

# Response to ‘Comment on “Topological Analysis of the Electron Density in the Carbonyl Complexes $M(\text{CO})_8$ ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ )”’

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**ABSTRACT:** The Comment by Holzmann *et al.* does not properly reflect the conclusions of the original article, as shown in the current response. New calculations on the title compounds, as well as on  $M(\text{CO})_2$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ) complexes with both  $D_{\infty h}$  and  $C_{2v}$  symmetry, included in the current response and based not only on the Quantum Theory of Atoms in Molecules but also on the Natural Bond Orbital approach, strengthen the arguments of the original article.

In a recent publication,<sup>1</sup> the bonding in alkaline-earth carbonyl complexes  $\text{Ca}(\text{CO})_8$  (**1**),  $\text{Sr}(\text{CO})_8$  (**2**), and  $\text{Ba}(\text{CO})_8$  (**3**) in their ground states ( $T$ ,  $O_h$ ), which had been previously synthesized and analyzed,<sup>2,3</sup> has been theoretically studied using both the Quantum Theory of Atoms in Molecules (QTAIM) and the Electron Localization Function (ELF) approaches, among others, through the calculation of several tools related to bond order, bond strength, and covalent/electrostatic character of bonds. In a Comment to that publication,<sup>4</sup> Holzmann *et al.* claim to have refuted one of its main conclusions (i.e. the absence of any significant  $\pi$ -backdonation) by focus themselves in just one of the many properties calculated, namely the delocalization indexes for non-bonding  $\text{M}\cdots\text{O}$  interactions ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) calculated using the QTAIM methodology. But, in the authors's opinion, this is far from being proved, as stated below.

Firstly, not only topological descriptors based on real-space partitioning methods are used in Ref. 1 to study the bonding in **1–3**, as Holzmann *et al.* claim. Bond orders (Table 4 of Ref. 1) are calculated directly from MO's (without any topological partition of the electron density) and, as explained in the 'Results and Discussion' section of Ref. 1, when only  $\pi$  MO's are used M–C bond orders are negligible in these complexes: “*This behavior is observed in other functions too, like in LBO- $\pi$  and WBO- $\pi$ , giving values of 0.001 and 0.058, respectively, for the Ba–C  $\pi$  bond order (compare with 0.120 and 0.626 in Table 4 for the global bond order), with equivalent results for the other two complexes.*”<sup>1</sup> It is highly unlikely that for any kind of bonding interaction (except for a pure electrostatic interaction), even for the highly polar M–C covalent bonds present in **1–3**, no trace of any significant  $\pi$  bond order for the M–C bond is present if  $\pi$ -backdonation existed.

Secondly, also in the 'Results and Discussion' section of Ref. 1, ELF and ELF- $\pi$  functions are analyzed, which are not based on the QTAIM approach used for the calculation of delocalization indexes, but on a completely different partition of the molecular space (namely, on the conditional same-spin pair density), leading to the same conclusion: “*In addition, when only  $\pi$  molecular orbitals are taken into account to calculate ELF (a procedure which is commonly known as ELF- $\pi$ ), a featureless picture is obtained in the metal-ligand bonding regions of **1–3** (see Figure S5 in the Supporting Information)*”<sup>1</sup> Here again, it is highly unlikely that for any kind of bonding interaction (except for a pure electrostatic interaction), even for the highly polar M–C covalent bonds present in **1–3**, no trace of any significant ELF- $\pi$  is present in the M–C bonding region if  $\pi$ -backdonation existed.

Thirdly, even within the QTAIM approach many of the properties calculated are not based on the electron density alone, as Holzmann *et al.* claim.<sup>4</sup> On the contrary most of them are obtained from the molecular wave function itself since they need the first- or second-order reduced density matrices, like, for instance, the delocalization indexes. This is the reason behind the fact that these indexes, among other properties, cannot be obtained from the *experimental* electron density, when available from X-ray data.

