Influence of reactant vibrational excitation on stereodynamics of C + NO → CN + O Reaction

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Abstract. Stereodynamics of the title reaction at different reagent vibrational states (v=0-2) are obtained using the quasiclassical trajectory method at collision energy of 0.06 eV on an accurate ^{4}A″ potential energy surface. The vector properties including angular momentum $P(\theta_r)$ and $P(\phi_r)$ distributions as well as polarization-dependent differential cross sections (PDDCS) of the product CN are presented. Furthermore, the influence of vibrational excitation on the product vector properties has also been studied in present work.

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Key words: stereodynamics; vibrational excitation; quasiclassical trajectory.

1 Introduction

The CNO reaction systems are relevant to astrochemistry under the cold conditions and are especially important for understanding the processes of NO reburning at high combustion temperatures. [1-2] Due to their eminence in gas phase chemistry, the CNO reaction systems have attracted much theoretical and experimental attention. A large number of experiments [3-11] have been carried out to measure the product energy partitioning and rovibrational distributions of CN, the reaction cross section as well as the rate coefficients at room temperature and low-temperature for the reaction.

From the theoretical viewpoint, the CNO potential energy surfaces have been builded and dynamical calculations have been carried out in recent years. The first *ab initio* study of the CNO PES was constructed by Persson *et al.* [12] The geometries and vibrational frequencies for the stationary points were determined for both ^{2}A′ and ^{2}A″ PESs. [13] Based on these surfaces, the followed work focused on the classical dynamics studies and rovibrational spectral of the linear triatomic molecules CNO. [14] However, the above ^{2}A′ and

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^{2}A″ potential energy surface was much too attractive for non-linear approaches of C to NO as pointed by Nyman and coworkers, which result in the overestimate the rate coefficient at room temperatures and were not good enough to describe the long-range interaction. To get more accurate rate coefficient and better simulate the results of the crossed molecular beam experiment, Nyman and coworkers improved and reconstructed the ^{2}A′ and ^{2}A″ PESs. [15-16] Thermal rate coefficients for formation of CN+O and CO+N in the temperature range from 200 K to 4500 K have been obtained using quasiclassical trajectory calculations and agreed excellent with experiment based on the new surface. [17-18] Very recently, Nyman and coworkers built a new ^{4}A″ PES for this reaction to explain the direct formation of ground state N atom in the crossed molecular beam experiment. [19] The inclusion of the ^{4}A″ surface in the QCT calculations gave more excellent agreement with experiments. In 2012, the thermal rate constants for reaction have been recalculated in ^{2}A′, ^{2}A″ and ^{4}A″ electronic states by using the adiabatic capture centrifugal sudden approximation and QCT method [20].

For fully understanding the dynamics of the title reaction, it is important to study not only its scalar properties as mentioned above, but also to study its vector properties such as relative velocities of reagent and product and the product rotational angular momentum etc. The vector properties of chemical reaction can provide the valuable information about chemical reaction stereodynamics. Ma and coworkers have carried out stereodynamics study for C+NO reaction at 0.06 eV based on the ^{2}A′ and ^{2}A″ PESs. [21-22] Very recently, we have carried out the QCT calculation to study the rotational excitation effect on the stereodynamics of this reaction on the new ^{4}A″ PES for comparison with the work of Ma and coworkers. [23-24] In the present paper, we applied the QCT method to study the vibrational excitation influence on the stereodynamics of the title reaction on ^{4}A″ PES.

2   Theory

The present calculations were performed by applying a standard QCT-stereodynamics procedure which has been successfully used to study a great deal of collision reactions. The center-of-mass (c.m.) frame is utilized in our calculations. The z-axis is parallel to the reagent relative velocity vector k, while the xz-plane (also called the scattering plane) contains k and k' with k' on the x $\geq$ 0 half plane. The y-axis is perpendicular to the scattering plane, θ_r is the angle between k and j', ϕ_r is the dihedral angle between the scattering plane and the plane containing k and j', θ_t is the angle between k and k'. In the c.m. frame, the product rotational polarization can be depicted through angular distributions $P(\theta_r)$, $P(\phi_r)$ and polarization-dependent generalized differential cross sections (PDDCSs). The product rotational polarization for the title reactions is investigated, using the stereo-QCT procedure which was developed by Han *et al.* [25-27]. Each reaction runs 100 000 trajectories and the integration step size is set as 0.1 fs to guarantee the conservation of total angular momentum and total energy. The calculations of the product