Fluorescence and Phosphorescence

Fluorescence and phosphorescence are types of **photoluminescence (/en-eu/pages/photoluminescence)**. Photoluminescence refers to radiative emissions where the **absorbance (/en-eu/pages/absorbance-spectroscopy)** of a photon is followed by the emission of a lower energy photon. The main empirical difference between fluorescence and phosphorescence is the time in between absorbance and the emission of photons. Fluorescence is where a material absorbs a photon, and almost immediately emits a lower energy photon. Phosphorescence occurs over a longer period as it requires a forbidden transition.

On an atomic level, the distinction between phosphorescence and fluorescence depends on the electron spin state during energy level transitions. In fluorescence transitions, this electron spin state is maintained throughout. Phosphorescence, however, requires the spin state to change when a photon is absorbed. This is reversed when the subsequent emission occurs. One key difference is that fluorescence only occurs when light is incident on the material, while phosphorescent materials can continue to glow sometime after the light source has been removed.

To find out more about photoluminescence, see **Photoluminescence Spectroscopy (https://www.ossila.com/en-eu/pages/photoluminescence)**

To find out more about absorbance, see **Absorption Spectroscopy (https://www.ossila.com/en-eu/pages/absorbance-spectroscopy)**

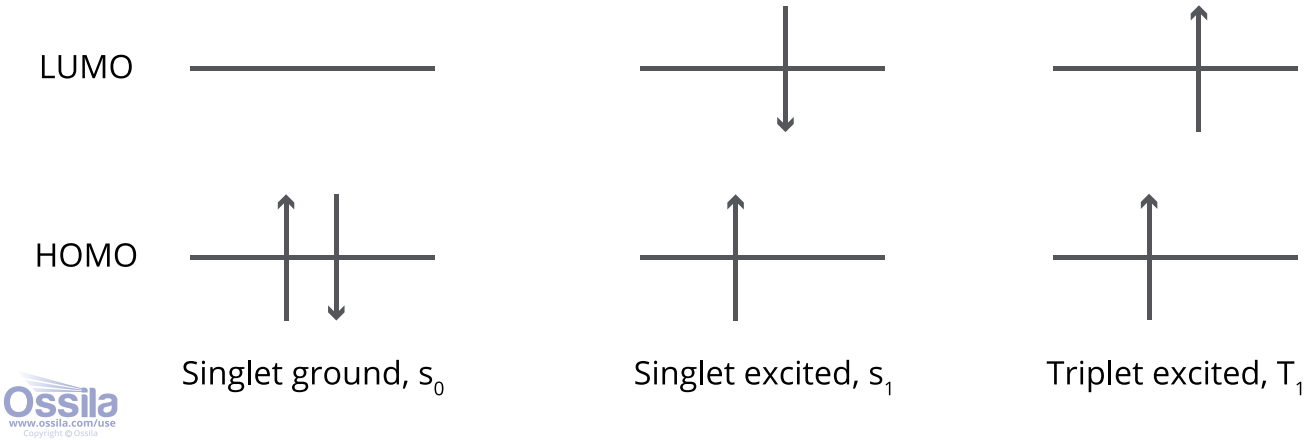
You can use fluorescent materials for many different purposes. These include bioluminescent technology, investigating optical properties of materials, or labelling molecules in medicine, microbiology, or chemistry.

On the other hand, the long emission life, high-signal-to-nose ratio, large stokes shift as well as the higher quantum yield of phosphorescent materials make them especially attractive for several other purposes. These include...

Singlet and Triplet States

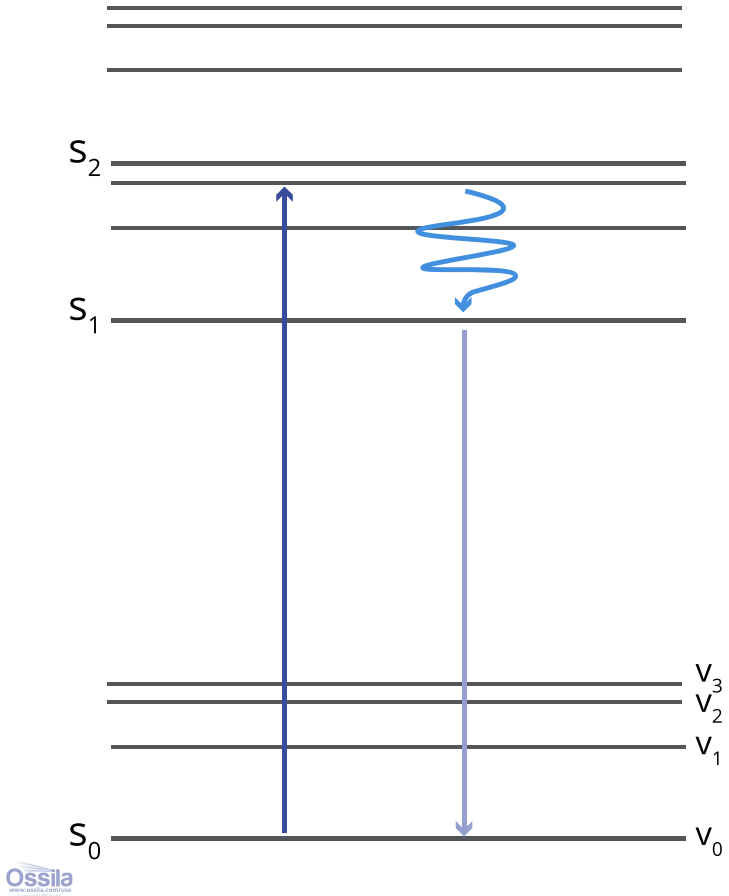
In its ground state, the total spin angular momentum of a molecule will be S=0. This is because all electronic orbitals are full (two electrons) and the electron spins in each orbital are anti-parallel (opposite direction). This is known as a singlet state. However, when an electron from the HOMO is excited to the LUMO, there are then two unpaired electrons, and the total spin angular momentum can be either S=0 or S=1. S=0 states are called singlets and S=1 states are called triplets. This is because the multiplicity of the spin states (the number of degenerate states) is given by 2S+1. When the excited electron retains its spin from the ground state (i.e. they

