

4.4: Fluorescence and Phosphorescence

This Chapter describes fluorescent spectroscopy based on the QM theory outlined in the previous Chapter. Electron energy levels within the sample define the spectra of absorption as well as of emission (fluorescence and phosphorescence). Relationship between fluorescent spectroscopy and UV range of light is described.

Learning Objectives

- Understand how irradiation absorption leads to the excitation of electrons in the system
- Distinguish emission via fluorescence from emission via phosphorescence
- Grasp the kinetics effect: why phosphorescence often occurs much slower than fluorescence within the same system
- Become familiar with the processes described by the Jablonski diagram
- Develop a sense of how the average wavelength values for related absorption, fluorescence and phosphorescence are related

Absorption

In a system with quantized energy levels, its particles (e.g. electrons) in general occupy the lowest energy levels/states. An incoming quantum of radiation with the energy E and frequency ν ($E = h\nu$) can excite an electron from a lower energy level (ground state) to an unoccupied higher energy level (excited state) if the energy of the incoming quantum (e.g. photon) matches or resonates with the difference between the energy levels of the excited and ground states ($E \geq E_{excited} - E_{ground}$). **Figure IV.4.A** shows the processes of irradiation absorption and subsequent emission via two types of pathways, fluorescence and phosphorescence.

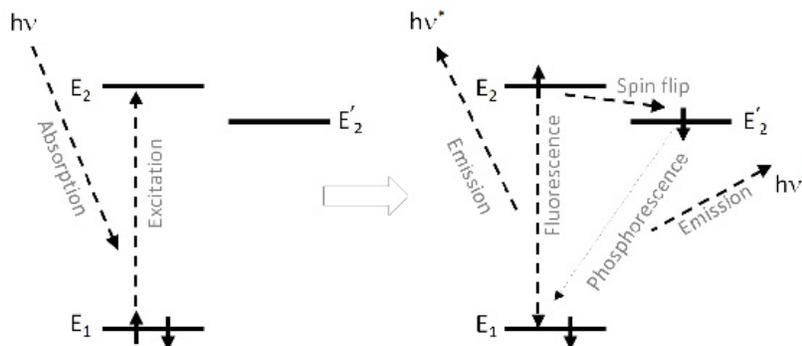


Figure IV.4.A The processes of radiation absorption (left) and emission (right).

If the energy of an incoming quantum is lower than the $E_{excited} - E_{ground}$ difference ($E < E_{excited} - E_{ground}$), the absorption of the incoming irradiation will not happen. For example, two incoming quanta of the same energy will not excite a “ground \Rightarrow excited” transition with the energy double of the individual quantum of radiation.

If the energy of an incoming quantum is equal to the $E_{excited} - E_{ground}$ difference ($E = E_{excited} - E_{ground}$), the upward transition will happen and the excited particle (e.g. electron) will have its energy increased. In terms of the quantum description (Schrödinger equation, equation IV.3.1), the potential energy function defining the states of the excited electron will stay the same, but the wave function will change to the one with a higher energy level and different orbital shape.

If the energy of an incoming quantum is greater than the $E_{excited} - E_{ground}$ difference ($E > E_{excited} - E_{ground}$), the absorption of the incoming irradiation will take place and the system can go to a higher energy state (excited). If the energy of the incoming quantum is high enough, its absorption might cause major alterations of the system, e.g. bond breakage (excited electrons leave shared molecular orbitals thus depopulating them), or ionization (excited electrons leaving the atom/molecule).

Fluorescence

An electron excited to a higher unoccupied level with energy value E_2 can “relax” back to the original ground level E_1 (**Figure IV.4.A**) via a process called fluorescence. Fluorescence takes place rather quickly, in 10^{-8} - 10^{-5} seconds, due to the fact that the excited electron simply comes back to its original ground state without any quantum number alterations apart from the orbital number. During fluorescence, most of the energy of the initial incoming irradiation is emitted back because the excitation and

relaxation occur between the same two levels with energies of E_2 and E_1 . Note that the fluorescence emission frequency ν^* is somewhat lower than the absorption frequency ($\nu^* < \nu$) due to inevitable energy losses during absorption and fluorescence.

Phosphorescence

Another pathway through which the energy of excitation can be recovered is called phosphorescence. During phosphorescence, the excited particle (e.g., an electron), first relaxes to another “excited state” with slightly lower energy level of E'_2 ($E'_2 < E_2$). With high likelihood, a spin flip occurs during such a step ($E_2 \Rightarrow E'_2$), which prevents this still excited electron from relaxing back to its original ground state (E_1) right away if there is another electron there with the same spin (**Figure IV.4.A**). Therefore, it will take a substantial time to reverse the spin flip and allow the excited electron to relax back to the ground state. As a result, phosphorescence may last a lot longer than fluorescence: from milliseconds to days and even years, depending on the specific chemical system. Because $E'_2 < E_2$, the main phosphorescence frequency $\nu^\#$ is smaller than fluorescence frequency ν^* ($\nu^\# < \nu^*$).

