Rare-earth ions and some types of organic molecules can undergo cross-relaxation (self-quenching), upconversion, fluorescence and other non-radiative relaxations. For rare-earth ions, these processes are important when used in lasers, optical amplifiers and for other applications.

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

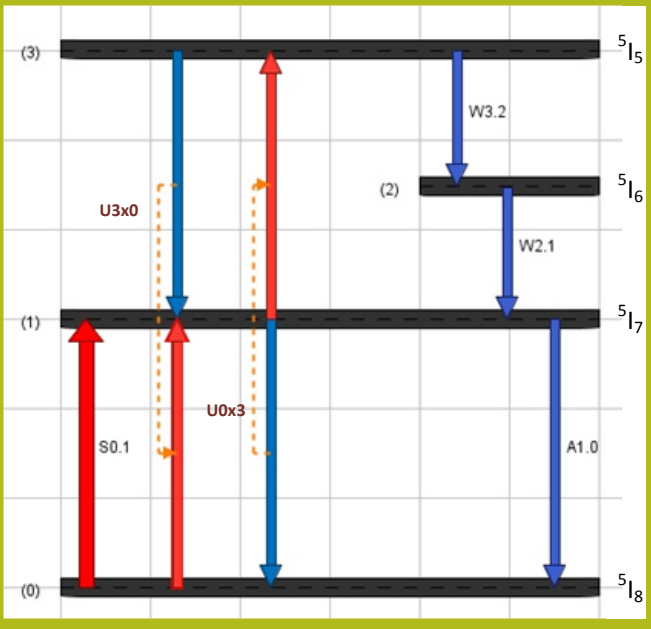
Cross-relaxation (self-quenching) occurs when a molecule or ion in an excited state exchanges energy with an identical molecule or ion that is in the ground state, resulting in each molecule or ion simultaneously undergoing energy transfer to an intermediate excited state that is energetically halfway between the upper excited state and the ground state.

SimphoSOFT can model both upconversion and cross-relaxation 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 cross-relaxation and upconversion: Holmium ($Ho^{3+}$)

The sample is composed of 0.5% $Ho^{3+}$ ions dispersed in yttrium lithium fluoride (YLF) host material. The ions have four important energy states for optical transitions, $^5I_8$, $^5I_7$, $^5I_6$, and $^5I_5$.

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




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

SimphoSOFT user creates 4 energy levels which represent Ho energy states $^5I_8$ (labeled 0 in the energy level diagram above), $^5I_7$ (excited state, labeled as 1), $^5I_6$ (excited state, labeled as 2) and $^5I_5$ (excited state, labeled as 3). For simplicity, other energy levels will not be shown but can be added if needed. The laser wavelength is 1900 nm.

To define an upconversion in the SimphoSOFT M-CAD dialog, only one stack of $Ho^{3+}$ energy levels is required since there is no need to illustrate the levels of a second, identical molecule. 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 molecules of the same type when the first molecule will relax to its ground state (relaxation transition module), while the second molecule 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 $Ho^{3+}$:

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 | 1 | $9 \times 10^{-21}$ cm$^2$ | | | |
| 3 | 2 | | 118 (non-radiative) | | |
| 3 | 1 | | 15 (radiative) | | |
| 2 | 1 | | 48 (non-radiative) | | |
| 1 | 0 | | 14 (radiative) | | |
| 3 and 0 | 1 | | | | $1.3 \times 10^{-16}$ cm$^3$ s$^{-1}$ |
| 1 | 0 and 3 | | | $1.5 \times 10^{-17}$ cm$^3$ s$^{-1}$ | |

| Other sample properties | |
|---|---|
| Molecular dopant density (concentration) in the host material | $7.0 \times 10^{19}$ molecules/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 |

