

The QCT calculation of the rate constants for the $\text{N}({}^4\text{S}) + \text{O}_2({}^3\Sigma_g^-) \rightarrow \text{NO}({}^2\Pi) + \text{O}({}^3\text{P})$ reaction

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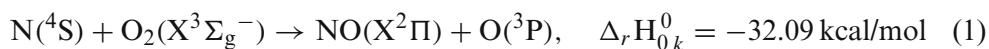
Received 18 November 2006; Revised 23 January 2007

A quasi-classical trajectory (QCT) calculation with the fourth-order explicit symplectic algorithm for the $\text{N}({}^4\text{S}) + \text{O}_2({}^3\Sigma_g^-) \rightarrow \text{NO}({}^2\Pi) + \text{O}({}^3\text{P})$ reaction has been performed by employing the ground and first-excited potential energy surfaces (PESs). Since the translational temperature considered is up to 5000 K, the larger relative translational energy and the higher vibrational and rotational level of O_2 molecule have been taken into account. The affect of the relative translational energy, the vibrational and rotational level of O_2 molecule in the reaction cross-sections of the ground and first-excited PESs has been discussed in a extensive range. And we exhibit the dependence of microscopic rate constants on the vibrational and rotational level of O_2 molecule at $T=4000$ K. The thermal rate constants at the translational temperature between 300 and 5000 K have been evaluated and the corresponding Arrhenius curve has been fitted for reaction (1). It is found by comparison that the thermal rate constants determined in this work have a better agreement with the experimental data and provide a more valid theoretical reference.

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

1. Introduction

The elementary atmospheric reaction,



play a meaningful role in the study of the Earth's atmospheric chemistry, infrared chemiluminescence and combustion processes [1–3]. The temperature

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dependence of thermal rate constants has been the focus of many experimental researches about reaction (1). The experimental data of thermal rate constants over the temperature range of $298 \leq T/K \leq 5000$ for reaction (1), which has been regarded as one of the best expression of experimental data to this day, have been recommended by Baulch et al. via the expression $k(T)=1.5 \times 10^{-14} T \exp(-3270/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [4].

It should be noted at this stage that the dynamical study of reaction (1) primarily involves the potential energy surfaces of $^2A'$ and $^4A'$ states of NO_2 , the $^6A'$ state of NO_2 makes no contribution for reaction (1) at the translational temperature considered [5, 6]. There have also been several *ab initio* studies on the ground ($^2A'$) and first-excited ($^4A'$) potential energy surfaces (PESs for brevity) of reaction (1) [7–12], where the complete active space self-consistent field (CASSCF) calculation, multi-reference contracted configuration interaction (MR-CI) calculation and the density functional method have been often employed. The analytical functions about the ground and first-excited PESs for reaction (1) [7, 8, 10, 11], based on these data of *ab initio* calculations, have also been provided with the many-body expansion formalism. To better explain the exoergicity and the corresponding experimental rate constant at 300 K for reaction (1), Sayós et al. constructed the improved ground and first-excited PESs on the basis of the accurate *ab initio* data published in [9, 12] along with their complemented data of second-order perturbation theory [13].

From the point of view of reaction dynamics, reaction (1) can be researched by the quasi-classical trajectory (QCT) method and the quantum dynamics method [6, 7, 10, 14]. Since the accurate full-dimension quantum dynamics calculation is computationally expensive for the large number of opening channels, we will present a QCT study for reaction (1) by the new ground and first-excited PESs reported by Sayós et al. [13]. In this work, the fourth-order explicit symplectic algorithm, which has been assessed an effective numerical integral scheme, has been adopted to improve the availability of the integration of Hamiltonian equations. And the extensive database about the reaction cross-section, the microscopic rate constant and the thermal rate constant of reaction (1) has been extended to the translational temperature of 5000 K. The present paper is organized as follows. In section 2, we provide a synopsis of the formalism about the determination of the reaction attributes by the QCT method. The effect of the relative translational energy, the vibrational and rotational level of O_2 molecule on the reaction cross-section of the ground and first-excited PESs is discussed in section 3, where the more extensive range about these parameters are involved because of the considered temperature up to 5000 K. The dependence of the net microscopic rate constants on the vibrational and rotational level of O_2 molecule have analyzed in detail at $T = 4000$ K. And we obtain the Arrhenius curve of thermal rate constants at the translational temperature between 300 and 5000 K in this work. Finally, some remarks about the results of this work are concluded in section 4.

