INTRODUCTION

Carbon dioxide is an important molecule in both the Earth’s atmosphere as one of the main greenhouse gases and interstellar media. Ultraviolet (UV) photodissociation of carbon dioxide is of considerable importance for atmospheric, planetary, and interstellar chemistry and has received much attention of the experimentalists. For example, CO2 photodissociation at 157 nm which involves state-to-state correlations between CO (1Σg+ ν) and O (3P) has been studied up to now [1–6]. Moreover, the reaction of CO (1Σg+ ν) with the electronic ground state oxygen atom O (3P) has also been studied with experimental [7–14] and theoretical methods [15, 16] so far. However, a full understanding of these two questions is hampered by the complex nature of its electronically excited states.

It was suggested that the mechanism of the recombination of an oxygen atom with a carbon monoxide molecule may occur through the 3B2 state crossing the 1B2 state [12, 17]:

\[ \text{CO}(X^\Sigma_g^+, \nu) + \text{O}(^3\text{P}) \rightarrow \text{CO}_2(^3\text{B}_2) \rightarrow \text{CO}_2(^1\text{B}_2) \rightarrow \text{CO}(X^\Sigma_g^+, \nu = 0) + \text{O}(^1\text{D}). \]

Simkin et al. [16] calculated the potential energy surfaces (PESs) of the ground state (1Σg+) and excited electronic states (^3B2, ^1B2) of the carbon dioxide molecule in order to make clear the recombination of an oxygen atom and a carbon monoxide molecule to give CO2. Their calculations indicated that no crossing point was found between ^1B2 and ^3B2 states. However, in Abe et al. work [11], they pointed that the seam between the ^1B2 and ^3A2 state surfaces ranges from 100° to 130°, R_{CO} = 1.2–1.5 Å for the bond length of the new CO bond; and in Spielfiedel et al. paper [18], there is a crossing point between ^1B2 and ^3B2 state when R_{CO} = 2.35 bohr and 90° < α_{OCO} < 100°.

Thus, whether the ^1B2 state crosses with the ^3B2 state is still not very clear. Sufficient calculation for the ground and excited states PESs of CO2 is necessary for understanding the mechanism. In the present paper ab initio PESs for the ground state (1Σg+) and excited electronic states (^3B2, ^1B2) of the carbon dioxide molecule were described by us.

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The three-dimensional potential energy surfaces for the electronic ground state 1\(\alpha\)\(^1\)A\(^1\)(\(1\)A\(_1\)), the first excited single state 2\(^1\)A\(^1\)(\(1\)B\(_2\)) as well as the lowest triplet state 1\(\alpha\)\(^3\)B\(^2\)(\(3\)B\(_2\)) of CO\(_2\) have been computed using complete active space self-consistent field (CASSCF) method and second order multiconfigurational perturbation theory (CASPT2). The grid for the ab initio calculation of the three potential energy surfaces has been varied from 1.8 to 4.0 bohr. The grid spacing is 0.2 bohr. The calculations have been repeated for thirteen bond angles, extending from 60° to 180° with a step size of 10°. For the three-dimensional global energy-surface computations, a reasonable compromise between accuracy and computational cost has to be found. For the present investigation, aug–cc–pvtz basis set was chosen. The multiconfiguration self-consistent field wave functions consist of a complete configuration expansion for 16 electrons distributed in the 12 active valence orbitals. The 1s orbitals for the oxygen and carbon atoms were kept doubly occupied but fully optimized during the CASSCF procedure. Two \(\sigma\) orbitals and one \(\pi^*\) orbital (obtained by combining the 1s orbitals for the oxygen and carbon atoms respectively) were kept doubly occupied but fully optimized during the CASSCF procedure.

