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## CO<sub>2</sub> activation by Zr<sup>+</sup> and ZrO<sup>+</sup> in gas phase

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**Abstract** The gas-phase reduction of carbon dioxide to carbon monoxide, induced by Zr<sup>+</sup> and ZrO<sup>+</sup> catalysts, was investigated at density functional level of theory. Calculations were carried out using both hybrid and pure exchange-correlation functionals in order to reproduce adequately the energetic gap between the Zr<sup>+</sup> <sup>4</sup>F and <sup>2</sup>D electronic states and experimental reaction heats. In agreement with a guided ion beam tandem mass spectrometer study, we have found that carbon dioxide activation by Zr<sup>+</sup> presents a spin-forbidden mechanism because of a spin inversion process occurring during reaction in the rate-determining step. ZrO<sup>+</sup> interacts with CO<sub>2</sub> through two possible pathways both endothermic: formation of ZrO<sub>2</sub><sup>+</sup> and CO products is less unfavourable. Information about ground and excited states of ZrO<sup>+</sup> and ZrO<sub>2</sub><sup>+</sup> oxides and bond dissociation energies of species present on the reaction paths was also given.

**Keywords** Carbon dioxide activation · Zirconium ions · Electronic states · Density functional theory

### 1 Introduction

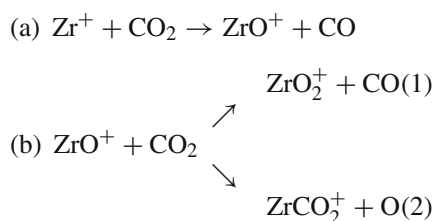
Continuous emission of carbon dioxide into the atmosphere represents the main cause of greenhouse effect because of the stratospheric ozone depletion. Since the first structural compounds containing CO<sub>2</sub> [1] were synthesized and characterized, many studies were performed to introduce new reaction mechanisms that allow the elimination of this gas in mild conditions [2–5]. However, till now, carbon dioxide chemistry is not developed much. CO<sub>2</sub> effective activation is still an unresolved problem because it is thermodynamically stable and kinetically inert. The possibility to convert

carbon dioxide into a non-dangerous species not only could limit the greenhouse environmental damages, but also constitutes a carbon source alternative to petroleum, natural gas and coal, that are all energetic resources destined to exhaust themselves. Besides, because of its large-scale availability at low cost, carbon dioxide could represent a precursor compound for the synthesis of useful chemical products, such as methanol, urea and salicylic acid. CO<sub>2</sub> natural mechanisms of activation have received much attention in recent years, through the simulation of photosynthesis processes and the study of metal-enzyme catalysed reaction paths on the model of carbonic anhydrase [6–8]. A great deal of experimental [9–15] and theoretical [16–20] works was based on the coordination of CO<sub>2</sub> to one or more metals. As far as the coordination modes are concerned, carbon dioxide gives rise to insertion mechanisms in bonds between a metal and elements such as H, O, N, P, Si, C, in intermetallic bonds and can interact with unsaturated substrates coordinated to transition metals.

To give insight into the thermodynamic and the work mechanisms of some zirconium compounds used as hydrogenation catalysts for CO and CO<sub>2</sub>, Sievers and Armentrout [21] studied the gas-phase reactions of Zr<sup>+</sup>, ZrO<sup>+</sup> and ZrO<sub>2</sub><sup>+</sup> cations with carbon mono- and dioxide. This investigation, performed at experimental level using the guided ion beam mass spectrometry, allowed to characterize all stable species involved in the reactions. Emphasis was put on the importance to consider the electronic states of the metal cation and its oxides. In fact, for some of these species, there is no information, either at experimental or at theoretical level, on both ground (i.e. for ZrO<sub>2</sub><sup>+</sup>) and excited states (i.e. for both ZrO<sup>+</sup> and ZrO<sub>2</sub><sup>+</sup>). Only speculative determinations of electronic excitation energies for two excited states of ZrO<sup>+</sup> were possible in this study. For several species involved in the examined reactions, these approximate assignments allowed an estimate of binding energies.

With the aim to corroborate the literature data on zirconium catalysts previously studied experimentally [21] and to check the utility of density functional theory in determining some missing information, we have retained interest in performing calculations on the following processes:

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Potential energy profiles, geometrical and electronic characterization of all stationary points on the energetic paths, heats of reaction and bond dissociation energy (BDE) values were objects of the present investigation.

## 2 Computational methods

All computations were performed using the Gaussian 03/DFT code [22].

Four different exchange-correlation functionals, namely B3LYP [23–25], B3LYP\* [26], BP86 [27, 28] and PBE1PBE [29], in connection with the 6-311++G\*\* basis set [30, 31] and LANL2DZ pseudo-potential [32–34] for non-metal and metal atoms, respectively, were used to carry out preliminary calculations addressed to the reproduction of the experimental heats of (a) and (b) reactions and of the energetic gap between ground and excited electronic states of Zr<sup>+</sup>.