2. The computational method

Because the QCT method is widely described in the dynamics calculations of the chemical reaction [10], here we only summarize the details relevant to the present calculations. The reaction cross-section on the given PES of reaction (1) assumes the general form

$$S_r(v, J, E_t) = \pi b_{\max}^2(v, J, E_t) [N_r(v, J, E_t) / N(v, J, E_t)], \quad (2)$$

where $b_{\max}(v, J, E_t)$ is the maximal impact parameter, $N_r(v, J, E_t)$ and $N(v, J, E_t)$ are the numbers of reactive collisions and total collisions at a given set of initial conditions (v, J, E_t) , respectively. For each set of initial conditions, a mean number of 10000 trajectories are enough to estimate the reaction cross-section with a standard deviation of less than 5%.

The microscopic rate constant on the given PES can be computed by the following equation

$$k'(T, v, J) = g_e(T) \left(\frac{2}{k_B T} \right)^{3/2} (\pi \mu)^{-1/2} \int_{E_0}^{E_m} S_r(v, J, E_t) E_t \exp\left(-\frac{E_t}{k_B T}\right) dE_t, \quad (3)$$

where $g_e(T)$ is the electronic degeneracy factor, k_B is the Boltzmann constant, T the translational temperature associated to the relative translational energy, μ is reduced mass of the reactants, E_0 and E_m are the energy threshold and the maximal relative translational energy, respectively. The electronic degeneracy factors of the ground and first-excited PESs for reaction (1) should be taken equal to 1/6 and 1/3, respectively. Neglecting the non-adiabatic coupling between $^2A'$ and $^4A'$ states of NO_2 , the net microscopic rate constants of reaction (1) can be evaluated by

$$k(T, v, J) = k'(T, v, J)(^2A') + k'(T, v, J)(^4A'), \quad (4)$$

where $k'(T, v, J)(^2A')$ and $k'(T, v, J)(^4A')$ are the microscopic rate constants on the ground and first-excited PESs, respectively.

The thermal rate constants for reaction (1) can be obtained by the weighted summation of the net microscopic rate constant

$$k(T) = \sum_{v, J} p_{v, J}(T) k(T, v, J), \quad (5)$$

where $p_{v, J}(T)$ is the distribution function of the rovibrational level of O_2 molecule which is regarded as the Maxwell–Boltzmann distribution in this work. In all, millions of trajectories have been run to estimate the thermal rate constants at the translational temperature range from 300 to 5000 K for reaction (1).

Because of the translational temperature considered up to 5000 K, the relative translational energy with a range from the energy threshold to 4.0 eV is

necessary. The ($J=0, 4, 8, 12, 16, 20, 40, 60, 80$ and $v=0, 1, 2, 4, 6, 8$) rovibrational levels of O_2 molecule have been chosen because the range represents the majority of the rovibrational levels of O_2 molecule at the high-translational temperatures considered. The fourth-order explicit symplectic algorithm that can conserve not only the symplectic structure of Hamiltonian system but also the total energy of the reaction system is used during the numerical integration with a constant time step size (1.0×10^{-16} s) [15]. 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. In calculations, we have employed a homemade parallel program that consists of the standard Fortran code and the MPICH function.

