JABLONSKI DIAGRAM

Project: C1

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Various relaxation processes can take place from the excited state. The possible transitions are illustrated using a simplified energy level diagram, the so-called Jablonski diagram (see Figure 1).[1]
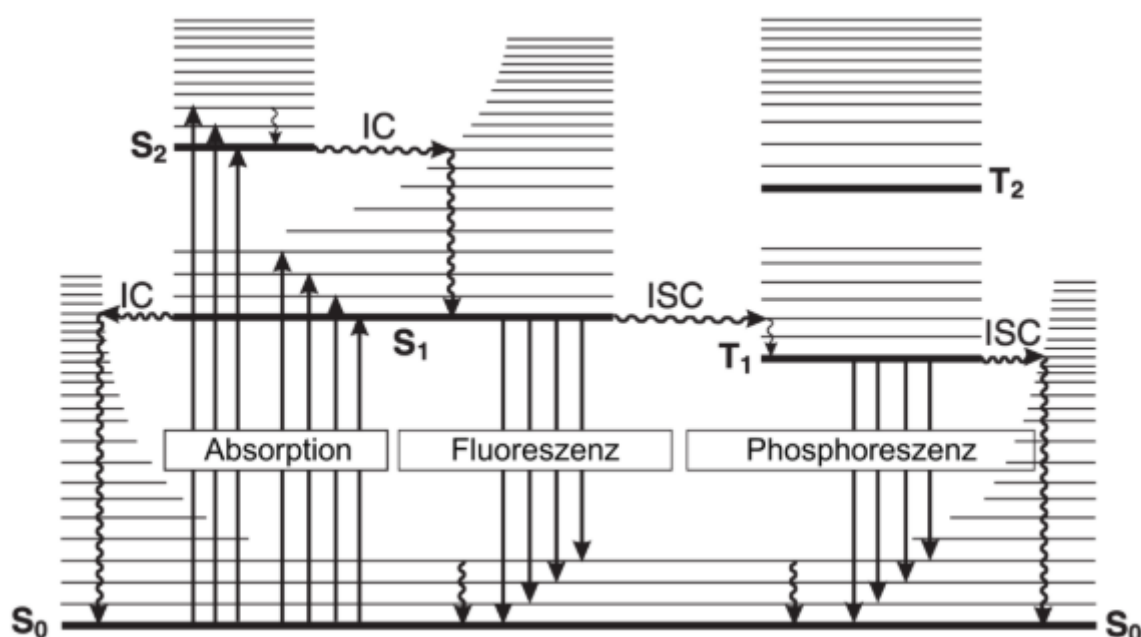

Figure 1: Illustration of a Jablonski diagram with various relaxation processes. Figure taken from reference [2]. Radiative processes between the different energy states, such as absorption, fluorescence or phosphorescence, are shown as vertical solid arrows. Non-radiative processes such as intercombination (ISC), internal conversion (IC) and vibrational relaxation are symbolised by wavy arrows. Vibrational relaxation is explicitly symbolised by vertical wavy arrows and ISC with IC by vertical wavy arrows. Electronic states (S_0, S_1, S_2, T_1, T_2) are represented by thick and vibronic states by thin horizontal lines in the energy level diagram. The characteristic times of the processes involved are given in Table 1.

Excitation

Most systems are usually in the singlet ground state S_0. By absorbing a photon, the system is excited into an energetically higher electronic state S_n. The spin multiplicity is maintained according to the selection rules and a spin-allowed $S_0 \rightarrow S_n$ ($n > 0$) transition occurs. After

excitation, the system also occupies an oscillation level ν of the S_n state. However, vibrational transitions are not subject to strict selection rules when switching between two different electronic states. A statement about the probability with which a vibronic state is occupied can be made using the Franck-Condon principle.

Relaxation transitions

Starting from the excited state, there are several processes that can occur to relax to the singlet ground state. In general, these can be divided into radiative and non-radiative processes. In most cases, these processes compete after reaching the vibrational ground state of the S_1 state. According to Kasha's rule, photons are emitted from the lowest excited state of a multiplicity (valid for both singlet and triplet states).[3] However, this rule is empirical and does not apply to all systems.

Internal conversion - IC

The S_1 state is achieved through radiation-free vibrational relaxation and internal conversion. At a speed of 10^{-12}–10^{-10} s, the vibrational relaxation is very fast and therefore unrivalled. The internal conversion then occurs from the lowest vibronic state. This is a transition between two electronic states with the same spin multiplicity. The electronic energy of the initial state is converted into the vibronic energy of the final state, whereby the system is then in a higher vibronic state. This transition is radiationless as the vibronic levels of the initial and final states are isoenergetic. This is followed by vibrational relaxation. This process continues until the S_1 state is reached at its lowest vibrational level or until the molecule is thermalised. The $S_{n+1} \rightarrow S_n$ transitions are more efficient than the $S_1 \rightarrow S_0$ transition due to the smaller energy differences between these states. The internal conversion takes place in a speed range of 10^{-11}–10^{-9} s, but the large energy gap between the S_0 and S_1 state leads to a slowdown due to the lower efficiency. This enables competition with the processes of intersystem crossing (ISC) with a speed range of 10^{-10}–10^{-8} s and fluorescence with a lifetime of 10^{-10}–10^{-7} s.

