

## DFT Study on the Gas Phase Reactions of Pt<sup>+</sup> and Pt with CO<sub>2</sub>

CHUAN-FENG WANG and GUO-LIANG DAI\*

School of Pharmaceutical and Chemical Engineering, Taizhou University, Linhai 317000, P.R. China

\*Corresponding author: E-mail: daigl@tzc.edu.cn

(Received: 24 May 2012;

Accepted: 6 March 2013)

AJC-13071

In order to better understanding the mechanism of third-row metal reacting with CO<sub>2</sub>, the reactions of Pt<sup>+</sup> cation and Pt atom with CO<sub>2</sub> have been investigated at B3LYP level of theory. The minimum energy reaction path is found to involve the spin inversion in the different reaction steps. This potential energy curve-crossing dramatically affects reaction exothermic. The present results show that the reaction mechanism is insertion-elimination mechanism along the C-O bond activation branch. All theoretical results not only support the existing conclusions inferred from early experiment, but also complement the pathway and mechanism for this reaction.

**Key Words:** Density functional theory, Carbon dioxide, Platinum, Reaction mechanism.

### INTRODUCTION

Carbon dioxide is a main contributor to global warming. To remove this long-lived greenhouse gas from industrial emission and to recycle it have become one of the most challenging subjects nowadays<sup>1</sup>. As it is difficult to reduce significantly CO<sub>2</sub> emissions from anthropic sources, in the past many years, considerable attention has been paid to convert this species into more useful chemical materials due to its abundance and renewability. But new ways must be found to activate the 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 CO<sub>2</sub> and much interest has been focused on the experimental and theoretical studies of transition metal-CO<sub>2</sub> complexes<sup>2-40</sup>, as such complexes have potential for practical application in activating CO<sub>2</sub>.

Zhang and Armentrout<sup>40</sup> have examined the reaction of Pt<sup>+</sup> with CO<sub>2</sub>, the metal-oxygen bond energies were determined in their experiment. In this reaction, PtO<sup>+</sup> is found to be the dominant product. Based on the experiment, they also investigated the gas-phase carbon dioxide activation by Pt<sup>+</sup> cation at the density functional level of theory and brought out that the CO<sub>2</sub> activation mediated by Pt<sup>+</sup> cation is an spin-forbidden process which resulted from a crossing between different energetic profiles. But they didn't locate the exact region of curve-crossing which may dramatically affect reaction mechanism. To the best of our knowledge, the detailed information for the reaction of Pt atom with CO<sub>2</sub> is still scarce. Can a similar reaction mechanism be applicable to the reactions of Pt<sup>+</sup> cation

and Pt atom with CO<sub>2</sub>? What are the different behaviours between them? Promoted by these questions, we investigated the reactions of Pt<sup>+</sup> cation and Pt atom with CO<sub>2</sub> by using DFT methods in order to shed some light on these reactions. A comparative theoretical study on the reactions of Pt<sup>+</sup> cation and Pt atom with CO<sub>2</sub> is interesting and important since platinum is a representative of the third-row transition metal.

### COMPUTATIONAL METHOD

The doublet, quartet potential energy surfaces for the reaction of Pt<sup>+</sup> + CO<sub>2</sub> and the triplet and singlet potential energy surfaces for the reaction of Pt + CO<sub>2</sub> have been considered in detail. We optimized all molecular geometries (reactants, intermediates, transition states and products) by employing the B3LYP density functional theory method<sup>41,42</sup>. The spin-unrestricted version of this methodology was used for the calculations of doublet, triplet and quartet potential energy surfaces. As for the singlet potential energy surface, we used the RB3LYP density functional theory method. 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<sup>43,44</sup>. In all of our calculations, the 6-311+G(2d) basis set was used for the carbon and oxygen atoms and the effective core potentials (ECP) of Stuttgart basis<sup>45</sup> set was used for the platinum, the 6s and 5d in Pt were treated explicitly by a (8s 7p 6d) Gaussian basis set contracted to [6s 5p 3d]. 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<sup>46</sup>. All calculations in the present study were performed using the Gaussian 03 program<sup>47</sup>.

## RESULTS AND DISCUSSION

The optimized geometries of the stationary points for the reactions of Pt<sup>+</sup> cation and Pt atom with CO<sub>2</sub> are depicted in Fig. 1. The profiles of the potential energy surfaces are shown in Fig. 2. The potential energies curve-crossing diagrams between the different potential energy surfaces are drawn in Fig. 3.

