WORK PLAN: Anharmonic IR spectroscopy of α-diimine complexes with tricarbonylrhenium halides and pseudohalides in ground, excited, and different redox states.

Complexes $[Re(CO)_3X(L)]$ with aromatic α-diimine ligands L (2,2'-bipyridines or 1,10-phenanthrolines) have been much studied because of their photophysics, photocatalytic [1,2] and electrocatalytic properties [1-5]. The variation of physical properties in the course of excitation or redox changes is monitored by CO stretching frequencies.

Effects of anharmonicity on previously explained the fine structure of IR spectra for [Re(X)(CO)3(α-diimine)] (α-diimine= 2,2'-bipyridine or pyridylimidazo[1,5 a]pyridine; X=Cl or NCS) complexes [6]. During planed stay the study shall be extended by calculations of anharmonic effects in IR spectra of oxidation and reduction products together with excited states.

The study shall be performed on compounds $[Re(CO)_3X(L)]$ with non-aromatic α-diimine ligand L - substituted 1,4-diaza-1,3-butadienes RN=CH-CH=NR (= R-DAB); axial ligand X= Cl, Br, CN and NCS (Fig. 1). For these systems geometry optimizations and following vibrational analyses will be performed. During calculations several implicit and explicit solvent models will be tested. The expertise of group at ScuolaNormaleSuperiore will be utilized in the following calculations of anharmonic frequencies and modelling of solvent effects. The calculated aharmonic frequencies will be used for interpretation of IR and time resolved IR spectra.

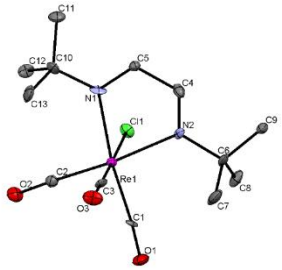

Fig. 1. Experimental structure of Re(^{t}Bu-DAB)$(CO)_3$Cl.

Referrences

[1] (a) B.P. Sullivan, T.J. Meyer, J. Chem. Soc., Chem. Commun. (1984) 1244;(b) B. Kumar, J.M. Smieja, A.F. Sasayama, C.P. Kubiak, Chem. Commun. 48 (2012) 272.

[2] J. Hawecker, J.-M. Lehn, R.J. Ziessel, J. Chem. Soc., Chem. Commun. (1983) 536.

[3] (a) E. Fujita, Coord. Chem. Rev. 185-186 (1999) 373;(b) D.H. Gibson, X. Yin, H. He, M.S. Mashuta, Organometallics 22 (2003) 337;(c) H. Takeda, K. Koike, H. Inoue, O. Ishitani, J. Am. Chem. Soc. 130 (2008) 2023.

[4] T. Scheiring, A. Klein, W. Kaim, J. Chem. Soc., Perkin Trans. 2 (1997) 2569.

[5] (a) J.M. Smieja, C.P. Kubiak, Inorg. Chem. 49 (2010) 9283;(b) J. Agarwal, R.P. Johnson, G. Li, J. Phys. Chem. A 115 (2011) 2677.

[6] H. Kvapilová, A. Vlček, Jr., V. Barone, M. Biczysko and S. Záliš, *J. Phys. Chem. A***119** (2015) 10137-10146.