

Title: Theoretical study of spin–orbit coupling on spectra and photophysics of rhenium complexes

Author: RNDr. Radka Heydová

Department: Physical and Macromolecular Chemistry

Supervisor: Ing. Stanislav Záliš, CSc., JHI AS CR, v.v.i.

Supervisor's e-mail address: stanislav.zalis@jh.inst-cas.cz

Abstract: Relativistic effects, especially spin–orbit coupling (SOC), play an essential role in transition metal chemistry and SOC treatment is indispensable for a correct theoretical description. To demonstrate the importance of SOC, the energies and oscillator strengths of vertical transitions for a series of $[\text{ReX}(\text{CO})_3(2,2'\text{-bipyridine})]$ ($X = \text{Cl}, \text{Br}, \text{I}$) and $[\text{Re}(\text{imidazole})(\text{CO})_3(1,10\text{-phenanthroline})]^+$ complexes were calculated in the spin-free (SF) and spin–orbit (SO) conceptual frameworks. Two different computational approaches were adopted: SO-MS-CASPT2 where SOC was added a posteriori using a configuration interaction model (SO-RASSI), and the approximate perturbative SO-TD-DFT method. Relativistic effects were included via the two-component Douglas–Kroll–Hess transformation and the zeroth-order regular approximation in the former and the latter technique, respectively. The SF (i.e. accounting only for the scalar relativistic effects) and SO results from both methods were compared with each other and to available experiments. The character of charge-transfer transitions was used to describe the SF states. The SO states were characterized by their parentages in terms of the SF states and double-group symmetries. In case of complexes with a halide ligand, several observed spectral trends, mainly on going from Cl to I, were studied. We have proven that the SO model is able to interpret absorption spectra, emission characteristics and excited-state behaviour correctly and it improves a quantitative agreement with the experiment. Moreover, only the inclusion of SOC can explain some of spectroscopic features (temperature-dependent emission decay, various picosecond relaxation times, enormous broadness of emission bands etc.) that cannot be captured by the SF model. The photophysical SO excited-state model was developed in order to elucidate ultrafast spectroscopic experimental data – the principal observations (emission, the presence of an intermediate emissive state, electronic/vibrational relaxation, nonradiative transitions, equilibration among the lowest SO states) and detected time constants can be associated with particular processes and SO states.

Several generalizations can be extracted from the SO model, which are applicable to many other closed-shell transition metal complexes, such as high excited-state density, highly spin-mixed character of SO states, and multiple electronic and vibrational excitation and relaxation pathways (occurring after optical excitation). When strong SOC is introduced, the assignment of spin multiplicity is no longer appropriate and hence a unified point of view should be adopted. To sum up, our calculations are capable of providing an insight into the excited-state dynamics of rhenium(I) tricarbonyl complexes, which can be utilized in many photonic applications, e.g. organic light-emitting diodes.

Keywords: rhenium, carbonyl, diimine, spin–orbit coupling, excited states, ultrafast intersystem crossing, luminescence, spectroscopy, photophysics, CASSCF, MS-CASPT2, TD-DFT