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Light • Interactions • Matter

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SimphoSOFT™ Modeling - Validation Testing

AF455 Two Photon Absorption Cross Section

Yb^{+3}/Er^{+3} Energy Transfer & Luminescence

Simphotek, Inc.

Introduction

Modeling the time-dependent interaction of light with optically active materials is an obviously useful tool in materials development. If results can be modeled prior to experimental work, experimental candidates can be pre-screened 'virtually' saving experimental effort, and allowing a focus on the most promising materials. Virtual experimentation with reliable modeling tools also allows the exploration of as-yet untested conditions and materials configurations, again accelerating development work and increasing the efficiency of resource utilization.

However, when modeling is approached on a case-by-case basis, specific sets of transition rate equations need to be defined and solved numerically for each case. With currently available modeling tools, extensive customization and programming are required for each new system studied, or whenever a new transition for an existing system comes into play. Existing programs cannot automatically create the proper set of partial differential equations to describe an arbitrary system. Clearly, if a generalized method were available that could use known, estimated or calculated energy levels and photo-physical parameters as a starting point, and relieve researchers of the mathematical and programming burden, it would be valuable. Furthermore, if this method were sufficiently general, it would allow nearly unlimited restructuring of energy levels and transitions for modeling existing or hypothetical materials; this would be a powerful new paradigm for photonics materials development.

The SimphoSOFT™ generalized photonics modeling application platform has precisely those capabilities. This application note reports on two test studies that illustrate the utility of SimphoSOFT modeling and show that the underlying mathematical foundation is valid. With SimphoSOFT modeling, literature or readily measured data are used to construct an energy level diagram and define key transitions for materials of interest. These energy levels and transitions, along with basic materials parameters like index of refraction, are then used by the SimphoSOFT engine to define internal 'transition modules'. These transition modules, in turn, are used to numerically model photonic behavior of materials. This application note demonstrates that SimphoSOFT modeling yields valid results for two-photon absorption by the well known chromophore AF455, and for energy transfer (time-dependent population densities) and luminescence in a Yb^{3}/Er^{+3} system.

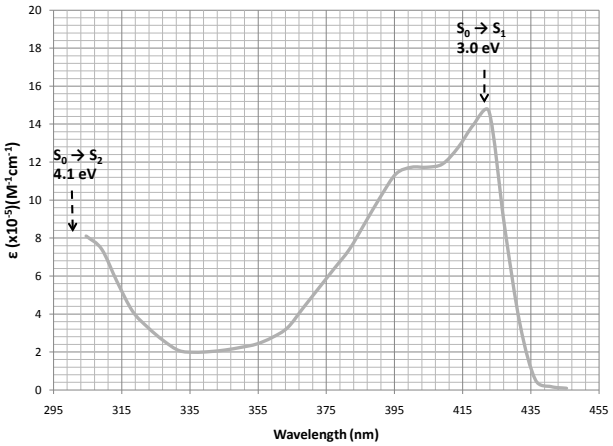
About Simphotek – Simphotek, Inc. is a NJ based technology company with roots at NYU and the US AFRL. Simphotek believes that photonics materials development demands better tools for modeling light-matter interactions for materials fabrication and data analysis. Simphotek has developed a generalized methodology for photonics modeling that circumvents traditional, resource intensive, modeling approaches that depend upon time-consuming programming. The SimphoSOFT™ modeling application is a GUI driven platform, using a CAD environment that embodies this methodology and relies upon a small set of possible photo-physical interactions handled within the software as Transition Modules. Transition Modules can be used to "construct" a nearly unlimited number of photonic interactions schemes for modeling. The underlying equations for modeling are generated without user intervention by a unique, proprietary differential equations engine linked to the Transition Modules diagram a user builds.

