

## DFT study of molecular properties, potential energy surface and Stability of the dioxide of the group 12 $M(O_2)$ : $M=Zn, Cd$ and $Hg$

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### Abstract

Two potential energy surfaces PESs in the lowest energy multiplicities triplet  $^3A''$  and singlet  $^1A'$  for the dioxide of heavy metals of the group 12  $Zn(O_2)$ ,  $Cd(O_2)$  and  $Hg(O_2)$  have been studied through DFT methods with the B3LYP functional. The core electrons of Zn (30 electrons), Cd (48 electrons) and Hg (60 electrons) are represented by pseudopotential ECP and the valences electrons are explicitly treated with the quasi-relativistic basis MWB and the full relativist basis AVTZ-PP. Both linear  $C_{\infty v}$  and  $D_{\infty h}$  or bent  $C_s$  and cyclic  $C_{2v}$  structures of  $M(O_2)$  have been considered in this work. The different pathways of dissociation and formation of  $M(O_2)$  and their dissociative limits  $M+O_2$  and  $MO+O$  have been examined to discuss the stability of these molecules. Structural, spectroscopic and thermodynamic properties of stationary points are presented and compared with previous theoretical and experimental studies.

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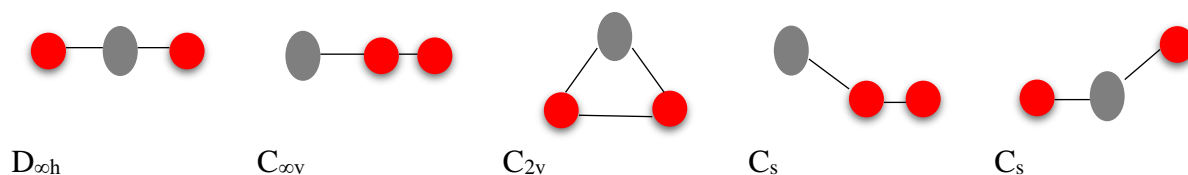
## 1. Introduction

Understanding the nature of chemical bonds, structure and reaction mechanism in mixed clusters between the group 12 metals (Zn, Cd and Hg) and small atoms (H, O, S, C, Cl, Br...) and diatomic molecules ( $\text{H}_2$ , OH, SH, CH,  $\text{O}_2$ ...) are of great interest in many areas of science, e.g., surface chemistry, catalysis, semiconductor, organometallic chemistry and recently have been proposed to play a role in the Earth's atmosphere. The structures, physicochemical properties and reactivity of these species have been the subject of intense experimental and theoretical studies, which have been described in numerous reviews as the initially formed species in most metal oxidation processes. Complexes of metal dioxide are particularly interesting in atmospheric chemistry. For the dioxides molecules of interest in this work  $\text{Zn}(\text{O}_2)$ ,  $\text{Cd}(\text{O}_2)$  and  $\text{Hg}(\text{O}_2)$ , experimental and theoretical studies have been limited. For the  $\text{Zn}(\text{O}_2)$  and  $\text{Cd}(\text{O}_2)$  molecules, experimental spectroscopic studies have been realized by the infrared measurements in rare gas matrices, vibrational frequency assigned by Chertihin and Andrews[1] to be 748.2 and 744.4, of  $\text{OZnO}$  in argon and nitrogen respectively, and 626.6 and 625.4  $\text{cm}^{-1}$  of  $\text{OCdO}$ , the authors found that equilibrium structure of Zinc dioxide and Cadmium dioxide is linear, but the asymmetric  $\text{CdOO}$  isomer was identified from bands at 1124 and 1129  $\text{cm}^{-1}$  [2] in solid argon and nitrogen following the reaction to ozone. Also, Chertihin and Andrews reported in their paper the calculations of vibrations frequency and Geometry parameters at DFT/B3LYP with an ECP and all-electron for  $\text{Zn}(\text{O}_2)$  and  $\text{Cd}(\text{O}_2)$  of linear and bent structure. A comparative density functional study and CCSD(T) calculation have been done by Uzunova[3] of dioxides  $\text{ZnO}_2$  ( $^3\Sigma_g^-$  et  $^1\text{A}'$ ) to calculate geometry parameters, dipole moment, vibrational frequencies and dissociation energy. He suggests in his work that all Zn dioxygen clusters are thermodynamically unstable. Systematic study of 3d-Metal Dioxides Isomers and their Anions has been reported by Gutsev et al.[4] which found the  $^3\Sigma_g^-$  state of  $\text{OZnO}$  linear isomer is the ground state. In his paper, the electronic and geometrical structures of the ground and excited states of the dioxides  $\text{ZnO}_2$  have been calculated using the BPW91/6-311+G\*. In 2009, Yu Gong and Zhou[5] in their review described advances in the spectroscopic and theoretical Studies of transition metal oxides and dioxides complexes (among them  $\text{ZnO}_2$ ). So, the reaction mechanisms of transition metal dioxides have been discussed in their paper. All experimental and theoretical studies found that  $\text{OZnO}$  isomer  $^3\Sigma_g^-$  is metastable than the  $\text{ZnOO}$  isomer that was found unstable. Excited intermediates in the Hg photosensitized reaction of  $\text{O}_2$  detected by energy transfer and that was realized by Hiplitter[6] in his work. However; Bulter[7] in his paper, Identification of  $\text{HgO}$ , Species by Matrix Isolation Spectroscopy suggested that a mercury superoxide complex has been observed in a solid matrix some qualitative evidence in favor of the formation of  $\text{HgO}_2$  is presented. Recently Dibble et al. in their study on modeling OH-Initiated Oxidation of Mercury in the Global Atmosphere, suggest that the calculations are needed to obtain reliable values of  $\text{Hg-O}_2$  bond energies in these radicals and to investigate the reactions of these compounds in the atmosphere. The topic of the present paper is described through theoretical investigation of the group 12 metal with dioxide  $\text{O}_2$ , to yield structure, thermochemical and spectroscopic constants of high accuracy. The two potential energy surfaces  $^1\text{A}'$  and  $^3\text{A}''$  have been studied at DFT/B3LYP methods in connection with accurate relativistic pseudopotentials to determine the different isomers. We examine the different pathways of dissociation and form of  $\text{M}(\text{O}_2)$  and their dissociative limits to discuss the stability of these molecules.