3. Results and discussion

In figure 1, we have plotted the variation of reaction cross-sections on the ground and first-excited PESs for reaction (1) with the relative translational energy at the ($v=0; J=20$) rovibrational level of O_2 molecule. As depicted by the plot of figure 1, the function of $S_r(v, J, E_t)$ on the ground and first-excited PESs versus E_t rises rapidly with the relative translational energy. When the relative translational energy exceeds the value of about 2.0 eV, the function of $S_r(v, J, E_t)$ versus E_t gradually becomes smooth and tends slowly to saturation. The character of the function of $S_r(v, J, E_t)$ versus E_t in this work is consistent to that of the reaction system with an energy barrier, which can be interpreted by the ADLOC model in the literature [16] at the relative translational energy range considered. Apparently, from the comparison in the plot of figure 1, the reaction cross-sections on the ground PES have a systematical enhancement than the ones on the first-excited PES at the ($v=0; J=20$) rovibrational level of O_2 molecule because the energy barrier of the ground PES is a clearly lower with respect to the one of the first-excited PES. As a result, the area under the curve of $S_r(v, J, E_t)$ versus E_t on the first-excited PES is lower than the one on the ground PES at the ($v=0; J=20$) rovibrational level of O_2 molecule.

The variation of reaction cross-sections on the ground and first-excited PESs with the rotational level of O_2 molecule has been analyzed in figure 2. In two plots of figure 2, the rotational level of O_2 molecule does not play a significant role in enhancing the reaction cross-sections of the ground and first-excited PESs as the rotational level of O_2 molecule is less than 20, which is attributed to that the O_2 molecule is rotationally frozen at the low rotational level of O_2 molecule and relative translational energy [16]. When the rotational level of O_2 molecule exceeds the value of 20, the reaction cross-sections on the ground and first-excited PESs have the rapidly ascending trend with the rotational level of O_2 molecule increasing. However, for the reaction system with an energy barrier like reaction (1), the general behavior of the reaction cross-sections varying with

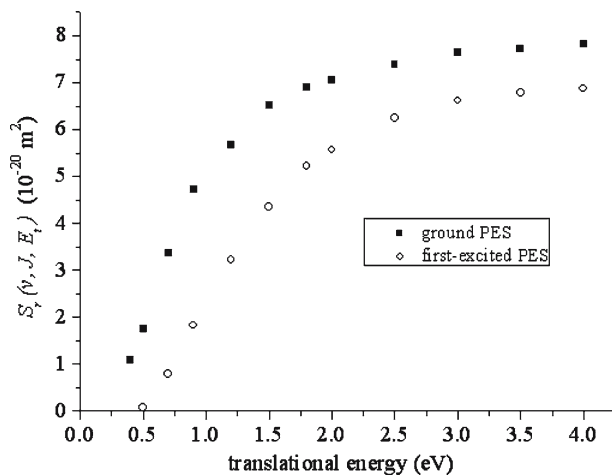


Figure 1. Dependence of the reaction cross-section on the relative translational energy for O_2 molecule at $v = 0$ and $J = 20$.

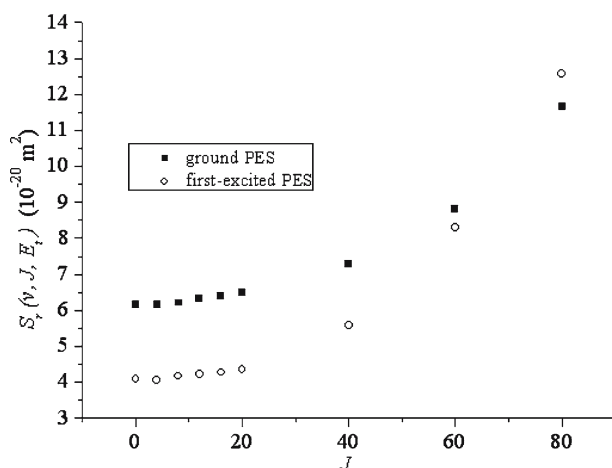


Figure 2. Variation of the reaction cross-section with the rotational level for O_2 molecule at $E_t = 1.50 \text{ eV}$ and $v = 0$.

the rotational level of reactant molecule indicates a fall in the reaction cross-section followed by a subsequent rise because of both the competing orientation and energy effects [17, 18]. Since the orientation effect unfavorable to the reaction has effectively compensated by the anisotropic character of the PESs and the system is forced back to the preferable orientation [18], the fall of reaction cross-sections with the rotational level of O_2 molecule does not happen in this work.

