Some types of rare-earth ions and some types of organic molecules can undergo both upconversion and cross-relaxation (self-quenching).

We define upconversion as occurring between molecules or ions that are chemically identical. Upconversion can occur, for example, if many molecules of the same type have electrons in their first excited states. Upconversion occurs with the de-excitation of a molecule from its first excited state to its ground state and the simultaneous excitation (via energy transfer) of another identical molecule from its first excited state to a higher excited state.

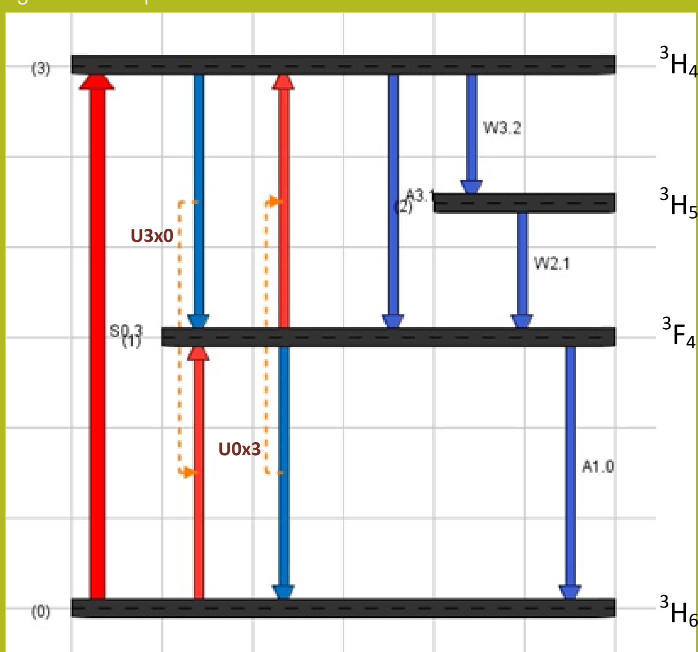
Cross-relaxation (or self-quenching) between identical molecules or ions occurs when a molecule or ion in an excited state exchanges energy with an identical molecule or ion that is in the ground state, resulting in both molecules or ions going to an intermediate excited state that is energetically approximately halfway between the upper excited state and the ground state.

SimphoSOFT can model both upconversion and self-quenching simultaneously. User can define upconversion transition modules for one type of molecule in M-CAD window. Cross-relaxation can be defined for the same type of molecule by using 'inverse' upconversion transition modules.[1]

Example SimphoSOFT simulation of upconversion and cross-relaxation: Thulium (Tm^{3+})

The sample is composed of 5% Tm^{3+} ions dispersed in yttrium lithium fluoride (YLF) host material. The ions have four important energy states for optical transitions, $^3H_6$, $^3F_4$, $^3H_5$, and $^3H_4$ for optical transitions.

Screenshot of SimphoSOFT® M-CAD with partial energy level diagram for Tm^{3+} containing 'inverse' upconversion transition module which mimics cross-relaxation



[1] Simphotek will develop separate transition modules for self-quenching in the next version of SimphoSOFT

SimphoSOFT user creates 4 energy levels which represent Tm energy states $^3H_6$ (labeled 0 in the energy level diagram above), $^3F_4$ (labeled as 1), $^3H_5$ (labeled as 2), and $^3H_4$ (labeled as 3). For simplicity, other energy levels will not be shown but can be added if needed. The laser wavelength is 780 nm.

To define an upconversion in the SimphoSOFT M-CAD dialog, only one stack of Tm^{3+} energy levels is required since there is no need to illustrate the levels of a second, identical ion. Upconversion transition module, labeled U0x3 in the diagram above, contains an additional arrow (an orange broken line – – – →), which connects relaxation transition module with absorption transition module. This symbolizes energy transfer between two ions of the same type when the first ion will relax to its ground state (relaxation transition module), while the second ion will be promoted to a higher energy state (absorption transition module).

Cross-relaxation transition, labeled U3x0, is mimicked by the same upconversion transition module, where the direction of the energy transfer (an orange broken line ← – – –) is reversed due to a swap of its relaxation and absorption transition modules.

Cross-section, relaxation times and rates for Tm^{3+}:

Energy levels are labeled from 0 to 3

The values listed below are representative values for 0.5% doping and will need to be modified for other sample compositions. Actual values can depend on the host material, the level of doping and the sample temperature.[2,3] Relaxation rates are from Walsh et al.[2] Cross-relaxation and up-conversion rates are from Dinndorf.[3]

From level(s):	To level(s):	Cross-section:	Relaxation time (ms):	Upconversion rate:	Cross-relaxation rate:
0	3	1×10^{-19} cm^2			
3	2		39 (non-radiative)		
3	1		15 (radiative)		
2	1		270 (non-radiative)		
1	0		9.3 (radiative)		
3 and 0	1				2.2×10^{-17} cm^3 s^{-1}
1	0 and 3			2.2×10^{-19} cm^3 s^{-1}	

Other sample properties	
Tm ion dopant density (concentration) in the host material	7.0×10^{20} ions/cm^3
The host material linear refractive index	$n_0 = 1.4$
Host material linear absorption	$\alpha = 0$ cm^{-1}
Host material nonlinear refractive index	$n_2 = 0$
Sample length	1 mm