## 2. Computational details

With the G09 code (Gaussian09)[8], calculations have been performed with the DFT[9,10] density functional methodology using the unrestricted (UKS) or restricted (RKS) Kohn-Sham formalism while adopting the

B3LYP hybrid functional [11], for the exchange part that contains the functions of local exchange, Becke exchange and HF exchange; and the local and corrected correlation functionalities of the Lee, Yang and Parr gradient for the correlation part. In our previous study of theoretical investigations of structural, thermal properties and stability of the group 12 metal M (XH) isomers in atmosphere[12], we have determined the quality of our choice. In the same paper we have made diatomic MO, MH and MS calculations at the B3LYP functional in connection with the large basis sets and pseudopotentials. These species are very well known in their fundamental state, either by experiment or by high-level theoretical calculations. A comparison of the functional B3LYP with this database will take place during the study of each fragment. Our calculated values reported at DFT results with the B3LYP functional of diatomic ground state are in good agreement with experimental and previous theoretical results. The same suggestions on the quality of use of the functional B3LYP are confirmed by our team in previous studies on the interaction of lead with atmospheric species[13–15]. Other theoretical researches are recommended the performance to use the DFT method for the structure properties of M-O [4,16,17]. We can reasonably expect that the same quality will be kept when the O<sub>2</sub> bonds to the Zn, Cd and Hg atoms. The interaction of Zn, Cd and Hg with the dioxide O<sub>2</sub> produced in different symmetries depending on whether the coordination is linear C<sub>∞v</sub> and D<sub>∞h</sub> or bent C<sub>s</sub> and C<sub>2v</sub> **Scheme 1**.



**Scheme 1**

The methodology used in the BOH study by Qian Peng et al.[18] have been followed to construct our PESs. The spheroid coordinate system ( $d$ ,  $R_{M-O}$ ,  $\alpha$ ) has been chosen to describe the potential energy surface isomerization. The potential energy surfaces are constructed by optimizing the  $R_{MO}$  and  $R_{OO}$  bond lengths and the pointwise variation of the angle  $\alpha$  (from 0° to 180°) in steps of 5°. The different structures bent and linear of M (O<sub>2</sub>) isomers have been optimized for the two-multiplicity singlet and triplet. The stability of these molecules has been discussed by the examination of dissociation energy, the enthalpy of reaction and the wavelength maxima  $\lambda_{max}$  that are necessary to break the bonds of M(O<sub>2</sub>) isomers found in the surface of their dissociative limits MO, O<sub>2</sub> M and O. In this study, the parameters properties such as structures, vibration frequencies, dissociation energies, reaction enthalpies of the stationary points in the surface are given and discussed. Also, the Mulliken populations were calculated to reveal both covalent and non-covalent effects in molecules and to predict dipole moment.

### Basis sets:

For the oxygen O and dioxide O<sub>2</sub> species, we adopted the base of correlation consistent Dunning polarized triple zeta quality for the valence orbitals and augmented by diffuse functions denoted aug-cc-pVTZ [19]. For the transition metal Zn and Cd with 3d orbitals and Hg with 5d orbitals, the treatment requires large relativistic effects, and for simplification, its core electrons are usually described by a pseudo-potential including these effects. In the present study, the core electrons of Zn (30 electrons), Cd (48 electrons) and Hg (60 electrons) are represented by pseudopotential and the valences electrons are explicitly treated with the

quasi-relativistic base ECPnMWB[20–22] and the full relativist base ECPnAVTZ-PP[23,24] (n: number of core electrons).

### 3. Results and discussions

#### 3.1. The potential energy surface

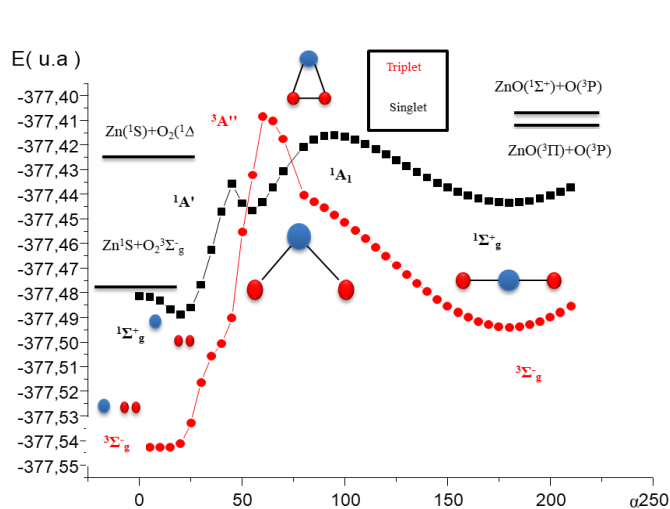
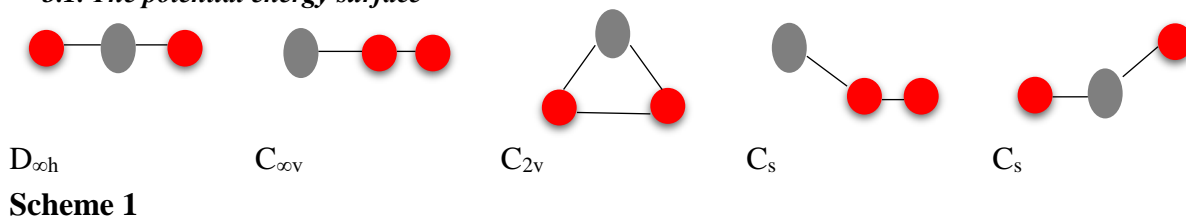


FIG.1. ZnOO-OZnO potential energy surfaces

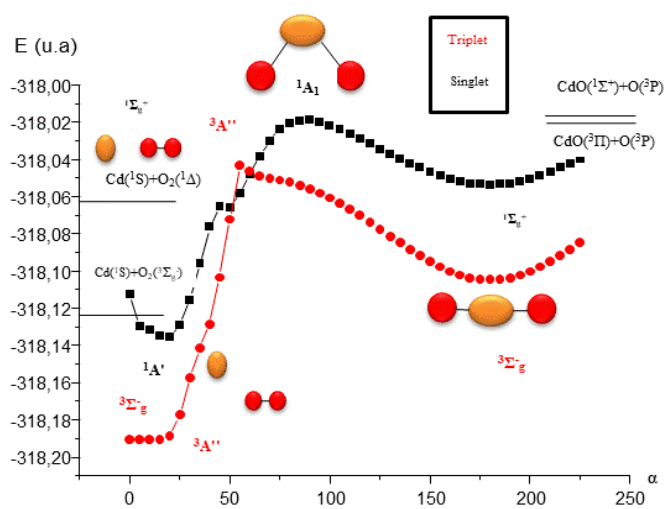


FIG.2. CdOO-OCdO potential energy surfaces

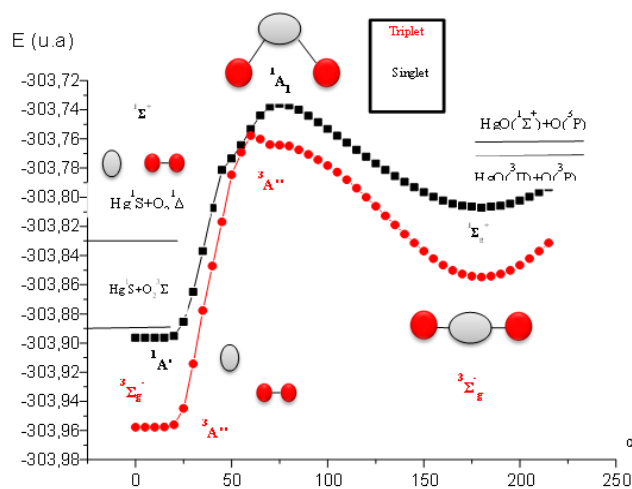


FIG.3. HgOO-OHgO potential energy surfaces

Exploring the potential triplet ground state surface Fig.1, Fig.2 and Fig.3 indicates that PES of the ground state is very flat in the region from 0 to 20°. The two states  $^3\Sigma_g^-$  and  $^3A''$  of the two isomers MOO linear and. This means that the two isomers are unstable and the two states of these isomers are repulsive. We can witness a predissociation of these compounds in the dissociative limit  $M + O_2$  by the broken of the bond liaison M-O<sub>2</sub> at an energy which is lower. On the other hand, for the OMO isomer, the PESs presents only a minimum that

