Fluorescence and Phosphorescence

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1 Introduction

Luminescence is most conveniently defined as the radiation emitted by a molecule, or an atom, after it had absorbed energy to go to an exited state. The main types of luminescence are consist of *fluorescence* and *phosphorescence*. The goal of this experiment is to investigate the properties of optical *excitations*[1] in organic crystals and to understand the processes that lead to phosphorescence and fluorescence.

2 Nature of Electronic States

When discussing the nature of electronic states, it is important to distinguish between the terms *electronic state* and *electronic orbital*. An *orbital* is defined as the volume element in which there is a high probability (99.9%) of finding an electron. It is calculated from a one-electron wave function and is assumed to be independent of all other electrons in the molecule. *Electronic states*, on the other hand, are concerned with the properties of all the electrons in all the orbitals. In other words, the wave function of an electronic state is a combination of the wave functions of each of the electrons in each of the orbitals of the molecule.

Another important distinction is that between exited electronic states and the transition state. Generally a transition state corresponds to a vibrationally exited ground state (*i.e.* ground state in a strained configuration), where as exited electronic states may contain no excess vibrational energy, but are still much higher in energy than the ground state. In fact a molecule in an exited state is best regarded as a completely new entity, only remotely related to the same molecule in the ground state. An exited state will have a completely different electron distribution from the ground state, a different geometry, and more than likely will undergo chemical reaction quite different from those of the ground state.

Electronic states of organic molecules can be grouped into two broad categories, *singlet states* and *triplet states*. A *singlet state* is one in which all of the electrons in the molecule have their spins paired. *Triplet states* are those in which **one** set of electron spin have become unpaired. As will be seen later, triplet states and singlet states differ significantly in there properties

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[1]exited states

as well as in there energies. A triplet state will always lie lower in energy than its corresponding singlet state.

2.1 The Nature of Absorption Processes

Figure 1 show a partial energy diagram for a photoluminescence system. One should note that each of the electronic states (ground or exited) has a number of vibrational levels superimposed on it. The vibrational levels arise because a molecule in a given electronic state may absorb small increments of energy corresponding to changes in vibrational modes, although retaining the same electronic configuration. Another significant fact to be noted is the degree of overlap between the vibrational levels of exited states such as S_2 and S_1. By convention the singlet states should be stacked in a column while the triplet states are stacked in another vertical column displaced to the right of the singlet column. One should also notice the overlap between the vibrational levels of the triplet state T_1 and its corresponding singlet state S_1.

The energy of a photon ($E = hc/\lambda$) required to produce a particular exited state is the difference in energy between that state and the ground state as shown in figure 1. Thus there is a range of wavelength that can lead to a transition between any two electronic states, which accounts for the fact that electronic absorption spectra generally occur as broad bands, rather than as single lines.

As one might notice there is no arrow describing a transition from the ground state to the triplet state T_1. These transitions are forbidden and thus highly improbable. A good role of thumb is that singlet-triplet processes have a probability of about 10^{-6} that of a corresponding singlet-singlet or triplet-triplet processes.

