By standard definition, energy transfer occurs between molecules or ions of different types. During energy transfer molecule of the first type (molecule 0) relaxes from its first excited state to its ground state, while molecule of the second type (molecule 1) simultaneously excites from its ground state to its first excited state. Note that for energy transfer, the ground states of both molecules are involved.

Energy transfer upconversion also occurs between molecules or ions of different types, but both molecules can be in their first excited states. Energy transfer upconversion may happen with the de-excitation of molecule 0 from its first excited state to its ground state and the simultaneous excitation of molecule 1 from its first excited state to a higher excited state. Once the molecule 1 is in the higher excited state, it may emit a photon that has a higher energy than photons emitted from the first excited state.

We define upconversion as occurring between identical molecules or ions.[1] Upconversion can occur, for example, if many molecules of type 0 have electrons in their first excited states. Upconversion happens with the de-excitation of a molecule of type 0 from its first excited state to its ground state and the simultaneous excitation of another identical molecule of type 0 from its first excited state to an another higher excited state.[2]

SimphoSOFT can simulate energy transfer and energy transfer upconversion between molecules (or ions) of different types and upconversion between identical molecules (or ions). Among other applications, these processes are important for

- some types of lasers,
- optical amplifiers,
- photodynamic therapy (PDT),
- photosynthesis,
- Forster resonant energy transfer (FRET).

The SimphoSOFT Materials-CAD (M-CAD) dialog allows a user to simultaneously set up energy level diagrams of two or more types of molecules or ions.

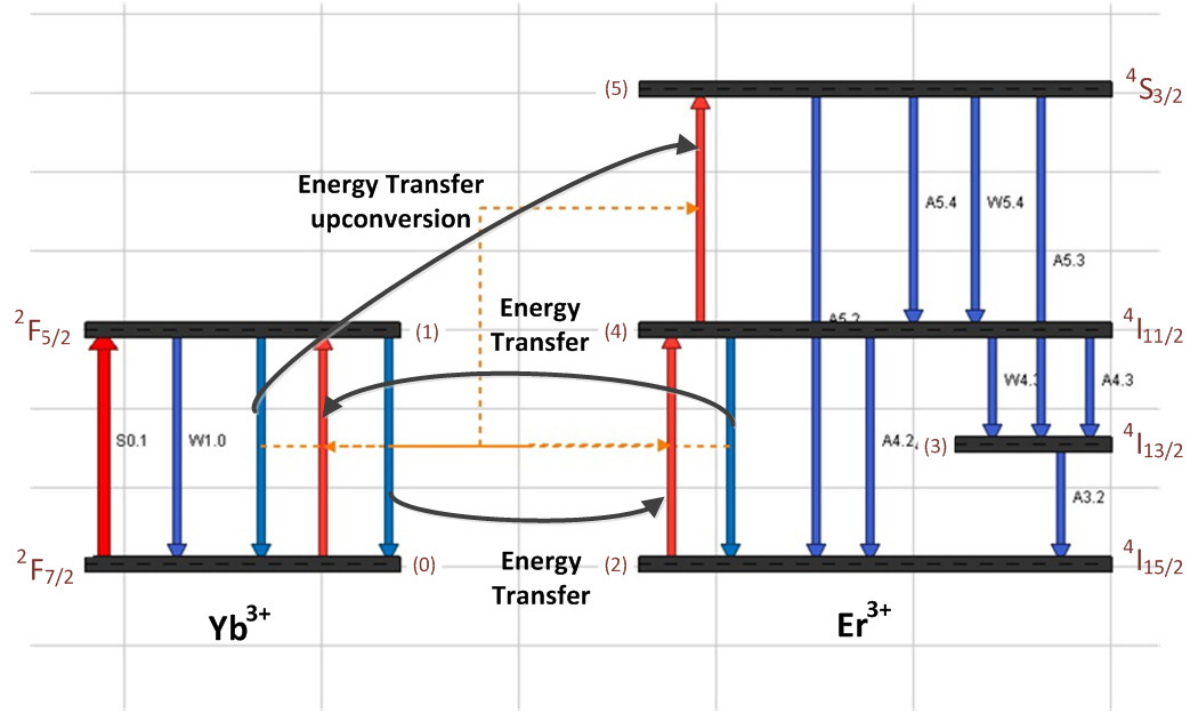
Example SimphoSOFT simulation of energy transfer between Yb^{3+} and Er^{3+} ions:

