Spin-Vibronic Excited-State Quantum Dynamics
# in Transition Metal Complexes

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Non-radiative relaxation processes of electronically excited states are mediated by vibronic and spin-orbit coupling, depending on spin and spatial symmetry. While the former is known to lead to ultrafast relaxation (fs – ps) since many years, the latter has been recognized more recently to be able to act on the same time scale. Spin-orbit coupling may play an important role in organic compounds, but its impact become crucial in most transition metal complexes. In order to study the excited-state quantum dynamics in such cases, we propose a model Hamiltonian comprising both spin-orbit and vibronic coupling [1]. The parameters are extracted from electronic structure calculations [2].

Applications on Rhenium α–diimine carbonyl complexes $[Re(L)(CO)_3(N,N)]^+$ are shown [3]. For Halide ligands (L = Cl, Br, I), an unexpected behavior has been experimentally observed [4]: despite a larger spin-orbit coupling constant with increasing mass of the Halide, the relaxation time increases. Our model is able to reproduce this trend, allowing use to shed new light on the ultrafast relaxation processes in this class of compounds.
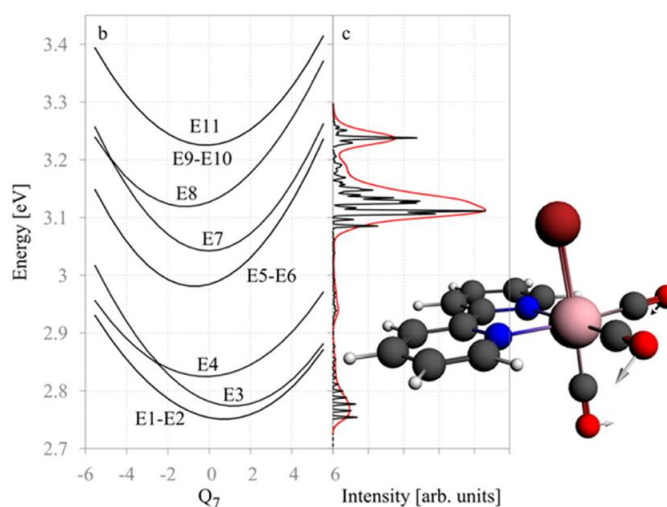
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