Excited-state RIXS of Cobaltates

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Hydrogen production through the water splitting reaction ($2H_2O$+energy $\rightarrow O_2+H_2$) 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 $LaCoO_3$ 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. $LaCoO_3$ and as well for example the cobalt oxide Co_3O_4 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 $LaCoO_3$ using pump-probe soft x-ray Cobalt L_3-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 $LaCoO_3$ system is also known for and capable of as function of temperature [9], [10].

References

[1] A. Singh and L. Spiccia, "Water oxidation catalysts based on abundant 1st row transition metals," *Coord. Chem. Rev.* 257 (2013) 2419.

[2] M. Grzelczak *et al.*, "Electro- and photochemical water oxidation on ligand-free Co_3O_4 nanoparticles with tunable sizes," *ACS Catal.* 3 (2013) 383.

[3] J. Suntivich, *et al.*, "A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles," *Science* 334 (2011) 1383.

[4] A. Vojvodic and J.K. Norskov, "Optimizing perovskites for the water-splitting reaction," *Science* 334 (2011) 1355.

[5] C. Zhang, *et al.*, "Water oxidation catalysis: tuning the electrocatalytic properties of amorphous lanthanum cobaltite through calcium doping," *ACS Catal.* 7 (2017) 6385.

[6] S. Zhou *et al.*, "Engineering electrocatalytic activity in nanosized perovskite cobaltite through surface spin-state transition," *Nat. Commun.* 7 (2016) 1151.

[7] F. de Groot and A. Kotani, *Core Level Spectroscopy of Solids*. 2008.

[8] P.S. Miedema, "X-ray spectroscopy of inorganic materials," PhD Utrecht Univ. 2012.

[9] M. Abbate *et al.*, "Electronic structure and spin-state transition of $LaCoO_3$," *PRB*, 47 (1993) 16124.

[10] M.W. Haverkort *et al.*, "Spin state transition in $LaCoO_3$ studied using soft X-ray absorption spectroscopy and magnetic circular dichroism," *PRL* 97 (2006) 38.