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## Reply to the 'Comment on "Revisiting $\pi$ backbonding: the influence of d orbitals on metal–CO bonds and ligand red shifts"' by G. Frenking and S. Pan, *Phys. Chem. Chem. Phys.*, 2019, 22, DOI: 10.1039/C9CP05951B

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We respond to the comment by Pan and Frenking with regard to our investigation on transition and alkaline earth metal d orbital influence on their bonding to carbonyl ligands to clarify misconceptions. We do not consider the points raised in the comment as affecting our conclusions.

In their comment on our work, Pan and Frenking raise several concerns with regard to our conclusions and methodology which we are pleased to address in order to eliminate any ambiguities about our computational approach and the aim of the investigation in ref. 1. We have identified several minor points which we would like to discuss first and that we consider as rather a semantic misconception than a deep conceptual disagreement.

Pan and Frenking state that our mentioning of the seminal work by Bauschlicher and Bagus<sup>2</sup> is misleading since their approach as well as conclusion are inherently different from ours. The latter is absolutely correct. We also have not claimed anything to the contrary. Our mentioning of the work by Bauschlicher and Bagus<sup>2</sup> served the purpose to give, as we believe, due credit for the earliest mentioning of a basis set restriction in the context of carbonyl complexes. We referred to the "No 4s/4p metal basis set" (NSPMBS) they introduced and their conclusion that "[the total energy difference between full metal basis set and NSPMBS] is a very small fraction of the total  $E_{\text{int}}$ : 12% for Ni(CO)<sub>4</sub> and 5% for Fe(CO)<sub>5</sub> [...] [t]his is, however, an upper limit to the contribution of the metal 4s and 4p orbitals to the bonding". In analogy to this we pointed out that our basis set truncation presents a limit to the "combined  $\sigma$ -donation/ $\pi$ -backdonation effect". We did not mention this work in support of our results and of course the constrained space orbital variation method is completely different from what we did; we mentioned this work to not imply that we are the first ones

restricting a basis to test the effect of certain contributions in the context of carbonyl complexes. We hope that this misunderstanding is clarified.

We furthermore wondered about the repeated mentioning of the Ca–C bond strengthening by d orbitals in the comment by Pan and Frenking, which seems to imply that we have not acknowledged this fact. However, we have reiterated the crucial role of d functions in the stabilization of the calcium-carbonyl bond on several occasions. In fact, it is the first point we raise in our conclusions section. In their comment Pan and Frenking referred to our conclusion that the "[c]harge transfer from the central atom on the ligands in metal carbonyl complexes is not dependent on metal d functions and the formation of M–C  $\pi$  bonds which are often used to rationalize the bonding in this kind of complexes" and made a statement that this challenges the validity of the Dewar–Chatt–Duncanson (DCD) model.<sup>3,4</sup> We do clearly show that significant charge transfer occurs regardless of d-orbitals and their covalent contribution to bonding, but we never claimed that d-orbitals are unimportant for M–C bonding. We absolutely agree that the transition metal–carbonyl bond is only stable due to the pronounced covalency brought in by the central atom d functions. While criticizing our statement that "the admixture of Ca d states in Ca(CO)<sub>8</sub> is not the inherent reason for the occurrence of a CO redshift in these complexes, but merely a stabilizing factor of the overall complex", Pan and Frenking again referred to the importance of d-orbitals for covalent bonding and complex stability, although this statement only concerns the red shifts of the CO ligands. When the d-orbitals are reintroduced, the covalent bonds are formed and the complex becomes stable. This is what we meant to express by "stabilizing factor". We believe there is a big difference between this statement and saying that "the orbitals of Li in LiF are unimportant for the charge transfer to F complexes, but merely a stabilizing factor of the overall complex".