Fluorescence

The radiative deactivation process into the singlet ground state S_0, while maintaining multiplicity, is fluorescence. The transition takes place under the emission of a photon, which is usually a $S_1 \rightarrow S_0$ transition. After the transition, as with excitation, different vibronic states are occupied according to the Franck-Condon principle. Exceptions such as fluorescence from

the S_2 state are shown by the example of azulene.[4] There are also substances that emit from both the S_1 and the S_2 state with a balanced ratio. Such 'balanced non-Kasha dual emission' can be observed, for example, in molecules of the triphenylmethane dye group.[5,6]

Intersystem crossing – ISC

A process that is similar to internal conversion is intercombination, which is also radiationless. This is also a transition between two isoenergetic vibration levels, but they belong to electronic states with different multiplicities. The transition from a singlet to a triplet state is formally spin-prohibited, but can occur with large spin-orbit coupling. Molecules containing atoms with high atomic mass such as Br, Pt, Ir, Au can exhibit strong spin-orbit coupling, which increases the efficiency of intercombination and thus the quantum yield and intensity of phosphorescence.[7,8]

Phosphorescence

After a $S_1 \rightarrow T_n$ transition, radiationless vibrational relaxation and internal conversion to the T_1 state at the lowest vibrational level occurs according to Kasha's rule. This can be followed by a $T_1 \rightarrow S_0$ transition with the emission of a photon. This emission is phosphorescence. The occupation of the oscillation levels in the S_0 state is analogous to that in fluorescence. The wavelength of the emitted radiation is usually lower in phosphorescence compared to fluorescence, as the T_1 state is lower in energy than the S_1 state. Since the $T_1 \rightarrow S_0$ transition is spin-forbidden, the radiation rate constant is very low. This means that the lifetime of the triplet state can be much longer than that of the singlet state. They are in the range of 10^{-10}– 10^{-7} s for the singlet state. However, the lifetime of the triplet state can be in the range of 10^{-6}–10 s.

Other relaxation pathways

In addition to the common processes, there are other rarer processes such as triplet-triplet transitions or delayed fluorescence. After an excited system occupies the T_1 state, a spin-allowed transition to an energetically higher triplet state T_n can occur through the absorption of photons. The T_1 states are usually metastable states with a sufficient population.[9] Such triplet-triplet transitions can occur in polyatomic molecules such as benzene or naphthalene.[10]

Thermally activated delayed fluorescence (TADF) occurs when the energy difference between the T_1 and S_1 state is small and the lifetime of the T_1 state is sufficiently long. A $T_1 \rightarrow S_1$ transition occurs with subsequent fluorescence. This process is thermally activated and is favoured at higher temperatures. The delayed fluorescence behaves analogue to the ordinary fluorescence, the only difference is the longer decay time constant, which is caused by the additional $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_1$ transitions. This case was observed for the first time with eosin.[11,12]

Life times

Table 1: Characteristic life times of the processes shown in Figure 1.[13]

Absorption	10^{-15} s
Vibrational relaxation	10^{-12}–10^{-10} s
S_1 life time (fluorescence)	10^{-10}–10^{-7} s
Intersystem crossing (ISC)	10^{-10}–10^{-8} s
Internal conversion (IC)	10^{-11}–10^{-9} s
T_1 life time (fluorescence)	10^{-6}–10 s

References

[1]   A. Jablonski, *Nature* **1933**, *131*, 839–840.
[2]   D. Graf, Master Thesis, Karlsruher Institut für technologie (KIT), **2023.**
[3]   M. Kasha, *Discuss. Faraday Soc.* **1950**, *9*, 14–19.
[4]   M. Beer, H. C. Longuet-Higgins, *J. Chem. Phys.* **1955**, *23*, 1390–1391.
[5]   A. Janowski, J. Rezeszotarska, *J. Lumin.* **1980**, *21*, 409–416.
[6]   S. K. Behera, S. Y. Park, J. Gierschner, *Angew. Chem. Int. Ed.* **2021**, *60*, 22624–22638.
[7]   H. Shi, Z. An, P.-Z. Li, J. Yin, G. Xing, T. He, H. Chen, J. Wang, H. Sun, W. Huang, Y. Zhao, Cryst. *Growth Des.* **2016**, *16*, 808–813.
[8]   Q. Zhao, C. Huang, F. Li, *Chem. Soc. Rev.* **2011**, *40*, 2508–2524.
[9]   M. K. Orloff, *J. Chem. Phys.* **1967**, *47*, 235–241.
[10]   D. S. McClure, *J. Chem. Phys.* **1951**, *19*, 670–675.
[11]   C. A. Parker, C. G. Hatchard, *Trans. Faraday Soc.* **1961**, *57*, 1894–1904.
[12]   A. Maciejewski, M. Szymanski, R. P. Steer, *J. Phys. Chem.* **1986**, *23*, 6314–6318.
[13]   B. Valeur, M. N. Berberan-Santos, *Molecular Fluorescence* **2012**.