Excited-state RIXS of Cobaltates

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Hydrogen production through the water splitting reaction (2H₂O+energy → O₂+H₂) is one of the most attractive sources of providing clean energy (fuel) for the future, provided it can be generated from renewable energy sources. Research on water splitting catalysis has been deflecting away from the high-performance catalytic oxides containing expensive elements (Ru, Ir) towards more earth-abundant ones [1], like cobalt-containing oxides [2]–[6], which have catalytic activities comparable to the precious metal oxides.

Cobaltates such as LaCoO₃ have been proposed as active photo- and electro-catalysts for water splitting [4]–[6]. In the case of photo-catalysis, it is essential that the photo-excited state has sufficient lifetime in order to catalyze the reaction of interest. LaCoO₃ and as well for example the cobalt oxide Co₃O₄ are known to have a relatively long photo-excited-state lifetime in the range of pico- to nano-seconds.

We have studied the first few picoseconds of the excited-state pathway of LaCoO₃ using pump-probe soft x-ray Cobalt L₃-edge Resonant Inelastic X-ray Scattering (RIXS) at the SSS beamline of PAL-XFEL with a laser using 400 nm as pump in order to understand where that long excited-state lifetime comes from.

Combined with semi-empirical crystal field multiplet simulations [7], [8] we could overall follow the excited-state pathway and we discuss the final reached excited-state in terms of stability referring to the low- to high-spin conversion that the LaCoO₃ system is also known for and capable of as function of temperature [9], [10].

References