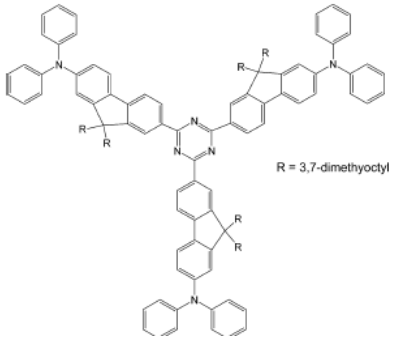
Based in part on E. Parilov and M. Potasek, *J. Opt. Soc. Am. B* **23**, 1894 (2006) and Simphotek pending-patents.

AF455 – Two Photon Absorption

AF455 is a well characterized two-photon absorber, and the relevant energy levels, absorption coefficients, and relaxation behavior are well known (see table, below).

In general terms, energy levels and linear absorption coefficients can be determined from optical absorbance spectra. In the spectrum shown below, single-photon absorptions corresponding to





Absorption spectrum of AF455. Molecular structure of AF455

Ref. J. E. Rogers et. al., J. Phys. Chem. A **108**, 5514 (2004).

transitions from the ground state (S_0) to the first excited singlet state (S_1), and to the second excited singlet state (S_2) define energy levels for those states. This information, combined with information from other sources on absorption cross-sections and relaxations, and a consideration of the energy levels that would interact with incident 800 nm photons (the energy for which this molecule is a two-photon absorber), yields the table of relevant parameters shown below.

Absorptions	Parameter	Value[a]	Relaxations	Parameter	Value[a]
$S_0 \rightarrow S_1$ (one photon)	(not relevant)	(not relevant)	$S_1 \rightarrow S_0$	k_{10}^{-1} (ns)	2.72
$S_0 \rightarrow S_1$ (two photon)	σ_{01} (cm^4/GW)	0.5×10^{-20} [b]			
$S_1 \rightarrow S_2$ (one photon)	σ_{12} (cm^2)	1.68×10^{-17}	$S_2 \rightarrow S_1$	k_{21}^{-1} (ps)	1.66[c]
$T_3 \rightarrow T_4$ (one photon)	σ_{34} (cm^2)	17.1×10^{-17}	$T_4 \rightarrow T_3$	k_{43}^{-1} (ns)	10[d]
			$S_1 \rightarrow T_3$	k_{13}^{-1} (ns)	45.3
			$T_3 \rightarrow S_0$	k_{30}^{-1} (μs)	0.368

(S indicates a singlet energy level, T indicates a triplet)

Table Notes:

[a] Unless otherwise noted, parameters are taken from R. L. Sutherland, M. C. Brant, J. Heinrichs, J. E. Rogers, J. E. Slagle, D. G. McLean, and P. A. Fleitz, "Excited state characterization and effective three-photon absorption model of two-photon-induced excited state absorption in organic push-pull charge-transfer chromophores," J. Opt. Soc. Am. B **22**, 1939 (2005).

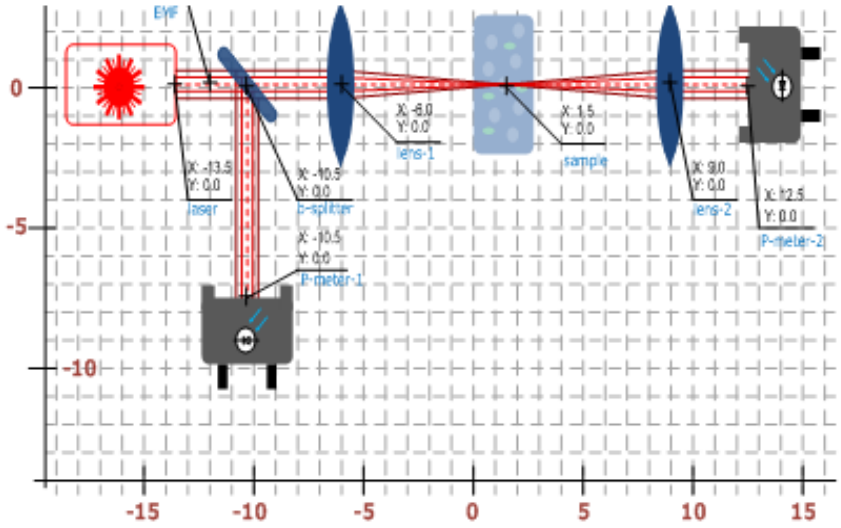
[b] The value shown in the table is taken from G. S. He, T.-C. Lin, J. Dai, P. N. Prasad, R. Kannan, A. G. Dombroskie, R. A. Vaia, and L.-S. Tan, "Degenerate two-photon-absorption spectral studies of highly two-photon active organic chromophores," J. Chem. Phys. **120**, 5275 (2004) and