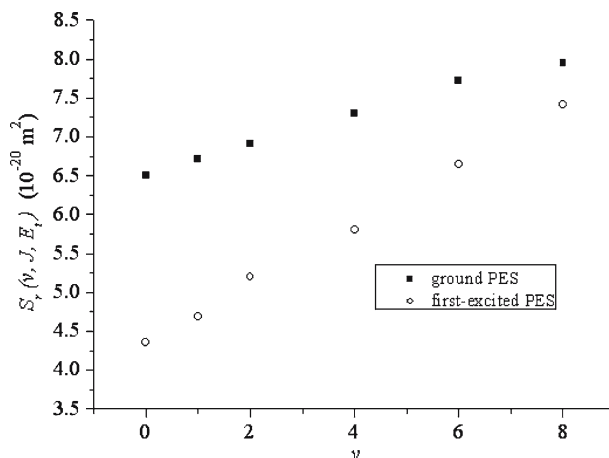


Figure 3. Variation of the reaction cross-section with the vibrational level for O_2 molecule at $E_t = 1.50 \text{ eV}$ and $J = 20$.

The plot of figure 3 has described the influence of the vibrational level of O_2 molecule placed at $E_t = 1.50 \text{ eV}$ and $J = 20$ on the reaction cross-sections of the ground and first-excited PESs. We can see that the reaction cross-sections enhance linearly with the vibrational level of O_2 molecule moving from 0 to 8, which indicates that the vibrational level of O_2 molecule contributes modestly to the enhancement of the reaction cross-sections. The moderate effect of the vibrational level of O_2 molecule on the reaction cross-sections is due to that the enhancement of the vibrational energy promotes the relative motion perpendicular to the coordinate over the energy barrier to reaction. As shown by the plot of figure 3, the difference between the reaction cross-sections on the first-excited PES and the ones on the ground PES is visible at the low vibrational level of O_2 molecule and slowly shortens at the high vibrational level of O_2 molecule. Thus, the fact has revealed that the gradient of the curve of $S_r(v, J, E_t)$ versus v on the first-excited PES is larger than the one on the ground PES at $E_t = 1.50 \text{ eV}$ and $J = 20$. It is suggested that the contribution of the first-excited PES to the thermal rate constants of reaction (1) will become important at the higher translational temperature.

We specifically show the net microscopic rate constant of reaction (1) and assess its dependence on the vibrational and rotational level of O_2 molecule at $T = 4000 \text{ K}$ in figure 4. The enhancements of $\log_{10} k(T, v, J)$ at $T = 4000 \text{ K}$ are almost identical while the vibrational level of O_2 molecule varies from 0 to 8 with the increment of 2 over the range of the rotational level of O_2 molecule. The linear variation of $\log_{10} k(T, v, J)$ with the vibrational level of O_2 molecule has been exhibited, although there casually is a little anomaly. The fact reveals that the vibrational level of O_2 molecule has a moderate affect on the net

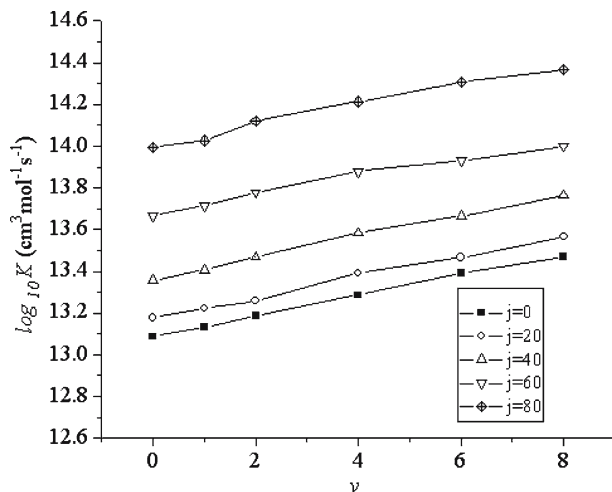


Figure 4. Variation of the net microscopic rate constants (4000 K) for reaction (1) with vibrational levels of O_2 molecule at various rotational levels.