Fourthly, when comparing theoretical data, in order to obtain reliable results, it is essential to use equivalent model chemistries, and this is not the case with the data reported in Table 1 of Ref. 4. The criticism in Ref. 4 is mainly based on their reported data for the complexes Ca(CO)<sub>2</sub> (**1'**), Sr(CO)<sub>2</sub> (**2'**), and Ba(CO)<sub>2</sub> (**3'**) in  $D_{\infty h}$  symmetry, which are calculated using “the same M–CO distance as in M(CO)<sub>8</sub>”.<sup>4</sup> By performing a frequency calculation with that geometry, at the M06-D3/def2-TZVPP level used in Ref. 4 for their calculations, the number of imaginary frequencies found is, respectively, 4, 5, and 4 for the triplet states, which are the ground states (see below), with similar results for the singlet states. When the M06-2X-D3/def2-TZVPP level (used in Refs. 1 and 2) is utilized instead the situation is not much better, as the number of imaginary frequencies found is, respectively, 2, 2, and 5, again for the triplet states, with similar inconsistent results for the singlet states. Although it is true that Holzmann *et al.* use optimized geometries in order to calculate *frequencies*, they still use the non-optimized frozen geometries to calculate the *delocalization indexes*, thus leading to unreliable results. A proper geometry optimization (at both M06-D3/def2-TZVPP and B3P86-D3/QZVP levels, see Table S1 of the Supporting Information) led to minima (no imaginary frequencies) in the three compounds **1'–3'** in their triplet states with  $D_{\infty h}$  symmetry. When these results are followed by an electronic structure calculation using all-electron basis sets equivalent to the ones used in Ref. 1 (M06-D3/6-311++G(3df,3pd),DKH3-QZP) the results included in Table 1 are found, which show  $\delta(\text{M}\cdots\text{O})$  values not only between 3 and 4 times higher than those calculated by Holzmann *et al.*, but also between 4 and 5 times higher than those obtained for complexes **1–3** (see Table 3 in Ref. 1). In addition,  $\delta(\text{M–C})$  values for **1'–3'** (Table 1) are three times higher than those of **1–3** (see Table 2 in Reference 1) and follow the correct tendency (increasing from **1'** to **3'**), which is not the case for the data reported by Holzmann *et al.* Moreover, if the following approximate relationship between the  $\delta^{\text{AB}}$  delocalization index and the exchange-correlation term of the A–B interaction energy is used,<sup>5</sup>

$$V_{xc}^{AB} \approx -\frac{\delta^{AB}}{2R}$$

(with  $R$  the interatomic distance in au), then the values in Table 2 are found (compare with Table 7 in Ref. 1), which show a relevant covalent contribution to the M–CO bonding of M⋯O interactions in **1'**–**3'**. To sum up, in complexes **1'**–**3'** the  $\delta(\text{M}\cdots\text{O})$  values obtained in the current study are consistent with a non-negligible  $\pi$ -backdonation which could account for the calculated red-shifts in these compounds, which is not the case for complexes **1**–**3**. Nevertheless, experimental results could well show a bent geometry with a  $C_{2v}$  symmetry instead of the  $D_{\infty h}$  symmetry proposed by Holzmann *et al*, and hence they could have strong  $\text{C}_{\text{CO}}\cdots\text{C}_{\text{CO}}$  interactions just like complexes **1**–**3**. As a matter of fact, the global minimum for the  $\text{M}(\text{CO})_2$  species ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) found by using both M06-D3/def2-TZVPP and B3P86-D3/QZVP levels of calculation is not given by the above linear **1'**–**3'** complexes but for the bent **1''**–**3''** compounds instead (see Figures S1–S3 and Table S1 in the Supporting Information), where bond critical points are found between C atoms, which are clear signs of some kind of non-covalent interaction between CO groups.  $\delta(\text{M}-\text{C})$  and  $\delta(\text{M}\cdots\text{O})$  delocalization indexes for **1''**–**3''** are included in Table 1, showing values very similar to those obtained for complexes **1'**–**3'**, but  $\delta(\text{C}_{\text{CO}}\cdots\text{C}_{\text{CO}})$  values obtained for the bent  $C_{2v}$  complexes, which are 0.407, 0.392, and 0.352, respectively, show that  $\text{C}_{\text{CO}}\cdots\text{C}_{\text{CO}}$  interactions are likely to be responsible for the red-shifts predicted for these compounds, just like for **1**–**3** complexes.