corresponds to OMO linear with a symmetry state  $^3\Sigma_g^-$  state, and a maxima OMO  $^3A''$  corresponds to possible transition state with a cyclic geometry. The values of relative energy for different states and isomers of Zn(O<sub>2</sub>) are reported in [Table 1] and for Cd(O<sub>2</sub>) and Hg(O<sub>2</sub>) are reassembled in [Table 2].

**Table 1: Relative energy (Te) between different states of Zn(O<sub>2</sub>)**

Te (eV)	B3LYP/M WB	B3LYP/AVTZ -PP	CCSD(T)/6- 311+G* <sup>a</sup>	B1LYP/6- 311+G* <sup>a</sup>	BPW91/6- 311+G* <sup>b</sup>
<b>Zn(O<sub>2</sub>)</b>					
OZnO ( $^3\Sigma_g^-$ )	0.00	0.00	0.00	0.00	0.00
ZnO <sub>2</sub> ( $^3A''$ ) TS	2.13	2.19	-	-	-
ZnOO ( $^1\Sigma^+$ )	1.23	0.47	-	-	-
ZnOO ( $^1A'$ )	0.34	0.26	0.134	-	-
ZnO <sub>2</sub> ( $^1A'$ ) TS	1.29	4.41	-	-	-
ZnO <sub>2</sub> ( $^1A'$ )	1.28	2.24	1.51	1.22	1.57
ZnO <sub>2</sub> ( $^1A_1$ ) TS	2.1	3.26	-	-	-
OZnO ( $^1\Sigma_g^+$ )	1.37	1.37	-0.47	1.47	-

<sup>a</sup> Ref. [3], <sup>b</sup> Ref. [4]

For the singlet excited state PESs  $^1A'$  of Zn(O<sub>2</sub>) Fig.1, six stationary points have been identified. One corresponds to the global minimum ZnOO  $^1A'$  bent, and two of them correspond to the local minimum of ZnO<sub>2</sub>  $^1A'$  bent and OZnO  $^1\Sigma^+$  linear. For the linear structure ZnOO  $^1\Sigma^+$ , it is found on these potential surfaces as being inversion transition states, whereas the two transition states with structure ZnO<sub>2</sub>  $^1A'$  bent and ZnO<sub>2</sub>  $^1A_1$  cyclic are involved in the isomerization process. The theoretical study reported by Uzunova et.al at CCSD(T)/6-311+G\* and B1LYP/6-311+G\* for ZnO<sub>2</sub> isomers [3] is in agreement with our suggestion obtained at B3LYP/MWB and B3LYP/AVTZ-PP level. They limited their work about  $^3\Sigma_g^-$ ,  $^1\Sigma_g^+$  and  $^1A_1$  for ZnO<sub>2</sub>, that suggests the relative energy between  $^3\Sigma_g^-$  and the two other states  $^1\Sigma_g^+$  and  $^1A_1$  is (-0.478eV) and (1.516eV) respectively at CCSD(T)/6-311+G\*, and 1.472 and 1.225eV respectively at B1LYP/6-311+G\*; for the other isomer ZnOO, his work is limited for the  $^1A'$  state that is found above 0.134eV in the ground state  $^3\Sigma_g^-$ . The other theoretical study by Gutsev et.al at BPW91/6-311+G\* [4] of the two isomers ZnO<sub>2</sub>  $^3\Sigma_g^-$  and ZnO<sub>2</sub>  $^1A_1$  suggests that ZnO<sub>2</sub>  $^1A_1$  is above ZnO<sub>2</sub>  $^3\Sigma_g^-$  by 1.57eV, the deviation between our results calculation at B3LYP is 0.2eV. To our knowledge no theoretical study is performed to assign the states for Cd(O<sub>2</sub>) and Hg(O<sub>2</sub>), so we based in our calculation at B3LYP level when discussing these compounds. For the PESs  $^1A'$  of Cd(O<sub>2</sub>) Fig.2, two minimum have been identified correspond to CdOO  $^1A'$  bent and OCdO  $^1\Sigma_g^+$  linear. For the linear structure CdOO  $^1\Sigma^+$ , it is found as inversion transition states and for the transition states CdO<sub>2</sub>  $^1A_1$  cyclic are involved in the isomerization process. The results of exploiting the two PESs of Zn(O<sub>2</sub>) and Cd(O<sub>2</sub>) are in accordance with the experimental study done by Chertihin and Anderws[1] who found the OZnO  $^3\Sigma_g^-$  and OCdO  $^3\Sigma_g^-$  triplet can excite in reaction of laser-ablated but no-identification of ZnOO isomers is suggested, so for the CdOO isomer was identified in solid and nitrogen flowing the reaction with to ozone. Our PESs calculations suggest that CdOO isomer can excite in  $^1A'$  state because it is the one global minimum found in the two PESs of this isomer. The value of T<sub>e</sub> between the OCdO  $^3\Sigma_g^-$  and CdOO  $^1A'$  in this work is -

0.85eV which suggests that the singlet PES may be under the triplet PES, so a high-level computation of state characterization is necessary.