On the basis of obtained results that we have reported in the Table 1, it was made the choice of the definitive protocol to be used for all next calculations.

The most reliable BP86/6-311++G\*\*/LANL2DZ protocol was then used for geometry optimizations and frequencies evaluation. Zero point energy (ZPE) corrections, derived from vibrational analysis, were included in all relative energy values.

Calculation type method STABLE [35, 36] that ensures wavefunction to be tested during optimization was used everywhere.

Lowest energy electronic state for all species was searched using the ALTER keyword.

## 3 Results and discussion

One of the problems inherent in density functional methods is the incorrect prediction of ground and excited states ordering and splitting for transition metals cationic species [37].

**Table 1** Heats ( $\Delta E$  in kcal/mol) of (a), (b1) and (b2) reactions and energetic gap between ground and excited states of zirconium ion computed at DF level together with available experimental data

| Functional | $\Delta E$ (a)         | $\Delta E$ (b1)   | $\Delta E$ (b2)    | Zr <sup>+</sup> 4F– <sup>2</sup> D gap |
|------------|------------------------|-------------------|--------------------|--|
| B3LYP      | –35.7                  | 37.5              | 100.0              | 9.4                                    |
| B3LYP*     | –37.7                  | 36.8              | 102.6              | 9.3                                    |
| BP86       | –41.4                  | 34.0              | 107.4              | 13.0                                   |
| PBE1PBE    | –26.9                  | 44.8              | 101.7              | 13.2                                   |
| Exp        | –53.3±2.5 <sup>a</sup> | 36.7 <sup>a</sup> | 114.6 <sup>a</sup> | 12. 2 <sup>a</sup>                     |

<sup>a</sup> Ref. [21]

For this reason, the study of the reactions in which they are involved cannot prescind from the preliminary evaluation of the reliability of the used theoretical protocol in the reproduction of these quantities.

The values in Table 1 that we have determined in the first step of the work indicate that BP86 and PBE1PBE reproduce the energy gap between the ground quartet and excited doublet states of zirconium ion better than the other selected functionals.

Because of the large discrepancy between the experimental and PBE1PBE, B3LYP and B3LYP\* values referring to the heats of the (a), (b)1 and (b)2 processes, we have chosen to employ the most reliable BP86 functional to perform the rest of the computations.

The electronic configuration of <sup>4</sup>F and <sup>2</sup>D states of zirconium ion was found to be 5s<sup>1</sup> 4d<sup>2</sup> and the separation energy value between them equal to 13.0 kcal/mol in good agreement with the experimental determination of 12.2 kcal/mol [21].

For ZrO<sup>+</sup> species, the ground state (<sup>2</sup>Σ<sup>+</sup>) is the doublet with 1σ<sup>2</sup>1π<sup>4</sup>2σ<sup>1</sup> configuration followed at 84.2 kcal/mol by the first excited 1σ<sup>2</sup>1π<sup>3</sup>2σ<sup>1</sup>1δ<sup>1</sup> state of quartet (<sup>4</sup>Φ). BP86 gap is abundantly higher than that of 67.6 ± 3.2 kcal/mol estimated by Sievers and Armentrout [21] but it is closer to that of YO species (77.0 kcal/mol) that these authors take as reference molecule to verify their assignments.

Stretching vibrational frequencies for ZrO<sup>+</sup> oxide in its ground and excited states were computed to be 963 and 695 cm<sup>–1</sup>, respectively. The first value, for which an experimental assignment of 1,114 cm<sup>–1</sup> exists [21], appears to be underestimated by about 16%. However, it is worth noting that the experimental value is only an approximation obtained by Morse potential scaling of the NbO<sup>+</sup> frequency, taken from a study of Dyke et al. [38]. To our knowledge, no information exists on Zr<sup>+</sup>–O distance. The value that we find (1.955 Å) is longer with respect to that of neutral oxide ZrO (1.781 Å), obtained by us at the same level of theory.

Calculations on ZrO were performed in order to test the reliability of findings pertaining to the cationic system, through comparison with some experimental determination (bond length [39, 40], vibrational frequency [39, 40] and ionization energy [41] values) concerning the neutral oxide. The accuracy in the reproduction of the Zr–O distance in the <sup>3</sup>Δ ground state (1.763 vs. 1.728 Å), of the stretching frequency (930 vs. 936 cm<sup>–1</sup>) and the ionization potential (158.4 vs. 161.9 ± 4.1 kcal/mol) make us confident about the spectroscopic and energetic data obtained for ZrO<sup>+</sup> oxide.

