Séminaire :

“Dispersion corrections in transition metal complexes: the nephelauxetic effect revisited”

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Résumé : We readdress the well-known nephelauxetic effect in coordination compounds of transition metal ions and analyze its possible origins presented in the literature. The initial hypothesis was to ascribe the reduction of the effective Racah parameters $B$ and $C$ of the electron-electron interaction in the complexes as compared to their respective free-ion values (which is the essence of the nephelauxetic effect) to expansion of $d$-orbitals in the complex due to their quantum mechanical mixing with the orbitals of the ligands leading to delocalization. This picture necessarily leads to a rigid positive correlation between the amount of the $d$-shell splitting controlled by the same delocalization and the amount of the renormalization of the interaction parameters. In fact such a rigid relation does not exist and the so-called spectrochemical and nephelauxetic series of the ligands composed according to the above amounts do not coincide in many points.

An alternative explanation based not on the delocalization, but on polarization of the ligands had been proposed about the same time as the delocalization-based one. Realistic estimates had been obtained on this basis, but the scheme had never been implemented on the atomic scale which is necessary to enable renormalization of the above interaction parameters as a “built-in” function of quantum-chemical software.

The required atomic resolution formulation of the polarization-based model of the nephelauxetic effect is constructed, where also a relation of such an approach to the general problematics of the "next generation" of semiempirical methods of quantum chemistry is discussed.