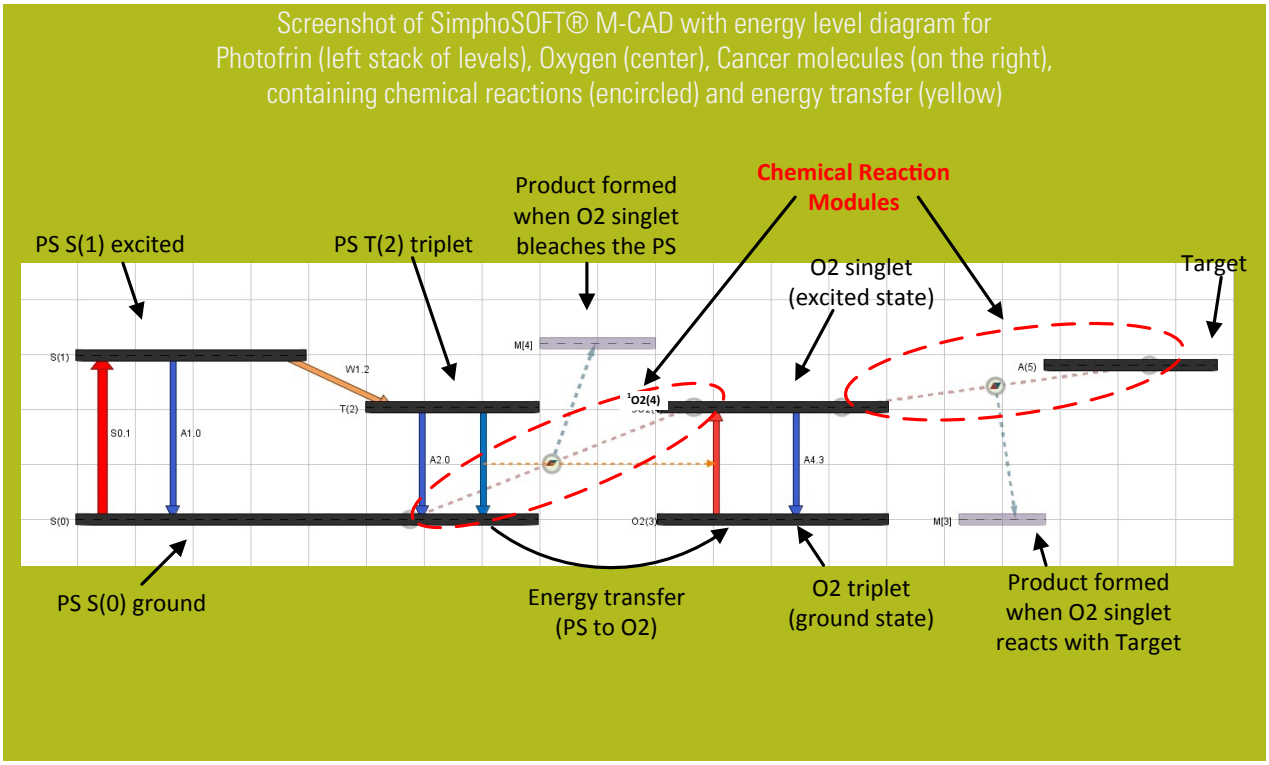
Light absorbed by a photo-sensitizer molecule can excite an electron from the ground state of the photo-sensitizer to an excited state and result in the direct or indirect chemical reaction of the optically excited molecule with a target molecule. Photo-induced chemical reactions are important processes that occur in both biology and chemistry. Biological applications include, for example, photodynamic therapy for the treatment of cancer and psoriasis, the process of photosynthesis that converts light energy into chemical energy, and the sterilization of water or medical equipment with ultraviolet light. Chemical applications involving photo-sensitizers include both positive and negative photoresists that are used in the manufacture of integrated circuits.

SimphoSOFT can simulate chemical reaction kinetics in addition to the standard photo-physical processes of single- and multi-photon absorption, relaxation, stimulated emission and energy transfer.

