Photophysics and photochemistry of 2nd and 3rd row transition metal complexes: A quantum chemical study

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Transition metal complexes are characterized by a high density of electronic excited states in the visible/ UV energy domain with a variety of metal-centered, metal-to-ligand-charge transfer, ligand-to-ligand-charge transfer and intra-ligand states that may interact leading to very complex spectroscopy. Two recent applications based on state-of-the-art *ab initio* calculations or on density functional theory will illustrate this complexity.

The first part of the lecture is dedicated to the spectroscopy and photophysics of Ru(II) complexes used as DNA intercalators.[1,2] The influence of the environment on the optical properties will be discussed under the light of recent results obtained by means of quantum mechanical/quantum chemical calculations performed on two reference systems, namely $[Ru(phen)_2dppz]^{2+}$ and $[Ru(tap)_2dppz]^{2+}$ (phen = 1,10-phenanthroline; tap = 1,4,5,8-tetraazaphenanthrene; dppz = dipyridophenazine) modelling the environment effects at different levels.

The second part of the lecture reports a comprehensive theoretical study of the ultra-fast steps leading to ligand *trans-cis* isomerization of Rhenium (I) tricarbonyl diimine complexes under visible light.[3,4] The chosen molecule is representative of a wide class of compounds largely studied experimentally. The electronic absorption spectroscopy and the photophysics of $[Re(CO)_3(2,2'$-bipyridine (t-4-styrylpyridine))$]^+$ and derivatives are analyzed on the basis of *ab initio* CASSCF/MS-CASPT2 and spin-orbit calculations. The mechanism of the *trans-cis* isomerization of the styrylpyridine ligand as function of the wavelength of irradiation is described by multi-dimensional potential energy surfaces associated to the low-lying ^{1,3}MLCT ($Re \rightarrow \pi^*_{bpy}$) and ^{1,3}IL ($\pi_{stypy} \rightarrow \pi^*_{stypy}$) excited states. The photoisomerization process is discussed under the light of recent ultra-fast time-resolved experiments reported for related complexes.

[1] Atsumi, M.; González, L.; Daniel, C. ***J. of Photochem. & Photobio A: Chem***. **2007**, *190*, 310.

[2] Ambrosek, D.; Loos, P.-F.; Assfeld, X.; Daniel, C**. *J. of Inorganic Biochemistry***, **2010**, *104*, 893-901.

[3] Bossert, J.; Daniel, C. *Chem. A Eur. J.* 12 **2006** 4835-4843.

[4] Gindensperger, E.; Köppel, H.; Daniel, C. *Chem. Comm.* 46 **2010** 8225-8227.