Finally, in order to rationalize the mechanism of the  $\text{C}_{\text{CO}}\cdots\text{C}_{\text{CO}}$  interactions observed in both **1**–**3** and **1''**–**3''** complexes, a Natural Bond Order (NBO) analysis has been performed,<sup>6</sup> leading to the existence of a significant charge transfer between the occupied  $\pi$  orbitals of each CO group and the empty  $\pi$  orbitals of their adjacent CO groups (see Figure 1). While no donation is detected from the metal  $d_{\pi}$  orbitals to  $\pi^*$  CO orbitals, the  $\pi(\text{CO}) \rightarrow \pi^*(\text{CO})$  charge transfer is estimated to be around 0.2 e for each CO ligand.

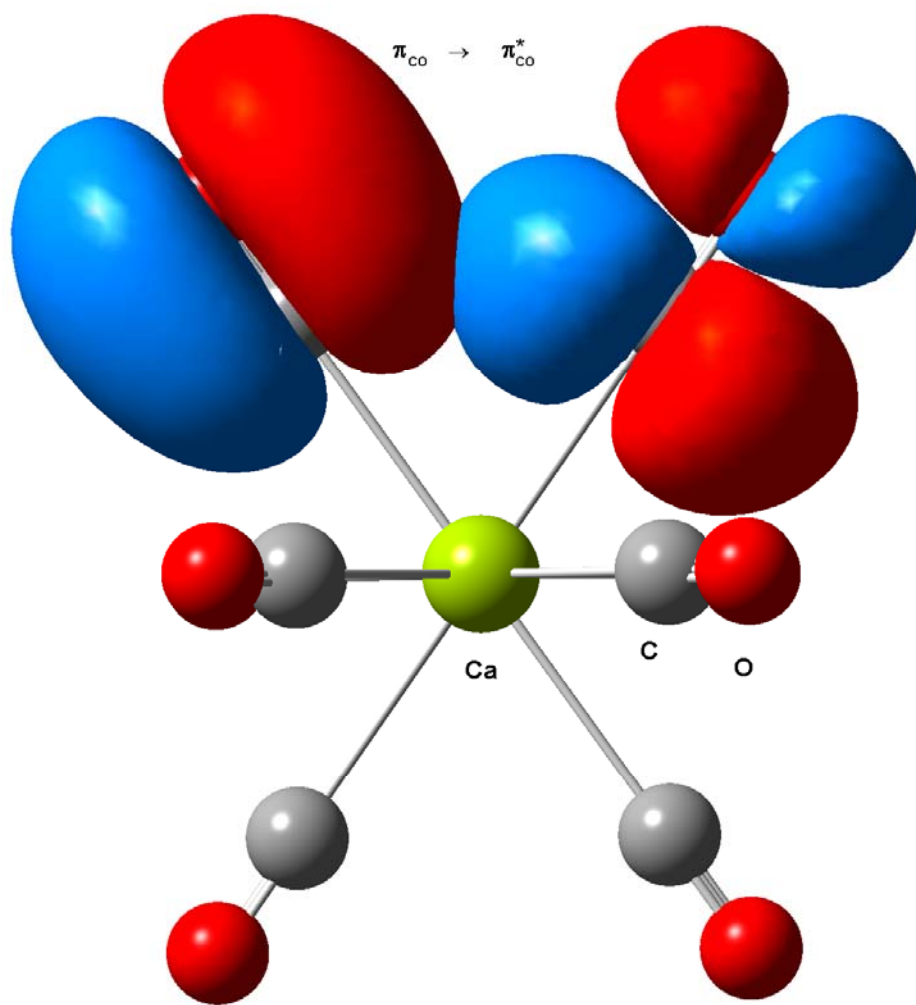
**Table 1. Delocalization indexes for M–C bonding and M⋯O non-bonding interactions, and CO stretch frequency shifts<sup>a</sup> (relative to free CO),  $\nu(\text{CO})-\nu_0(\text{CO})$  (in  $\text{cm}^{-1}$ ) for complexes 1'–3' ( $D_{\infty h}$ ), and 1''–3'' ( $C_{2v}$ )**

