Non-Adiabatic Quantum Dynamics for Ultrafast Intersystem Crossing in [Re(bipyridine)(CO)$_3$(X)] (X = Cl, Br, I)

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Rhenium (I) α-diimine carbonyls complexes [Re(L)(CO)$_3$(N,N)]$^{n+}$ are thermally and photochemically robust and highly flexible synthetically. Structural variations of the N,N and L ligands affect the spectroscopy, the photophysics and photochemistry of these choromophores easily incorporated into complex environment. Visible light absorption opens the route to a wide range of applications such as sensors, probes or emissive labels for imaging biomolecules. Halide complexes [Re(X)(CO)$_3$(bpy)] (X= Cl, Br, I; bpy = 2,2'-bipyridine) exhibit complex electronic structure and large spin-orbit effects that do not correlate with the heavy atom effects. Indeed, the ^{1}MLCT $\rightarrow$ ^{3}MLCT intersystem crossing (ISC) kinetics is slower than in [Ru(bpy)$_3$]$^{2+}$ or [Fe(bpy)$_3$]$^{2+}$ despite the presence of a third-row transition metal. Counter intuitively, singlet excited-state lifetime increases on going from Cl (85 fs) to Br (128 fs) and to I (152 fs). Moreover, correlation between the Re-X stretching mode and the rate of ISC is observed.[1]

In this contribution we emphasize on the role of spin-vibronic coupling on the mechanism of ultrafast ISC in [Re(X)(CO)$_3$(bpy)] (X= Cl, Br, I). For this purpose we have developed a model Hamiltonian for solving an eleven electronic excited states multi-mode problem including vibronic and spin-orbit couplings within the linear vibronic coupling (LVC) approximation and the assumption of harmonic potentials.[2] The presence of a central metal atom coupled to rigid ligands, such as α-diimine, assures nuclear motions of small amplitudes and justifies the use of the LVC model. The simulation of the ultrafast dynamics by wavepacket propagations using the multi-configuration time-dependent Hartree (MCTDH) method is based on density functional theory (DFT) and it's time-dependent extension to excited states (TD-DFT) electronic structure data. We believe that the interplay between time-resolved experiments and these pioneering simulations covering the first ps and including spin-vibronic coupling, will promote a number of quantum dynamical studies that will contribute to a better understanding of ultrafast processes in a wide range of organic and inorganic chromophores easily incorporated in bio-systems or supramolecular devices for specific functions.

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[1] Cannizzo A, Blanco-Rodriguez AM, El Nahhas A, Sebera J, Zalis S, Vlcek A Jr, Chergui M J. Am. Chem. Soc. 130 (2008) 8967; Heydova R, Gindensperger E, Romano R, Sykora J, Vlcek A Jr, Zalis S, Daniel C J. Phys. Chem. A 116 (2012) 11319.

[2] 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).