Relativistic effects in molecules: metal carbonyl cations $[M(CO)_n]^{x+}$

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Abstract

The benchmark results for isoelectronic metal carbonyl complexes of the groups 11 and 12 of the periodic table are presented. The focus is on the geometry, vibrational frequencies, bond dissociation and chemical bonding. The correct description of these complexes requires a balanced account of electron correlation and relativistic effects. The relativistic corrections grow with the atomic number of the metal atom and are responsible for the M-C bond length contraction, the decrease of M-C stretching and the increase of the bond dissociation energy. These effects are not negligible for complexes with first and second row TM atoms and are huge for molecules with heavy and superheavy elements. The results demonstrate that the combination of the effective core potential and MP2 method give quantitative results for the first- and the second-row transition metal complexes and only qualitative agreement for the third-row complexes. In order to obtain quantitative results for the whole series the use of four-component or X2C methods is mandatory. The metal-carbon bond strength pattern along the group is shown to be highly dependent on the correct description of the relativistic effects. Finally, the relativistic effects on the bonding are studied by means of electron density difference maps, the analysis of the bond critical points of the electron density and the mechanism for σ-donation and π-backdonation. The relativistic effects shrink the size of the metal within the molecule and displace the electron density from the CO fragment towards the metal. They also significantly increase the σ-donation of the CO to the TM, thus enhancing the covalent character of the M-C bond.