R. Kannan, G. S. He, T.-C. Lin, P. N. Prasad, R. A. Vaia, and L.-S. Tan, "Toward highly active two-photon absorbing liquids. Synthesis and characterization of 1,3,5-triazine-based octupolar molecules," Chem. Mater. **16**, 185 (2004).

[c] J. E. Rogers, J. E. Slagle, D. G. McLean, R. L. Sutherland, B. Sankaran, R. Kannan, L.-S. Tan, and P. A. Fleitz, "Understanding the one-photon photophysical properties of a two-photon absorbing chromophore", J. Phys. Chem. A **108**, 5514 (2004).

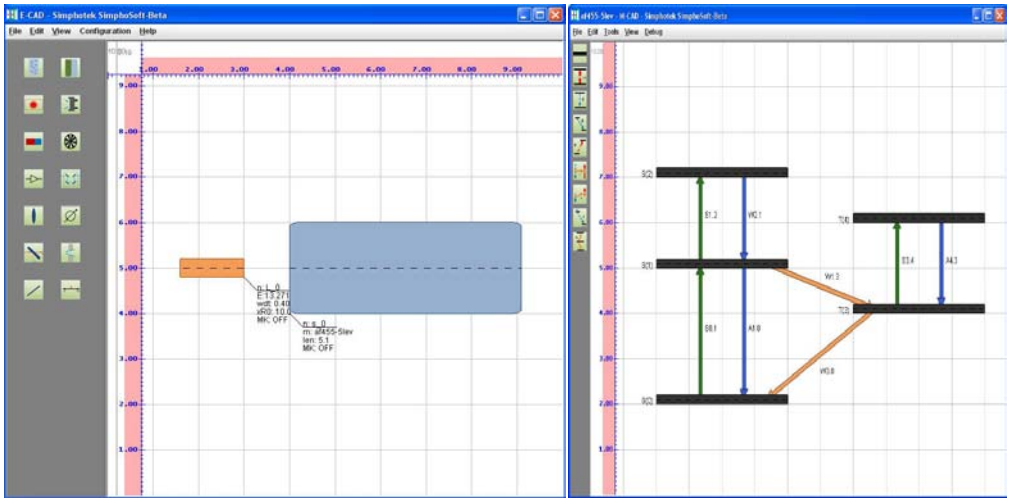
[d] J. Kleinschmidt, S. Rentsch, W. Tottleben, and B. Wilhelmi, “Measurement of strong nonlinear absorption in stilbene-choloform solution, explained by the superposition of two-photon absorption and one-photon absorption from the excited state,” Chem. Phys. Lett. **24**, 133 (1974).

A key test for model performance is whether correct results are predicted for laser transmission at the wavelength corresponding to two-photon absorption as the incident pulse energy is varied, in an experimental set up similar to that shown below.



Schematic diagram of laser transmission experiment showing laser, beam splitter, detectors, lens, and sample.

Within SimphoSOFT E-CAD and M-CAD windows, the preceding combination of experimental setup and materials properties are symbolized as shown below:

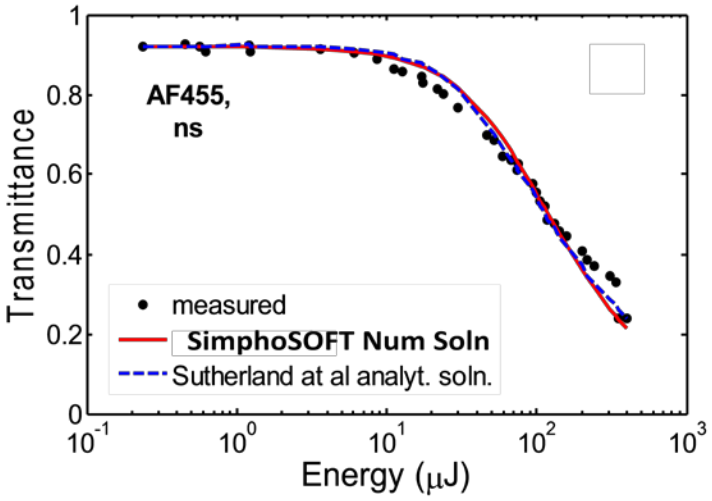


E-CAD M-CAD

Other key parameters for the simulation include chromophore concentration in the sample layer matrix (a.k.a. carrier density, in this case 1.2 x 10^{-2} nm^{-3}).

The laser is at 800 nm, emitting pulses with 1.92 ns duration (FWHM, Gaussian shape), and a radius of 13.0 µm at the entrance to the material (R_o, Gaussian shape). The sample in this case is 1.0 mm thick, and is sufficiently wider than the laser beam radius that it is not relevant here.

Once set up, SimphoSOFT can be used to simulate the laser transmission at a range of laser pulse energies (in this case from 0.2 µJ to 300 µJ). The following graph compares output from SimphoSOFT to the experimental data, and to a custom model of the results based on an analytical solution to the relevant set of differential equations. Transmittance is the output energy divided by the input energy.



Laser transmission as a function of incident energy. The black dots are measurements, the red line is from **SimphoSOFT**, and the dashed blue line is an analytical solution. Ref. *J. Opt. Soc. Am. B* **23**, 1894-1910 (2006)

The excellent agreement between the SimphoSOFT generalized numerical approach and both the data and the reported analytical solution demonstrate the validity of the transition module approach and the SimphoSOFT mathematical kernel.

Note that the SimphoSOFT-OPT application package provides tools that allow users to conduct modeling to find an optimum fit to experimental results, in order to extract experimental parameters. In this case, were the two-photon absorption coefficient not known, SimphoSOFT-OPT tools can be used to determine it, by finding the value providing the best fit to experimental data.

Yb^{+3}/Er^{+3} Coupling – Energy Transfer with Up-conversion

The Yb^{+3}/Er^{+3} system in a $LiNiO_3$ matrix is a well-known example of a rare-earth ion system (see Table Notes a-d, below) with utility in applications like optical amplifiers and lasers. This is a fairly complex system with multiple energy levels and complex transitions between them. Modeling this system with conventional software tools is quite complex.

In this case, the laser is at 920 nm, delivering 20 mJ with 10 ns duration (FWHM, Gaussian shape). The sample in this case is 1.0 mm thick ($LiNbO_3$ matrix), and sufficiently wide (relative to the beam diameter) to not impact results. The matrix has an index of refraction of 2.007 and concentrations are: $[Yb^{+3}]$ = 0.1 mol % (2.1×10^{19} cm^{-3}) or 2.0 mol % (5.0×10^{20} cm^{-3}) and $[Er^{+3}]$ = 0.5 mol % (1.13×10^{20} cm^{-3}). Relevant transitions and parameters are given in the table below.

