Light that is incident on a molecule or ion that is in an excited electronic state may trigger radiative relaxation of the molecule and thereby cause the molecule to emit a coherent photon. This process, known as a stimulated emission, may result in depletion of the excited state of the molecules, which in some cases is desirable and in other cases is an unwanted effect.

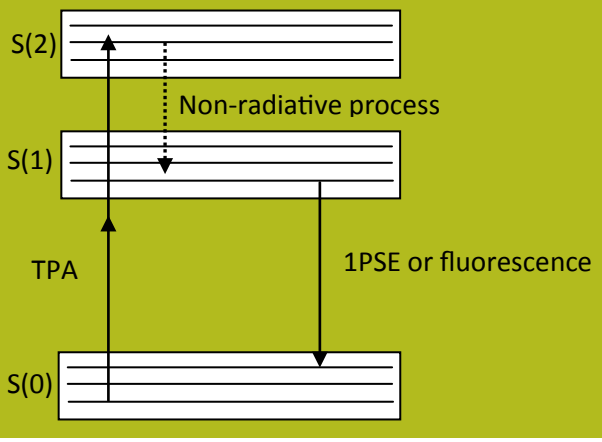
The SimphoSOFT mathematical model includes stimulated emission, which allows a user to accurately analyze photo-activated materials and optimize their performance.

Stimulated emission can reduce fluorescence emission

A type of optical microscopy called stimulated emission depletion (STED) microscopy has been developed by Stefan Hell and co-workers in Germany[1]. In STED microscopy, fluorescence emission from nanoparticles or single molecules is generated by the diffraction-limited focused spot of a laser pulse. A second STED laser pulse that is donut-shaped and red-shifted is directed at the focus of the first pulse after a short delay. The second STED beam de-excites and depletes the fluorescence emission from the first pulse except in the region of the donut hole where the STED pulse has zero or low intensity. Fluorescence emission will then occur only at the center of the focal spot of the exciting light pulse, resulting in an effective resolution for fluorescence emission that can be much smaller than the diffraction spot size of the exciting pulse.

Although STED microscopy is normally done with two laser pulses, an exciting pulse and a time-delayed STED pulse, it is also possible to demonstrate stimulated emission depletion with a single pulse. See, for instance, an example shown in Figure 1(d) of a paper by Belfield et al[2]. In this example, a molecule with at least three singlet states is excited by two-photon absorption (TPA) from state S(0) to S(2). The molecule quickly relaxes to the S(1) state by a non-radiative process and fluoresces from the S(1) state to the ground state S(0). One-photon stimulated emission (1PSE) from the same laser pulse can deplete the S(1) state to reduce fluorescence emission. A simplified energy level diagram is shown below.

Stimulated emission occurs in the presence of a photon with energy matching S(0)-S(1) gap by relaxation from level S(1) to level S(0). It compotes with fluorescence.



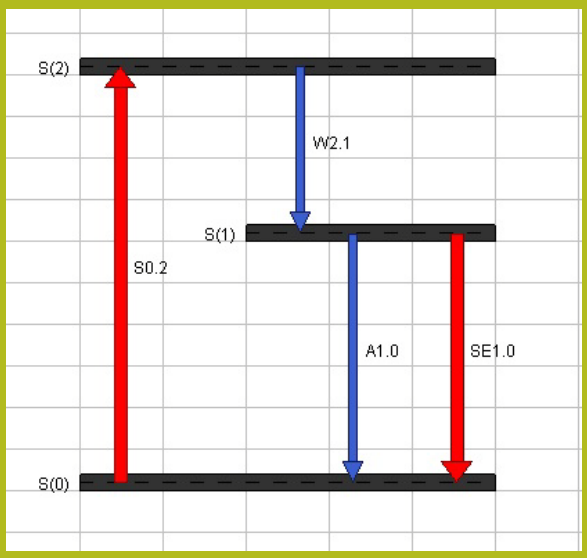
[1] S. W. Hell and J. Wichmann, "Breaking the diffraction resolution limit by stimulated emission: stimulated emission depletion microscopy," Opt. Lett. 19, 780-782 (1994)

[2] Belfield, K. D.; Bondar, M. V.; Yanez, C. O.; Hernandez, F. E.; Przhonska, O.V. "One- and Two-Photon Stimulated Emission Depletion of a Sulfonyl-Containing Fluorene Derivative," J. Phys. Chem. B 113, 7101-7106 (2009)

Example SimphoSOFT simulation: TPA and one-photon stimulated emission (1SPE)

The results of an example SimphoSOFT calculation using a single laser pulse for both two-photon absorption (TPA) and one-photon stimulated emission (1PSE) are shown below. The sample is composed of molecules dispersed in a host material. The molecules have three important energy states for optical transitions: Singlet states S(0), S(1) and S(2) (other states will be ignored).