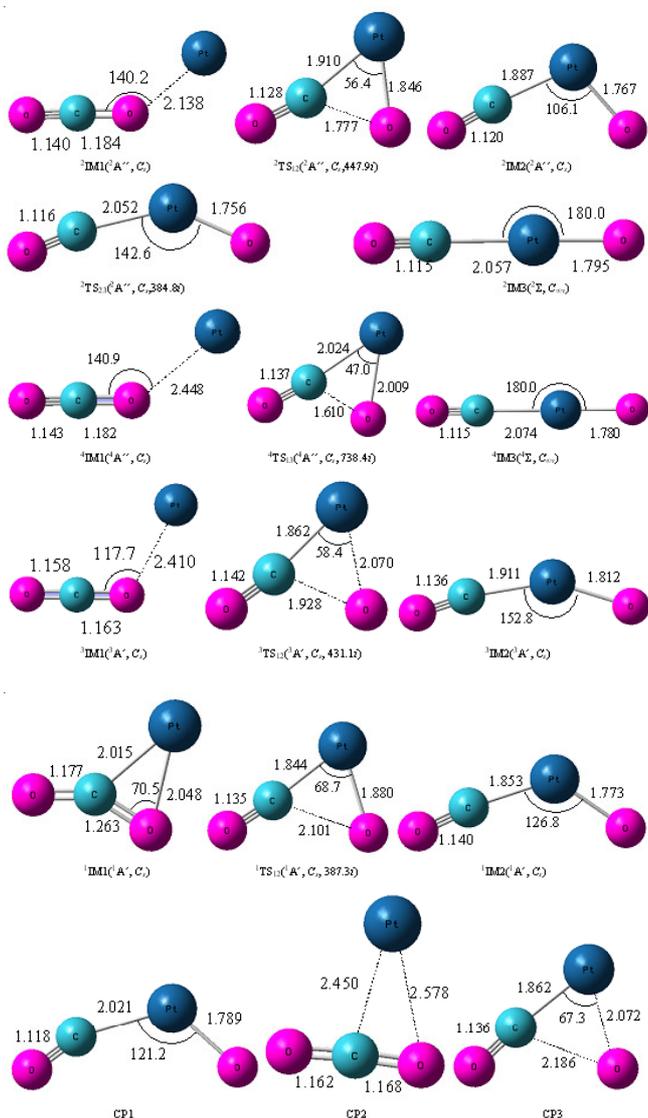


Fig. 1. Optimized geometries for the various stationary points and crossing points located on the Pt<sup>+</sup> cation and Pt atom with CO<sub>2</sub> potential energy surfaces [distances in angstroms, angles in degrees]

**Reaction between Pt<sup>+</sup> and CO<sub>2</sub>:** If CO<sub>2</sub> approaches the ground state <sup>2</sup>Pt<sup>+</sup> cation *via* its oxygen side, an encounter complex denoted as <sup>2</sup>IM1 is formed, 109.1 kJ/mol more stable than the reactants. It should be pointed out that although numerous trials are taken to search for possible transition states