are anti-parallel), S=0 and the multiplicity = 2(1/2 + -1/2) + 1 = 2(0) + 1 = 1. Hence, singlet states. When the excited state electron changes spin state so it's the same as the ground state (parallel), S=1 and the multiplicity = 2(1/2 + 1/2) + 1 = 2(1) + 1 = 3. Hence, triplet states.



Electron spins in singlet and triplet states

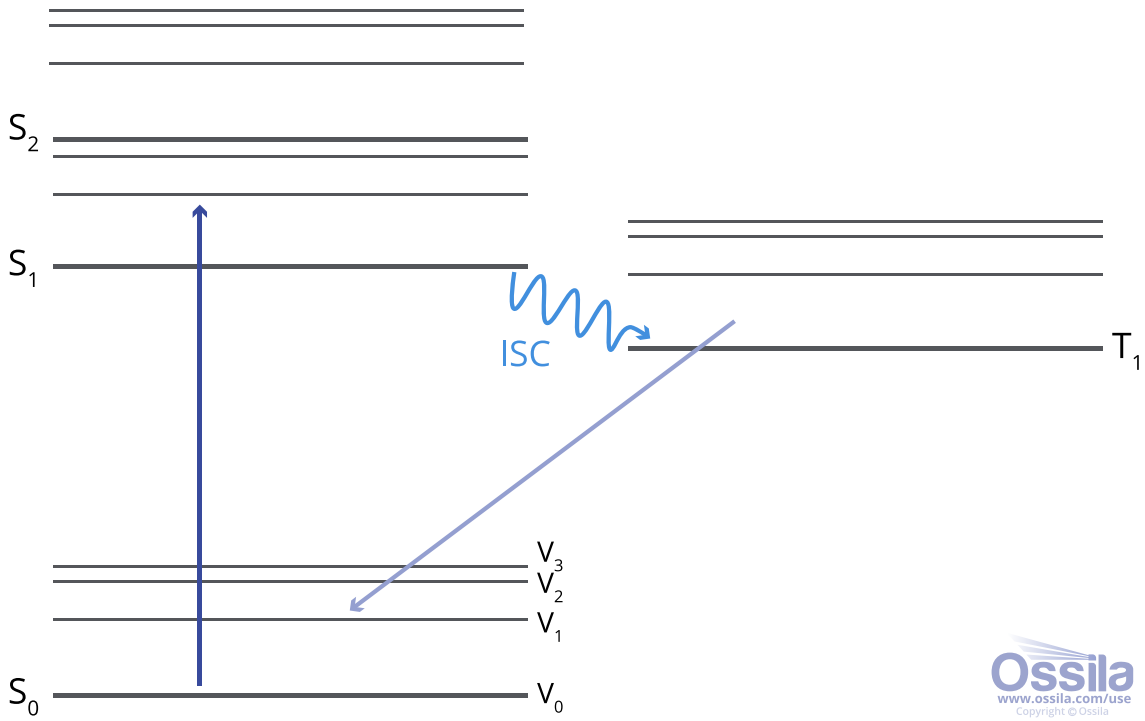
According to Hund's rule of maximum multiplicity, the lowest energy state will be the one in which the multiplicity is largest. This means that electrons will fill orbitals singly and with parallel spins before pairing up. Triplets therefore tend to have a slightly lower energy than singlets.



Jablonski diagrams (https://www.ossila.com/en-eu/pages/jablonski-diagrams) showing fluorescence energy transitions

Fluorescence consists of only spin-allowed transitions. As photons have spin-0, only transitions between states of the same spin, i.e. singlet-singlet, are spin-allowed. Therefore, where S_0 is the singlet ground state (or highest occupied molecular orbit), and S_1 is the singlet excited state (or lowest occupied molecular orbit), the absorption edge will tend to correspond to the $S_0 \rightarrow S_1$ transition. Similarly, the emission peak will also tend to correspond to the $S_1 \rightarrow S_0$ transition.

The emission of a photon when an electron relaxes from the $S_1 \rightarrow S_0$ state is known as **fluorescence** and has a very short lifetime (~ns).



Jablonski diagrams showing phosphorescence energy transitions. Absorbance of a photon (blue), intersystem crossing (green) and phosphorescent emission (green).

Just like for fluorescence emissions, in phosphorescence, an electron is initially excited through absorbance of a photon. The electron can then non-radiatively relax into the triplet state through **intersystem crossing (/en-eu/pages/jablonski-diagrams)** (ISC). This transition is not spin-allowed but can occur due to spin-orbit coupling. Once the electron is in the triplet state, it will eventually radiatively relax into the ground state (S_0) or one of the vibrational states above. Although singlet-triplet transitions are forbidden by spin selection rules, they can still occur over a longer time period. This type of emission is termed **phosphorescence** and can have lifetimes of seconds or even as long as several hours.

To find out more about Jablonski diagrams, see **Jablonski diagram (https://www.ossila.com/en-eu/pages/jablonski-diagrams)**

References

1. T.-S. Ahn, *et al*. Rev. Sci. Instrum. 78, 086105 (2007).

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