ZrO<sup>+</sup> cation has an electronic ground state of doublet with <sup>2</sup>B<sub>2</sub> symmetry. The first excited state with different multiplicity is a quartet <sup>4</sup>A' that lies at 87.2 kcal/mol above <sup>2</sup>B<sub>2</sub>. The two Zr<sup>+</sup>–O bond lengths, in the ground state, are 1.818 Å and the O–Zr<sup>+</sup>–O valence angle is equal to 94.25°. Zr<sup>+</sup>–O symmetric (ss) and asymmetric (as) stretchings and O–Zr<sup>+</sup>–O bending (bd) modes fall at the frequency values of 859, 501 and 185 cm<sup>–1</sup>, respectively. Sievers and Armentrout [21] reported for ZrO<sub>2</sub><sup>+</sup> molecule in the ground state, the following values of frequencies: 502, 813, 960 cm<sup>–1</sup>.

As it is evident, there is no agreement between our theoretical and their experimental determinations.

On the other hand, if we compare the BP86 Zr–O bond lengths (1.806 Å) and O–Zr–O bond angle (106.09°) values in the neutral ZrO<sub>2</sub> dioxide, with those reported by Brugh et al. [42] by microwave spectroscopy (1.771 ± 0.001 Å and 108.11 ± 0.1°), we can note a respectable agreement. This same agreement is found between BP86 theoretical (210.3 kcal/mol) and experimental (216.3 ± 8.1 kcal/mol) [21] values of ionization potential of neutral zirconium dioxide. Thus, as in the previous case, we can also retain the results obtained for ZrO<sub>2</sub><sup>+</sup> cation reliable.

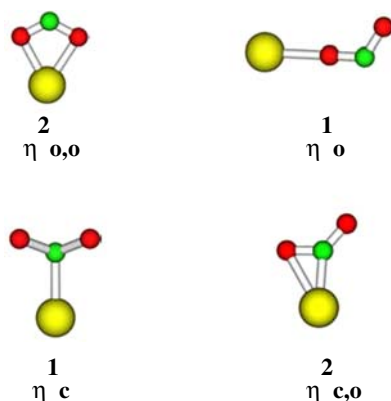
In the excited state of ZrO<sub>2</sub><sup>+</sup>, the Zr<sup>+</sup>–O distances assume the value of 1.935 Å and the O–Zr<sup>+</sup>–O angle measures 132.9°. The set of frequencies for the three vibrational modes is 594 (ss), 349 (as) and 78 (bd) cm<sup>-1</sup>. No comparison is possible in this case for the lack of literature data.

### 3.1 Path (a): activation of CO<sub>2</sub> by Zr<sup>+</sup>

Starting geometries for the stationary points lying on the potential energy surfaces (PES) corresponding to Zr<sup>+</sup> quartet and doublet spin multiplicities were derived from the main coordination modes of CO<sub>2</sub> on a single transition metal atom [43]. The picture of these structures (see Fig. 1) shows that, in principle, carbon dioxide can interact with metal ions, through both its oxygens ( $\eta_{\text{O},\text{O}}^2$ ), with one oxygen ( $\eta_{\text{O}}^1$ ), with carbon ( $\eta_{\text{C}}^1$ ) and with oxygen–carbon couple ( $\eta_{\text{C},\text{O}}^2$ ).

Energy profiles were reported in Fig. 2a with solid and dashed lines for quartet and doublet states, respectively. Table 2 lists the absolute and relative energy values of all the species (see Fig. 3) involved in the reaction (a) in the two different spin states.

Despite the different multiplicities of the cation, the first species encountered in both reaction profiles are the  $\eta_{\text{O}}^1$  adducts. From a structural point of view, these two compounds seem to be very similar: the differences concerning valence angle values are near zero and the deviation on the Zr<sup>+</sup>–O distance is 0.018 Å. Energetically,  $\eta_{\text{O}}^1$  in the electronic spin state of doublet  $^2A'$  is more stabilized than the analogous



**Fig. 1** Main coordination modes of CO<sub>2</sub> on a single transition metal atom

quartet  $^4A''$  with respect to the relative reactants. They lie at 29.4 and 24.8 kcal/mol below the references, respectively.

On both PES, the molecular complexes  $\eta_{\text{O}}^1$  evolve in as many  $\eta_{\text{C},\text{O}}^2$  species through a transition state (TS).

The  $^4A''$  transition state, whose imaginary frequency of 159 cm<sup>-1</sup> corresponds to the Zr<sup>+</sup>–O–C bending coupled with the Zr<sup>+</sup>–C incoming bond stretching, was found to be at 13.0 kcal/mol above the reactants asymptote. As can be noted, this implies that a quite high barrier of 37.8 kcal/mol must first be overcome by the  $^4A''\eta_{\text{O}}^1$  complex to reach the  $\eta_{\text{C},\text{O}}^2$  minimum next.