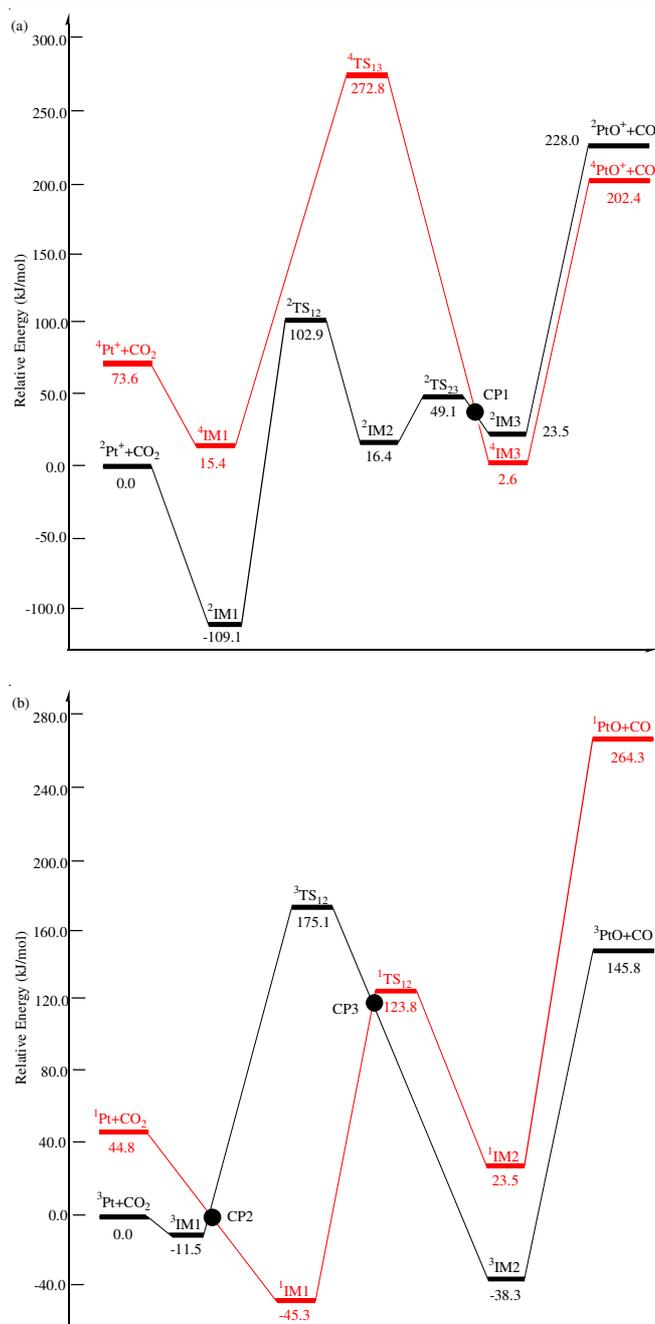
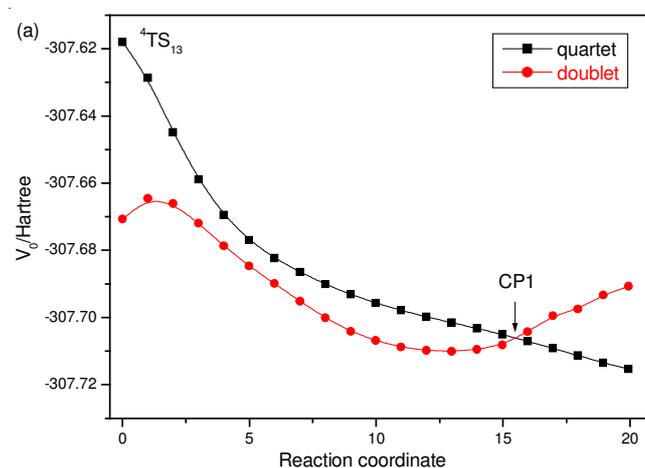


Fig. 2. Potential energy surface profiles for the reaction of (a) Pt<sup>+</sup> cation with CO<sub>2</sub>; (b) Pt atom with CO<sub>2</sub>



