

Effect of Spin-Orbit Coupling on Electronic Transitions in Transition Metal Complexes

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Starting from the very simple case of the hydrogenic atom, the basic theory of spin-orbit coupling (SOC) for atoms or monoatomic cations (with special emphasis for transition metals (TM)) will be briefly reviewed.

Then the discussion will be extended to TM complexes where SOC is considerably lowered with respect to the naked neutral (or cationic) TM. The transition energies to the low-lying singlet and triplet electronic states of the TM dihydrides $H_2M(CO)_4$ ($M = Fe, Os$) will be discussed in detail (1), as well as the influence of SOC effects on these transition energies (2).

The calculations are carried out in two steps:

- in a first step, the spin-free vertical transitions are calculated with the CASSCF/MS-CASPT2 method (3).
- in a second step, SOC effects are taken into account by building a determinantal model space which includes a set of reference configurations able to represent all the desired states along with singly excited configurations selected with respect to the SO operator within the atomic mean-field approximation. This is achieved with the EPCISO code (4).

It is shown that while SOC is of little influence on the absorption spectrum of $H_2Fe(CO)_4$ it does affect significantly the electronic spectroscopy of the third row TM complex $H_2Os(CO)_4$ leading to a large mixing between the low-lying states and to a splitting exceeding 3000 cm^{-1} for the lowest 3B_2 state.

However these SOC effects are not responsible for the remarkable photostability of the Os complex as opposed to the high photoreactivity of the Fe analog.

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