In the doublet potential energy profile, the  $^2A''$  transition state lies 20.5 kcal/mol below the reference point. The barrier to go from the  $^2A''\eta_{\text{O}}^1$  adduct to the  $\eta_{\text{C},\text{O}}^2$  minimum is much lower (only 8.9 kcal/mol) than in the previous case. The imaginary frequency of 169 cm<sup>-1</sup> describes the Zr<sup>+</sup>–O–C bending vibrational mode. Valence angle assumes the value of 117.4° that is visibly smaller than the corresponding one in the  $\eta_{\text{O}}^1$  species. Contrary to what happens in the quartet, the Zr<sup>+</sup>–C distance is still too long (2.847 Å) to hypothesize a bond, thus the relative stretching is absent in the simulated IR spectrum.

Geometrical parameters of the  $^4A'$  and  $^2A''\eta_{\text{C},\text{O}}^2$  species are fairly different, especially as far as the Zr<sup>+</sup>–O (1.976 vs. 1.744 Å) and Zr<sup>+</sup>–C (2.245 vs. 2.271 Å) bond lengths are concerned.

The quartet species is only 3.3 kcal/mol more stable than the previous TS. This fact is, however, not surprising because of the similarity between the two structures whose only relevant difference lies in the O–Zr<sup>+</sup>–C valence angle value (64.37° for TS and 96.36° for  $\eta_{\text{C},\text{O}}^2$ ).

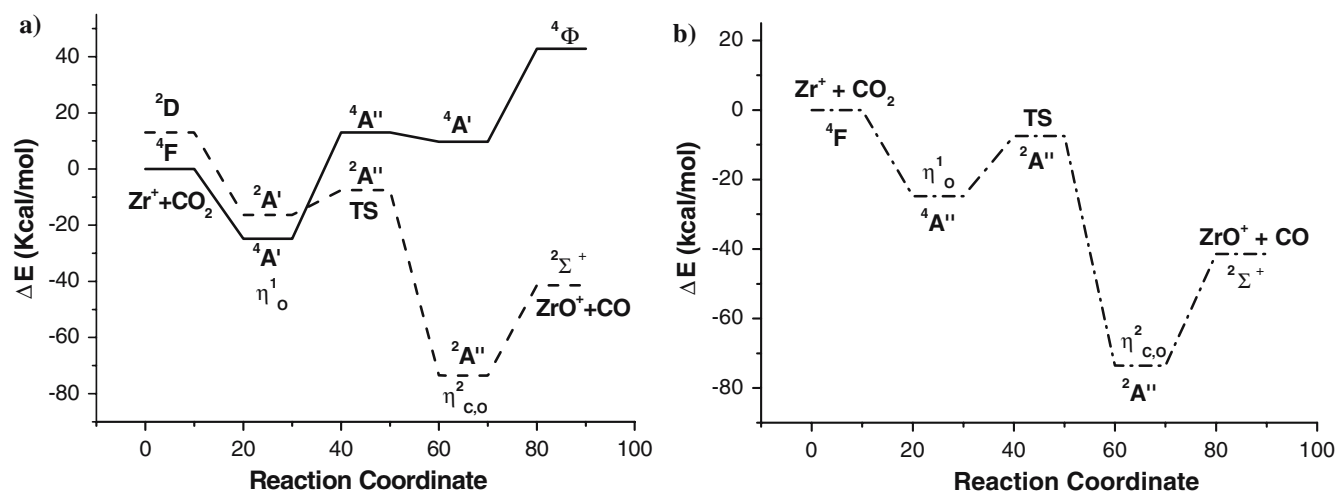
Instead, the  $^2A''\eta_{\text{C},\text{O}}^2$  complex was found to be strongly stabilized with respect to the previous minimum. As can be noted from Table 2 and Fig. 2a, the energy of this species is 86.5 kcal/mol lower than that of reactants.

In both doublet and quartet  $\eta_{\text{C},\text{O}}^2$  species, the distance value of the coordinated C–O (1.140 and 1.142 Å, respectively) is already very close to that assumed by the free molecule (1.139 Å).

Irrespective of the multiplicity, reaction proceeds towards the formation of ZrO<sup>+</sup> and CO products with a barrier-less mechanism. The energy required for the dissociation of  $^2A''$  and  $^4A'\eta_{\text{C},\text{O}}^2$  is a quite big amount (32.1 and 33.1 kcal/mol, respectively) but the natural bond analysis (E.D. Glendening, A.E. Reed, J.E. Carpenter and F. Weinhold, NBO version 3.1 as implemented in Gaussian 03) suggests that in both cases the Zr<sup>+</sup>–C bond has a covalent character, thus the energetic cost to break is clearly high.

In the case of quartet, reaction is endothermic the products being 42.8 kcal/mol less stable than reactants. On the contrary, for doublet, we have an exothermic process with a gain of 54.4 kcal/mol.