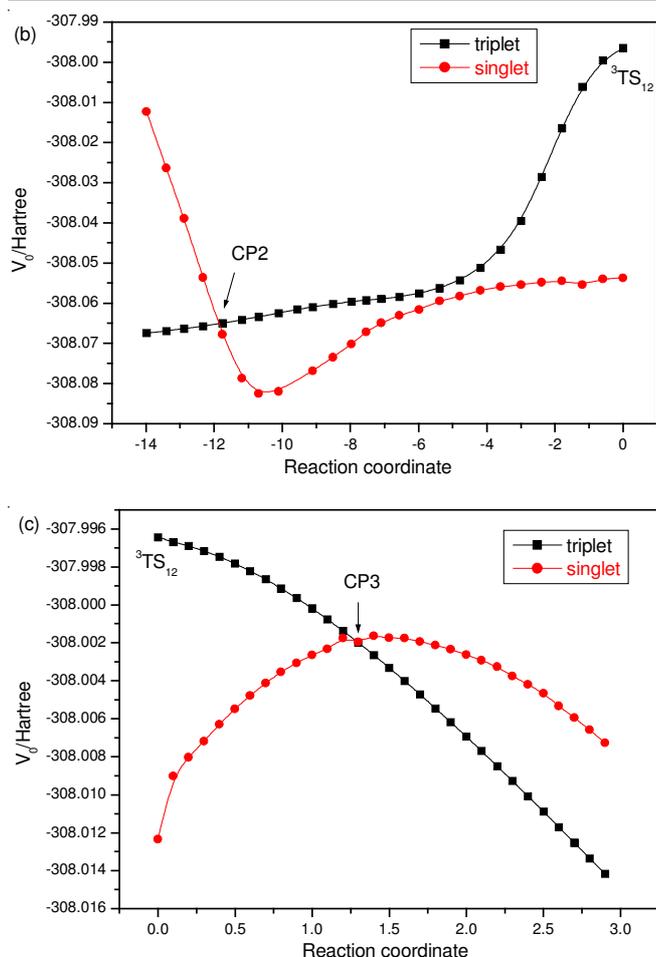


Fig. 3. (a) Potential energies from  ${}^2\text{TS}_{23}$  to  ${}^4\text{IM}3$  along the quartet IRC; (b) potential energies from  ${}^3\text{IM}1$  to  ${}^1\text{IM}1$  along the triplet IRC; (c) potential energies from  ${}^1\text{TS}_{12}$  to  ${}^3\text{IM}2$  along the triplet IRC

that connect reactants and original complex, no such structures are obtained. For example, in case of the formation of this linear encounter complex  ${}^2\text{IM}1$ , for a given Pt-O bond length, all other geometrical degrees of freedom are optimized, as Pt approaches the oxygen atom, the energy of the complex decreases monotonically until formation of the encounter complex  ${}^2\text{IM}1$ . Clearly, the formation of  ${}^2\text{IM}1$  is spontaneous and it is a barrier free process. Starting from the complex  ${}^2\text{IM}1$ , the next step in the reaction mechanism is the insertion of the Pt<sup>+</sup> cation into the C-O bond generating  ${}^2\text{IM}2$ . This step is endothermic by 125.5 kJ/mol and requires an high energy barrier of 212.0 kJ/mol. These results show that it is much difficult for ground state Pt<sup>+</sup> cation to cleave the C-O bond in CO<sub>2</sub>. Further transformation of the  ${}^3\text{IM}2$  complex to a linear complex  ${}^2\text{IM}3$  ( ${}^2\Sigma$ ,  $C_{\infty v}$ ) goes through the transition state called  ${}^2\text{TS}_{23}$  with an energy barrier of 32.7 kJ/mol. In  ${}^2\text{IM}3$ , the OPt-CO binding energy is 204.5 kJ/mol which can be basically attributed to the Pt-C bond arising from a strong Pt→CO  $\pi$ -back-donation. This species can be considered as a bound complex between  ${}^2\text{PtO}^+$  and CO, the dissociation of the insertion product  ${}^2\text{IM}3$  into  $2\text{PtO}^+ + \text{CO}$  requires 204.5 kJ/mol energy at the UB3LYP levels.

With respect to the quartet state pathway, the first step of the reaction over this potential energy surface starts with the formation of an initial complex  ${}^4\text{IM}1$  ( $4A''$ ,  $C_s$ ), 58.2 kJ/mol

more stable than the reactants  ${}^4\text{Pt}^+ + \text{CO}_2$ . Similar with the reaction over the doublet potential energy surface, the next step corresponds to the activation of C-O bond. Starting from  ${}^4\text{IM}1$ , it can rearrange to form  ${}^4\text{IM}3$ , which undergoes a rupture of C-O bond *via* a transition state  ${}^4\text{TS}_{13}$  that is 257.4 kJ/mol above  ${}^4\text{IM}1$ . As shown in Fig. 1, the distance between Pt and O in  ${}^4\text{TS}_{13}$  is shortened from 2.448-2.009 Å. This fact indicates that the weak electrostatic interaction between Pt<sup>+</sup> and CO<sub>2</sub> strengthens when it is converted into  ${}^4\text{TS}_{13}$  and the Pt-O bond is nearly formed. At the same time, the activated C-O bond is almost broken and the bond length is elongated by 0.428 Å. The imaginary frequency of  ${}^4\text{TS}_{13}$  is 738.4i cm<sup>-1</sup> and the normal mode corresponds to the rupture of C-O bond with the result of Pt<sup>+</sup> cation insertion into C-O bond. Similar with the intermediate  ${}^2\text{IM}3$ , The Pt-C bond rupture can form  ${}^4\text{PtO}^+ + \text{CO}$ , which is calculated to be endothermic by 199.8 kJ/mol. The whole reaction  ${}^4\text{Pt}^+ + \text{CO}_2 \rightarrow {}^4\text{PtO}^+ + \text{CO}$  is calculated to be endothermic by 128.8 kJ/mol. It should be pointed out that we have tried to locate the insertion species similar with  ${}^2\text{IM}2$  over quartet potential energy surface, but all our attempts failed. So, different from doublet state, this insertion complex does not exist over quartet potential energy surface.