Example SimphoSOFT simulation of photodynamic therapy including photo-induced chemical reactions: Photofrin

In photodynamic therapy (PDT), light excites a photo-sensitizer that undergoes intersystem crossing from a singlet excited state to a triplet state. The excited photo-sensitizer triplet state transfers energy to an oxygen molecule (O_2), causing the oxygen molecule to be excited from the triplet ground state to an excited singlet state. Singlet oxygen is highly reactive, and can attack target molecules in nearby cancer cells and subsequently kill the cancer cells. Photobleaching is also possible when singlet oxygen can also attack and neutralize the photo-sensitizer molecules in an undesirable side reaction. But this occurs at a slower rate than the desired therapeutic rate.

Screenshot of SimphoSOFT® M-CAD with energy level diagram for Photofrin (left stack of levels), Oxygen (center), Cancer molecules (on the right), containing chemical reactions (encircled) and energy transfer (yellow)



The energy level diagram for the PDT simulation is shown on the previous page. The photo-sensitizer (PS) ground state PS S(0) is excited with 630 nm light having an intensity of 100 mW/cm^2 for at time period of up to 20 seconds. Electrons that are excited to the PS S(1) excited state can undergo intersystem crossing to the PS T(2) triplet state. In order to generate singlet O_2 in the O2(4) state, energy transfer occurs from PS to O_2 via triplet-triplet interactions. The resulting highly reactive singlet O2(4) state decays via three pathways shown in the diagram: (1) chemical reaction and destruction of the Target molecules; (2) chemical reaction with PS molecules, which bleaches the PS molecules and renders them inactive; or (3) decay by radiative emission.

Cross-section, relaxation times and rates for Photofrin, Oxygen, Target:

Energy levels are labeled from 0 to 5

SimphoSOFT user creates three stacks of energy levels: molecule 0 represents PS (three levels S(0), S(1), and T(2) on the left), molecule 1 represents O_2 (two levels O2(3) and ^{1}O2(4) in the center), and molecule 3 represents the Target (A(5) on the right). The most important transitions for PDT are the energy transfer transition (yellow arrow which connects the energy levels involved in energy transfer) and chemical reactions between singlet oxygen $^1O_2$ and PS and between $^1O_2$ and the Target (encircled in red). To track the concentrations of chemical reactions, one can create "fictitious" levels representing the products of the reactions (M[3] and M[4] on the picture).

From level(s):	To level(s):	Cross-section:	Relaxation time:	Energy transfer rate:	Chemical reaction rate:
0	1	5.966×10^{-18} cm^2			
1	0		50 ns (radiative)		
1	2		12.5 ns (ISC; non-radiative)		
2	0		800 μs (radiative)		
4	3		1 μs (radiative)		
2 to 0	3 to 4			1.66×10^{-13} cm^3 s^{-1}	
4 and 5	M[3]				4.32×10^{-9} cm^3 s^{-1}
4 and 0	M[4]				2.40×10^{-16} cm^3 s^{-1}

Other sample properties	
Starting PS concentration in the host material	5.112×10^{15} molecules / cm^3
Starting O_2 concentration in the host material	4.998×10^{16} molecules / cm^3
Starting Target concentration in the host material	7.500×10^{16} molecules / cm^3
Starting M[3] (molecule 3) concentration in the host material	1 molecule/ cm^3
Starting M[4] (molecule 4) concentration in the host material	1 molecule/ cm^3
The host material linear refractive index	$n_0 = 1.4$
Host material linear absorption	$\alpha = 0.0306$ cm^{-1}
Host material nonlinear refractive index	$n_2 = 0$
Sample length	0.05 mm

Laser beam properties	
Beam intensity	100 mW/cm^2
Beam radius (HW1/e^{2}M)	5 mm
Pulse FWHM (simulates CW)	up to 20 s
Wavelength	630 nm

Results of SimphoSOFT simulations for the populations of the Photofrin and Oxygen energy levels:

Fig 1 shows the time dependences of the energy level populations from about 2 ns to 10 μs. During this time interval, the populations of the PS triplet state (PS--T0) and the $^1O_2$ singlet state (O_2 active) are growing. The PS S(1) state population grows to about 10 ns and then comes to quasi-equilibrium.