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At this point we also want to mention that we agree with the notion that Ca indeed shows some transition metal-like behavior, even if a preprint of our work was previously cited to in defense of a somewhat contrarian statement.<sup>5</sup> Upon the re-introduction of Ca d functions into the basis, one can observe a similar significant stabilization of the complex and increased covalency (charge back-transfer to Ca and reduction of the CO stretch red shift) as with the true transition metal Ti<sup>2+</sup>, while Mg behaves qualitatively differently. We therefore do not share the interpretation of Landis *et al.* that “nominal calcium-centered d-type basis orbitals [are] acting primarily to augment the basis functions of the [(CO)<sub>8</sub>]<sup>2-</sup> dianion”. Our observation also aligns well with the repeatedly reported covalent character of transition metal bonds in solid state chemistry<sup>6–10</sup> and the charge retention or, as Raebiger, Lany and Zunger have called it in their work,<sup>11</sup> “charge self-regulation” of transition metals. The observation of this behavior (in a weaker form) on Ca can be potentially very informative far beyond carbonyl chemistry. Other than that, we certainly do not contest the fact that metal to CO charge donation is key to binding; indeed we emphasize the oxidized nature of Ca in spite of its zero formal oxidation state. What we have seen from the basis set truncation, however, is a restoration of the covalency of the Ca–C bond *via* the  $\pi$  contributions, which leads to a transfer of 0.3  $e^-$  from the CO ligands to Ca and in turn, and this should not be surprising, to a stabilization of the CO bond. Without any d contributions the metal–CO interaction is very weak (unstable), highly ionic and leads to strong red shifts. However, the quantitative comparison between different metals and the red shifts they introduce on CO ligands is rather meaningless if one wants to probe the influence of one specific type of metal orbitals, which is why we made use of truncated basis sets. We do not see a principal disagreement between our findings and what has been stated about the interpretation of our results in the comment by Pan and Frenking.

One of the reasons we want to highlight the effect of d functions in contrast to a (also artificial) non-d system is that in the ground-breaking work on neutral heavy group II carbonyls by Wu *et al.*<sup>12</sup> (to which also the authors of the comment, Pan and Frenking, have contributed) the CO red shift in these complexes itself was presented as indicator for transition metal-like behavior in contrast to what would be expected if Ca would be a true s block element. This is the view we want to challenge with our investigation, not the validity of the DCD model which itself is not concerned with contrasting the behavior of s and d block metals.

With all this being said, we want to address the methodological criticisms of the comment. Pan and Frenking referenced the work by Landis, Hughes and Weinhold<sup>5</sup> to point towards a perceived methodological shortcoming, claiming that “Landis *et al.* optimized the geometry of Ca(CO)<sub>8</sub> where they not only deleted the calcium d functions, but they also deleted all Fock matrix elements which contain Ca d-orbital Fock matrix elements.”. However, we do not find this extra step in the original work, which states that “[o]ptimization of the geometry using basis sets that lack d orbitals on Ca or optimization after deletion of all Fock matrix elements involving calcium d-type natural atomic orbitals lead to modest changes in geometry”. When we do not use the Ca d basis functions, there cannot be matrix elements over them by construction.

As Pan and Frenking pointed out, the d-truncated Ca(CO)<sub>8</sub> system with O<sub>h</sub> symmetry is not a minimum of the electronic potential energy surface (PES) anymore, although an electronically stable calcium octacarbonyl complex exists with a distorted (C<sub>1</sub>) geometry, and possesses imaginary (doubly degenerate) e<sub>u</sub> and (triply degenerate) t<sub>1u</sub> vibrational modes (with magnitudes of 40.08 cm<sup>-1</sup>, and 27.61 cm<sup>-1</sup>, respectively). We, however, stuck with the O<sub>h</sub> symmetry to remain consistent in the chosen complex geometry as well as orbital type and ordering to simplify the comparative discussion. Our focus was

**Table 1** Optimized complex geometry in Cartesian coordinates of the Ca(CO)<sub>8</sub> complex in O<sub>h</sub> symmetry (left) and C<sub>1</sub> symmetry (right) with the M06-2X functional and a truncated cc-pVQZ basis set containing only s- and p-type functions. Convergence thresholds of 10<sup>-6</sup> E<sub>h</sub> for the total energy and 1.5 × 10<sup>-5</sup> E<sub>h</sub>/a<sub>0</sub> for the interatomic forces were applied

