Supporting Information: Charge-displacement analysis via natural orbitals for chemical valence in the four-component relativistic framework

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Contents

1 BERTHA versus ADF: the $[Li–CO]^+$ complex

1.1 NOCVs and Charge Displacement curves

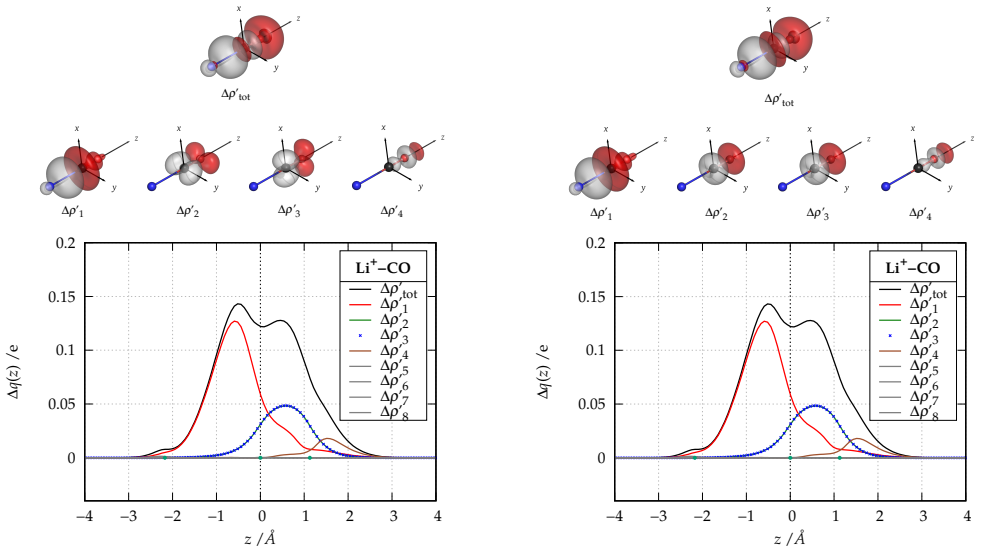

Figure S1: Lower panel: CD functions associated with the eight $\Delta\rho_k^{'}$ components for $[Li–CO]^+$ evaluated using the NOCV implementation of ADF suite program (left) and using the present implementation in BERTHA (right). Upper panel: isodensity surfaces (± 0.0014 e a.u.$^{-3}$) for the first four $\Delta\rho_k^{'}$ components. Grey surfaces (positive values) represent density accumulation, and red surfaces (negative values) identify depletion.

1.2 Charge Displacement curves for $\Delta\rho'_2$ and $\Delta\rho'_3$

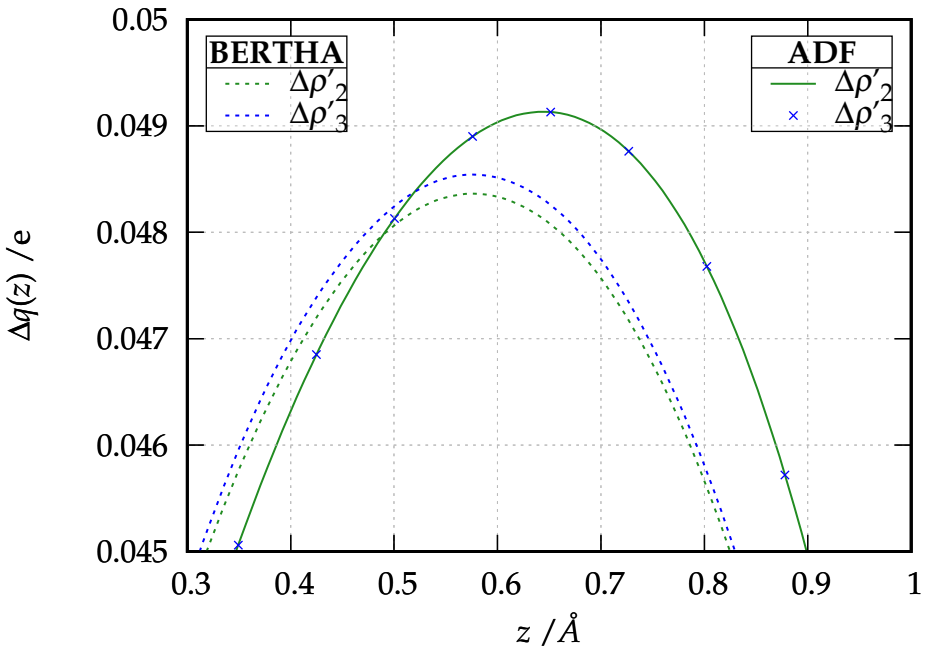

Figure S2: Enlarged view of CD curves in Figure S1.