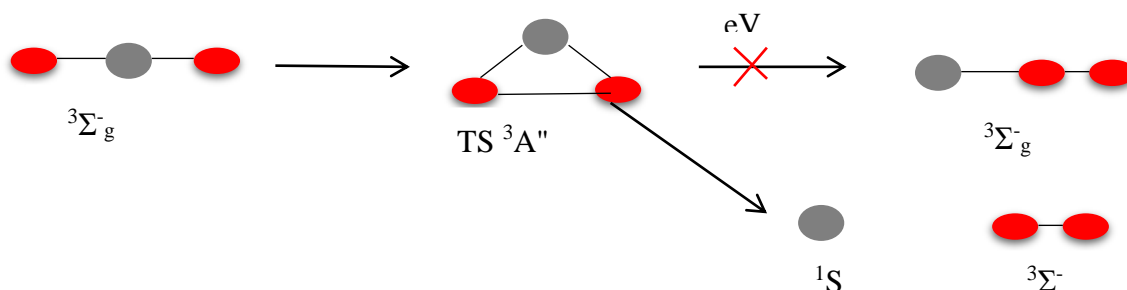
**Table 2:** Relative energy (Te) between different states of Cd(O<sub>2</sub>) and Hg(O<sub>2</sub>)

Cd(O <sub>2</sub> )	Te (eV)		Hg(O <sub>2</sub> )	Te (eV)	
	B3LYP/MWB	B3LYP/AVTZ-PP		B3LYP/MWB	B3LYP/AVTZ-PP
OCdO ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )	0.00	0.00	OHgO ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )	0.00	0.00
CdO <sub>2</sub> ( <sup>3</sup> A'') TS	1.80	1.81	HgO <sub>2</sub> ( <sup>3</sup> A'') TS	2.64	2.38
CdOO ( <sup>1</sup> Σ <sup>+</sup> )	-0.21	-0.659	HgOO ( <sup>1</sup> Σ <sup>+</sup> )	-	-
CdOO ( <sup>1</sup> A')	-0.84	-0.82	HgOO ( <sup>1</sup> A')	-	-
CdO <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> ) TS	4.10	4.09	OHgO ( <sup>1</sup> A <sub>1</sub> ) TS	3.82	3.82
OCdO ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	1.39	1.38	OHgO ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )	1.29	1.29

For the PES singlet state of Hg (O<sub>2</sub>) Fig.3, the shape of the curve is similar at to the PES triplet state. The two states <sup>1</sup>Σ<sup>+</sup> and <sup>1</sup>A' of the two isomers HgOO linear and HgOO bent cannot be a minimum in the potential energy surface, then the two states of these isomers are repulsive. This means that the two isomers HgOO in the two multiplicity singlet and triplet <sup>1,3</sup>Σ<sup>+</sup> and <sup>1,3</sup>A' are dissociative. The linear OHgO <sup>1</sup>Σ<sup>+</sup> isomer is the only minimum found in the PES, and the maximum which corresponds to OHgO <sup>1</sup>A' can be a transition state. The relative energy found in this work at B3LYP between OHgO (<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) and OHgO <sup>1</sup>Σ<sup>+</sup> is 1.3eV.

#### 4. Isomerization and dissociation

For the PES triplet, the passage from the two linear form OMO ↔ MOO (scheme 2) via the transition state TS <sup>3</sup>A'' of bent structure, the energy barrier involved which is relative to the OZnO is of the order of 2.13-2.19eV at B3LYP/MWB and B3LYP/AVTZ-PP level respectively. For CdO<sub>2</sub> and HgO<sub>2</sub> triplet, the isomerization barrier is 1.80eV and 2.38eV at B3LYP/MWB and B3LYP/AVTZ-PP level respectively. But this transition state is higher than the fundamental M + O<sub>2</sub> limit, so, a direct isomerization OMO ↔ MOO is impossible. Experimental or theoretical T<sub>e</sub> for this transition state is not given.

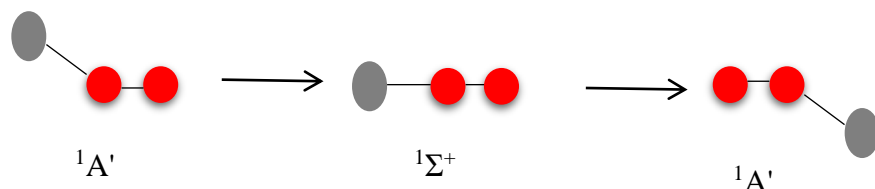


**Scheme 2**

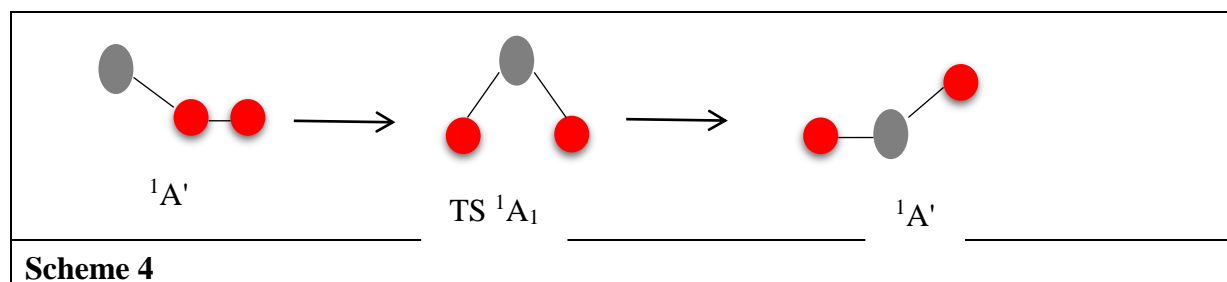
Following the singlet PES of Zn(O<sub>2</sub>), three processes have been identified; the first one concerns the zinc inversion process in the coordination ZnOO (<sup>1</sup>A') → ZnOO (<sup>1</sup>A') via the linear structure [TS] ZnOO (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) (scheme 3), and the other two processes correspond to the isomerization between the two isomers ZnOO (<sup>1</sup>A') and ZnO<sub>2</sub> via the transition state ZnO<sub>2</sub> (<sup>1</sup>A') bent with an isomerization barrier 2.61eV ZnOO(<sup>1</sup>A') → OZnO



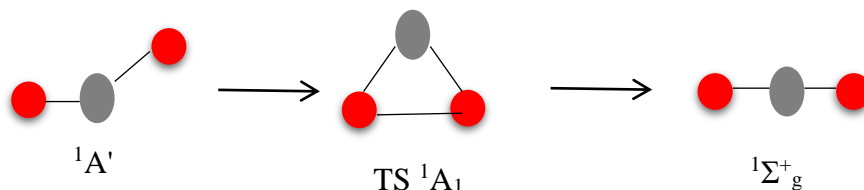
( $^1A'$ ) (scheme 4). The second isomerization pathway that is between the two isomers  $ZnO_2$  and  $OZnO$  ( $^1\Sigma_g^+$ ) linear is done via the transition state  $ZnO_2$  ( $^1A_1$ ) cyclic form with an activation barrier 3.42eV  $ZnO_2$  ( $^1A'$ )  $\rightarrow OZnO$  ( $^1\Sigma_g^+$ ) (scheme 5). For the cadmium dioxide  $Cd(O_2)$  PES singlet, an isomerization pathway  $CdO_2$  ( $^1A'$ )  $\rightarrow OCdO$  ( $^1\Sigma_g^+$ ) (scheme 4) involves via the transition state  $CdO_2$  ( $^1A_1$ ) cyclic with an activation barrier 4.94eV. For the two dioxide  $Zn(O_2)$  and  $Cd(O_2)$ , the low height of the barrier for the two isomerization processes suggests that isomerization is easily achievable. Finally, for the PES singlet of mercury dioxide, the only isomerization process observed that  $OHgO \longleftrightarrow HgOO$  can't be done because the transition state between the two forms is above that the asymptote  $Hg + O_2$ .