Jablonski Diagram

In real systems, most molecules consist of multiple atoms, which complicates the set of absorption, fluorescence and phosphorescence transitions. In addition, most electronic quantum energy levels (E_1 , E_2 , E'_2 etc) undergo internal split due to vibrational motion of the relevant nuclei (vibrational relaxation). Thus, the overall picture includes many transitions of each type and many levels and sub-levels. A complete set of relevant transitions for a specific molecule is referred to as the Jablonski diagram (**Figure IV.4.B**).

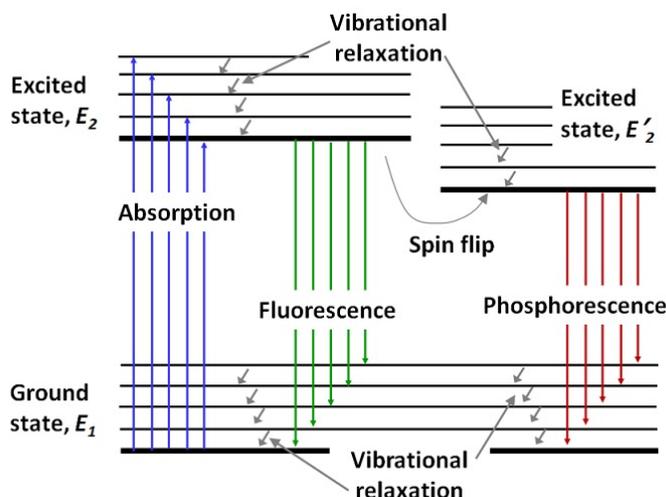


Figure IV.4.B The Jablonski diagram. Note, that each electronic energy level (E_1 , E_2 , E'_2 etc) is in turn split into vibrational sublevels. The energy difference between these vibrational sublevels within an electronic level are small enough, so vibrational relaxation between the sublevels occurs actively all the time, which complicates the overall absorption/excitation and relaxation/emission spectra and their interpretation.

Because of the complexity of the Jablonski diagram for real molecules, the respective absorption, fluorescence and phosphorescence spectra can be messy in terms of the line shapes (**Figure IV.4.C**). But in general and on average, the relationship between the energy (and thus frequency ν as $E=h\nu$) of the absorption, fluorescence and phosphorescence is clear : $E_{\text{absorption}} \geq E_{\text{fluorescence}} \geq E_{\text{phosphorescence}}$. Due to the inverse relationship between the frequency ν and wavelength λ ($c=\lambda\nu$), the trends in wavelength values are the opposite: $\lambda_{\text{absorption}} \leq \lambda_{\text{fluorescence}} \leq \lambda_{\text{phosphorescence}}$ (**Figure IV.4.C**).

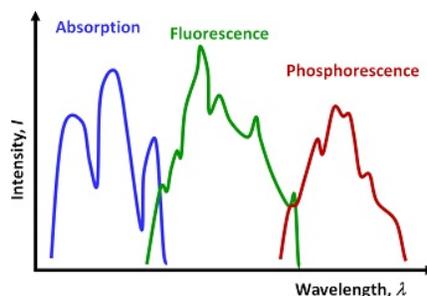
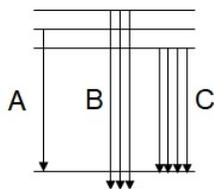


Figure IV.4.C General spectra for absorption, fluorescence and phosphorescence. Note, that the relative wavelengths of the three respective groups are based on the energy of the respective transition presented on the Jablonski diagram (Figure IV.4.B).

Practice problems



In a certain system, three pathways, A, B and C (see figure above), are available for relaxation of excited electrons via **fluorescence**. The energy change of the downward transitions are as follows:

$$\Delta E_A = 7.9 \times 10^{-22} \text{ kJ}, \Delta E_B = 9.9 \times 10^{-22} \text{ kJ}, \text{ and } \Delta E_C = 4.9 \times 10^{-22} \text{ kJ}$$

The number of arrows for each transition is proportional to the probability of each relaxation pathway: the more arrows for the pathway, the more excited electrons follow the pathway to relax.

Practice problem 1. Which pathway(s) generate photons which are capable of disrupting a double $\text{C}=\text{C}$ bond? Justify quantitatively.

Practice problem 2. Provide a spectrum representing the three transitions with the X axis in nm. The spectrum should accurately represent the relative probability of the transitions. Each spectral line should be drawn as a thin vertical bar: assume uniform line widths for all the peaks.

Practice problem 3. Consider the same system at thermal equilibrium. If the system has at its ground state energy levels 1,000,000 moles of electrons, how many electrons will spontaneously occupy all of the “excited” states combined? Justify quantitatively.

Practice problem 4. You are analyzing the Jablonski diagram for two molecules **X** and **Y**. Molecule **X** is double the size of molecule **Y** (has twice as many atoms). In what ways do you expect the Jablonski diagram for molecule **X** could be different from that of molecule **Y**?

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