The experimental information on reaction (a) suggests that it is exothermic and that it follows a spin-forbidden mechanism. As we have seen, both high- and low-multiplicity



**Fig. 2** Energetic profile of Zr<sup>+</sup> + CO<sub>2</sub> reaction for quartet and doublet multiplicity. **a** Crossing of potential energy profiles; **b** global path along its spin-forbidden channel

**Table 2** Absolute ( $E$  in a.u.) and relative ( $\Delta E$  in kcal/mol) energies for the species having quartet and doublet multiplicities involved in path (a)

| Species                           | quartet            |            | doublet            |            |
|-----------------------------------|--------------------|------------|--------------------|------------|
|                                   | $E$ (stable) + ZPE | $\Delta E$ | $E$ (stable) + ZPE | $\Delta E$ |
| Zr <sup>+</sup> + CO <sub>2</sub> | -234.859648        | 0          | -234.838906        | 0          |
| $\eta_o^1$                        | -234.899059        | -24.8      | -234.885742        | -29.4      |
| TS                                | -234.838763        | +13.0      | -234.851672        | -20.5      |
| $\eta_{co}^2$                     | -234.844050        | +9.7       | -234.976770        | -86.5      |
| ZrO <sup>+</sup> + CO             | -234.791281        | +42.8      | -234.925531        | -54.4      |

pathways are spin allowed because total spin of reactants and products is identical, but they have a different energetic cost.

From the overlap of the two potential energy profiles (see Fig. 2a), we can note that a crossing point is present at TSs level. This means that a spin conversion can occur that switches over the reaction from a spin-allowed to a spin-forbidden channel.

The phenomenon is termed two-state reactivity (TSR) and usually involves the participation of spin inversion in the rate-determining step [44–46].

Taking into account this possibility, the reaction profile can assume the definitive aspect depicted in Fig. 2b.

The process starts with reactants in their ground state ( $^4F$  for Zr<sup>+</sup> and  $^1\Sigma^+$  for CO<sub>2</sub>) and finishes with products in their ground state ( $^2\Sigma^+$  for ZrO<sup>+</sup> and  $^1\Sigma^+$  for CO).

The rate-determining step is represented by a transition state with doublet character that lies at 17.3 kcal/mol with respect to the first adduct  $\eta_o^1$  that maintains the quartet multiplicity.

These results are in agreement with the qualitative description of the process done by Sievers and Armentrout [21] but the theoretical value of the heat of reaction, calculated with respect to new reference (41.4 kcal/mol), is found to be 11.9 kcal/mol lower than the experimental determination (53.3 kcal/mol). However, it is important to underline that this

experimental determination was also obtained by literature thermochemistry data and not by direct measurement.

### 3.2 Path (b): activation of CO<sub>2</sub> by ZrO<sup>+</sup>

It is known from experimental evidences [21] that ZrO<sup>+</sup> oxide deriving from reaction (a) can interact with CO<sub>2</sub> through two different mechanisms, namely (b)1 and (b)2, both endothermic.

BP86 functional reproduces well the measured heats of these reactions (see Table 1).

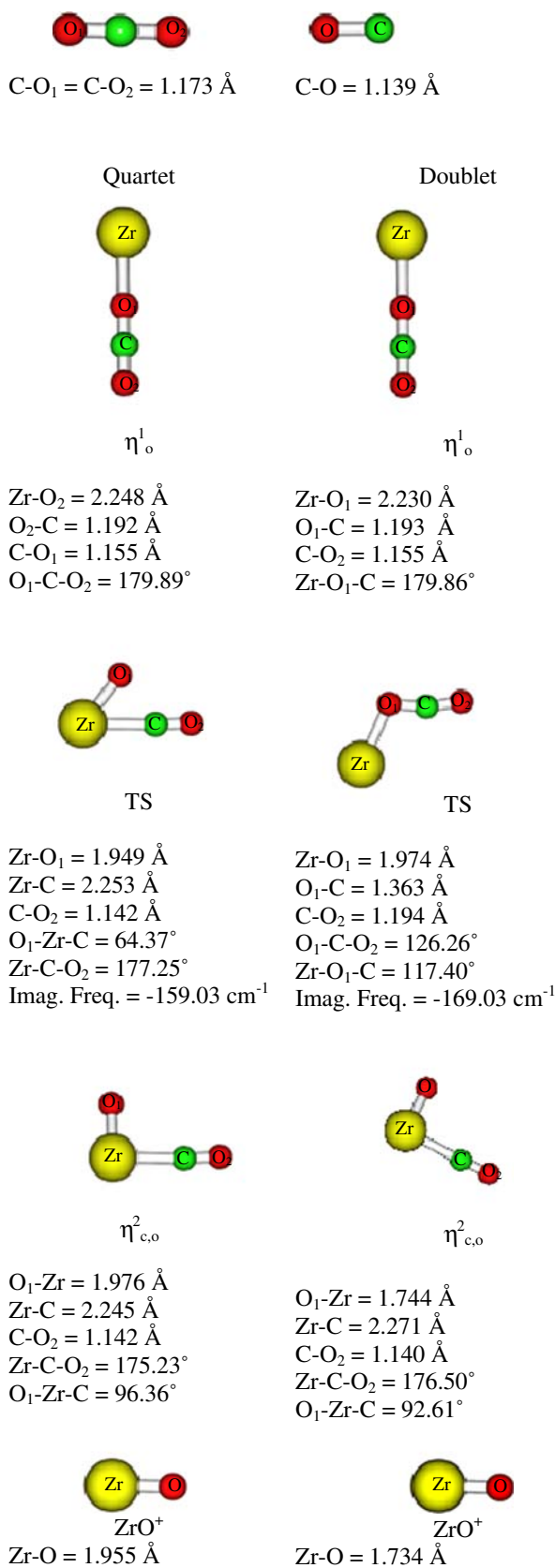
Since the first steps are common for the two processes, we have reported the energetic profiles together (see Fig. 4). Energetic and geometrical parameters of involved species are collected in Table 3 and shown in Fig. 3, respectively.