**Scheme 3**



**Scheme 4**



**Scheme 5**

To our knowledge, no experimental data is known for the dissociation energies of the isomers of the  $Zn(O_2)$ ,  $Cd(O_2)$  and  $Hg(O_2)$  complex.

Theoretically, G. L. Gutsev et al.[4] have assigned the value of dissociation energy  $D_0$  for  $Zn(O_2)$  in the ground state at BPW91/ 6-311+G\* level, taking into account the two dissociation paths of  $ZnO_2$  ( $Zn+O_2$   $D_0=0.6$  eV and  $ZnO+O$   $D_0=3.5$  eV) to their fundamental states. According to our bibliographic research on  $Cd(O_2)$  and  $Hg(O_2)$ , no theoretical study was found to attribute the dissociation energy of those compounds. In this present work, we will try to give qualitative values of  $D_0$  at B3LYP/AVTZ-PP level. In order to be able to correctly determine these energies, it is important that their states are adiabatically correlated to the appropriate dissociation limits. Fig.1, Fig.2, Fig3 and Table 3 and 4 shows these correlations. For  $ZnOO$  ( $^3\Sigma_g^-$ ) and  $ZnOO$  ( $^3A''$ ) correlated with the three fundamental asymptotes  $Zn(^1S)+O_2(^3\Sigma^-)$ ,  $ZnO(^1\Sigma^+)+O(^3P)$  and  $ZnO(^3\Pi)+O(^3P)$ , the involved dissociation energy is 1.76eV to break the Zn-O bond and 4.1eV to break the O-O bond. For  $OZnO(^3\Sigma_g^-)$  isomer, two dissociation channels are possible,  $ZnO(^1\Sigma^+)+O(^3P)$  and

$\text{ZnO}(^3\Pi)+\text{O}(^3\text{P})$  and the value for breaking the Zn-O bond is 2.7eV. For the first excited state  $\text{ZnOO}(^1\Sigma^+)$  and  $\text{ZnOO}(^1\text{A}')$ , the adiabatic correlation is towards the  $\text{Zn}(^1\text{S})+\text{O}_2(^1\Delta_g)$  and  $\text{ZnO}(^3\Pi)+\text{O}(^3\text{P})$ . The dissociation energy involved in this case is 1.73eV and 1.93eV respectively to rupture the Zn-O bond and 2.37eV to rupture the O-O bond. As for isomer singlet state  $\text{ZnO}_2(^1\text{A}')$  that presents a local minimum which correlates with the same limit, the dissociation energy is 0.46eV and 1.1eV for Zn-O and O-O bonds respectively. We also noticed for  $\text{OZnO}(^1\Sigma_g^+)$  isomer which is correlated with the one excited state  $\text{ZnO}(^3\Pi)+\text{O}(^3\text{P})$ , the dissociation energy obtained is 1.33eV to break the Zn-O bond. We can see that  $\text{OZnO}$  isomers in the two-multiplicity singlet and triplet are more strongly bound than its  $\text{ZnOO}$  isomers because breaking the Zn-O bond is much easier.

**Table 3:** Dissociation energy ( $D_0$ ) and enthalpy of reaction for  $\text{M}(\text{O}_2)$  triplet

$\text{M}(\text{O}_2)$	$\text{M}(^1\text{S})+\text{O}_2(^3\Sigma^-)$		$\text{MO}(^1\Sigma^+)+\text{O}(^3\text{P})$		$\text{MO}(^3\Pi)+\text{O}(^3\text{P})$	
	$D_0$ eV	$\Delta H_{298}^\circ$	$D_0$ eV	$\Delta H_{298}^\circ$	$D_0$ eV	$\Delta H_{298}^\circ$
		Kcal/mol		Kcal/mol		Kcal/mol
<b>M(O<sub>2</sub>) triplet</b>						
$\text{ZnOO}(^3\Sigma_g^+)$	1.75	40.62	4.012	94.33	4.04	93.1
$\text{ZnOO}(^3\text{A}'')$	1.76	40.83	4.11	94.88	4.10	93.47
$\text{OZnO}(^3\Sigma_g^-)$	-	-	2.78	64.78	2.71	63.29
Ref	-0.6 <sup>a</sup>	-	3.5 <sup>a</sup>	93 <sup>b</sup>	-	-
$\text{CdOO}(^3\Sigma_g^-)$	1.73	40.53	4.58	106.38	4.29	99.14
$\text{CdO}_2(^3\text{A}'')$	1.76	40.82	4.61	106.67	4.30	81.89
$\text{OCdO}(^3\Sigma_g^-)$	-	-	2.28	53.28	2.13	46.04
$\text{HgOO}(^3\Sigma_g^-)$	1.75	40.52	5.26	121.36	4.86	112.24
$\text{HgO}_2(^3\text{A}'')$	1.76	41.41	5.26	121.65	4.86	112.54
$\text{OHgO}(^3\Sigma_g^-)$	-	-	2.45	57.40	2.05	48.28

<sup>a</sup> Ref [4] , <sup>b</sup> Ref [1]

**Table 4:** Dissociation energy ( $D_0$ ) and enthalpy of reaction for  $\text{M}(\text{O}_2)$  singlet

$\text{M}(\text{O}_2)$	$\text{M}(^1\text{S})+\text{O}_2(^1\Delta_g)$		$\text{MO}(^3\Pi)+\text{O}(^3\text{P})$	
	$D_0$ eV	$\Delta H_{298}^\circ$	$D_0$ eV	$\Delta H_{298}^\circ$
		Kcal/mol		Kcal/mol
<b>M(O<sub>2</sub>) singlet</b>				
$\text{ZnOO}(^1\Sigma^+)$	1.73	58.99	2.37	54.75
$\text{ZnOO}(^1\text{A}')$	1.93	45.2	2.57	59.99
$\text{ZnO}_2(^1\text{A}')$	0.46	48.34	1.10	26.32
$\text{OZnO}(^1\Sigma_g^+)$	-	-	1.33	30.03
$\text{CdOO}(^1\Sigma^+)$	1.26	30.28	2.16	51.03
$\text{CdOO}(^1\text{A}')$	1.89	44.38	2.79	65.13
$\text{OCdO}(^1\Sigma_g^+)$	-	-	0.57	13.93
$\text{HgOO}(^1\Sigma^+)$	1.73	39.96	3.19	73.82
$\text{HgOO}(^1\text{A}')$	1.74	40.71	3.21	74.57
$\text{OHgO}(^1\Sigma_g^+)$	-	-	0.75	18.33



