Supporting Information for *Spin trapping and flipping in FeCO through relativistic electron dynamics*

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1 Bonding in FeCO

The MOs and populations for the triplet ground and lowest-lying quintet state are shown in Fig. 1. In the triplet ground state, the 11σ and 1δ MOs are populated, but not the antibonding 12σ MO. In the lowest-lying quintet state, the antibonding 12σ is populated, leading to a weakening of the metal-ligand bonding and a reduced dipole moment.

In Fig. 2, the optically accessible electronic excited states starting from the lowest-lying singlet state S_0 are illustrated. The energy difference is represented on the y-axis relative to the triplet ground state, and the magnitude of the transition dipole moment, which dictates the coupling between initial and final state, is represented through the size of the circles. The accessible excited states are classified according to their spin multiplicity by different colors.

The dominant electron configurations in the LS $X^3\Sigma$ ground and HS target state $^5\Pi$ state are shown in Fig. 3. In the LS state, the 1δ MOs both contain one unpaired electron, while the HS target state is a superposition of excitations from the x and y 4π orbitals into the antibonding 12σ MO. The occupancy of the relevant MOs during a 2 fs propagation without a laser pulse in the $X^3\Sigma$ and $^5\Pi$ electronic states (Fig. 4) confirms the above configurations as the major contributions to the electronic states.