Because of the large energetic gap between ground and excited states of ZrO<sup>+</sup>, only the low-spin paths were explored.

The reactions start with the formation of OZrOCO<sup>+</sup> adduct. This species, having  $^2A'$  symmetry, lies at 20.9 kcal/mol below the reactant's energy. The two Zr<sup>+</sup>–O bond lengths are very different. In particular, zirconium ion maintains with the original oxygen atom a distance almost equal to that in the free cationic oxide and establishes a weaker interaction (2.280 Å) with one of CO<sub>2</sub> oxygen. Consequently, one of C–O bonds lengthens (1.193 Å) and the other shortens (1.152 Å) with respect to the gas-phase value in the carbon dioxide (1.173 Å). This creates the necessary

**Table 3** Absolute ( $E$  in a.u.) and relative ( $\Delta E$  in kcal/mol) energies for the species involved in paths (b)1 and (b)2

| Species   | $E$ (stable) + ZPE | $\Delta E$ |
|---|--------------------|------------|
| ZrO <sup>+</sup> + CO <sub>2</sub> ( $^2\Sigma^+$ ) | -310.227568        | 0          |
| ZrO <sup>+</sup> /CO <sub>2</sub> ( $^2A'$ )        | -310.260964        | -20.9      |
| ZrO <sub>2</sub> <sup>+</sup> + CO ( $^2B_2$ )      | -310.173417        | +34.0      |
| ZrCO <sub>2</sub> <sup>+</sup> + O ( $^2A''$ )      | -310.056568        | +107.3     |



**Fig. 3** Optimized structures and geometrical parameters of species relating to path (a)

conditions for an easy detachment of CO without the involvement of any barrier.  $ZrO_2^+$  in its electronic ground state and CO fragments lie at 34.0 kcal/mol above the reactants asymptote.

At 107.3 kcal/mol over the reference we have located the alternative products  $OZrCO^+$  and O. The first of these compounds is structurally and energetically identical to the  ${}^2A''\eta^2_{C_2O}$  complex involved in the path (a).

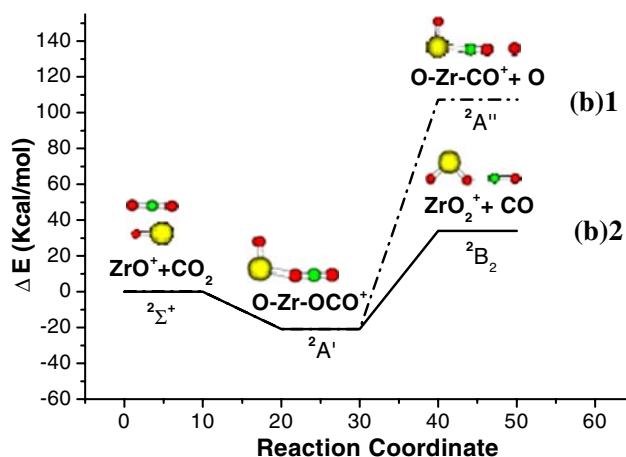
Also in this case, as is evident from Fig. 4, we are in the presence of a barrier-less process.

#### 4 Bond dissociation energies

Bond dissociation energies were computed at BP86 level for all species encountered on the paths of reaction (a) (see Fig. 2b) and (b) (see Fig. 4).

Results were reported in Table 4 together with experimental estimate [21].