For CdOO ( $^3\Sigma_g^-$ ) and CdOO ( $^3A''$ ), the dissociation energy involved is 1.76eV to break the Cd-O bond and 4.3eV to break the O-O bond. For OCdO( $^3\Sigma_g^-$ ) isomer, the value for breaking the Zn-O bond is 2.13eV. For the excited state CdOO ( $^1\Sigma^+$ ) and CdOO ( $^1A'$ ), the dissociation energy involved in this case is 1.26eV and 1.89eV respectively to rupture the Cd-O bond, 2.16 and 2.79eV to rupture the O-O bond. We also noticed for OCdO ( $^1\Sigma_g^+$ ), the dissociation energy obtained is 0.57eV to break the Cd-O bond. For HgOO ( $^3\Sigma_g^-$ ) and HgOO ( $^3A''$ ), the dissociation energy involved is 1.76eV to break the Hg-O bond and 4.86eV to break the O-O bond. For OHgO( $^3\Sigma_g^-$ ) isomer, the value for breaking the Hg-O bond is 2.05eV. For the excited state HgOO ( $^1\Sigma^+$ ) and HgOO ( $^1A'$ ), the dissociation energy involved in this case is 1.73eV and 1.74eV respectively to rupture the O-O bond and 3.2eV to rupture the Cd-O bond. As for isomer singlet state OHgO ( $^1\Sigma_g^+$ ), the dissociation energy obtained is 0.75eV to break the Hg -O bond. The examination of the PESs and the dissociation energies at B3LYP predict that OMO isomer has appreciable stability than the MOO.

## 5. Structural parameters

The equilibrium geometries, frequencies and the moment dipole obtained at the different levels of approximation for the M(O<sub>2</sub>) isomers are reported in [Table 5, 6 and 7]. It can be seen that the two bases used MWB and AVTZ-PP with the functional B3LYP give values quite close to each other, that's why we will just give the values obtained by AVTZ-PP during the discussion. For the two triplet isomers linear ( $^3\Sigma_g^-$ ) and bent ( $^3A''$ ) of zinc, cadmium and mercury superoxide ZnOO, CdOO and HgOO which are found to be repulsive states in the PES, the values of the M-O bond lengths obtained are of the order of 6-7 Å. The most intense mode corresponds to the O-O stretching vibration (1600cm<sup>-1</sup>) is comparable to the vibration frequency of the free O<sub>2</sub> molecule (1584cm<sup>-1</sup>) and the very low frequency 1-6 cm<sup>-1</sup> corresponds to the second stretching mode M-O. The values obtained for the geometry and spectroscopic proprieties of these isomers are in agreement with the reasoning above which is based on the values of dissociation energies which suggests that the two form of MOO are unstable and the interaction between these metals and dioxide O<sub>2</sub> is difficult to establish, so these two forms of dioxides cannot be formed under atmospheric conditions. For the linear OZnO, OCdO and OHgO ( $^3\Sigma_g^-$ ) isomers which have the minimum on the triplet PES, the bond length of Zn-O 1.72 Å is in agreement with the value (1.74 Å) obtained at CCSD(T) [3] and BPW91[4]. For the Cd-O and Hg-O bond length obtained in this work, they are 1.90 and 2.80 Å respectively. The length of the M-O bond in isomeric OMO remains almost unchanged compared to free M-O (Zn-O (1.7 Å), Cd-O (1.90 Å) and Hg-O (2.23 Å)[12]). For the OZnO and OCdO isomers whose experimental vibrational frequency values are given by Chertihin and Anderws [1], the symmetric Zn-O and Cd-O stretching mode calculated at the B3LYP level is 807.90cm<sup>-1</sup> and 651.82 cm<sup>-1</sup> respectively. They are higher than the values observed at 748.2 and 625.1 cm<sup>-1</sup> respectively and the deviation is between 60 et 30 cm<sup>-1</sup>. The calculation for OZnO at CCSD (T) leads to a value of 755 cm<sup>-1</sup> and the other calculation predicts 821 cm<sup>-1</sup> at BPW91/ 6-311+G\*. It can be noticed that the values obtained at the CCSD (T) estimate the values of the frequencies obtained experimentally in comparison with the values obtained at B3LYP and BPW91.

**Table 5:** Structural parameters calculated for stable forms and transition state of the Zn(O<sub>2</sub>) complexes in the lowest singlet and triplet states.

Methods	Basis	R <sub>O-O</sub> (Å)	R <sub>Zn-O</sub> (Å)	α(°)	μ(D)	ω <sub>1</sub>	ω <sub>2</sub> (cm <sup>-1</sup> ) <sup>1</sup>	ω <sub>3</sub> (cm <sup>-1</sup> )
ZnOO ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )								
B3LYP	AVTZ-PP	1.20	7.24	180.0	0.00	0.70	29.30	1626.28
	MWB	1.20	4.770	180.0	0.01	6.48	12.45	1614.75
ZnO <sub>2</sub> ( <sup>3</sup> A'')								
B3LYP	AVTZ-PP	1.20	7.144	160.727	0.00	3.26	27.96	1626.47
	MWB	1.2	4.698	160.219	0.012	5.23	27.77	1626.34
ZnO <sub>2</sub> TS ( <sup>3</sup> A <sub>2</sub> )								
B3LYP	AVTZ-PP	-	1.81	60.00	1.95	-782.0	411.42	542.00
	MWB	-	1.82	60.00	1.77	-235.0	545.75	609.91
OZnO ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )								
B3LYP	AVTZ-PP	-	1.72	180.0	0.00	179.7	641.55	807.90
	MWB	-	1.72	180.0	0.00	179.2	636.4	799.33
	Ref1	-	1.74	180.0	0.00	-	-	-
	Ref2	-	1.74	180.0	0.00	166	587	755
	Ref3	-	1.74	180.00	-	122	634	821
	Exp3							748.2
ZnOO ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )								
B3LYP	AVTZ-PP	1.20	7.057	180.0	0.00	4.20	35.40	1614.8
	MWB	1.20	4.760	180.0	0.012	6.53	29.59	1626.18
ZnOO ( <sup>1</sup> A')								
B3LYP	AVTZ-PP	1.25	2.137	123.32	2.67	148.4	321.38	1299.53
	MWB	1.25	2.164	123.543	2.60	135.8	310.79	1314.19
	Ref1	1.24	2.217	124.2	-	-	-	-
	Ref2	1.28	2.057	124.4	3.32	199	350	1196
ZnO <sub>2</sub> cyclic TS ( <sup>1</sup> A')								
B3LYP	AVTZ-PP	1.80	1.44	45.00	7.00	-519.2	258.12	1503.26
	MWB	1.78	2.053	45.00	5.57	-564.1	568.64	745.37
ZnO <sub>2</sub> ( <sup>1</sup> A')								
B3LYP	AVTZ-PP	1.80	1.90	55.00	7.64	61.88	419.70	507.92
	MWB	1.81	1.817	55.00	6.94	488.9	553.49	747.58
	Ref1	1.66	1.83	53.9	-	-	-	-
	Ref2	1.72	1.84	55.8	6.68	438	521	682
	Ref3	1.36	2.044	39.0	-	423	170	1150
ZnO <sub>2</sub> TS ( <sup>1</sup> A <sub>1</sub> )								
B3LYP	AVTZ-PP	1.80	2.23	95.00	5.73	-432.7	55.57	344.97
	MWB	-	1.73	95.00	5.02	-208.3	661.94	703.39
OZnO ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )								
B3LYP	AVTZ-PP	-	1.71	180.0	0.00	207.9	651.28	844.10
	MWB	-	1.713	180.0	0.00	207.3	644.52	834.54
	Ref1	-	1.73	180.00	0.00	-	-	-

**Table 6:** Structural parameters calculated for stable forms and transition state of the Cd(O<sub>2</sub>) complexes in the lowest singlet and triplet states.