Absorptions	Parameter	Value	Relaxations	Parameter Radiative	Value	Parameter Non-Radiative	Value
Yb^{+3}							
$S_1 \rightarrow S_2$ (one photon)	σ_{12} (cm^2)	7.96×10^{-21} [a]	$S_2 \rightarrow S_1$	A_{21}^{-1} (ms)	0.39 [b]	W_{21} (ms)	0.26 [b]
Er^{+3}							
$S_3 \rightarrow S_4$ (one photon)	(not relevant)	(not relevant)	$S_4 \rightarrow S_3$	A_{43}^{-1} (ms)	3.6 [c]	W_{43}^{-1} (ms)	2.3 [c]
			$S_5 \rightarrow S_4$	A_{54}^{-1} (ms)	12.99 [c]	W_{54}^{-1} (ms)	1.61 [c]
			$S_5 \rightarrow S_3$	A_{53}^{-1} (ms)	0.24 [c]	W_{53}^{-1} (ms)	None [c]
			$S_6 \rightarrow S_5$	A_{65}^{-1} (ms)	8.75 [c]	W_{65}^{-1} (ms)	1.67 [c]
			$S_6 \rightarrow S_4$	A_{64}^{-1} (ms)	0.11 [c]	W_{64}^{-1} (ms)	None [c]
			$S_6 \rightarrow S_3$	A_{63}^{-1} (ms)	0.04 [c]	W_{63}^{-1} (ms)	None [c]
Energy Transfer Yb^{+3} / Er^{+3}			**Forward/Back Energy Transfer**	**Parameter**	**Value**		
			$S_2 \rightarrow S_5$	C_{25} (cm^3/s)	2.4×10^{-16} [d]		
			$S_5 \rightarrow S_2$	C_{52} (cm^3/s)	1.8×10^{-16} [d]		
Upconversion Yb^{+3} / Er^{+3}			**Upconversion**	**Parameter**	**Value**		
			$S_2 \rightarrow S_6$	C_{52} (cm^3/s)	4.8×10^{-16} [d]		

(S indicates a singlet energy level)

Yb^{+3}/Er^{+3} and Yb^{+3}/Er^{+3} Table Notes:

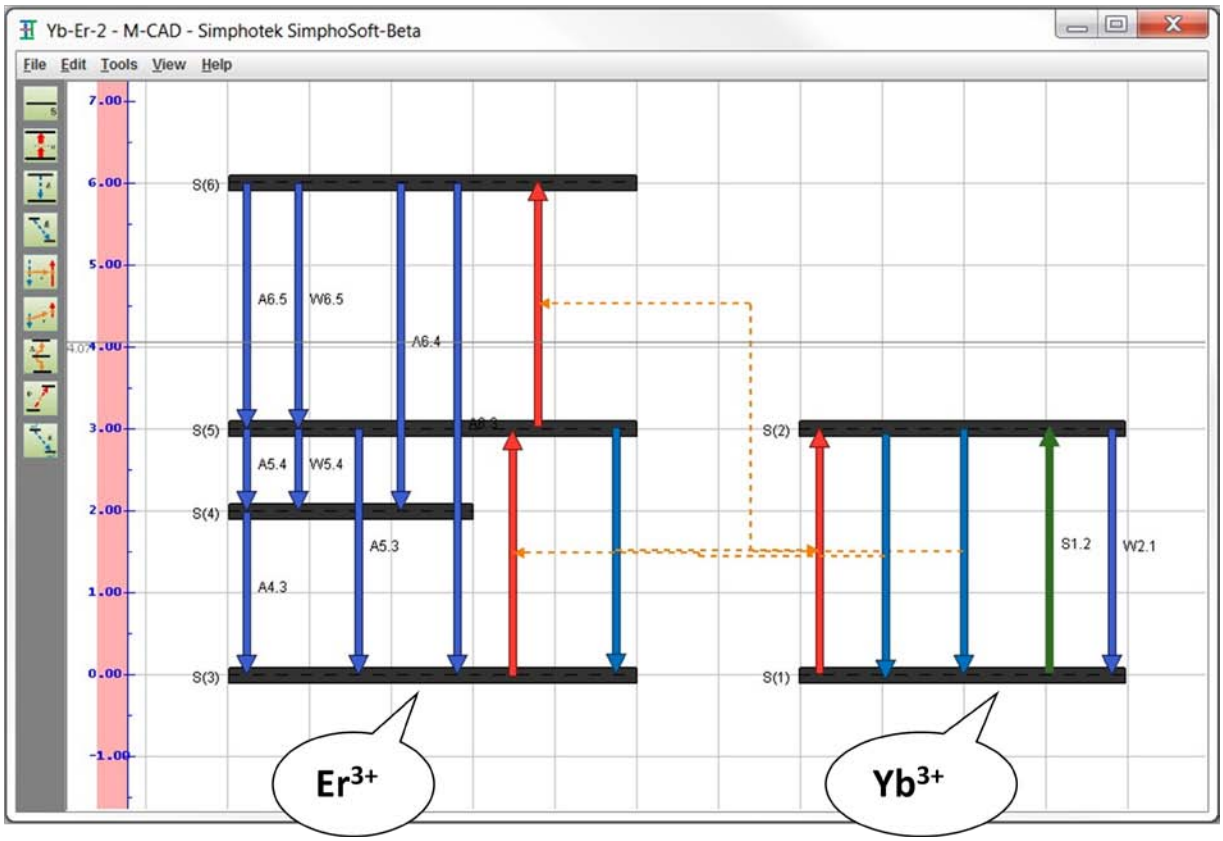
[a] E Cantelar and F Cusso, "Analytical solution of the transfer rate equations in $LiNbO_3:Er^{3+}$ /Yb^{3+}", J. Phys: Condens. Matter **12,** 521 (2000).