2 NOCVs orbital densities decomposition for the [Au–CO]$^+$ system.

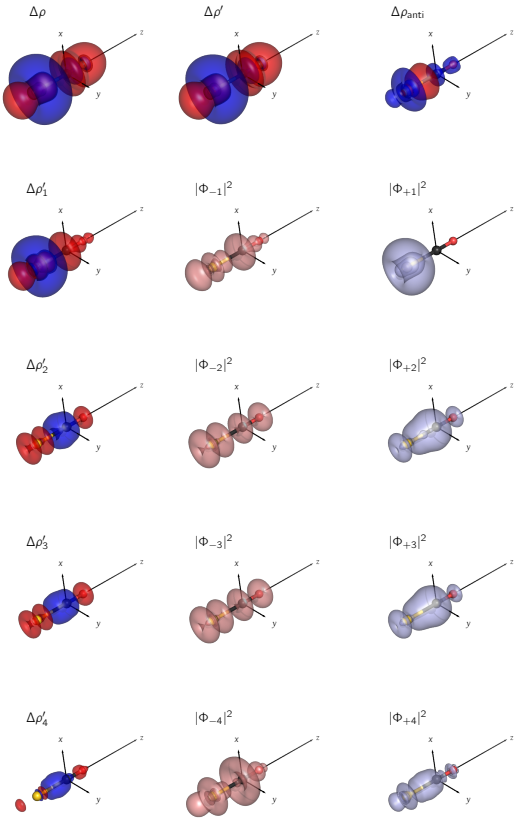

Figure S3: On top of the panel $\Delta\rho$, $\Delta\rho'$ and $\Delta\rho_{anti}$ are depicted as isodensity surfaces (± 0.0014 e/a.u^3) for $[AuCO]^+$. Below the NOCV pairs ($|\Phi_{+k}|^2$, $|\Phi_{-k}|^2$) and the associated $\Delta\rho'_k$, with $k = 1, 2, 3, 4$, are also shown by means of isodensity surfaces (± 0.005 a.u).

3 Eigenvalues of NOCVs for the $[Cu–CO]^+$, $[Ag–CO]^+$, $[Au–CO]^+$ systems.

Table S1: Eigenvalues corresponding to the first seven NOCVs pairs for the $[Cu–CO]^+$, $[Ag–CO]^+$, $[Au–CO]^+$ metal carbonyl complexes. [a]data obtained with DKS calculation increasing the speed of light of one order of magnitude (c = 10·c) to approximate the non-relativistic hamiltonian.

	$[Cu–CO]^+$	$[Ag–CO]^+$	$[Au–CO]^+$	$[Au–CO]^+$ [a]
v_1	0.51108	0.42896	0.79043	0.48396
v_2	0.30460	0.20313	0.36518	0.27950
v_3	0.29742	0.19592	0.32377	0.27950
v_4	0.21699	0.16035	0.24912	0.21422
v_5	0.05192	0.04310	0.05923	0.04145
v_6	0.05166	0.04278	0.04986	0.04144
v_7	0.04628	0.04232	0.05432	0.04025

4 Non-relativistic [Au–CO]$^+$.

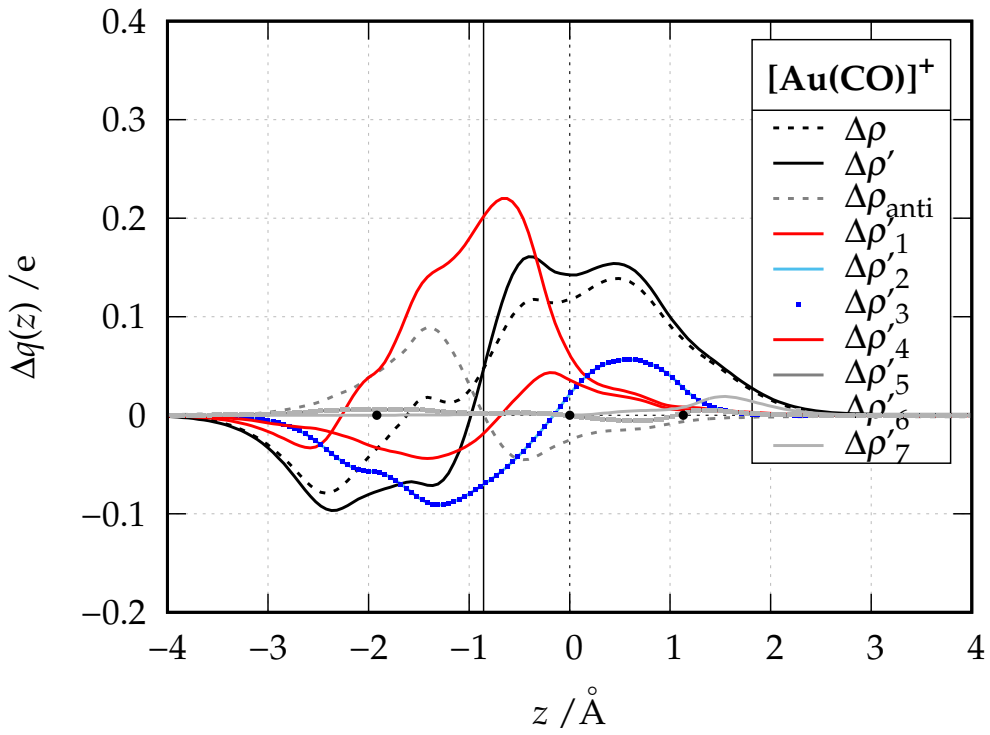

Figure S4: CD analysis for the Au-CO bond in the complex [Au(CO)]$^+$ calculated in non-relativistic limit (i.e. increasing the speed of light by one order of magnitude). The dots on the axis mark the z coordinate of the atoms. The vertical line marks the boundary between the Au$^+$ and the CO fragments (see text for details).