Data concerning the  $Zr^+-O$  BDE appear to be in good agreement especially if the experimental uncertainty is taken into account. The situation is different in the case of  $OZr^+-O$ . In fact, BP86 BDE value of 105.4 kcal/mol falls outside of the wide experimental range ( $91.5 \pm 4.6 - 76.3 \pm 3.0$  kcal/mol) [21]. Sievers and Armentrout [21] proposed as most probable one the value of  $89.0 \pm 1.6$  kcal/mol since this appeared to be in reasonable agreement with a previous literature determination ( $80.7 \pm 9.2$  kcal/mol) [47] whose precision was primarily limited by ionization energy measurements. However, these



**Fig. 4** Interaction between  $ZrO^+$  (ground state  ${}^2\Sigma^+$ ) and  $CO_2$ : (b)1 and (b)2 paths

**Table 4** Bond dissociation energies (BDE in kcal/mol) for the most significant species involved in the paths (a) and (b)

| Species     | BDE <sub>BP86</sub> | BDE <sub>EXP</sub> <sup>a</sup> |
|-------------|---------------------|---------------------------------|
| $Zr^+-O$    | 180.8               | $178.9 \pm 2.5$                 |
| $OZr^+-O$   | 105.4               | $89.0 \pm 1.6$                  |
| $OZr^+-CO$  | 32.1                | $19.4 \pm 1.8$                  |
| $OZr^+-OCO$ | 20.9                | $17.1 \pm 1.4$                  |

<sup>a</sup> Ref. [21]

authors seem to be not utterly convinced of the large decrease that they find in the bond energy value from the first to the second oxide ligand of ZrO<sub>2</sub><sup>+</sup>. In fact, this result is in contrast to those obtained for the metal (or metal ion) oxides and dioxides of Zr and Nb<sup>+</sup> for which the ratio BDE (OM<sup>(+)</sup>-O)/BDE (M<sup>(+)</sup>-O) was about 0.8 [48,49]. They explain their finding on the basis of the presence of a different number of unpaired electrons on the ZrO<sup>+</sup> (only one unpaired electron) towards ZrO and NbO<sup>+</sup> (two unpaired electrons) that should determine, respectively, a weaker or a stronger double bond in the corresponding dioxides and hence a greater or smaller decrease of the binding energies.

This explanation is quite persuasive but, in the case of the isovalent neutrals YO and YO<sub>2</sub> systems [49], the ratio between BDE is 0.56 and incontrovertibly closer to that of 0.58 that we find for ZrO<sup>+</sup> and ZrO<sub>2</sub><sup>+</sup> oxides. Thus, our value of 105.4 kcal/mol seems to go in a more appropriate direction.

Theoretical and experimental predictions of OZr<sup>+</sup>-CO BDE are very different. In particular theoretical values are higher by 12.7 kcal/mol.

We dealt in the elucidation of this result travelling over the PES of the reaction (a) in the doublet multiplicity where the fragmentation of this species into ZrO<sup>+</sup> and CO involved an expense of 32.1 kcal/mol because of the presence of a covalent bond between Zr<sup>+</sup> and C.

Finally, BP86 BDE value for OZr<sup>+</sup>-OCO (20.9 kcal/mol) is substantially in agreement with the experimental counterpart (17.1 ± 1.4 kcal/mol) [21].

## 5 Conclusions

In this work the gas-phase conversion of carbon dioxide into carbon monoxide catalysed by Zr<sup>+</sup> and ZrO<sup>+</sup> oxides was examined. The study was performed at density functional level of theory using the BP86 exchange-correlation potential.

ZrO<sup>+</sup>, formed in a first step on interaction of Zr<sup>+</sup> with CO<sub>2</sub>, reacts in turn with CO<sub>2</sub> to form ZrO<sub>2</sub><sup>+</sup> and CO in the most energetically favoured channel.

Two different electronic spin states were considered for cationic Zr<sup>+</sup> and ZrO<sup>+</sup> species.

A crossing occurring between the high- and low-spin PESs indicated that ZrO<sup>+</sup> in its doublet ground state is obtained through an exothermic spin-forbidden pathway in which Zr<sup>+</sup> reactant has a multiplicity of quartet. Instead, the following endothermic conversion of ZrO<sup>+</sup> into ZrO<sub>2</sub><sup>+</sup> was confirmed to be spin allowed.

Findings concerning the followed reaction mechanisms were in agreement with the experimental predictions from a qualitative point of view.

Energetic gap between ground and excited states of Zr<sup>+</sup> and ZrO<sup>+</sup>, BDE values for all stationary points on potential energy profiles and the heats of considered processes were accurately determined, and the comparison with the previous literature estimates showed that there is no quantitative agreement as far as the energy separation of ZrO<sup>+</sup> doublet and

quartet states, the BDE of OZr<sup>+</sup>-CO species and reaction heat of process (a) are concerned.

The characterization of ZrO<sub>2</sub><sup>+</sup> dioxide brought to the individuation of an electronic ground state of doublet with <sup>2</sup>B<sub>2</sub> symmetry and to a first excited state with different multiplicity of quartet <sup>4</sup>A' lying at 87.2 kcal/mol above <sup>2</sup>B<sub>2</sub>.

