Non-Adiabatic Dynamics for Ultrafast Excited States Processes in Transition Metal Complexes

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This lecture will illustrate the progress made in the past few years in our understanding of ultrafast events underlying photophysical and photochemical processes in transition metal complexes taking into account spin-orbit and vibronic couplings.
Related experiments, based on ultrafast picosecond (ps) and femtosecond (fs) transient absorption or luminescence spectroscopies, and optical laser pump-X-ray probe techniques using ps and fs X-ray pulses, are still subject to unresolved questions.[1]
One of these questions is the interplay between spin-orbit coupling (SOC) and vibronic coupling. Indeed, spin-orbit and vibronic couplings directly influence the probability of elementary processes such as internal conversions and intersystem crossing (ISC). The interpretation of ultrafast structural changes, time-resolved spectra, quantum yields and time-scales of elementary processes or transient lifetimes not only needs robust theoretical tools in quantum chemistry but developments in quantum dynamics for solving the electronic and nuclear problems. Quantum dynamics has to treat dynamical processes that are not confined to a single electronic PES and that violate the Born-Oppenheimer (BO) separation of electronic and nuclear motions, taking into account nonadiabatic coupling between two or more electronic states via several vibrational modes.
Up to now three types of dynamical simulations, far from being routine, have needed specific developments to be applicable to transition metal complexes and ultrafast phenomena circumscribed by spin-vibronic coupling: i) the time-dependent formalism within the Condon approximation; ii) the non-adiabatic surface-hopping semi-classical method; iii) the multi-mode quantum wavepacket dynamics.[2]
Recent applications, based on these developments, will illustrate the complexity of ultrafast excited states processes in 1^{rst}, 2nd and 3rd row transition metal complexes.

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[1] Juban EA, Smeigh AL, Monat JE, McCusker JK (2006) Coord. Chem. Rev. 250: 1783; McCusker J K (2003) Acc. Chem. Res. 36: 876; Chergui M (2012) Dalton Trans. 41: 13022; Bräm O, Messina F, Baranoff E, Cannizzo A, Nazeeruddin MK, Chergui M (2013) J. Phys. Chem. C 117: 15958; El Nahhas A, Consani C, Blanco-Rodríguez AM, Lancaster KM, Braem O, Cannizzo A, Towrie M, Clark IP, Záliš S, Chergui M, Vlček A Jr. (2011) Inorg. Chem. 50: 2932; Renske M, van der Veen RM, Cannizzo A, van Mourik F, Vlček A Jr., Chergui M (2011) J. Am. Chem. Soc. 133: 305

[2] Etinski M, Tatchen J, Marian CM (2011) J. Chem. Phys. 134: 154105 ; Etinski M, Rai-Constapel V, Marian CM (2014) J. Chem. Phys. 140: 114104; Curchod BFE, Rothlisberger U, Tavernelli I (2013) Chem. Phys. Chem. 14 :1314 and references therein; Gourlaouen C, Eng J, Otsuka M, Gindensperger E, Daniel C (2015) J. Chem. Theory Comput. DOI: 10.1021/ct500846n; Eng J, Gourlaouen C, Gindensperger E, Daniel C (2015) Acc. Chem. Res. "Ultrafast Excited States Dynamics in Transition Metal Containing Systems" Special Issue (accepted); Daniel C chapter in Topics in Current Chemistry "Density Functional Methods for Excited States" Eds. Ferré, Filatov, Huix-Rotlant, in press 2015.