The selected active space comprises of 16 electrons in 12 orbitals, which includes two \(\sigma\) orbitals, four \(\sigma^*\) orbitals, two \(\pi\) orbitals, two \(\pi^*\) orbital and two oxygen nonbonding orbitals. The C\(_2\) point group was employed for the PESs calculations at the different geometries. The resulting numbers of configuration state functions (CSFs) in C\(_2\) symmetry are 35793 and 56592, respectively in \(1\)A\(^1\) and \(3\)A\(^1\) representations. The reference wave functions for \(1\)A\(^1\) and \(2\)A\(^1\) states have been optimized together in a state-averaged procedure with equal weights for both states. The reference wave functions for \(1\)A\(^2\) and \(2\)A\(^2\) states also have been optimized together in a state-averaged procedure with equal weights for both states. The deep core orbitals are not involved in the perturbation calculation when CASPT2 level is used. In order to obtain continuous potential energy functions, level shift 0.3 is used for the three surfaces.

### Computational Details

The selected active space comprises of 16 electrons in 12 orbitals, which includes two \(\sigma\) orbitals, four \(\sigma^*\) orbitals, two \(\pi\) orbitals, two \(\pi^*\) orbital and two oxygen nonbonding orbitals. The C\(_2\) point group was employed for the PESs calculations at the different geometries. The resulting numbers of configuration state functions (CSFs) in C\(_2\) symmetry are 35793 and 56592, respectively in \(1\)A\(^1\) and \(3\)A\(^1\) representations. The reference wave functions for \(1\)A\(^1\) and \(2\)A\(^1\) states have been optimized together in a state-averaged procedure with equal weights for both states. The reference wave functions for \(1\)A\(^2\) and \(2\)A\(^2\) states also have been optimized together in a state-averaged procedure with equal weights for both states. The deep core orbitals are not involved in the perturbation calculation when CASPT2 level is used. In order to obtain continuous potential energy functions, level shift 0.3 is used for the three surfaces.

The equilibrium geometries of \(1\)A\(_1\), \(1\)A\(_2\), \(1\)B\(_2\), \(3\)A\(_2\), and \(3\)B\(_2\) states and crossing point between \(1\)B\(_2\) state and \(3\)A\(_2\) state have been optimized by CASSCF (16e/12o) method, and single-point energies were calculated at the CASPT2 level of theory based on CASSCF wave function to consider the dynamical correlation effects. When calculated the adiabatic excitation energy, IPEA shift = 0.8 was used to reduce the systematic error which leads to a relative overestimation of the correlation energy for open shell system. Frequency calculations were performed at the same theory level as the optimizations to obtain zero-point vibration energies (ZPVE) and to confirm the nature of the stationary points.

One-dimensional full valence CASSCF and CASPT2 potential energy sections for the \(3\)B\(_2\), \(3\)A\(_2\), \(1\)A\(_2\), and \(1\)B\(_2\) states along the bending coordinate \(\alpha\)\(_{OCO}\) from 90° to 150° with \(R\)\(_{CO}\) = 2.35 bohr were calculated with C\(_2\)\(_\infty\) symmetry. This part of calculation was performed with aug–cc–pvtz and aug–cc–pvdz basis set, respectively. All the calculations above were performed with Molcas 6.4 quantum chemistry software [19].

### RESULTS AND DISCUSSIONS

#### Equilibrium Geometries, Adiabatic Excitation Energy, Dissociation Limits

The minimum-energies configurations of the \(1\)A\(_1\), \(3\)B\(_2\), \(3\)A\(_2\), \(1\)A\(_2\), and \(1\)B\(_2\) states optimized at the CASSCF level is the same as the geometries optimized at the CASPT2 level (see Table 1). Thus, the geometries were optimized at CASSCF(16e/12o)/aug–cc–pvtz level of theory, and the final energies were evaluated with CASPT2 method at this part of calculation. The ground state of CO\(_2\) (\(1\)A\(_1\)) adopts well-known D\(_{\text{oh}}\) symmetry, where the C–O bond is 1.166 Å and O–C–O angle is 180°. This is in agreement with the experiment value of 1.161 Å [20]. The ordering of the lowest valence excited states of CO\(_2\) has been calculated to be \(3\)B\(_2\), \(3\)A\(_2\), \(1\)A\(_2\), followed by \(1\)B\(_2\), and all these states have bent equilibrium structures. The \(1\)B\(_2\) and \(1\)A\(_2\) states differ in their equilibrium angles (118° and 127°, respectively), and have much longer equilibrium dis-