Fig 2 shows the time dependences of the energy level populations from about 2 μs to 10 ms. At approximately 100 μs, the PS T0 triplet and $^1O_2$ singlet state populations both come to quasi-equilibrium. The reactions of $^1O_2$ singlet molecules with the Target molecules or with the PS molecules are not readily apparent on this time scale.

Fig 1. Time period from about 2 ns to 10 μs.

Fig 2. Time period from about 2 μs to 10 ms.

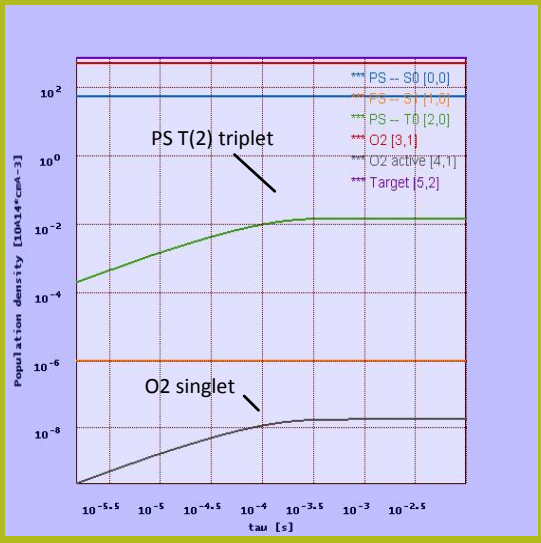


Fig 3 shows the time dependences of the energy level populations from about 3 ms to 20 s. The O_2 triplet ground state and the $^1O_2$ singlet excited state populations are both significantly depleted in the time interval from 1 s to 20 s due to chemical reaction with the Target. The Target population partially depletes and then stabilizes. Since the starting Target population was 50% larger than the starting O_2 population, only 2/3 of the Target molecules can be attacked by O_2 before the O_2 is depleted. Therefore after the O_2 is depleted, about 1/3 of the Target molecules remain. Note that in this example, the O_2 is depleted before any significant bleaching of the PS occurs.

Fig 4 shows an expanded view of the Target population from about 3 ms to 20 s. In units of 10^{14} cm^{-3}, the target population drops from about $10^{2.87} = 741$ to about $10^{2.4} = 251$. At 20 s, the Target population is about 34% of the starting value.

Fig. 3. Time period from about 3 ms to 20 s.

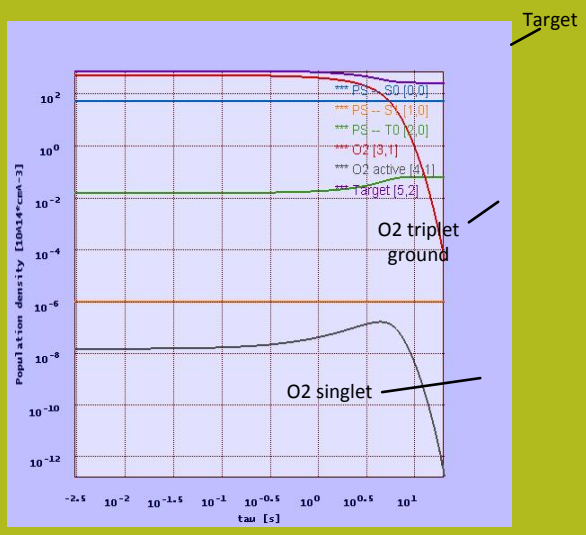


Fig 4. Target population from about 3 ms to 20 s.

This PDT example illustrates the versatility of SimphoSOFT for modeling complex problems that include both photo-physical processes and chemical reactions.