From the previous experiment<sup>40</sup>, one can see that the dominant product of the reaction Pt<sup>+</sup> toward CO<sub>2</sub> is PtO<sup>+</sup> and the product PtO<sup>+</sup> is predicted to has ground state  ${}^4\Sigma$  from the above discussion. Based on the B3LYP calculations, Zhang and Armentrout<sup>40</sup> indicate the  ${}^4\Sigma$  state of PtO<sup>+</sup> is lower in energy than that of the  ${}^2\Sigma$  about 26.1 kJ/mol. Obviously, the reaction between ground state Pt<sup>+</sup> (2D) cation and CO<sub>2</sub> to generate PtO<sup>+</sup> is spin-forbidden and has to go through intersystem crossing. From the calculation based on the B3LYP level, we can acquire the following information: (1) The ground state  ${}^2\text{Pt}^+$  is calculated to be 73.6 kJ/mol more stable than excited state  ${}^4\text{Pt}^+$ ; (2) The initial complex  ${}^2\text{IM}1$  is more stable than  ${}^4\text{IM}1$  by 124.5 kJ/mol; (3) the insertion species  ${}^2\text{IM}3$  is less stable than  ${}^4\text{IM}3$  by 20.9 kJ/mol; (4) the products  ${}^2\text{PtO}^+ + \text{CO}$  are less stable than  ${}^4\text{PtO}^+ + \text{CO}$  by 25.6 kJ/mol. All these facts suggest that the formation of the PtO<sup>+</sup> ( ${}^2\Sigma$ ) + CO ( ${}^1\Sigma$ ) products involves a change of spin and must therefore proceed through a crossing point of the different potential energy surfaces.

From the previous experiment<sup>40</sup> and our calculations above, we speculate that the intersystem crossing occur during the process of  ${}^2\text{IM}1 \rightarrow {}^4\text{IM}3$ . Our following calculation is aimed at determining the region where the spin inversion occur and acquiring the structure and energy informations of crossing point between the two different potential energy surfaces. We choose a simple approach suggested by Yoshizawa *et al.*<sup>48</sup> for approximately locating the crossing points of two potential energy surfaces of different multiplicities. The main idea of this approach is to perform a series of single-point computations of one spin state along the intrinsic reaction coordinate of the other spin state. Using this method, we computed potential energy profile of the doublet state along the quartet intrinsic reaction coordinate. In Fig. 3(a), one can see that a crossing point CP1 (between doublet and quartet potential energy surface) is after  ${}^2\text{TS}_{23}$ . As can be seen from Fig. 3(a), after passing point CP1, the quartet potential energy surface can provide a low-energy reaction pathway until the formation of  ${}^4\text{IM}3$ . To conclude, the minimum energy pathway may proceed

as  ${}^2\text{Pt}^+ + \text{CO}_2 \rightarrow {}^2\text{IM1} \rightarrow {}^2\text{TS}_{12} \rightarrow {}^2\text{IM2} \rightarrow {}^2\text{TS}_{23} \rightarrow \text{CP1} \rightarrow {}^4\text{IM}_3 \rightarrow {}^4\text{PtO}^+ + \text{CO}$ , which is calculated to be endothermic by 202.4 kJ/mol.

Actually, the reactions catalyzed by metallic systems may often involve a change in the spin states and proceed *via* a non-adiabatic way on two or more potential energy surfaces, denoted as "two state reactivity" (TSR)<sup>49-52</sup>, which has been confirmed by experimental studies. In previous theoretical researches about  $\text{CO}_2$  activation by  $\text{Nb}^+$  and  $\text{Zr}^+$  cations, Toscano *et al.*<sup>2,3</sup> have ascertained the presence of some spin inversion during the reaction process,  $\text{CO}_2$  activation mediated by metal cations was found to be an exothermic spin-forbidden process which resulted from a crossing between different energetic profiles.