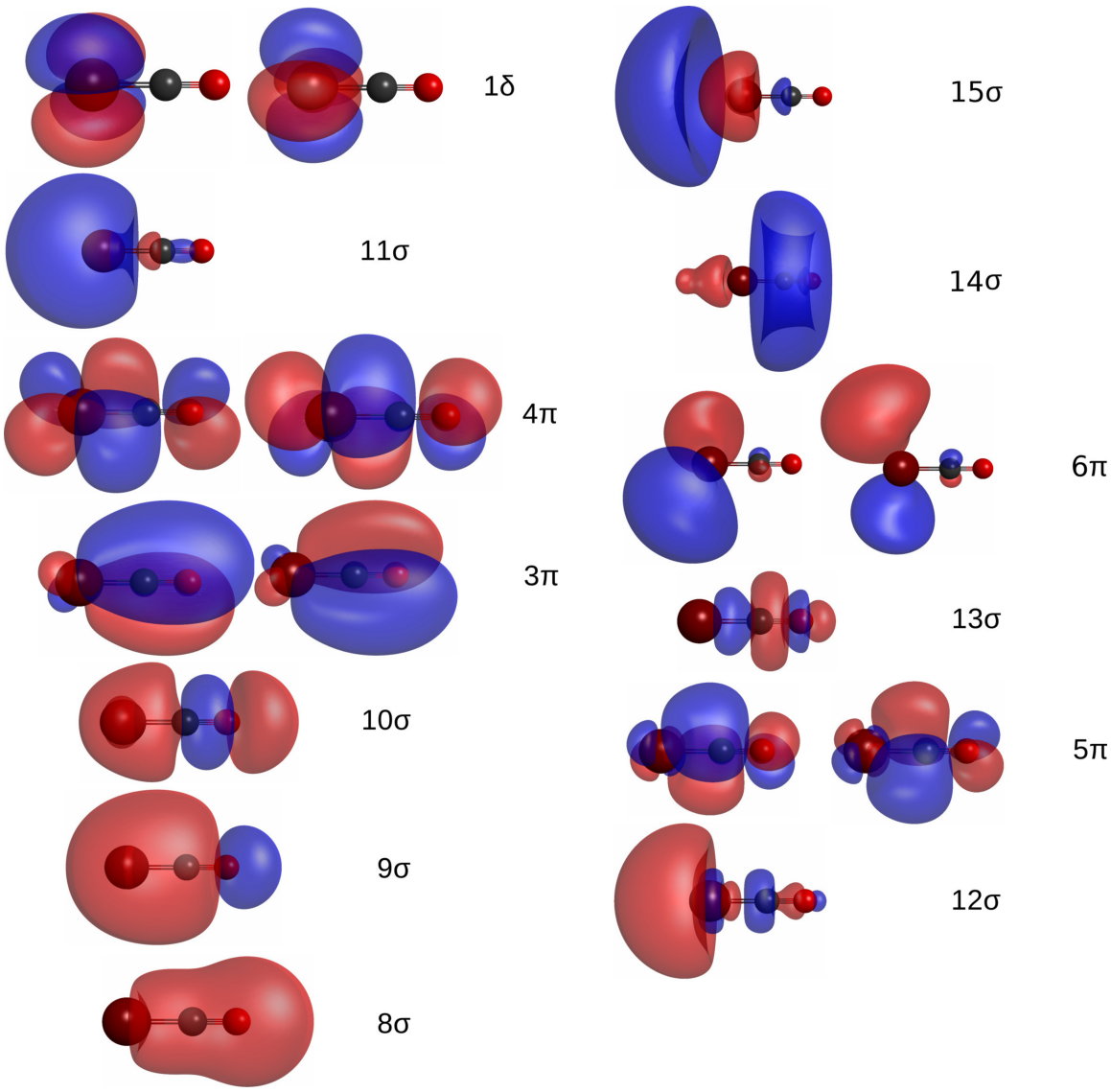

Figure 1 MOs in the active space. The 10σ MO is involved in the σ-donation from the CO ligand to Fe, while the 3π and 4π MOs are involved in the back-donation from Fe to the CO ligand. In the triplet ground state, all MOs up to 11σ are doubly occupied, and the two 1δ MOs contain the two uncoupled electrons. In the lowest-lying quintet state, one electron is removed from the 11σ MO and instead resides in the 12σ MO. A large variety of transitions between 3π (4π) and 1δ, as well as involving the virtual π MOs and the σ MOs are possible.

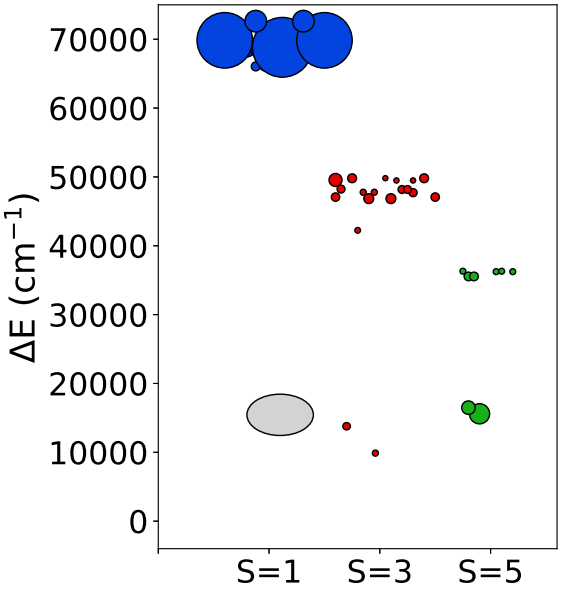

Figure 2 Electronic excitations out of the lowest-lying singlet state S_0 that can be induced optically. The initial state is marked with grey, while the accessible excited states are classified according to their spin multiplicity (blue – singlet, red – triplet, green – quintet), and the magnitude of the transition dipole moment is reflected through the size of the circles. The y-axis corresponds to the relative energy of the electronic states with respect to the triplet ground state.

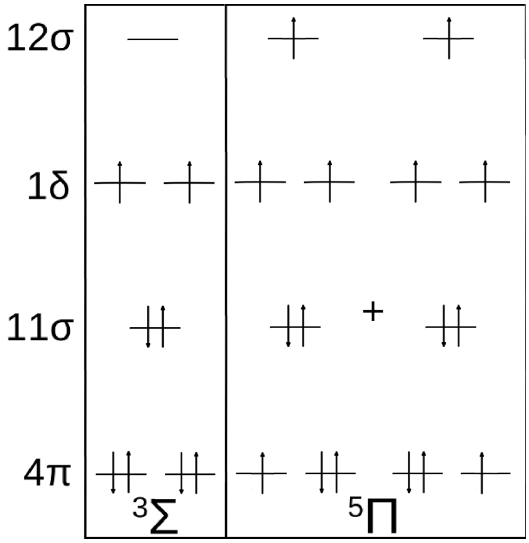

Figure 3 Dominant electronic configurations in the LS $X^3\Sigma$ ground and HS $^5\Pi$ target state. In the $^5\Pi$ state $\leftarrow$ $X^3\Sigma$ transition, an electron from the 4π MOs is excited into the antibonding 12σ MO and undergoes a spin flip.

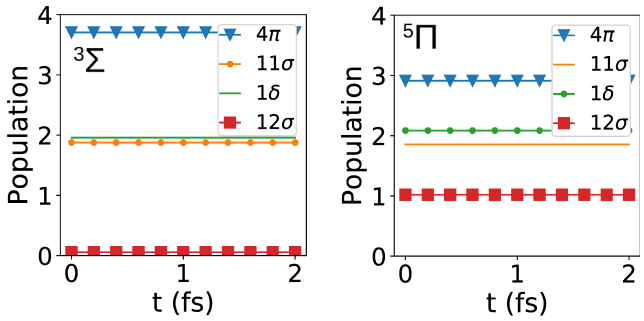

Figure 4 SO occupancies in the LS $X^3\Sigma$ ground and HS $^5\Pi$ target state. In the LS state, two unpaired electrons reside in the 1δ MOs, while in the HS state, one electron is excited from the 4π to the 12σ MO and undergoes a spin flip, leading to four unpaired electrons with same spin.