3 Luminescence Processes

Luminescence processes can be interpreted only in terms of the exited state from which luminescence emission occurs and its relationship to the ground state of the molecule. Although the simple picture of photon absorption by a molecule subsequent by a reemission of a photon to give luminescence seems to be quite straightforward, there are nonradiative processes which
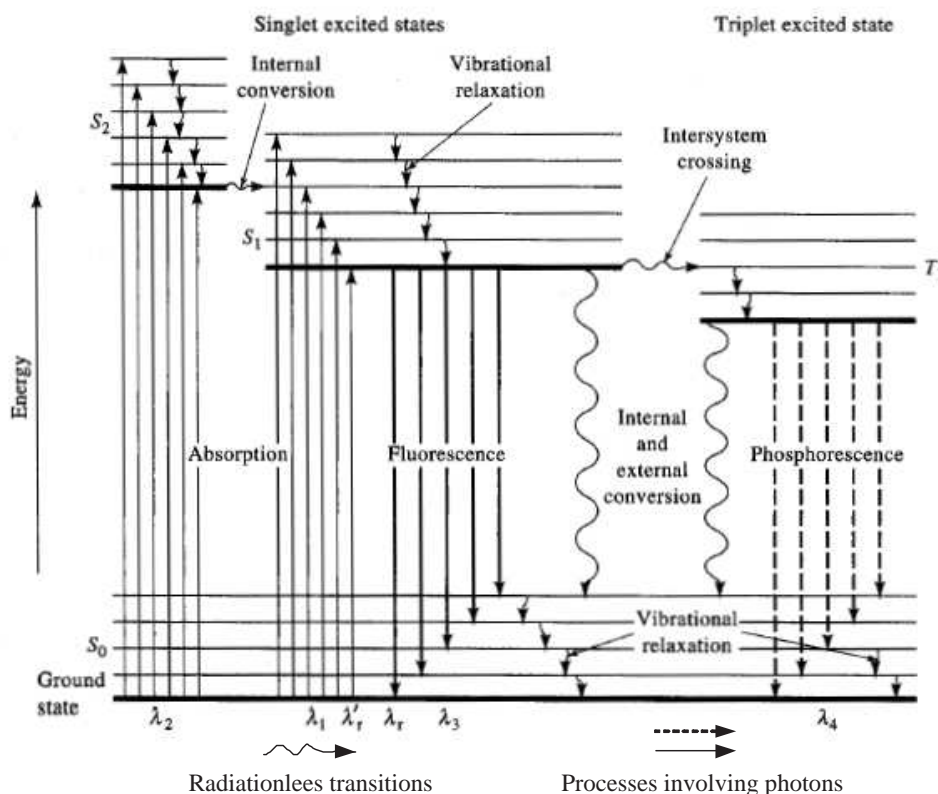
Figure 1: Partial energy diagram for a photoluminescence system(Jablonski diagram)

precede and/or compete with photon emission. In the following section mean lifetimes of all processes will be stressed as they are important for determining the luminescence behavior of a molecule.

3.1 Vibrational Relaxation

One may assume that all molecules are in the lowest vibrational level of the ground state at room temperature. The actual time required for a photon absorption, *i.e.* the time required for a molecule to go from one electronic state to another, is 10^{-15} sec. This time is short relative to the time required for all other electronic processes and nuclear motion. This

means that immediately after excitation a molecule has the same geometry and is in the same environment as it was in the ground state. In this situation it can do one of two things:

- emit a photon from the same vibrational level to which it was excited initially.

- undergo changes in vibrational levels prior to emission of radiation.

Which of these two processes is dominant depends on the environment of the molecule. For an isolated molecule in the gas phase, the only way to lose vibrational energy is to emit an infrared photon, which is less probable than undergoing an electronic transition to return to the ground state. Therefore one tends to see photon emission from higher vibrational levels of exited states in gas phase spectra at low pressures. In a solution, however, thermal relaxation of a vibrationally excited molecule is quite rapid through transfer of excess vibrational energy from the solute molecule to the solvent. In fact, this process is so efficient that all the excess vibrational energy of the excited state is lost, this process occurs in 10^{-13} to 10^{-11} sec. This means that before an excited molecule in a solution can emit a photon , it will undergo vibrational relaxation, and therefore photon emission will always occur *from the lowest vibrational level of an excited state.*

3.2   Fluorescence

Once a molecule arrives at the lowest vibrational level of an exited singlet state, it can do a number of things, one of which is to return to the ground state by photon emission. This process is called *fluorescence.* The lifetime of an excited singlet state is approximately 10^{-9} to 10^{-7} sec and therefore the decay time of fluorescence is of the same order of magnitude. If fluorescence is unperturbed by competing processes, the lifetime of fluorescence is the intrinsic lifetime of the excited singlet state. The *quantum efficiency* of fluorescence is defined as the fraction of molecules that will fluoresce. It should be noted that even though a quantum of radiation is emitted in fluorescence this quantum will be lower in energy on the average than the quantum absorbed by the molecule, due to vibrational relaxation (both after absorption and after emission). The change in photon energy causes a shift of the fluorescence spectrum to longer wavelength, relative to the absorption spectrum, this is referred to as the Stokes Shift.