microscopic rate constants. It is also observed from figure 4 that $\log_{10} k(T, v, J)$ rapidly increase as the rotational level of O_2 molecule moves from 0 to 80 at the given vibrational level, and the higher rotational level of O_2 molecule contributes much more to the enhancement $\log_{10} k(T, v, J)$ than the lower rotational level. The phenomenon in figure 5 of Ref. [6] that there is a slight reduction of $\log_{10} k(T, v, J)$ when the rotational level of O_2 molecule rises from 0 to 40 at the ($v = 0, 1, 2$) vibrational level of O_2 molecule, which is possibly irrational, does not appear in this present work.

The thermal rate constants determined in this work can conform to the following Arrhenius expression of the standard three-parameter equation

$$k = AT^n e^{B/T}, \quad (6)$$

where A , n and B are the parameters that can optimize by means of a non-linear least-squares procedure. The corresponding Arrhenius equation to thermal rate constants calculated in this work has the form of $k(T) = 1.6467 \times 10^8 T^{1.5576} \exp(-3089/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Figure 5 has exhibited the Arrhenius curve of thermal rate constants at the translational temperature between 300 and 5000 K determined in this work, and these curves of the previously experimental and theoretical study have also been inserted for comparison [4, 6]. As depicted by the plot of figure 5, the Arrhenius curve of $\log_{10} k(T)$ versus T fitted in this work is in good agreement with that of the experimental data under the translational temperature value of 2000 K [4]. The Arrhenius curve given by Bose and Candle is clearly below that of the experimental data, especially the difference is about an order of magnitude at $T = 300$ K [6]. The main reason is that

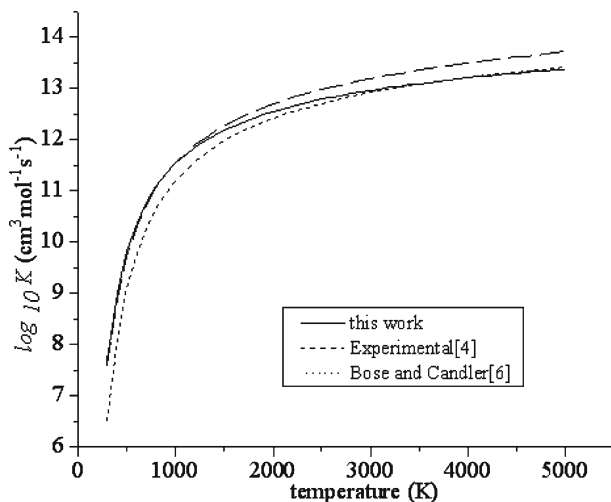


Figure 5. Comparison of thermal rate constants (300–5000 K) for reaction (1) obtained in this work with previously theoretical and experimental values.

the barrier heights of the ground and first-excited PESs employed by Bose and Candler have the higher values than those of both PESs adopted in this work. While the translational temperature is over 2000 K, we can obviously see a good agreement between the Arrhenius curve fitted by Bose and Candler and that of the experimental data. But this agreement may be of no significance because the experimental data of thermal rate constants for reaction (1) have a possible greater underestimate at the higher translational temperatures [6]. From the point of view, it is concluded that the thermal rate constants of the QCT study in this work have contributed the more accurate theoretical data of reaction (1) at all the translational temperatures considered for reference.