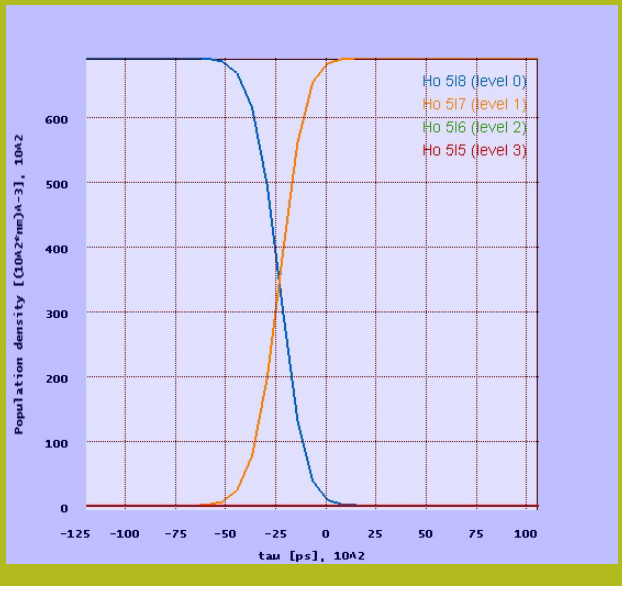
[2] Walsh, B. M, Barnes, N. P., Di Bartolo, B., J. Appl. Phys. 83(5), 2772 (1998). (for relaxation rates and times)
[3] Dinndorf, K. M., "Energy transfer between thulium and holmium in laser hosts", PhD thesis, Massachusetts Institute of Technology (1993). (for cross relaxation and upconversion rates)

| Laser beam properties | |
|---|---|
| Pulse energy | 10 mJ |
| Pulse radius (HW1/$e^2$M) | 50 µm |
| Pulse FWHM | 4 ns |
| Wavelength | 1900 nm |

## Results of SimphoSOFT simulations for the populations of the $Ho^{3+}$ energy levels:

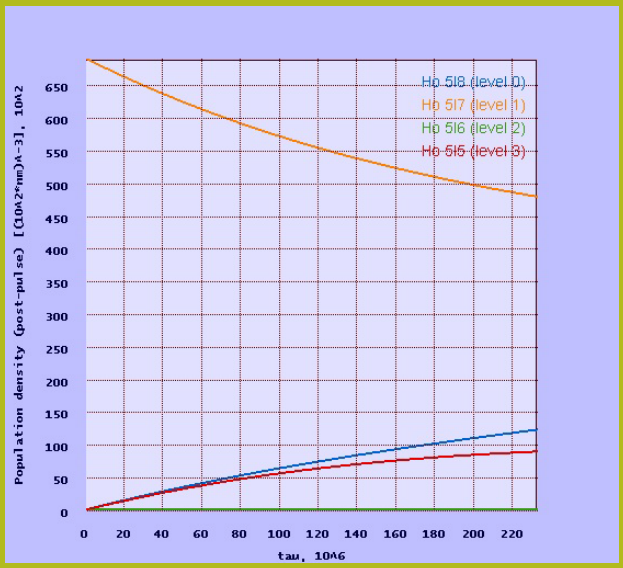
Near the sample entrance and at the spatial center of the laser pulse (rho = 0) , the populations of the four states during the initial simulation time domain (24,000 ps or 24 ns) are plotted below as a function of time tau. The $^5I_8$ (ground state 0; blue line) is depleted during the laser pulse. Most of the electrons are excited into $^5I_7$ (excited state 1; orange line). However, very few electrons get to the other two states during the initial 24,000 ps (24 ns) time period.

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




The second plot covers a time period of approximately 240 x $10^6$ ps or 240 µs, after the end of the laser pulse. As shown in the plot, where the illustrated data are at the spatial center of the laser pulse, most of the electrons are in $^5I_7$ (excited state 1; orange line) immediately after the laser pulse has passed (tau = 0 on the plot). During this longer time period, upconversion causes electrons in $^5I_7$ (excited state 1; orange line) to transfer to state $^5I_5$ (excited state 3; red line). Electrons also start to return to $^5I_8$ (ground state 0; blue line).

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




Although an ion in $^5I_5$ (excited state 3; red line) and an ion in $^5I_8$ (ground state 0; blue line) can also exchange energy and undergo cross-relaxation to state $^5I_7$ (excited state 1; orange line), cross-relaxation will not be as important as upconversion for early times in this calculation since the population of $^5I_5$ (excited state 3; red line) is relatively small compared to the population of $^5I_7$ (excited state 1; orange line).

SimphoSOFT can do these types of simulations, which are important both for photo processes in rare-earth materials and for organic molecules.