To summarize, the process of fluorescence consist of photon absorption by a molecule to go to an excited singlet state, relaxation from higher vibrational levels of that state to its lowest vibrational level, photon emission to a vibrationally exited level of the ground state, and again relaxation of the molecule to the lowest vibrational level of the ground state.

3.3   Internal Conversion

In addition to fluorescence, one also encounters *radiationless* processes where molecules in an excited singlet state may return to the ground state without the emission of a photon, converting all the excitation energy into heat. The process called *internal conversion*, is not well understood and its efficiency is very difficult to measure. Generally internal conversion is an inefficient process and is probably only a small fraction of the total excitation energy in most molecules. This is particularly true in aromatic hydrocarbons, which we use in this experiment.

So far the discussion was limited to the $S_0 \rightarrow S_1$ transitions, and the question might arise as to the nature of exited state processes if a molecule is excited to a higher singlet state such as S_2. In such cases the molecule will undergo vibrational relaxation as discussed before. The fate of the molecule as it reaches the zeroth vibrational level of S_2 depend of the energy separation between the exited singlet states. Generally the separation between excited singlet states in an aromatic molecule is smaller than the energy separation between the lowest singlet state S_1 and the ground state S_0. This means that the lowest vibrational level of S_2 will overlap with higher vibrational levels of the S_1 state, that do not involve extremely large differences in configuration from the zeroth vibrational level of the S_1 state. This situation gives rise to a high degree of coupling between the vibrational levels of the S_2 and S_1 states, which provides an extremely efficient path for crossing from the S_2 state to the S_1 state. In fact this process is so efficient that the molecule undergoes internal conversion from the S_2 state to the lowest vibrational level of the S_1 state in about the same time that it requires to convert from an exited vibrational level of the S_1 state to its zeroth vibrational level (*i.e.* 10^{-13} to 10^{-11} sec). Because of this situation one may formulate the following rule: a molecule may be considered to undergo internal conversion to the *lowest vibrational level of its lowest excited singlet state* in a time that is short, relative to photon emission , *regardless of the singlet state to which it was excited initially*

3.4   Phosphorescence and Intersystem Crossing

Although population of triplet states by direct absorption from the ground state is insignificant, a more efficient process exists for population of triplet states from the lowest excited singlet state in many molecules. This process is referred to as *intersystem crossing*, and is a spin-dependent internal conversion process. As singlet-triplet processes are generally less probable than singlet-singlet processes, one may be startled that a singlet-triplet process such as intersystem crossing can occur within the lifetime of an excited singlet state (10^{-8} sec). The mechanism for intersystem crossing involve vibrational coupling between the excited singlet state and a triplet state. Remembering that singlet-triplet processes are less probable than singlet-singlet processes by a factor of 10^{-5} to 10^{-6}, and that radiationless vibrational processes (such as internal conversion) occur in approximately 10^{-13} sec, the time required for a spin-forbidden vibrational process would be approximately 10^{-8} to 10^{-7} sec, which is the same order of magnitude as the lifetime of an excited singlet state. Therefore intersystem crossing can compete with fluorescence emission from the zeroth vibrational level of an excited singlet state but cannot compete with vibrational deactivation from higher vibrational level of a singlet state.

