COMMENT

Comment on "Revisiting π backbonding: the influence of d orbitals on metal–CO bonds and ligand red shifts" by D. Koch, Y. Chen, P. Golub and S. Manzhos, *Phys. Chem. Chem. Phys.*, 2019, 21, 20814

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We challenge the statement of Koch *et al.* that the M → CO charge transfer and the decrease of the CO stretching frequency in metal carbonyl complexes do not depend on the metal d orbitals. The approach of the authors is severely flawed and leads to misleading conclusions.

In the title publication Koch *et al.* report quantum chemical calculations of $Mg(CO)_8$, $Ca(CO)_8$, and $[Ti(CO)_8]^{2+}$ focusing on the influence of d orbitals on metal–CO bonds and ligand red shifts.[1] The authors claim that the charge transfer of the metal atom to the carbonyl ligands and the decrease of the CO stretching frequency do not depend on the metal d orbitals. We think that the conclusions of Koch *et al.* are not valid and that their arguments are flawed. In the following we will focus on the results for $Ca(CO)_8$, which has recently been synthesized along with the heavier homologues $Sr(CO)_8$ and $Ba(CO)_8$.[2]

The authors optimized the complexes first at the M06-2X/cc-pVQZ level, which contains a sufficiently large quadruple basis set for the valence electrons augmented by polarization functions that has up to spdfgh quality. The molecules are then reoptimized with truncated basis sets for the metals that only have sp and spd functions, while the basis set for the CO ligands remains at the cc-pVQZ level. They report that the CO stretching frequency, which has a large red-shift in the complex relative to free CO, hardly changes when the Ca basis set is truncated to spd functions and that the red shift becomes even stronger when Ca has only an sp basis set. But they do not inform the finding that $Ca(CO)_8$ with an sp basis set on Ca is not an energy minimum structure anymore! The calculation of the vibrational frequencies using exactly the same method, basis set (a 7s,6p truncated cc-pVQZ basis set for Ca but full basis set for CO) and convergence criteria as the authors gives five imaginary modes for the e_u and t_{1u} vibrations. They are

shown in Fig. 1, where the arrows indicate the direction of the imaginary modes. The imaginary modes do remain in calculations when higher convergence constraints (OPT = VeryTight) are used. It becomes clear that the imaginary modes refer to the $Ca-(CO)_8$ π interactions. Without the Ca d(π) orbitals the complex $Ca(CO)_8$ strongly distorts towards a structure with C_1 symmetry. In other words, the $Ca-(CO)_8$ π bonds are crucially important for the observed cubic (O_h) structure of the octacarbonyl.

The relevance of the Ca d(π) functions for the calculated geometry changes the conclusion about the role of the $Ca-(CO)_8$ π bonding on the structure and properties of the molecule completely. The authors are saying that "*Charge 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 π bonds which are often used to rationalize the bonding in this kind of complexes.*" This challenges the validity of the Dewar–Chatt–Duncanson (DCD) model[3,4] for transition metal complexes,
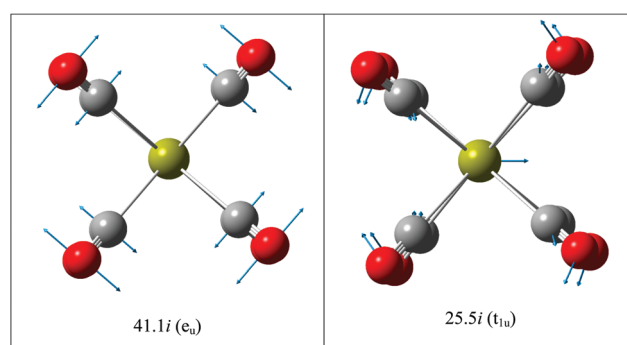
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41.1*i* (e_u)   25.5*i* (t_{1u})

Fig. 1 Pictorial depiction of one of the degenerate imaginary vibrational modes corresponding to e_u and t_{1u} of $Ca(CO)_8$ complex at the M06-2X/cc-pVQZ level but only s and p functions for Ca.

which has been supported by a variety of previous studies on numerous transition metal complexes.[5] Careful examination of the calculated data suggests that the DCD model holds also for $Ca(CO)_8$.

The small variation of the CO stretching frequency upon basis set truncation at Ca and the further red shift in going to an sp basis set is due to the high polarity of the $Ca–(CO)_8$ π bonds and the very large radius of the 3d AOs of the electropositive calcium atom. The electronic charge of the $Ca–(CO)_8$ π bonds is mainly localized in the antibonding region of the CO ligands, which have the largest coefficient at carbon. Removal of the calcium 3d functions changes the location of the π charges very little towards the CO ligands and enhances the red shift, but this does not mean that the $Ca–(CO)_8$ π bonds are unimportant for the stability of the complex. On the contrary, they provide the dominant part of the covalent $Ca–(CO)_8$ interactions. This has been shown in EDA-NOCV calculations[6,7] where either the total interactions of the separated CO ligands and Ca were calculated[2] or where the finally formed bonds in $Ca(CO)_8$ were considered.[8] These are two different questions, both of which can be addressed by EDA-NOCV calculations by using different fragments. The two options have been criticized as ambiguity of the EDA-NOCV method by Koch *et al.*[1] and by others,[9] but in reality it is rather a strength of the method that it can be used for both questions.[8] The contribution of $Ca–(CO)_8$ π bonding to the covalent interactions is 86% when neutral fragments are used[2] and it is 53% when singly charged fragments are employed, which are the best reference states for the bonds eventually formed.[8] The interactions between neutral Ca and 8 CO have according to the EDA-NOCV method 79% covalent character[2] whereas covalent bonding between Ca^+ and $(CO)^-$ provides 48% to the attractive interactions.[8]

