

Effect of the initial rotational and vibrational state on the stereodynamics of $\text{N}(^4\text{S})+\text{O}_2(\text{X}^3\Sigma_g^-) \rightarrow \text{O}(^3\text{P})+\text{NO}(\text{X}^2\Pi)$ reaction

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Abstract. The stereodynamics of the atom-molecule reaction $\text{N}(^4\text{S})+\text{O}_2(\text{X}^3\Sigma_g^-) \rightarrow \text{O}(^3\text{P})+\text{NO}(\text{X}^2\Pi)$ has been studied using quasi-classical trajectory method with the lowest $2\text{A}'$ potential energy surfaces (PESs) given by Sayós *et al.* [R. Sayós, C. Oliva, M. González, J. Chem. Phys. 117 (2002) 670]. Four generalized polarization-dependent differential cross-sections $[(2\pi/\sigma)(d\sigma_{00}/d\omega_t), (2\pi/\sigma)(d\sigma_{20}/d\omega_t), (2\pi/\sigma)(d\sigma_{22+}/d\omega_t), (2\pi/\sigma)(d\sigma_{21-}/d\omega_t)]$ and distributions $P(\theta_r)$, $P(\phi_r)$ were calculated. The effects of the different initial rotational and vibrational states were analyzed. It found that the degree of the forward scattering and the product polarizations show obviously change along with the initial vibration number, which leads to the increase of alignment and decrease orientation of product rotational angular momentum j' . Although the influence of the initial rotational excitation effect on the aligned and oriented distribution of product is not stronger than that of the initial vibration excitation effect, the initial rotational excitation makes the alignment of the product rotational angular momentum small change in a certain range. Moreover, the $P(\theta_r)$ distribution and $P(\phi_r)$ distribution change noticeably by varying the initial vibration number.

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Key words: quasiclassical trajectory, vector correlations, stereodynamics, rotational and vibrational excitation.

1 Introduction

The gas-phase reaction $\text{N}(^4\text{S})+\text{O}_2(\text{X}^3\Sigma_g^-) \rightarrow \text{O}(^3\text{P})+\text{NO}(\text{X}^2\Pi)$ and its reverse reaction play an important role in the Earth's atmospheric chemistry [1-2] and combustion processes

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[3]. This reaction is a source of infrared chemiluminescence in the thermosphere [4]. In previous works, several *ab initio* studies have been reported about the ground $^2A'$ and the first excited $^4A'$ potential energy surfaces (PESs) involved in this reaction. [5-11]. Based on the PESs, some scalar properties of this reaction were studied by using quasiclassical trajectory (QCT) [12-14], the variational transition state theory [8-10], and quantum dynamics methods [15-16], such as the reaction cross-sections, the temperature dependence of the rate constant and the ro-vibrational distributions of product NO molecule. The angular momentum polarizations of the product and the vector correlations between the reagent and product were also calculated with QCT, quantum scattering and wave packet dynamics methods. [17-24] Defazio *et al.* [16] reported the first quantum mechanical calculations of NO rovibrational distributions for the title reaction on the potential energy surface of Sayós *et al.* [7] Ramachandran *et al.* [13] also studied this reaction, but they used QCT on the other PES of Duff *et al.* [25]. It should be noted that their results are in good accord. Meanwhile, on the basis the two PESs, He *et al.* [14] not only calculated the total reaction cross section and the temperature dependence of microscopic rate constants using QCT method, but also compared their results with the experimental results of Gilbert *et al.* [26]. As for the reaction of the vector properties, just recently, Ma *et al.* [27] reported vector correlations between products and reagents for $N(^4S)+O_2(X^3\Sigma_g^-) \rightarrow O(^3P)+NO(X^2\Pi)$ reactions in the different collision energy for the $^2A'$ PES and the $^4A'$ PES. They found that the product rotational angular momentum is more strongly aligned on the $^4A'$ PES than on the $^2A'$ PES at the same collision energy.

As mentioned above, most previous studies basically deal with the scalar properties, such as reaction cross-sections, microscopic and macroscopic rate constants, and rovibrational distributions of the product NO molecule. In this work, we focus on stereodynamics characters of the $N(^4S)+O_2(X^3\Sigma_g^-) \rightarrow O(^3P)+NO(X^2\Pi)$ reaction on the $^2A'$ PES by Sayós *et al.* [7] and comprehensively analyze the effect of the vibrations and the rotational levels of the reactant molecules on the cross-sections and distributions.

2 Computational theory and details

2.1 QCT calculations

In this work, the standard QCT method [28-30] is used to study the stereodynamics of the title reaction based on Sayós *et al.* PES [7]. Only the details relevant to the present reaction will be given here. The initial vibrational and the rotational states of the O_2 molecule were taken to be $v=0-6$ and $j=0, 4, 8, 12, 16, 20, 24, 28, 32, 36$, respectively. Batches of 100000 trajectories were run for each run with an integration step of chosen to 0.1fs and collision energies 1.80eV. The trajectories start at an initial distance of 10 Å between the N atom and the center-of-mass (CM) of the O_2 molecule.

The total reaction cross section is defined as

$$\sigma_r = \pi b_{max} \frac{N_r}{N_T}. \quad (1)$$