

Ultrafast Excited-State Decays in $[\text{Re}(\text{CO})_3(\text{N,N})(\text{L})]^{n+}$: Non-Adiabatic Quantum Dynamics

Maria Fumanal, Etienne Gindensperger, Chantal Daniel

*Laboratoire de Chimie Quantique, Institut de Chimie Strasbourg, UMR-7177 CNRS/
Université de Strasbourg, 1 Rue Blaise Pascal BP 296/R8, F-67008 Strasbourg, France*

E-mail: fumanal@unistra.fr

The ultrafast luminescent decay of $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$,^[1] representative of Re(I) carbonyl-diimine photosensitizers, is investigated by means of wavepacket propagations based on the multiconfiguration time-dependent Hartree (MCTDH) method.^[2] On the basis of electronic structure data obtained at the time-dependent density functional theory (TD-DFT) level^[3,4] the luminescence decay is simulated by solving a 14 electronic states multimode problem including both vibronic^[5] and spin-orbit coupling (SOC) up to 15 vibrational modes. A careful analysis of the results provides the key features of the mechanism of the intersystem crossing (ISC) in this complex. The intermediate state, detected by means of fs-ps time-resolved spectroscopies, is assigned to the T_3 state corresponding to the triplet intraligand (^3IL) transition localized on the phen ligand. By switching off/on SOC and vibronic coupling in the model it is shown that efficient population transfer occurs from the optically active metal-to-ligand-charge-transfer $^1,^3\text{MLCT}$ states (S_2/T_4) to T_3 and to the lowest long-lived phosphorescent $^3\text{MLCT}$ (T_1) state (see Fig. 1). The early ultrafast SOC-driven decay followed by a T_3/T_1 equilibration controlled by vibronic coupling underlies the photoluminescent properties of $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$.^[6]

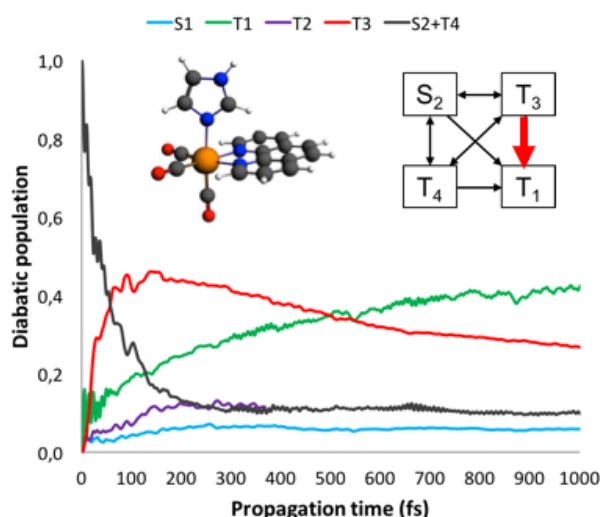


Figure 1. Diabatic electronic populations of the 6 low-lying excited states of $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$ as a function of time. Inset: Molecular structure of $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$ (left). Schematic deactivation pathways that contribute to the population transfer among the diabatic excited states and characterize the relaxation dynamics of $[\text{Re}(\text{CO})_3(\text{phen})(\text{im})]^+$ (right).

Funding: Labex “*Chimie des Systèmes Complexes*” (ANR-10-LABX-0026_CSC).

Acknowledgement: The European actions COST perspect-H₂O and CODEC are acknowledged as well as the Labex “*Chimie des Systèmes Complexes*” (ANR-10-LABX-0026_CSC). The quantum chemical calculations have been performed on the computer nodes of the LCQS, Strasbourg and thanks to the computer facilities of the High Performance Computing (HPC) regional center of University of Strasbourg.

References:

- [1] El Nahhas, A.; Consani, C.; Blanco-Rodríguez, A. M.; Lancaster, K. M.; Braem, O.; Cannizzo, A.; Towrie, M.; Clark, I. P.; Zálíš, S.; Chergui, M.; Vlček, A., Jr, *Inorg. Chem.* **2011**, *50*, 2932–2943.
- [2] Meyer, D. – H.; Manthe, U.; Cederbaum, L. S., *Chem. Phys. Lett.* **1990**, *165*, 73–78.
- [3] Fumanal, M.; Daniel, C. *J. Comput. Chem.* **2016**, *37*, 2454–2466.
- [4] Fumanal, M.; Daniel, C. *J. Phys. Chem. A* **2016**, *120*, 6934–6943.
- [5] Köppel, H.; Domcke, W.; Cederbaum, L. S. *Adv. Chem. Phys.* **1984**, *57*, 59-246.
- [6] Fumanal, M.; Daniel, C. *J. Chem. Theory Comput.* **DOI:** 10.1021/acs.jctc.6b01203