Methods	Basis	R <sub>O-O</sub> (Å)	R <sub>Cd-O</sub> (Å)	α(°)	μ(D)	ω <sub>1</sub>	ω <sub>2</sub> (cm <sup>-1</sup> ) <sup>1)</sup>	ω <sub>3</sub> (cm <sup>-1</sup> )
CdOO ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )								
B3LYP	AVTZ-PP	1.20	8.31	180.00	0.00	1.98	29.44	1626.28
	MWB	1.20	6.929	180.00	0.00	3.23	29.44	1626.28
CdO <sub>2</sub> ( <sup>3</sup> A'')								
B3LYP	AVTZ-PP	1.20	7.018	141.52	0.00	4.45	34.79	1626.75
	MWB	1.20	7.02	141.72	0.00	4.28	34.65	1626.75
CdO <sub>2</sub> TS ( <sup>3</sup> A'')								
B3LYP	AVTZ-PP	1.83	1.9	55	3.24	-1075.	446.54	717.15
	MWB	1.83	1.9	55	3.21	-1065	448.17	715.27
OCdO ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> )								
B3LYP	AVTZ-PP	-	1.90	180.00	0.00	136.7	548.40	654.57
	MWB	-	1.91	180.00	0.00	139.0	546.93	651.82
	Ref1							626.6
CdOO ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )								
B3LYP	AVTZ-PP	1.20	7.16	180.00	0.00	1.80	35.37	1614.82
	MWB	1.31	2.049	180.0	5.77	-510.3	354.96	1220.12
CdOO ( <sup>1</sup> A')								
B3LYP	AVTZ-PP	1.24	2.48	123.75	2.51	109.2	264.47	1364.86
	MWB	1.24	2.47	123.75	2.51	105.4	260.93	1367.49
	Ref1							1124
CdO <sub>2</sub> TS ( <sup>1</sup> A <sub>1</sub> )								
B3LYP	AVTZ-PP	2.75	1.94	90.00	8.46	-224.0	-82.99	574.79
	MWB	2.75	1.94	90.00	8.49	-223.9	-83.02	573.46
OCdO ( <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> )								
B3LYP	AVTZ-PP	-	1.9	180.00	0.00	163.3	555.53	692.64
	MWB	-	1.90	180.00	0.00	164.9	554.99	689.94

As for the singular multiplicity isomers, the two bent forms of ZnOO and CdOO (<sup>1</sup>A') that present a global minimum on the singlet PES. The geometric equilibrium structure shows that this isomer is weakly bent, the angle being 123.32° for ZnOO comparable to that was found at CCSD(T) 124°, and for the CdOO the angle being 123.75° is similar at to ZnOO angle. For Zn-O and Cd-O, the length bond is 2.137Å-2.479Å respectively. Relative to regarding the free M-O molecule (Zn-O 1.7Å and Cd-O 1.9Å), the M-O bond in OMO underwent an appreciable elongation of the order of 0.5Å. As for the length of the O-O bond 1.24 Å, it remains almost unchanged compared to that of free O<sub>2</sub>. For the asymmetric CdOO isomer, it was identified from bands at 1124 and 1129 cm<sup>-1</sup> in solid argon and nitrogen following the reaction with to ozone which is close with the value found in this work 1220.12 cm<sup>-1</sup>. For ZnOO (<sup>1</sup>A'), this isomer is not identified

experimentally, the different frequency values obtained in this present work are 148.4, 321.38 and 1299.53  $\text{cm}^{-1}$ , so theoretically at BPW91 suggest 199, 350 and 1196  $\text{cm}^{-1}$ . For  $\text{HgOO} (^1\text{A}')$ , this isomer is not identified as minimum in our PES. For the other isomer  $\text{OMO} (^1\Sigma_g^+)$  which is found as a local minimum on the singlet PES has a linear form, and the Zn-O bond found 1.71 Å is in agreement with CCSD(T) 1.73 Å. For Cd-O and Hg-O, the bond length is 1.90 Å and 1.859 Å respectively. For the symmetric Zn-O, Cd-O and Hg-O, the stretching modes calculated in this work was found 844.10, 689.94 and 772.82  $\text{cm}^{-1}$  respectively.

**Table 7:** Structural parameters calculated for stable forms and transition state of the  $\text{Zn}(\text{O}_2)$  complexes in the lowest singlet and triplet states.

Methods	Basis	$R_{\text{O-O}}$ (Å)	$R_{\text{Hg-O}}$ (Å)	$\alpha(^{\circ})$	$\mu(\text{D})$	$\omega_1$	$\omega_2(\text{cm}^{-1})$ <sup>1)</sup>	$\omega_3(\text{cm}^{-1})$
<b>HgOO (<math>^3\Sigma_g^-</math>)</b>								
B3LYP	AVTZ-PP	1.20	6.00	180.00	0.00	7.01	29.31	29.31
	MWB	1.20	6.09	180.00	0.00	3.27	29.29	1626.28
<b>HgOO (<math>^3\text{A}''</math>)</b>								
B3LYP	AVTZ-PP	1.20	6.00	160.00	0.00	7.3	29.04	1626.43
	MWB	1.20	6.13	160.31	0.00	1.69	28.55	1626.45
<b>HgO<sub>2</sub> TS (<math>^3\text{A}_2</math>)</b>								
B3LYP	AVTZ-PP	2.12	2.12	60.00	5.60	-231.6	293.02	396.55
	MWB	2.12	2.12	60.00	5.79	277.7	463.11	465.37
<b>OHgO (<math>^3\Sigma_g^-</math>)</b>								
B3LYP	AVTZ-PP	-	1.86	180.00	0.00	202.4	654.11	735.84
	MWB	-	1.86	180.00	0.00	202.9	652.44	734.35
<b>HgOO (<math>^1\Sigma_g^+</math>)</b>								
B3LYP	AVTZ-PP	1.2	6.94	180.00	0.00	4.95	35.12	1614.84
	MWB	1.6	6.10	180.00	0.00	2.74	35.53	1614.84
<b>HgOO (<math>^1\text{A}'</math>)</b>								
B3LYP	AVTZ-PP	1.21	3.06	123.97	0.71	52.92	136.4	1545.46
	MWB	1.21	3.062	124.01	0.718	52.68	134.18	1547.29
<b>HgO<sub>2</sub> TS (<math>^1\text{A}_1</math>)</b>								
B3LYP	AVTZ-PP	-	1.98	75.00	5.85	-222.9	-123.79	514.61
	MWB	-	1.98	75.00	5.87	-222.9	-122.8	513.84
<b>OHgO (<math>^1\Sigma_g^+</math>)</b>								
B3LYP	AVTZ-PP	-	1.85	180.00	0.00	238.7	674.79	776.48
	MWB	-	1.85	180.00	0.00	239.0	670.47	772.82