[2] Walsh, B. M, Barnes, N. P., Di Bartolo, B., J. Appl. Phys. 83(5), 2772 (1998). (for relaxation rates and times)
[3] Dinndorf, K. M., "Energy transfer between thulium and holmium in laser hosts", PhD thesis, Massachusetts Institute of Technology (1993). (for cross relaxation and upconversion rates)

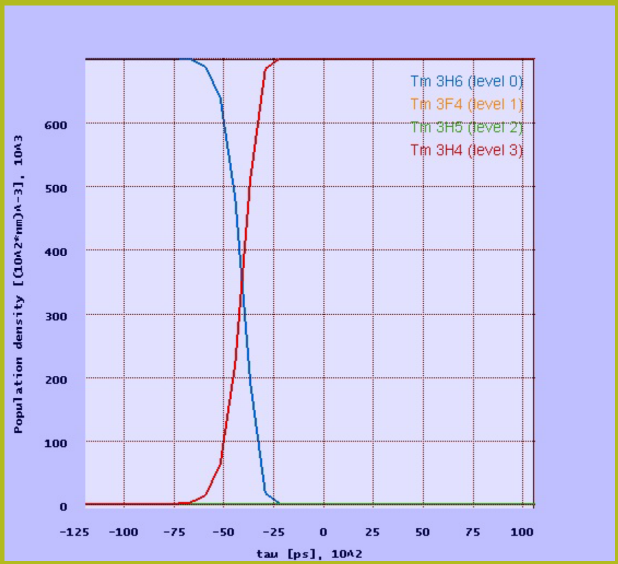
Laser beam properties	
Pulse energy	10 mJ
Pulse radius (HW1/e^2M)	50 µm
Pulse FWHM	4 ns
Wavelength	780 nm

Results of SimphoSOFT simulations for the populations of the Tm^{3+} energy levels:

Near the sample entrance, the populations of the four states as a function of radius rho are shown below. At rho = 0, the ground state 0 (blue line) is depleted. Most of the electrons are in state 3 (red line). However, some electrons can get to state 1 (orange line) both by self-quenching and by relaxation through state 2. Self-quenching dominates during the time period (10 ns) of the laser pulse.

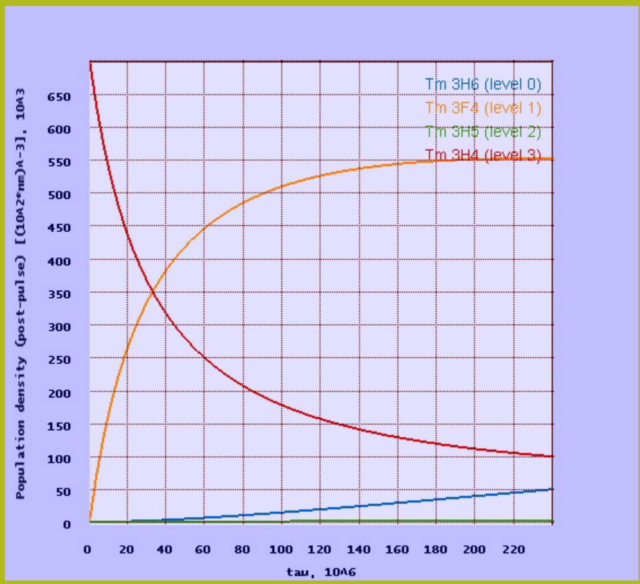
Near the sample entrance and at the spatial center of the laser pulse (rho = 0), the populations of the four states during the initial simulation time domain (24,000 ps or 24 ns) are plotted below as a function of time tau. The $^3H_6$ (ground state 0; blue line) is depleted during the laser pulse. Most of the electrons are excited into $^3H_4$ (excited state 3; red line). However, very few electrons get to the other two states during the initial 24,000 ps (24 ns) time period, which makes absorption the dominating process.

Dynamics of populations densities of Tm^{3+} at the entrance of the sample where upconversion and cross-relaxations are insignificant



The second plot covers a time period of 240 × 10^6 ps or 240 µs, after the end of the laser pulse. As shown in the resulting plot, where the illustrated data are at the spatial center of the laser pulse, most of the electrons are in $^3H_4$ (excited state 3; red line) immediately after the laser pulse has passed (tau = 0 on the plot). During this longer time period, cross-relaxation causes electrons in $^3H_4$ (excited state 3; red line) to transfer to state $^3F_4$ (excited state 1; orange line). Electrons also start to return to $^3H_6$ (ground state 0; blue line).

Dynamics of populations densities of Tm^{3+} after the pulse passes the entrance where cross-relaxation dominates upconversion



Although any two ions in $^3F_4$ (excited state 1; orange line) can also exchange energy and undergo upconversion, where one ion gains energy and goes to $^3H_4$ (excited state 3; red line) and the other ion loses energy and goes to $^3H_6$ (ground state 0; blue line), upconversion will not be important for this calculation since the upconversion rate is relatively small compared to the cross-relaxation rate.

SimphoSOFT allows users to determine whether processes of cross-relaxation and upconversion are important to be taken into account. This is essencial both for photo processes in rare-earth laser materials and for organic molecules.