Electronic Supplementary Information

How π back-donation quantitatively controls the CO stretching response in classical and non-classical metal carbonyl complexes

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Contents

1 Effect of the exchange correlation functional

We tested the effect of the exchange correlation functional by comparing the Charge Displacement functions (CDFs) obtained with the BLYP functional with the ones obtained with the LDA, BP86 and B3LYP functionals in $[Au(CO)]^+$ and [(Cl)Au(CO)] (S1). All functionals give very similar CDFs over the whole molec-

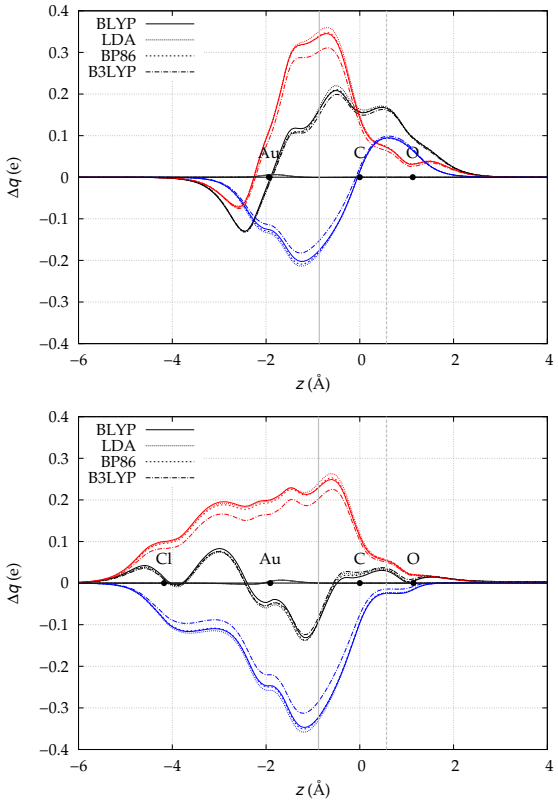

Figure S1 CDFs for the complexes $[Au(CO)]^+$ (top panel) and [(Cl)Au(CO)] (bottom panel). red and blue lines refer to the A_1 and B_1+B_2 components, respectively.

ular space. In particular, BLYP, BP86 and LDA give essentially the same values for the DCD components of the Au-C bond whilst the B3LYP functional gives slightly different results. For $[Au(CO)]^+$, back-donation values are -0.18 (BLYP) and -0.15 (B3LYP) electrons and donation values are 0.34 (BLYP) and 0.30 (B3LYP) electrons. For [(Cl)Au(CO)], back-donation values are -0.33 (BLYP) and -0.28 (B3LYP) electrons and donation values are 0.23 (BLYP) and 0.20 (B3LYP) electrons. Remarkably enough, the total CDFs are almost independent by the functional used, since the differences on donation and back-donation compensate each other.

2 Effect of basis set and hamiltonian

The CDFs computed at the ZORA/TZ2P level are well converged with respect to the basis set. S2 shows that the ZORA/TZ2P CDF for both $[Au(CO)]^+$ and [(Cl)Au(CO)] is almost identical to that obtained with the limit basis set QZ4P. Moreover, both curves almost coincide with the CDF obtained by employing the

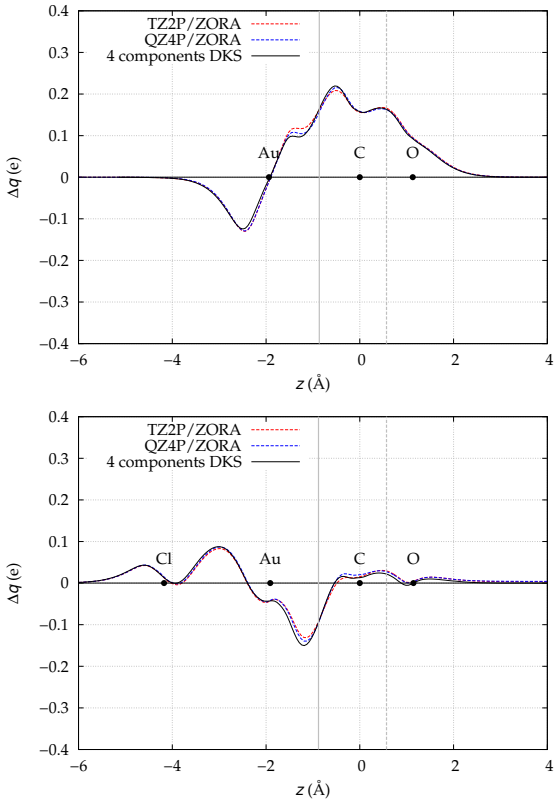

Figure S2 CDFs for the complexes $[Au(CO)]^+$ (top panel) and [(Cl)Au(CO)] (bottom panel). Solid black, dotted red and dotted blue lines refer to the net CD curve computed with the four component Dirac-Kohn-Sham (DKS) hamiltonian, BLYP/TZ2P/ZORA and BLYP/QZ4P/ZORA levels, respectively.

all-electron 4-component Dirac-Kohn-Sham (DKS) hamiltonian. We used the BLYP exchange-correlation functional in all cases. In the four-component calculation we used, for the large component, the basis set obtained by decontracting the Dyall basis set of triple zeta quality augmented with the related polarization and correlating functions (30s24p15d11f3g1h) on gold. The corresponding small component basis was generated using the restricted kinetic balance relation[1]. The calculation has been carried out with the DKS implementation of the molecular relativistic code BERTHA[2–4].

3 ν_{CO} vs CT^{π}_{back}

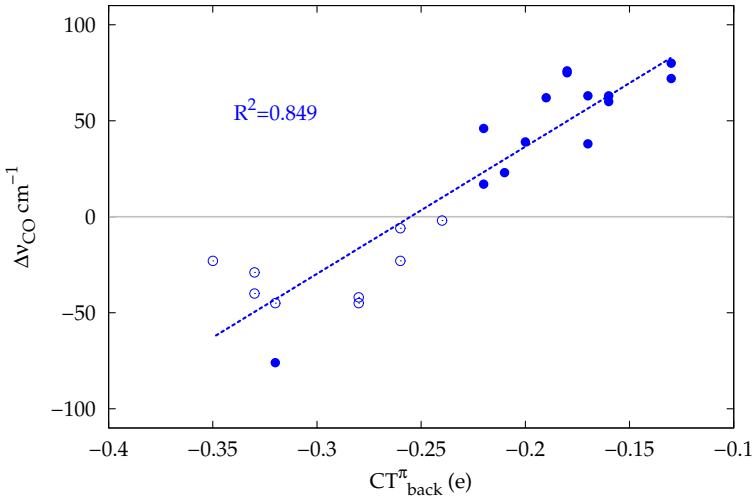

Figure S3 Correlation between the computed $\Delta\nu_{CO}$ in the considered series of $[(L)Au(CO)]^{0/+}$ complexes and the CT^{π}_{back}.

References

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