Er^{3+} ions can be doped in silica optical fiber waveguides to make efficient optical amplifiers for optical communications networks. However, Er^{3+} ions have a relatively small absorption cross-section and cannot be doped to high concentrations due to aggregation, leading to long amplifier lengths. This is not a problem for optical communication amplifiers, but limits the use of Er^{3+} ions as the sole dopant for shorter devices such as fiber lasers. However, it has been found that Yb^{3+} ions can be doped to higher concentrations than Er^{3+} ions and that efficient energy transfer can occur between Yb^{3+} and Er^{3+} ions that are co-doped in host materials. These advantages lead to shorter and more efficient devices.

The example material, which energy level diagram is illustrated below, is composed of Yb^{3+} and Er^{3+} ions co-doped in a host material, lithium niobate ($LiNbO_3$). Several references listed below describe the energy transfer dynamics. The Yb^{3+} ions have two important energy states for optical transitions at 920 nm: $^2F_{7/2}$ (ground state 0 in the diagram below) and $^2F_{5/2}$ (excited state 1). The Er^{3+} ions have four important energy states for optical transitions at 920 nm: $^4I_{15/2}$ (ground state 2), $^4I_{13/2}$ (excited state 3), $^4I_{11/2}$ (excited state 4) and $^4S_{3/2}$ (excited state 5).

[1] In the SimphoSOFT M-CAD dialog, only one type of molecule will be illustrated since there is no need for a second type of molecule.
[2] Upconversion will not be illustrated in the following example.

Screenshot of SimphoSOFT® M-CAD with important energy levels of Yb^{3+} and Er^{3+} for excitation, energy transfer and energy transfer upconversion at 920 nm



SimphoSOFT user creates a stack of 2 energy levels for Yb^{3+} on the left portion of Material CAD (M-CAD) and a stack of 4 energy levels for Er^{3+}, connecting the resulting levels with absorption and relaxation transitions (mentioned below). First stack becomes the molecule 0, while the second becomes the molecule 1. Finally, the user defines energy transfer transitions between energy levels of molecules 0 and 1.

Cross-section and relaxation times for Yb^{3+} - Er^{3+}:

Energy levels are labeled from 0 to 5 in brackets
References (1, 2 and 3)

From level(s):	To level(s):	Cross-section:	Relaxation time (ms):	
Ytterbium				
0	1	7.96×10^{-21} cm^2		
1	0		0.26	non-radiative
Erbium				
3	2		3.6	radiative
4	2		0.24	radiative
5	2		0.04	radiative
4	3		12.99	radiative
5	4		8.75	radiative
5	3		0.11	radiative
5	4		1.67	non-radiative
4	3		1.61	non-radiative

The energy transfer, back energy transfer, and energy transfer upconversion rates:

Reference (4)

From:	To:	Energy transfer rate:	Energy transfer upconversion rate:
Yb (1 to 0)	Er (2 to 4)	2.4×10^{-16} $cm^3 s^{-1}$	
Yb (1 to 0)	Er (4 to 5)		4.8×10^{-16} $cm^3 s^{-1}$
Er (4 to 2)	Yb (0 to 1)	1.8×10^{-16} $cm^3 s^{-1}$	

Other sample properties	
Yb^{3+} ion dopant density (concentration) in the host material (0.1 mol %)	2.1×10^{19} ions/cm^3
Er^{3+} ion dopant density (concentration) in the host material (0.5 mol %)	1.13×10^{20} ions/cm^3
The host material linear refractive index	$n_0 = 1.4$
Host material linear absorption	$\alpha = 0.075$ cm^{-1}
Host material nonlinear refractive index	$n_2 = 0$
Sample length	1 mm