Atom	O <sub>h</sub> Complex Coordinates [a <sub>0</sub> ]			C <sub>1</sub> Complex Coordinates [a <sub>0</sub> ]		
	X	Y	Z	X	Y	Z
Ca	0.000000	0.000000	0.000000	0.127746	0.121863	-0.001464
C	2.851639	2.851639	2.851639	3.241567	2.529935	2.986569
O	4.081715	4.081715	4.081715	4.626454	3.511796	4.271598
C	2.851639	-2.851639	2.851639	2.410043	-3.273237	2.723929
O	4.081715	-4.081715	4.081715	3.323976	-4.807598	3.885200
C	2.851639	2.851639	-2.851639	2.526376	3.279454	-2.950074
O	4.081715	4.081715	-4.081715	3.504125	4.685483	-4.215060
C	-2.851639	-2.851639	-2.851639	-2.311367	-3.267027	-2.654235
O	-4.081715	-4.081715	-4.081715	-3.297791	-4.780440	-3.785032
C	-2.851639	2.851639	-2.851639	-3.275804	2.385015	-2.730106
O	-4.081715	4.081715	-4.081715	-4.812833	3.289384	-3.895520
C	-2.851639	2.851639	2.851639	-2.475191	3.278430	2.831288
O	-4.081715	4.081715	4.081715	-3.546568	4.665108	4.042135
C	2.851639	-2.851639	-2.851639	3.291138	-2.442462	-2.858541
O	4.081715	-4.081715	-4.081715	4.679108	-3.497412	-4.082110
C	-2.851639	-2.851639	2.851639	-3.251922	-2.324324	2.651735
O	-4.081715	-4.081715	4.081715	-4.763119	-3.311015	3.785359

the effect of metal d orbitals on the CO stretch frequencies in these metal–carbonyl complexes, whose modes remain non-imaginary and therefore could be utilized for comparison. We do not claim that an imaginary  $O_h$  calcium octacarbonyl complex without d functions is a stable geometry, but rather that the red shift does not vanish in such an imaginary system and the charge transfer to the carbonyl ligands becomes even more pronounced as covalency decreases. We also want to give some attention to the fact that the stable  $C_1$ -symmetric complex (which is an electronic PES minimum, although only  $4 \text{ kJ mol}^{-1}$  more stable than the  $O_h$ -symmetric complex) has a very similar CO red shift ( $-138 \text{ cm}^{-1}$ ) and Ca–C–O bond angles close to  $180^\circ$  ( $\sim 177.3^\circ$ – $178.5^\circ$ ). The molecular geometries of the  $O_h$  and  $C_1$  complexes are given in Table 1 for comparison. The SOMO level remains CO  $\pi^*$ -dominated, but Ca contributions become noticeable ( $\sim 11\%$  for HOMO-1,  $\sim 42\%$  for HOMO level according to eqn (2) in the manuscript, splitting caused by the lifted degeneracy) due to the distorted symmetry which leads to Ca s and p contributions similar to what we reported with Mg. While it lacks the correct, experimentally observed geometry, it still implies that d functions on Ca are the reason for increased covalency and mitigate the red shift caused by charge transfer to the CO ligands in a bound energy regime (while making the complex significantly more stable).

Finally, we believe the criticism with respect to the basis set superposition error (BSSE) is misplaced. In the Supporting Information in ref. 1, we analyzed the effects of basis size and BSSE for the octacarbonyl complexes not only of Ca, but also of  $Ti^{2+}$  and Mg (which does not have significant metal d contributions), showing that they are small for all systems. In any case, the BSSE argument does not fully apply here as the whole purpose to remove the d functions is precisely to test the effect of such controlled incompleteness. Basis functions, however diffuse, of an atom-centered basis set, which are localized on the ligand cannot possibly replace the deleted d functions centered on Ca as they do not span the same space. There is a BSSE effect, but it cannot in principle compensate for the removal of the d functions.

All in all, we hope that our response clarifies the picture we wanted to provide about the influence of d orbitals in contrast

to the behavior of “genuine” group II metals, which we believe is not as counter-intuitive as it might seem on the first glance and is in agreement with well-documented behavior of transition metals in bulk compounds. We moreover disagree that our approach for some reason does not eliminate residual Ca d contributions in contrast to other, similar investigations<sup>5</sup> and that the weak cohesion of an ionized  $(CO)_8^{2-}$  cage is somehow result of a basis set superposition error, for which no supporting evidence was provided.

## Conflicts of interest

There are no conflicts to declare.

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