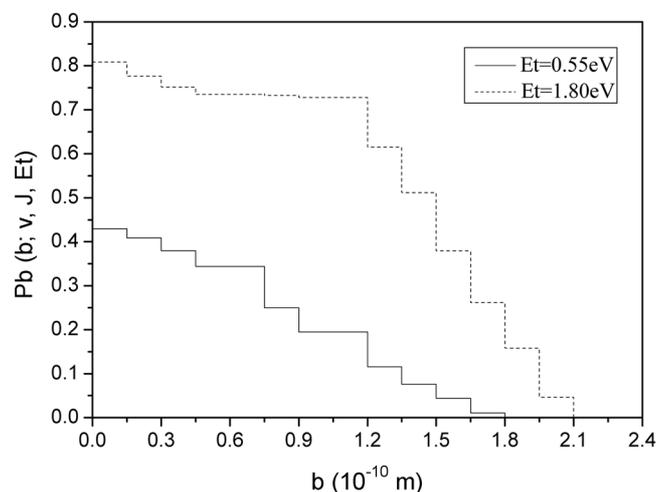


Figure 4. Variation of the reaction probability with the impact parameter at the ($v = 0$, $J = 8$) rovibrational level of O_2 molecule.

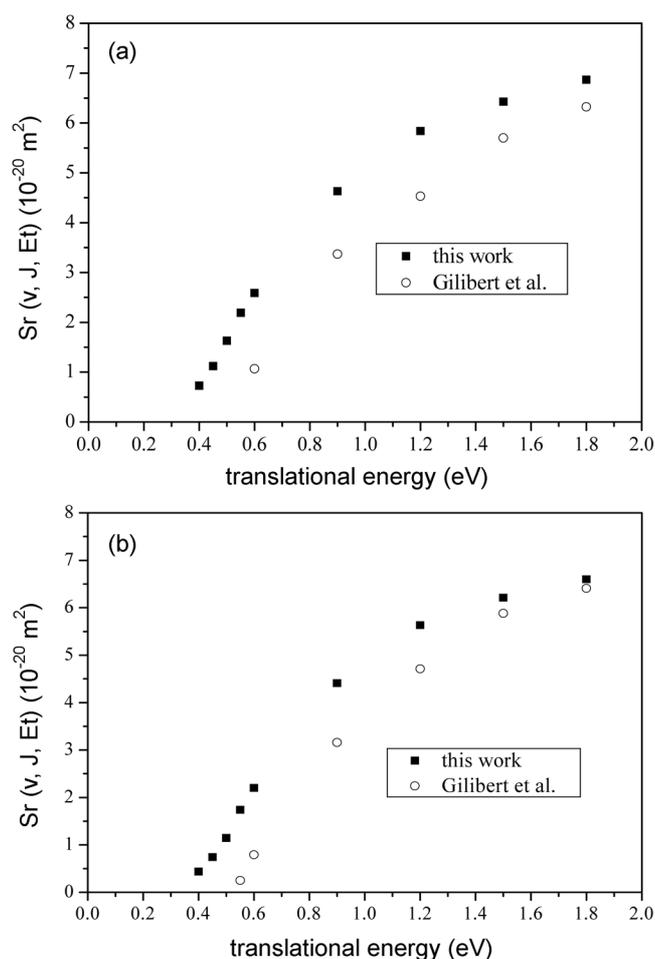


Figure 5. Function of the reaction cross-section versus the relative translational energy in this work compared with that of Gilibert *et al.*¹⁹ for reaction (1): (a) $v = 0, J = 0$; (b) $v = 1, J = 8$.

results in the reaction probability less than one. The second difference is that the situation of a slight increase of the reaction probability at the low impact parameter like the Figure 4 in Ref. [19] cannot be discovered in the Figure 4 of this work at the lower relative translational energy (less than 1.20 eV). Though Gilibert *et al.*¹⁹ consider that the differential phenomenon is attributed to the poor statistics at the low impact parameter by Monte Carlo sampling from a uniform distribution between 0 and $b_{\max}^2(v, J, Et)$, the declining trend of the reaction probability with the impact parameter in this work is seem to be more reasonable. Finally, the maximal impact parameter determined in this work has obviously larger values than those in the Figure 4 of Ref. [19] at the same initial conditions, especially at the low relative translational energy.

