INTRODUCTION

As a long-lived greenhouse gas, carbon dioxide is the main contributor to global warming. Nowadays, it has become one of the most challenging subjects to remove this gas from industrial emission and to recycle it. As it is very difficult to reduce significantly CO₂ emissions from anthropic sources, in the past many years, considerable attention has been paid to convert this species into more useful chemical materials, such as fine chemicals and clean fuels due to its abundance and renewability. But new ways must be found to activate this molecule if its potential has to be realized. Activation is one of the effective routes to induce inert molecules to react. In previous years, many types of metal and metal oxide were used as catalysts to activate CO₂, and much interest has been focused on the experimental and theoretical studies of transition metal–CO₂ complexes [1–40], as such complexes have potential for practical application in activating CO₂.

Sievers et al. [11] have examined the reaction of Zr⁺ with CO₂, where metal–oxygen bond energies were determined. In this reaction, ZrO⁺ is found to be the dominant product at the low energy condition. Based on their experiment, Tommaso et al. [2] investigated the gas-phase carbon dioxide activation by Zr⁺ cation at the density functional level of theory recently. They brought out that the CO₂ activation mediated by Zr⁺ cation is an exothermic spin-forbidden process resulting from a crossing between quartet and doublet energetic profiles, but they didn’t locate the exact region of curve-crossing which may dramatically affect the reaction energetic. Qin et al. [17, 18] reported an IR study on the reaction of laser-ablated Zr atom with CO₂, they also carried out a DFT calculation on the Zr–CO₂ complex. From the experiment, they found the interaction of ground state Zr atom with CO₂ leads eventually to the insertion product OZrCO and this process is barrierless. But detailed information for the potential energy surface of reaction Zr + CO₂ is still scarce. Can a similar reaction mechanism be applicable to the reactions of Zr⁺ cation and Zr atom with CO₂? What are the different behaviors between them? Promoted by these questions, we investigated the reactions of Zr⁺ cation and Zr atom with CO₂ by using DFT methods in detail in order to shed some light on these reactions. A comparative theoretical study on the reactions of Zr⁺ cation and Zr atom with CO₂ is interesting and important since Zr is a representative of the second-row early transition metals.

COMPUTATIONAL METHODS

The doublet and quartet PESs for the reaction Zr⁺ + CO₂ and the quintet, triplet PESs for the reaction Zr + CO₂ have been considered in detail. We optimized all molecular geometries by employing the B3LYP density functional theory method [41, 42]. The spin-unrestricted version of this methodology was used for the calculations of different PESs. These methods are chosen in this study since the previous calibration calculations on transition-metal compounds have shown that this hybrid functional provides accurate results for the geometries and vibrational frequencies of systems containing transition-metal ions [43, 44]. In all of our calculations, the 6–311 + G(2d) basis set was used for the carbon and

1 The article is published in the original.
oxygen atoms, and the effective core potentials (ECP) of Stuttgart [45] basis set was used for the zirconium, the 5s and 4d in zirconium were treated explicitly by a (8s7p6d) Gaussian basis set contracted to [6s5p3d]. The harmonic vibration analyses were performed at the same level of theory for all optimized stationary points to determine their characters (minimum or first-order saddle point) and to evaluate the zero-point vibrational energies (ZPEs). To verify whether the located transition states connect the expected minima, intrinsic reaction coordinate (IRC) calculations were carried out for each transition state at the same level [46]. All calculations in the present study were performed using the Gaussian 03 program [47].

RESULTS AND DISCUSSION

In order to evaluate the computational accuracy, before the discussion on the mechanisms of the titled reactions, we first calculated the bond dissociation energies (BDE) for several species involved in the reactions. As shown in Table 1, where some available experimental values are also listed for comparison, most of the theoretical values are in agreement well with experimental findings. In addition, in the present work, our main goals are to examine the detailed mechanism of the reaction and obtain the relative energy level of the species involved, so the theoretical level chosen in this work is reliable for describing the features of the PESs of titled reactions. The optimized geometries of the stationary points for the reactions of Zr+ and Zr with CO2 are depicted in Figs. 1a and 1b respectively. The profiles of the PESs are shown in Fig. 2. The relevant energies of various compounds in the reactions are listed in Tables 2 and 3, and the potential energies curve-crossing diagrams between the different potential energy surfaces are drawn in Fig. 3.

The Reaction between Zr+ Cation and CO2

First, we will discuss the quartet PES. The reaction starts with the formation of a linear encounter complex 4IM1(4\Sigma, C∞v), which is 19.14 kcal/mol below the