Mulliken population analyses for different species have been performed to determine the dipole moment and charge distribution [Table 8]. For all linear forms, the computed results found predict dipole moment values  $\mu=0.00\text{D}$ . For  $\text{ZnOO}$  and  $\text{CdOO } ^1\text{A}'$ , the calculations suggest that they have a moment dipole of  $\mu=2.67\text{D}$  and  $\mu=2.51\text{D}$  respectively. For  $\text{HgOO } ^1\text{A}'$ , it is not identified in our PES calculation as a minimum. The analysis of the distribution of the charges suggests the oxygen atoms are nucleophiles in all dioxides and the metals

have a positive charge, so we can conclude that the interaction of dioxides with metals produce the  $M^{2+}O_2^{2-}$ . This suggestion is in accordance with the theoretical works done at CCSD(T) and B1LYP and at BPW91 on  $Zn(O_2)$  isomers.

**Table 8:** charge distribution obtained from Milliken population analysis for  $M(O_2)$

	$ZnOO\ ^3\Sigma_g^-$	$ZnOO\ ^3A''$	$OZnO\ ^3\Sigma_g^-$	$ZnOO\ ^1\Sigma_g^+$	$ZnOO\ ^1A'$	$Zn(O_2)\ ^1A'$	$OZnO\ ^1\Sigma_g^+$
$q_M$	0.0010	0.0011	1.14	0.0011	0.26	1.16	1.18
$q_M^a$	-	-	1.52	-	0.39	1.47	-
$q_O$	0.0053	0.0030	-0.57	0.0048	-0.09	-0.53	-0.59
$q_O^a$	-	-	-0.76	-	-0.24	-0.73	-
$q_{O1}^b$	-0.0064	-0.0041	-	-0.0059	-0.17	-0.62	-
$q_{O1}^a$	-	-	-	-	-0.15	-	-
	$CdOO\ ^3\Sigma_g^-$	$CdOO\ ^3A''$	$OCdO\ ^3\Sigma_g^-$	$CdOO\ ^1\Sigma_g^+$	$CdOO\ ^1A'$	$Cd(O_2)\ ^1A'$	$OCdO\ ^1\Sigma_g^+$
$q_M$	-0.00	-0.00	1.43	0.74	0.269	-	1.48
$q_O$	0.0039	0.00129	-0.719	-0.50	-0.133	-	-0.74
$q_{O1}^b$	-0.0039	-0.00128	-	-0.238	-0.136	-	-
	$HgOO\ ^3\Sigma_g^-$	$HgOO\ ^3A''$	$OHgO\ ^3\Sigma_g^-$	$HgOO\ ^1\Sigma_g^+$	$HgOO\ ^1A'$	$Hg(O_2)\ ^1A'$	$OHgO\ ^1\Sigma_g^+$
$q_M$	-0.00	-0.00	1.28	-0.00	0.044	-	1.33
$q_O$	0.0078	0.0057	-0.64	0.0075	-0.009	-	-0.66
$q_{O1}^b$	-0.007	-0.0057	-	-0.00749	-0.035	-	-

Ref <sup>a</sup> [3]

<sup>b</sup>In superoxides, O-oxygen atom bonded to the metal; O1-terminal oxygen atom.

**Table 9:** wavelengths  $\lambda$  (nm) and the existence domain of isomers  $M(O_2)$  calculated at B3LYP

	$M+O_2$		$MO+O$	
	$\lambda$ (nm)	Domain	$\lambda$ (nm)	Domain
ZnOO	703	Visible	303	UV
OZnO	-	-	441	Visible
ZnOO	484	Visible	522	Visible
ZnOO	632	Visible	476	Visible
OZnO	-	-	952	IR
CdOO	705	Visible	269	UV
OCdO	-	-	539	Visible
CdOO	944	IR	560	Visible
CdOO	644	Visible	439	Visible
OCdO	-	-	2052	IR
HgOO	705	Visible	236	UV
OHgO	-	-	501	Visible
HgOO	714	Visible	386	Visible – UV
OHgO	-	-	1559	IR

## 6. Possible existence and stability of dioxide in the atmosphere

The analysis of the wavelengths obtained from the enthalpies of the reaction collected in table 9 indicates that the maxima wavelengths corresponding are in the visible regions and Ultra-violet for the MOO, whereas for the linear OMO where the maxima of wavelengths absorbed 952, 2052 and 1559 nm of  $\text{OZnO}$ ,  $\text{OCdO}$  et  $\text{OHgO}$  respectively, in the infrared domain show some stability compared to MOO isomers. This result confirmed the above data of the dissociation energies, the vibration frequencies, the geometries and the experimental studies of these species which suggest that MOO isomers are unstable and OMO isomers are metastable and possible exists in the gas phase as well in the atmosphere.

## 7. Conclusion

In this work, we presented a detailed theoretical study of the dioxide compounds of group 12  $\text{Zn}(\text{O}_2)$ ,  $\text{Cd}(\text{O}_2)$  and  $\text{Hg}(\text{O}_2)$  resulting from the two dissociative limits  $\text{M} + \text{O}_2$  and  $\text{MO} + \text{O}$ . In the first step, we were able to identify the stable forms and the intermediates as well as the transition states involved according to the two PESs  $^3\text{A}''$  and  $^1\text{A}'$ . The exploration of potential surfaces, structural properties, dissociation energies, reaction enthalpies and wavelengths allowed us to show that OMO linear forms are more stable than their MOO isomers. For the bent isomers of  $\text{M}(\text{O}_2)$ , only the  $\text{ZnOO } ^1\text{A}'$  and  $\text{CdOO } ^1\text{A}'$  states have been identified as minimum in the PES, whereas for  $\text{Hg}(\text{O}_2)$ , no bent isomer can be presented. All calculations confirm that the MOOs triplet are unstable and cannot exist in different forms and states. These suggestions presented in this work are in accordance with the experimental studies and theoretical investigations at high level of stability on the  $\text{Zn}(\text{O}_2)$  and  $\text{Cd}(\text{O}_2)$ .

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