Complex	$\delta(\text{M–C})$	$\delta(\text{M}\cdots\text{O})$	$\Delta\nu$
$\text{Ca}(\text{CO})_2$ ( $D_{\infty h}$ )	0.555	0.101	–225
$\text{Sr}(\text{CO})_2$ ( $D_{\infty h}$ )	0.572	0.102	–230
$\text{Ba}(\text{CO})_2$ ( $D_{\infty h}$ )	0.650	0.121	–220
$\text{Ca}(\text{CO})_2$ ( $C_{2v}$ )	0.519	0.101	–176
$\text{Sr}(\text{CO})_2$ ( $C_{2v}$ )	0.520	0.103	–182
$\text{Ba}(\text{CO})_2$ ( $C_{2v}$ )	0.676	0.144	–198

<sup>a</sup>The calculated values refer to the harmonic antisymmetric stretching frequencies, scaled by a correction factor of 0.9567, obtained from the quotient of the calculated value for free CO ( $2240 \text{ cm}^{-1}$ ) and its experimental value:  $\nu_0(\text{CO}) = 2143 \text{ cm}^{-1}$  (taken from Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand-Reinhold: New York, 1979.).

**Table 2. Approximate exchange-correlation term contribution,  $V_{xc}^{AB}$  (in  $\text{kcal mol}^{-1}$ ), to the bonding interaction energy for complexes 1', 2', and 3'**

Interaction	$\text{Ca}(\text{CO})_2$	$\text{Sr}(\text{CO})_2$	$\text{Ba}(\text{CO})_2$
M–C	–39.427	–37.811	–39.550
M⋯O	–4.798	–4.618	–5.178



**Figure 1.** NBO representation of the overlap between a  $\pi$  orbital of a CO group and an empty  $\pi$  orbital of an adjacent CO group in complex **1** (isosurfaces value: 0.022 au).

## ASSOCIATED CONTENT

**Supporting Information.** Atomic coordinates of optimized structures in xyz format at M06-D3/def2-TZVPP and B3P86-D3/QZVP levels of complexes **1'**–**3'** and **1''**–**3''** (Table S1), and representations of the molecular graph for complexes **1''**–**3''** (Figures S1–S3). The Supporting Information is available free of charge on the ACS Publication website at DOI: 10.1021/cas.organomet.0000000.

## Notes

The author declares no competing financial interest.

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## REFERENCES

- (1) Van der Maelen, J. F. Topological Analysis of the Electron Density in the Carbonyl Complexes  $M(CO)_8$  ( $M = Ca, Sr, Ba$ ). *Organometallics* **2020**, *39*, 132-141.
- (2) Wu, X.; Zhao, L.; Jin, J.; Pan, S.; Li, W.; Jin, X.; Wang, G.; Zhou, M.; Frenking, G. Observation of Alkaline Earth Complexes  $M(CO)_8$  ( $M = Ca, Sr, or Ba$ ) that Mimic Transition Metals. *Science* **2018**, *361*, 912–916.
- (3) (a) Landis, C. R.; Hughes, R. P.; Weinhold, F. Comment on “Observation of Alkaline Earth Complexes  $M(CO)_8$  ( $M = Ca, Sr, or Ba$ ) that Mimic Transition Metals”. *Science* **2019**, *365*, aay2355.  
(b) Zhao, L.; Pan, S.; Zhou, M.; Frenking, G. Response to Comment on “Observation of Alkaline Earth Complexes  $M(CO)_8$  ( $M = Ca, Sr, or Ba$ ) that Mimic Transition Metals”. *Science* **2019**, *365*, aay5021.
- (4) Holzmann, N.; Fernández, I.; Frenking, G. Comment on “Topological Analysis of the Electron Density in the Carbonyl Complexes  $M(CO)_8$  ( $M = Ca, Sr, Ba$ )”. *Organometallics* **2020**, *39*, 2956-2958.
- (5) Popelier, P. L. A. Quantum Chemical Topology. *Struct. Bond.* **2016**, *170*, 71–118.

(6) Glendening, E. D.; Badenhop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Karafiloglou, P.; Landis, C. R.; Weinhold, F. *NBO 7.0*; Theoretical Chemistry Institute; University of Wisconsin: Madison, WI, 2018.