The peculiar behavior of the valence d orbitals of the heavier alkaline earth atoms, which leads to unexpected molecular structures, had previously been demonstrated for $Ba(CO)^+$.[10] The interaction of a positively charged atom, which binds to CO only *via* a σ bond, leads to a strengthening of the CO bond and a blue-shift of the C–O stretching mode due to the change in the polarization of the bond.[11] A prominent example is the formyl cation HCO^+, which has a C–O stretching mode of 2184 cm^{-1} that is 41 cm^{-1} higher than in free CO (2143 cm^{-1}).[12] But even metal cations such as Li^+, Cu^+, Ag^+, Au^+ and others yield a blue-shift in MCO^+ whereas $M^+ \rightarrow CO$ π back donation becomes effective only at distances that are shorter than the equilibrium bond length.[11b] The $M^+ \rightarrow CO$ π back donation is negligibly small in late transition metal complexes,[13] which have been termed non classical carbonyls, because they exhibit a blue-shift of the C–O stretching mode.[14] The opposite effect is observed for the early transition metal complexes and for $Ba(CO)^+$, where the unpaired electron is in a π orbital that is Ba–CO bonding and antibonding for BaC–O. The rather diffuse d orbital of barium leads to the unusual situation that positively charged Ba^+ having a valence configuration $6s^05d^1$ becomes a donor for neutral CO.[10] A similar situation exist for the octacarbonyls $M(CO)_8$ (M = Ca, Sr, Ba).

The authors state that "*the admixture of Ca d states in Ca(CO)$_8$ is not the inherent reason for the occurrence of a CO redshift in these complexes, but merely a stabilizing factor of the overall complex.*" This statement is like saying that the orbitals of Li in LiF are unimportant for the charge transfer to F but merely a stabilizing factor for the formation of LiF. But the orbital interactions are crucial for the energy stabilization and for the associated charge transfer! The authors show in their Fig. 3 that omission of the d functions at Ca lowers the binding energy of the CO ligands in $Ca(CO)_8$ by more than 50% whereas the red-shift of the CO stretching frequencies becomes even larger. But the strong $Ca–(CO)_8$ π bonds are strongly polarized towards the CO end where they occupy the π^* orbital. The deletion of the calcium d orbitals moves the charge in the π^* orbital a bit further towards the carbonyl and enhances the red shift, but without the metal d functions there would not be any strong $Ca–(CO)_8$ π bonds. It is the interference of the wave functions of the interacting fragments that leads to covalent bonding.[15]

There is an important aspect of the basis set truncation procedure, which was not recognized by the authors. It concerns the large basis set superposition effect, which is introduced when the calcium basis set is reduced to sp functions while the cc-pVQZ basis set is retained for the ligands. The large basis set of the ligands, which includes diffuse functions, largely replaces the deleted metal d functions and thus leads only to a slight elongation in the $Ca–(CO)_8$ bond lengths. Landis *et al.* optimized the geometry of $Ca(CO)_8$ 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.[9,16] This procedure effectively deletes the basis set superposition effects and annihilates the $Ca–(CO)_8$ π bonds. As a result the $Ca(CO)_8$ bonds become longer by 0.4 Å, which indicates the crucial significance of the metal d functions and the associated π bonds. The basis set superposition error is not recognized by the counterpoise correction method, because the large fragment orbitals of the ligands cage mimic the metal d orbitals.

The authors say that their approach is similar to a previous study by Bauschlicher and Bagus (ref. 22 in their work), who analyzed the metal-carbonyl bond in $Ni(CO)_4$ and $Fe(CO)_5$.[17] The statement is misleading. Bauschlicher and Bagus used the constrained space orbital variation (CSOV) method,[18] which considers a stepwise bond formation using frozen and electronically relaxed fragments where metal–ligand donation and back donation as well as charge redistribution and polarization effects are separated. The CSOV method does not consider artificial basis set truncation effects. Bauschlicher and Bagus come to the conclusion that "*the metal to CO π donation is energetically much more important than the CO to metal σ donation.*"[17] This is opposite to the statement made by Koch *et al.* Finally, we want to mention that in the meantime the isoelectronic complexes $M(N_2)_8$ (M = Ca, Sr, Ba)[19] and the benzene complexes $M(Bz)_3$ (M = Sr, Ba) have been observed.[20] The bonding analysis suggests that the d orbitals of the heavier alkaline earth atoms play a dominant role for the covalent interactions. It appears that calcium, strontium and barium

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may exhibit the full scenario of transition metal chemistry in molecular complexes.

In summary, the conclusion of Koch *et al.* that the M → CO charge transfer and the decrease of the CO stretching frequency in metal carbonyl complexes do not depend on the metal d orbitals is not valid. The authors did not recognize that the basis set truncation introduces a large basis set superposition error and leads to a O_h structure of $Ca(CO)_8$ which is not an energy minimum. The DCD model is a valid description for the metal–CO bonding in $Ca(CO)_8$. The approach of the authors is severely flawed and leads to misleading conclusions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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