Energy transfer and upconversion in Tm^{3+}-doped β-$NaYF_4$: comparison between models and theory

P. Villanueva-Delgado[1,*], K. W. Krämer[1], Rafael Valiente[2]

[1]Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland
[2]Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain.

* corresponding author: *pedro.villanueva@dcb.unibe.ch*

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Tm^{3+} ions in close proximity interact non-radiatively in different ways so that, for example, blue $^3H_6 \rightarrow {}^1G_4$ excitation (473 nm) results in UV $^1D_2 \rightarrow {}^3H_6$ upconverted emission (361 nm) in a β-$NaYF_4$: 0.3% Tm^{3+} sample, see Fig 1.

The strength of an energy transfer (ET) interaction can be summarized by a single number: the critical radius R_c. This is the distance at which the probability of ET and radiative decay are equal. At shorter distances ET dominates, while at longer distances radiative decay is more important.

A recent model is able to obtain the R_c of different interactions by fitting luminescence decay curves, see Fig 1(b). [1] For the cross-relaxation interaction shown in Fig. 1(a), this model determines R_c =11.8 Å. An analysis based on the Inokuti-Hirayama model results in R_c =12.1 Å.

An equation due to T. Kushida determines R_c as a function of the donor state lifetime, refractive index, transition energy, emission and absorption oscillator strengths, and spectral overlap. [2]

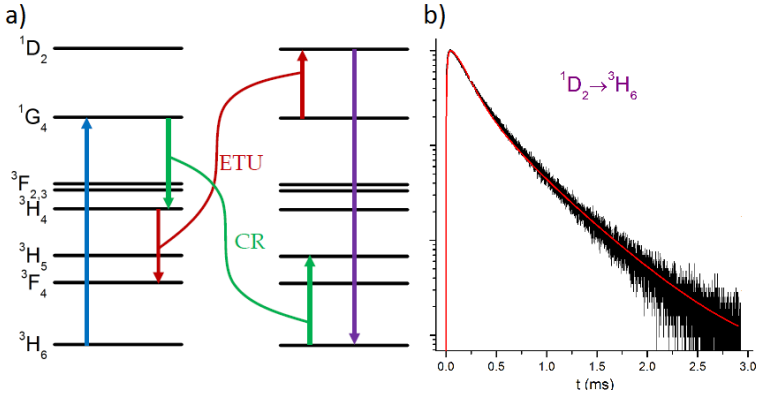

Fig. 1. a) Electronic structure of Tm^{3+} and relevant absorption, emission, and energy transfer processes in β-$NaYF_4$: 0.3% Tm^{3+}. b) $^1D_2 \rightarrow {}^3H_6$ luminescence decay curve (361 nm) after $^3H_6 \rightarrow {}^1G_4$ excitation (473 nm) with model fit (red line).

These parameters have been determined for a β-$NaYF_4$: 0.3% Tm^{3+} powder sample and a β-$NaGdF_4$: Yb^{3+}, Tm^{3+} single crystal. [1,3] The predicted critical radius is R_c=7.6 Å. The disagreement between the model and theory can be explained by the difficulty in measuring the spectral overlap, due to the disorder in the β-$NaYF_4$ lattice.

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