[b] E. Cantelar and F. Cusso, "Dynamics of the Yb^{3+} to Er^{3+} energy transfer in $LiNbO_3$**",** Appl. Phys. B **69**, 29 (1999).

[c] J. Amin, B. Dussardierb, T. Schweizer, M. Hempstead, "Spectroscopic analysis of Er^{3+} transitions in lithium niobate", Journal of Luminescence **69,** 17 (1996).

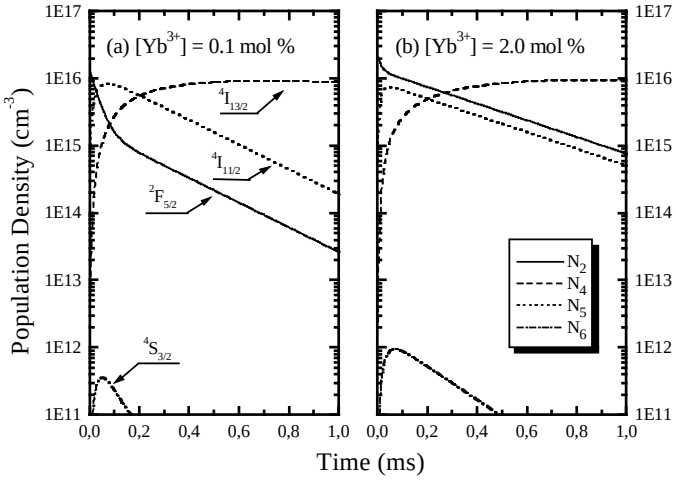
[d] E Cantelar, J A Munoz, J A Sanz-Garcıa and F Cusso, "Yb^{3+} to Er^{3+} energy transfer in $LiNbO_3$"**,** J. Phys: Condens. Matter **10,** 8893 (1998).

The resulting energy level diagram (M-CAD window) is shown below.

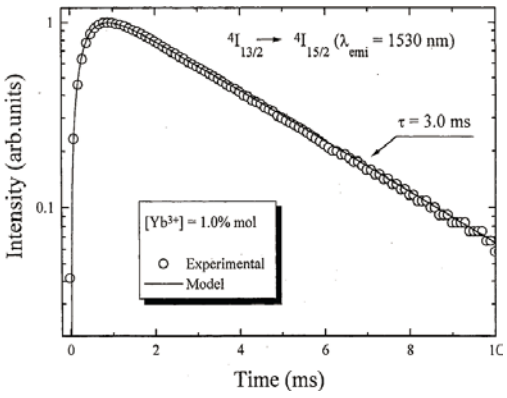


M-CAD window from SimphoSOFT for Er^{3+} and Yb^{3+}

Once the SimphoSOFT program is configured, it can be used to simulate the dynamic energy level populations and luminescence of this sample as it relaxes, post irradiation. Literature results are shown first (From Table Notes a, b above):