**Reaction between Pt atom and  $\text{CO}_2$ :** As for the triplet potential energy surface, the reaction starts with the formation of an encounter complex  ${}^3\text{IM1}$  ( ${}^3\text{A}'$ ,  $\text{C}_s$ ), which is 11.5 kJ/mol below the entrance channel  ${}^3\text{Pt} + \text{CO}_2$ . Subsequently, this encounter species proceeds to form the insertion complex  ${}^3\text{IM2}$  through the transition state  ${}^3\text{TS}_{12}$ . This insertion process is exothermic by 26.8 kJ/mol with a high barrier of 186.6 kJ/mol. This result shows that it is much different for ground state  ${}^3\text{Pt}$  atom to cleave the C-O bond in  $\text{CO}_2$ . As shown in Fig. 1, the Pt-O distance in  ${}^3\text{TS}_{12}$  is shortened from 2.410 to 2.070 Å and the Pt-C bond is shortened to 1.862 Å. These facts indicate that the weak electrostatic interaction between Pt and  $\text{CO}_2$  has strengthened when it converts into  ${}^3\text{TS}_{12}$ . Synchronously, the C-O bond breaks gradually, the bond length is increased by 0.765 Å.  ${}^3\text{TS}_{12}$  has a three-member-ring structure with  $\text{C}_s$  symmetry. The imaginary frequency is 431.1i  $\text{cm}^{-1}$  and the normal model corresponds to the rupture of C-O bond and the formation of Pt-O and Pt-C bonds.

As shown in Fig. 1,  ${}^3\text{IM2}$  ( ${}^3\text{A}'$ ,  $\text{C}_s$ ) is an insertion species of Pt atom into the C-O bond. NBO calculation shows that in  ${}^3\text{IM2}$  two single bonds have formed between Pt and O, Pt and C atoms, respectively. The NBO charge on the Pt atom increases to *ca.* +0.536e, whereas the atomic charge on carbon atom decreases to 0.245e (it is 0.997e in free  $\text{CO}_2$ ). The OPt-CO binding energy is 184.1 kJ/mol which can be basically attributed to the Pt-C bond arising from a  $\text{CO} \rightarrow \text{Pt}$   $\sigma$ -donation and a simultaneous  $\text{Pt} \rightarrow \text{CO}$   $\pi$ -back-donation. The next step is the nonreactive-dissociation of  ${}^3\text{IM2}$  to generate products. After calculation, we found the insertion species  ${}^3\text{IM2}$  can dissociate directly without exit barrier to products  ${}^3\text{PtO} + \text{CO}$ , endothermic by 184.1 kJ/mol. It is clear that the reaction mechanism of  ${}^3\text{Pt}$  with  $\text{CO}_2$  over triplet potential energy surface is the typical insertion-elimination mechanism.

With respect to the singlet state pathway, the first step of the reaction over this potential energy surface starts with the formation of a  $\eta^2$ -OC encounter complex  ${}^1\text{IM1}$  ( ${}^1\text{A}'$ ,  $\text{C}_s$ ), which is a barrierless process. The relative energy of  ${}^1\text{IM1}$  is calculated to be 33.8 kJ/mol lower than that of the triplet analogue,  ${}^3\text{IM1}$ . With reaction proceeding, this species may isomerize into an insertion complex through  ${}^1\text{TS}_{12}$ . This step is endothermic by 68.8 kJ/mol, with a barrier of 169.1 kJ/mol.  ${}^1\text{TS}_{12}$  has a three-member-ring structure with  $\text{C}_s$  symmetry. The distance between Pt and O is shortened to 1.880 Å and the C-O bond increased to 2.2101 Å simultaneously. The imaginary frequency of  ${}^1\text{TS}_{12}$  is 387.3i  $\text{cm}^{-1}$  and the normal model corres-

ponds to the breakage of C-O bond and the formations of Pt-O and Pt-C bonds. The rupture of Pt-C bond in  ${}^1\text{IM2}$  can form  ${}^3\text{PtO} + \text{CO}$  directly, which is calculated to be endothermic by 240.8 kJ/mol.

