

Density functional theory study of the catalytic reaction of N_2O ($^1\Sigma$) with CO ($^1\Sigma^+$) by Ni^+

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Abstract. The mechanism of the cyclic reaction $\text{CO}(\text{C}_{\infty v}, ^1\Sigma^+) + \text{N}_2\text{O}(\text{C}_{\infty v}, ^1\Sigma^+) \rightarrow \text{N}_2(\text{D}_{\infty h}, ^1\Sigma_g^+) + \text{CO}_2(\text{D}_{\infty h}, ^1\Sigma_g^+)$ catalyzed by Ni^+ has been investigated on both double and quartet potential energy surfaces (PESs). The reactions were studied by the UB3LYP density functional theory. The calculated results of different spin PES show that the reaction proceeds in a two-step manner and spin crossing between different PES occurs. The involved crossing between the PES has been discussed by means of the intrinsic reaction coordinate approach used by Yoshizawa *et al.*, and the crossing points were located. Furthermore, the spin-orbit coupling (SOC) is calculated between electronic states of different multiplicities at the crossing points to estimate the inter-system crossing probabilities.

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Key words: density functional theory, crossing point, molecule orbital(MO), natural bond orbital (NBO), spin-orbit coupling (SOC)

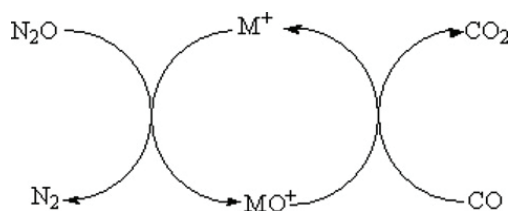
1 Introduction

It is generally known that the nitrous oxide impact is even more negative than CO_2 and methane effects toward the environment. N_2O is so steady to reach the troposphere, where it is responsible for the depletion of the ozone layer. Carbon monoxide is a significant toxic gas. How to reduce the environmental pollution resulted from N_2O and CO , which has been a hot subject for many experiments and theoretical calculations. Recently,

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the catalytic reactions mechanism of CO with N₂O by Fe⁺, Co⁺ and Mn⁺ were systematically investigated on potential energy surface using the quantum chemistry density functional theory [1-4]. Their research showed one oxygen atom of N₂O was directly extracted by metal ions to formate metal oxide ion. There does not exist NO insertion in all reaction process. The reactions of N₂O with Ge⁺ and Se⁺ were direct extracted oxygen mechanism using B3LYP/SDD+6-311+G(d) method by Chiodo *et al.* Additionally, the catalytic reactions mechanism of N₂O with CO by Pt⁺ and CO with NO₂ by Sc⁺ were studied using density functional method by Wang *et al.* [5-6]. Spin forbidden is an important factor to influence the reaction rate in gas phase reaction [7]. Many metal ions catalytic effect are not ideal because there is crossing and spin forbidden in different potential energy surfaces in their reactions. The reactions of Ti⁺ (²F and ⁴F) with N₂O and Cu⁺ (¹S and ⁴D) with N₂O were investigated by Lv *et al.*[8] and Delabie *et al.*[9], respectively. They confirmed crossing phenomenon was existed in the export of reactions between potential energy surface. Experimental measurements are carried out by using an inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer, which tests the efficiency of many atomic cations to catalyze the activation of nitrous oxide by carbon monoxide [10-12].

While the experimental procedure and the rate coefficients for this kind of O-atom transport reactions are there for all to see, few theoretical researches were performed to compute the potential energy landscapes for the catalytic cycle, illustrated in the Scheme as follows:



So far, 26 atomic cations were experimentally checked for their catalytic performance, but only ten activate nitrous oxide at room temperature[10]. Therefore, the theoretical study of the potential energy surface (PES) is the only tool to understand the reason of the catalytic efficiency about different cations. In our work, we considered the performance of Ni⁺, which gives rise to a very slow reaction and it is insufficient information available about the energy profile for reaction to provide an explanation for its low O-atom transfer reactivity. Ni⁺ reacts sufficiently quickly with N₂O to establish large enough concentrations of NiO⁺ to obtain meaningful results for its reaction under experimental conditions with $k = 6.5 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, but for the NiO⁺ with CO the measured shown the rate coefficient could not be measured because NiO⁺ could not be established in sufficient amounts[10].

In this paper we will report the detailed mechanisms of the reactions Ni/N₂O/CO by using density functional theory. Calculated results are expected to calibrate experimental