Screenshot of SimphoSOFT® M-CAD with energy level diagram of STED material containing TPA, labeled S0.2, and stimulated emission, SE1.0



SimphoSOFT user creates 3 energy levels – S(0), S(1), and S(2) – connecting the resulting levels with two-photon absorption (S0.2 on the diagram), non-radiative relaxation (W2.1), fluorescence (A1.0), and one-photon stimulated emission (SE1.0). Vibrational states are not shown since vibrational relaxations are very fast and usually do not affect the overall results. However, a user may add vibrational relaxations to the simulation if desired.

Cross-sections and relaxation times:

3-level model

From level:	To level:	Transition parameter:	
		TPA cross-section	
S(0)	S(2)	5×10^{-21} cm^4 GW^{-1}	

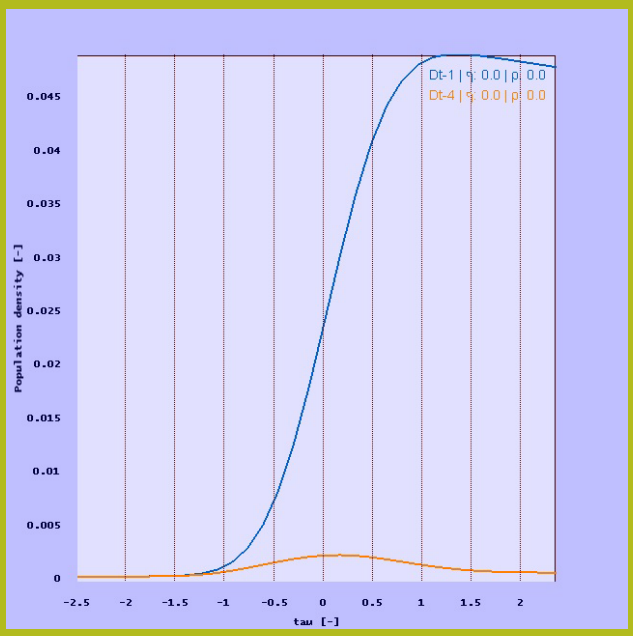
		Relaxation time (ps)	
S(2)	S(1)	1.0	non-radiative
S(1)	S(0)	800.0	fluorescence

		One-photon stimulated emission cross-section	
S(1)	S(0)	2×10^{-17} cm^2	

Other sample properties	
Molecular dopant density (concentration) in the host material	1.8×10^{20} molecules/cm^3
The host material linear refractive index	$n_0 = 1.4$
Host material linear absorption	$\alpha = 0.0$ cm^{-1}
Host material nonlinear refractive index	$n_2 = 0$
Sample length	1 mm

Laser beam properties	
Pulse energy	1000 mJ
Pulse radius (HW1/e^{2}M)	0.3 mm
Pulse FWHM	40 ps
Wavelength	532 nm

Results of SimphoSOFT® calculations with
fluorescence and 1PSE (1PSE is either turned 'OFF' or 'ON'):



1PSE turned 'OFF': The blue line shows the electronic population of state S(1) at the sample entrance during the time of the laser pulse (tau = 0 is the center of the pulse). With 1PSE turned 'off', the population rises during the first half of the 40 ps laser pulse and then starts to decay via fluorescence with a time constant of 800 ps after the peak of the pulse has passed.

1PSE turned 'ON': The orange line shows the electronic population of state S(1) during the time of the laser pulse when both fluorescence and 1PSE are activated. The population of S(1) is greatly depleted by 1PSE, which will result in significantly reduced fluorescence from the S(1) state.

This example illustrates the importance of including stimulated emission in simulations for some types of optical materials. Stimulated emission is a built-in feature of SimphoSOFT.