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## References

- Jegat C, Mascetti J, Fouassier M, Tranquille M, Aresta M, Tommasi I, Dedieu A (1993) *Inorg Chem* 32:1279
- Hwang CS, Wang NC (2004) *Mater Chem Phys* 88:258
- Tominaga K, Sasaki Y (2004) *J Mol Cat A Chem* 220:159
- Gallucci F, Paturzo L, Basile A (2004) *Chem Eng Process* 43:1029
- Jansen A, Pitter S (2004) *J Mol Cat A Chem* 217:41
- Muguruma C (1999) *J Mol Struct (Theochem)* 461:439
- Marino T, Russo N, Toscano M (2005) *J Am Chem Soc* 127:4242
- Walther D, Ruben M, Rau S (1999) *Coord Chem Rev* 182:67
- Yin X, Moss JR (1999) *Coord Chem Rev* 181:27
- Lu Y, Xue J, Liu Y, Shen S (1998) *React Kinet Catal Lett* 64:365
- Ramaraj R, Rajan Premkumar J (2000) *Curr Sci* 79:884
- Akolekar DB, Bhargava SK (2004) *J Mol Cat A Chem* 219:301
- Herdohelyi A, Fador K, Szailer T (2004) *Appl Catal B Environ* 53:153
- Chen HW, Wang CY, Yu CH, Tseng LT, Liao PH (2004) *Catal Today* 97:173
- Pandey KK (1995) *Coord Chem Rev* 140:37
- Hwang DY, Mebel AM (2004) *Chem Phys Lett* 396:75
- Wang GC, Jiang L, Morikawa Y, Nakamura J, Cai ZS, Pan YM, Zhao XZ (2004) *Surf Sci* 570:205
- Habas MP, Mele F, Sodupe M, Illas F (1999) *Surf Sci* 431:208
- Isaacs M, Canales JC, Aguirre MJ, Estiù G, Caruso F, Ferraudi G, Costamagna J (2002) *Inorg Chim Acta* 339:224
- Ricart JM, Habas MP, Clotet A, Curulla D, Illas F (2000) *Surf Sci* 460:170
- Sievers MR, Armentrout PB (1999) *Int J Mass Spectrom* 185:117
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian, Inc, Wallingford
- Becke AD (1993) *J Chem Phys* 98:5648
- Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785
- Miehlich B, Savin A, Stoll H, Preuss H (1989) *Chem Phys Lett* 157:200
- Reiher M, Salomon O, Hess BA (2001) *Theor Chem Acc* 107:48
- Becke AD (1988) *Phys Rev A* 38:3098
- Perdew JP (1986) *Phys Rev B* 33:8822
- Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77:3865
- Krishnan R, Binkley JS, Seeger R, Pople JA (1980) *J Chem Phys* 72: 650
- Clark T, Chandrasekhar J, Schleyer PvR (1983) *J Comp Chem* 4:294

32. Hay PJ, Wadt WR (1985) *J Chem Phys* 82:270
33. Hay PJ, Wadt WR (1985) *J Chem Phys* 82:284
34. Hay PJ, Wadt WR (1985) *J Chem Phys* 82:299
35. Seeger R, People JA (1977) *J Chem Phys* 66
36. Bauernschmitt R, Ahlrichs R (1996) *J Chem Phys* 104:9047
37. Bauschlicher CW Jr, Ricca A, Patridge H, Langgloff SR (1997) In: Chong DP (ed) *Recent advances in density functional theory*. World Scientific, Singapore, Part II and references therein
38. Dyke JM, Ellis AM, Fehér M, Morris A, Paul AJ, Stevens JCH (1987) *J Chem Soc Faraday Trans* 83:2
39. Weltner W Jr, McLeod D Jr (1965) *Nature* 206:87
40. Tatum JB, Balfour WJ (1973) *J Mol Spectrosc* 48:292
41. Sievers MR, Chen YM, Armentrout PB (1996) *J Chem Phys* 105:6322
42. Brugh DJ, Suenram RD, Stevens WJ (1999) *J Chem Phys* 111:3526
43. Schaftenaar G, Noordik JH (2000) *J Comput Aided Mol Des* 14:123
44. Schröder D, Shaik S, Schwarz H (2000) *Acc Chem Res* 33:139
45. Armentrout PB, Beauchamp JL (1989) *Acc Chem Res* 2:315
46. Armentrout PB (1991) *Science* 251:175
47. Murad E, Hildenbrand DL (1975) *J Chem Phys* 63:1133
48. Sievers MR, Armentrout PB (1998) *Int J Mass Spectrom* 179/180:103
49. Pedley JB, Marshall EM (1988) *J Phys Chem Ref Data* 12:2160