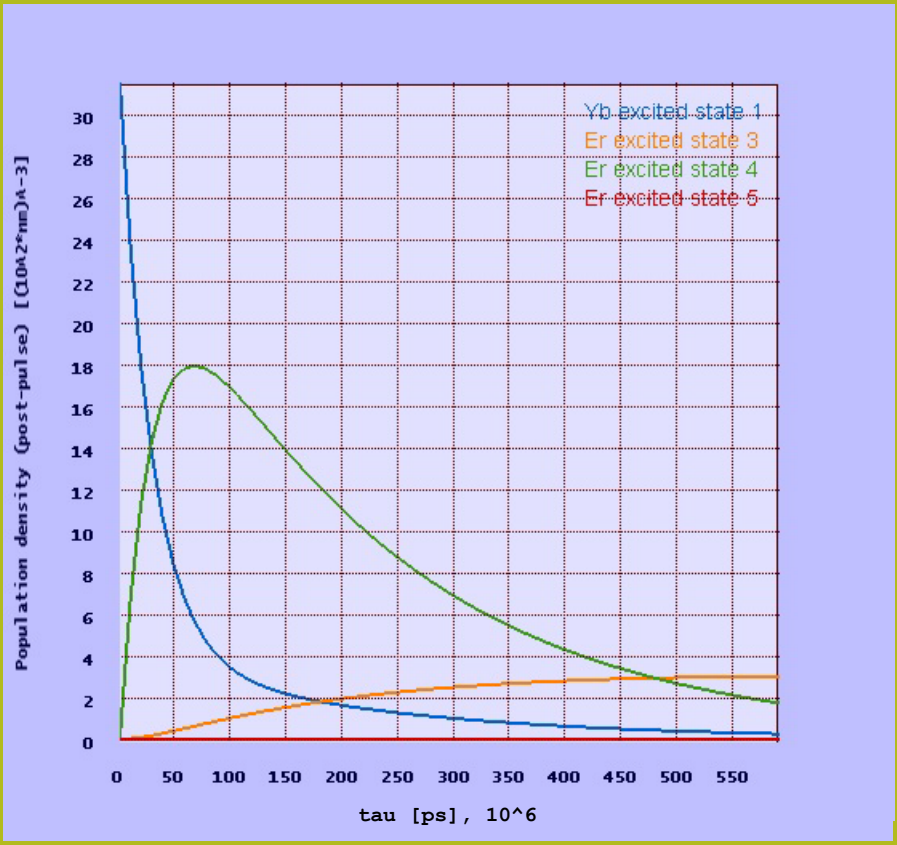
Laser beam properties	
Pulse energy	20 mJ
Pulse radius (HW1/e^2M)	5.52 mm
Pulse FWHM	10 ns
Wavelength	920 nm

SimphoSOFT helps to improve energy transfer efficiency.

Using the above specified conditions, SimphoSOFT can calculate the energy transfer and energy transfer upconversion dynamics during the passage of a laser beam or after the laser beam has passed through the sample.

The results shown below are the time dependences of the electronic populations of energy levels 1, 3, 4 and 5 after the laser pulse has left the sample. In the figure, full scale of the tau axis is 600×10^6 ps or 600 µs. The electronic population of Yb excited state 1 (blue line) of Yb^{3+} decreases as energy is transferred to Er excited states 3 (orange line), 4 (green line) and 5 (red line) of Er^{3+}. The electronic population of Er excited state 4 peaks at approximately 70×10^6 ps or 70 µs.

Results of SimphoSOFT® calculations:
electronic populations of energy levels
1,3,4, and 5 after the laser pulse left the sample.



The numerical results shown above are consistent with the results in Figure 2 of Reference (1) illustrating efficient energy transfer from Yb^{3+} to Er^{3+}.

Using SimphoSOFT for the numerical simulations is much easier and faster than laboriously setting up and solving the analytical equations shown in Reference (1). Utilizing SimphoSOFT, it is easy to change the type of rare earth ion used for energy transfer and choose another type, which in combination with erbium, improves the resulting hybrid material.

References:
(1) Cantlar, E. & Cusso, F., *J. Phy: Condens. Matter 12*, 521-527 (2000).
(2) Cantelar, E., & Cusso, F,*Appl. Phys. B , 69*, 29-33 (1999). (first rate only)
(3) Amin, J., Dussardier, B., Schweizer, T., & Hempstead, M, *Journal of Luminescence , 69*, 17-26 (1996).
(4) Cantelar, E., Munoz, J. A., Sanz-Garcia, J. A., & Cusso, F., , *10*, 8893 (1998).