Similar with the C-O bond activation by  $\text{Pt}^+$  cation, the potential energy surface crossing behaviour occurs along the reaction between Pt atom and  $\text{CO}_2$  also. On the basis of the analysis of Fig. 2(b), several spin crossings can be found to be possible along the optimal reaction pathway of the C-O bond activation in  $\text{CO}_2$  by Pt atom. First, the reaction may start with the formation of an encounter complex  ${}^3\text{IM1}$  on the triplet potential energy surface. Then, the triplet surface could likely cross the singlet surface somewhere between the region from  ${}^3\text{IM1}$  to  ${}^3\text{TS}_{12}$ . After passing the crossing point, the reaction may jump to the singlet potential energy surface. With reaction proceeding, the reaction may jump to the triplet potential energy surface again since  ${}^3\text{IM2}$  is 61.8 kJ/mol below  ${}^1\text{IM2}$ , *i.e.*, the C-O bond activation complex  $\text{IM2}$  over the triplet potential energy surface is thermodynamically more favourable than the corresponding singlet species.

Fig. 3(b) gives the potential energy profiles of the singlet state from the complex  $\text{IM1}$  to  $\text{TS}_{12}$  along the triplet intrinsic reaction coordinate. Along the triplet intrinsic reaction coordinate we find a triplet-singlet crossing point CP2, which lies before  ${}^3\text{TS}_{12}$ . From Fig. 3(c), one can see that the singlet-triplet crossing point CP3 lies before  ${}^1\text{TS}_{12}$ . Thus, the reaction may jump from the singlet potential energy surface to the triplet one near the crossing point CP3 and this potential energy surface can provide a low-energy reaction pathway toward the dissociation products  ${}^3\text{PtO} + \text{CO}$ .

Totally, two spin states are involved in the whole reaction, specifically, the minimum energy pathway can be described as  ${}^3\text{Pt} + \text{CO}_2 \rightarrow {}^3\text{IM1} \rightarrow \text{CP2} \rightarrow {}^1\text{IM1} \rightarrow \text{CP3} \rightarrow {}^3\text{IM2} \rightarrow {}^3\text{PtO} + \text{CO}$ . The whole reaction is endothermic by 145.8 kJ/mol.

From the discussion above, we conjecture that the insertion reaction and 'two state reactivity' could be general mechanisms for the reactions of  $\text{Pt}^+$  cation and Pt atom with  $\text{CO}_2$ . Further, we have reported the theoretical studies on the reactions of  $\text{La}^+$  and La with  $\text{CO}_2$ <sup>25</sup>. The results indicate that different from that of platinum atom, the reaction between La atom and  $\text{CO}_2$  is most likely to proceed over doublet potential energy surface throughout the whole process. As for the reaction between cation and  $\text{CO}_2$ , the lowest energy path corresponds to the initial coordination of  $\text{CO}_2$  followed by the insertion of  $\text{La}^+$  or  $\text{Pt}^+$  into the C-O bond, the minimum energy reaction path requires the crossing of two adiabatic surfaces with different spin states. In addition, both the reactions between  $\text{La}^+$  cation and La atom with  $\text{CO}_2$  are energy spontaneously and greatly exothermic. As for the reactions between  $\text{Pt}^+$  cation and Pt atom with  $\text{CO}_2$ , both are greatly endothermic.

## Conclusion

Density functional calculations have been performed to investigate the reactions of  $\text{Pt}^+$  cation and Pt atom with  $\text{CO}_2$  in gas phase. The ground and excited potential energy surfaces of the titled reactions have been explored. The following conclusions can be drawn from the present calculations.

(1) The reactions of  $\text{Pt}^+$  cation and Pt atom toward  $\text{CO}_2$  proceed according to the insertion-elimination mechanism.

(2) For the reaction between Pt<sup>+</sup> cation and CO<sub>2</sub>, the minimum energy channel requires the crossing of different spin states. The reactions start with the formation of a doublet encounter complex, after passing one crossing point, the reaction systems move on the quartet potential energy surface toward the products <sup>4</sup>PtO<sup>+</sup> + CO.

(3) For the reaction between Pt atom and CO<sub>2</sub>, we found the reaction system would likely change its spin multiplicity twice in going from the entrance channel to the exit channel. Specifically, it can be described as <sup>3</sup>Pt + CO<sub>2</sub> → <sup>3</sup>IM1 → CP2 → <sup>1</sup>IM1 → CP3 → <sup>3</sup>IM2 → <sup>3</sup>PtO + CO.

### ACKNOWLEDGEMENTS

This work was supported by the Zhejiang Provincial Natural Science Foundation of China under grant No. Y4090387 and No. Y4100508.

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