The plot of Figure 5 has described the variation of the reaction cross-section of reaction (1) with the relative translational energy, where the ($v = 0, J = 0$ and $v = 1, J = 8$) rovibrational level of O_2 molecule and the relative translational energy range from 0.40 to 1.80 eV are chosen in order to compare with the results carried out by Gilibert *et al.*¹⁹ As shown by the plot of Figure 5, the reaction cross-

section determined in this work rapidly increases with the relative translational energy above the energy threshold, which are equal to about 0.35 and 0.30 eV at the ($v = 0, J = 0$ and $v = 1, J = 8$) rovibrational level of O_2 molecule predicted by the calculation of this work. Although the functions of $Sr(v, J, Et)$ versus Et at $v = 0, J = 0$ and $v = 1, J = 8$ begin to become smooth at the high relative translational energy, they do not rapidly reach to saturation. The variational curve of $Sr(v, J, Et)$ versus Et in the plot of Figure 5 is consistent with that of the reaction system with an early energy barrier, which can be interpreted by the ADLOC model at the given initial condition. By the comparison in the plot of Figure 5, it is obvious that the energy thresholds determined in this work on the basis of the new ground PES provided Sayós *et al.*²⁰ are much lower than those predicted by Gilibert *et al.*¹⁹ at the rovibrational levels of O_2 molecule considered. The plot of Figure 5 also suggested that the reaction cross-section of reaction (1) calculated in this work have a systematical enhancement than those carried out by Gilibert *et al.*¹⁹ at all relative translational energies considered, especially at the low relative translational energy. And the curve of $Sr(v, J, Et)$ versus Et determined in this work has apparently covered a larger area with respect to that evaluated by Gilibert *et al.*¹⁹ Since the thermal rate constant of reaction (1) at the given translational temperature can be derived from the reaction cross-section value according to the QCT method, it can be prospective that they will have a great improvement relative to the values of Gilibert *et al.*¹⁹ The enhancements of the reaction cross-sections are owing to the fact that the energy barrier of the new ground PES employed in this work is obviously lower than the one of the ground PES adopted by Gilibert *et al.*¹⁹ In addition, it should be noticed that the 6th-order explicit symplectic algorithm is also benefited to the accurate prediction of the energy threshold and the enhancement of the reaction cross-section.

Conclusions

We have presented a QCT calculation with the 6th-order explicit symplectic algorithm for reaction (1), based on a new analytical ground PES reported by Sayós *et al.*²⁰ The fact has been documented that the 6th-order explicit symplectic algorithm can conserve both the total energy and the total angular momentum of the reaction system during the numerical integration of canonical equations, which make the reaction probabilities of reaction (1) calculated by SL6 more accurate than those determined by RK4. The reaction probability of reaction (1) has a declining trend with the impact parameter increasing, and do not exhibit a slight increase at the low impact parameter like the Figure 4 in Ref. [19] when the relative translational energy is less than 1.20 eV. The reaction cross-section of reaction (1) rapidly enhances with the relative translational energy until it becomes gradually smooth at the high relative translational energy. Since we employ the new ground PES and the 6th-order explicit symplectic algorithm during the QCT calculation in this work, the energy thresholds are much

lower than those predicted by Gilibert *et al.*¹⁹ at the rovibrational levels of O₂ molecule considered, and the reaction cross-section have a systematical enhancement than those carried out by Gilibert *et al.*¹⁹ at all relative translational energies considered.

Acknowledgements. The authors are grateful to “State Key Laboratory of Scientific and Engineering Computing, Chinese Academy of Sciences” for providing a part of the computer time on the NO.1 parallel computer cluster.

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