4. Conclusions

In this work, we have used the ground and first-excited PESs reported by Sayós et al. [13] to carry out an extensive QCT study with the fourth-order explicit symplectic algorithm for reaction (1). At the relative translational energy regime, the function of $S_r(v, J, E_t)$ on the ground and first-excited PESs versus E_t indicates a rapidly rise followed by a trend to reach saturation. The reaction cross-sections on the ground and first-excited PESs are almost not sensitive to the rotational level of O_2 molecule as the rotational level is less than 20, however, they rise rapidly with the rotational level of O_2 molecule while the rotational level exceeds the value of 20. And the vibrational level of O_2 molecule has a modest contribution to the enhancement of the reaction cross-sections on the ground and first-excited PESs at the given relative

translational energy. By the study of the dependence of the net microscopic rate constant on the vibrational of O_2 molecule, we have found that the value of $\log_{10} k(T, v, J)$ varies almost linearly with the vibrational level of O_2 molecule. The Arrhenius curve of thermal rate constants in this work with the form of $k(T) = 1.6467 \times 10^8 T^{1.5576} \exp(-3089/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ show excellent agreement with the experimental data at the translational temperature range from 300 to 2000 K, and provides a good theoretical reference of reaction (1) at the higher translational temperature.

References

- [1] M.W. Chase, Jr., C.A. Downey, J.R. Downey, D.J. Frurip, R.A. McDonald and A.N. Syverud, *J. Phys. Chem. Ref. Data* 4 (1985) 1.
- [2] P. Warneck, *Chemistry of the Natural atmosphere* (Academic, San Diego, 1998), chapter 3.
- [3] A. Burcat, G. Dixon-Liwes, M. Frenklach, W.C. Gardiner, R.K. Hanson, S. Salimian, J. Troe, J. Warnatz and R. Zellner, *Combustion Chemistry*, ed. W.C. Gardiner Jr. (Springer-Verlag, New York, 1984).
- [4] D.L. Baulch, C.J. Cobos, R.A. Cox, P. Frank, G. Hayman, Th. Just, J.A. Kerr, T. Murrells, M.J. Pilling, J. Troe, R.W. Walker and J. Warnatz, *J. Phys. Chem. Ref. Data* 23 (1994) 847.
- [5] M. Gilibert, A. Aguilar, M. González and R. Sayós, *Chem. Phys.* 108 (1998) 99.
- [6] D. Bose and G.V. Candler, *J. Chem. Phys.* 107 (1997) 6136.
- [7] J.W. Duff, F. Bien and D.E. Paulsen, *Geophys. Res. Lett.* 21 (1994) 2043.
- [8] R. Sayós, J. Hijazo, M. Gilibert and M. González, *Chem. Phys. Lett.* 284 (1998) 101.
- [9] R. Sayós, C. Oliva and M. González, *J. Chem. Phys.* 115 (2001) 1287.
- [10] M. Gilibert, A. Aguilar, M. González and R. Sayós, *Chem. Phys.* 172 (1993) 99.
- [11] D. Reignier, T. Stoecklin, A. Voronin and J.C. Rayez, *Phys. Chem. Chem. Phys.* 3 (2001) 2726.
- [12] M. González, C. Oliva and R. Sayós, *J. Chem. Phys.* 117 (2002) 680.
- [13] R. Sayós, C. Oliva and M. González, *J. Chem. Phys.* 117 (2002) 670.
- [14] P. Defazio, C. Petrongolo, C. Oliva, M. González and R. Sayós, *J. Chem. Phys.* 117 (2002) 3647.
- [15] M.Z. Qin, D.L. Wang and M.Q. Zhang, *J. Comp. Math.* 9 (1991) 211.
- [16] R. Sayós, A. Aguilar, M. Gilibert and M. González, *J. Chem. Soc. Faraday Trans.* 89 (1993) 3223.
- [17] N. Sathyamurthy, *Chem. Rev.* 83 (1983) 601.
- [18] J.A. Harrison, L.J. Isakson and H.R. Mayne, *J. Chem. Phys.* 91 (1989) 6906.