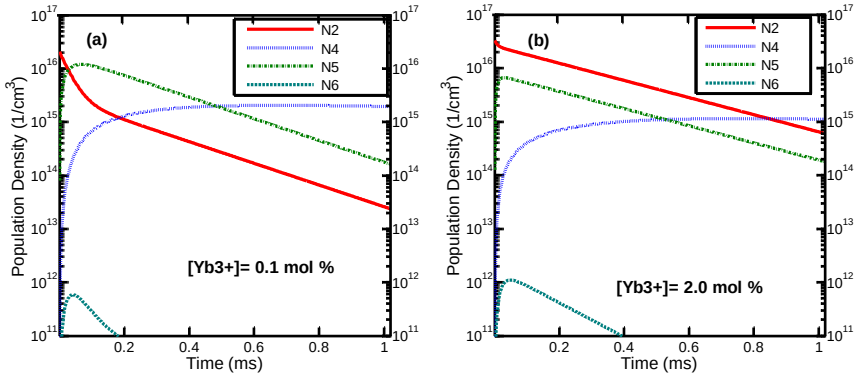


Calculated temporal evolution (log scale) of the population densities after ytterbium excitation, From Table Note a.

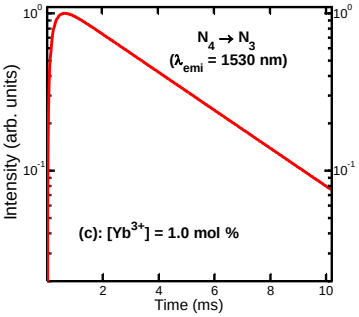


Temporal evolution (log scale) of the luminescence of Er^{3+} ions measured at 1.53 µm after pulsed excitation of the Yb^{3+} ions at 920 nm. The sample was co-doped with 0.5mol% Er^{3+} and 1.0 mol% Yb^{3+}. From Table Note b.

Results based on modeling with the SimphoSOFT-ET application (the energy-transfer version) are shown next.



Numerical calculations of the temporal evolution (log scale) of the population densities after ytterbium excitation using **SimphoSOFT**.



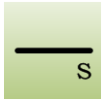
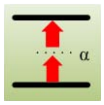
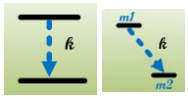
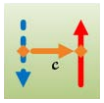
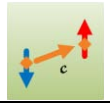
Numerical calculation of the temporal evolution (log scale) of the luminescence of Er^{3+} ions using **SimphoSOFT**.

As was the case for two-photon absorption, SimphoSOFT (in this case, SimphoSOFT-ET) modeling yields excellent agreement with reported results.

It is important to note in this case that time dependent modeling of the dynamic energy level population densities is an intrinsic element of SimphoSOFT modeling.

Supplemental Information

In designing SimphoSOFT, Simphotek personnel examined thousands of energy level diagrams that have been used to describe photo-physical interactions. Several repetitive elements occur throughout these diagrams, and Simphotek has selected six basic transition modules for use in modeling, that can be combined to make nearly any energy level diagram required for modeling materials described by electronic energy levels.

Material-CAD Component and Icons	Description/parameters-patents pending
Energy level 	**Simphotek's unified (computational) energy level.** An electronic, vibrational, rotational level, continuum level, degenerate levels, or a hypothetically added level
Absorption 	**Simphotek's absorption (computational) transition module.** Single- or multi-photon absorption or stimulation emission.
Relaxation 	**Simphotek's relaxation (computational) transition module.** Electron relaxation happening between the states of the same or different type, e.g. singlet-singlet or singlet-triplet.
Energy transfer 	**Simphotek's energy transfer (computational) transition module** Simultaneous relaxation event in the donor molecule and excitation event in the acceptor molecule due to energy transfer between molecules.
Energy transfer/up-conversion 	**Simphotek's energy transfer up-conversion (computational) transition module .** Simultaneous relaxation event in the donor molecule and up-conversion event in the acceptor molecule due to energy transfer between molecules.
Up-conversion 	**Simphotek's up-conversion (computational) transition module.** Energy exchange between two excited molecules when one is promoted to higher excited state and the other relaxes.