Once intersystem crossing has occurred the molecule undergoes the usual internal conversion process (10^{-13} to 10^{-11} sec) and falls to the zeroth vibrational level of the triplet state. Since the difference in energy between the zeroth vibrational level of the triplet state and the zeroth vibrational level of the lowest exited singlet state is large compared to thermal energy, repopulation of a singlet state from a triplet state is highly improbable. There are two factors which tend to enhance a *radiationless* transition between the lowest triplet state and the ground state. First the energy difference between the triplet state and the ground state is smaller than the difference between the lowest singlet state and the ground state. This tends to enhance vibrational coupling between these two states, and therefore to enhance internal conversion. Second, and more important, the life time of a triplet state is much longer than that of an excited singlet state (about 10^{-4} to 10 sec) and therefore loss of excitation energy by collisional transfer is generally enhanced. In fact, this second process is so important that in solution at room temperature it is often the dominant pathway for the loss of triplet state excitation energy.
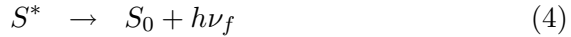
If a molecule is placed in a rigid medium where collisional processes are

minimized, a *radiative transition* between the lowest triplet state and the ground state is observed. This emission is called *phosphorescence*. As phosphorescence originates from the lowest triplet state, it will have a decay time approximately equal to the lifetime of the triplet state (ca. 10^{-4} to 10 sec). Therefore phosphorescence is often characterized by an afterglow which is not observed for fluorescence.

3.5   Delayed Fluorescence

Delayed fluorescence is a non-collisional energy transfer process. This process has the fluorescence characteristic emission spectrum but a lifetime only a bit shorter than phosphorescence. Studies of delayed fluorescence in a variety of aromatic hydrocarbons show that the intensity of delayed fluorescence is proportional to the square of the intensity of the exciting radiation and to the square of the phosphorescence intensity, indicating that it is a *biphotonic process* involving two triplet states. These data suggest the following mechanism for delayed fluorescence:

$$
\begin{align}
S_0 + h\nu &\rightarrow S^* \tag{1} \\
S^* &\rightarrow T \tag{2} \\
T + T &\rightarrow S^* + S_0 \tag{3} \\
S^* &\rightarrow S_0 + h\nu_f \tag{4}
\end{align}
$$

The molecule in its ground state, S_0, absorbs a photon and goes to the lowest exited singlet state, S^*. This, in turn, undergoes intersystem crossing to the triplet state T. The long life time of interaction between these triplet excitons and the molecules allows the these quasi particles to diffuse through the crystal and interact according to equation (3) producing an excited singlet state and a ground singlet state; the excited singlet state then emits its normal fluorescence as shown in (4). The process descried above is referred to as *P-type delayed fluorescence* and is one of the processes we witness in this experiment. In this biphotonic process the lifetime of delayed fluorescence is half the value of the concomitant phosphorescence. However, if the crystal contains impurities the excitons are trapped by them with high probabilities due to favorable energy ratios. Doping with impurities has a negative influence on the intensities and lifetimes of the triplet excitons, The intensities can be reduced and the lifetimes shortened by orders of magnitude.

4 Experimental System

4.1 Kinematics

In this experiment we will investigate the processes of phosphorescence and delayed fluorescence. As these two processes are both decays from the triplet state T_1 we are interested in the time dependence of triplet exciton density n. We shall thus start our discussion with the following ansatz,

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \alpha i - \beta n - \gamma n^2 + D\overrightarrow{\nabla}^2 n \tag{5}$$

The terms on the right side describe from left to right: dependence from excitation intensity i, direct decay (phosphorescence), annihilation (delayed fluorescence) and diffusion.

The observables in the experiment are linked to n by the following relationships:

$$\text{Intensity of phosphorescence: } \Phi_p \propto n \tag{6}$$

$$\text{Intensity of delayed fluorescence: } \Phi_f \propto n^2 \tag{7}$$

To solve equation 5 we neglect two terms: (αi), since we will not excite the crystal during observation (as can be seen later) and the diffusion term, because it can be considered a small perturbation in first order. This leads to the following equation:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\beta n - \gamma n^2 \tag{8}$$

$$\Rightarrow \frac{\mathrm{d}n}{\gamma n^2 + \beta n} = -\mathrm{d}t$$

$$\Rightarrow \frac{\mathrm{d}n}{n} - \frac{\mathrm{d}n}{n + \frac{\beta}{\gamma}} = -\beta\mathrm{d}t$$

Integration yields:

$$\log \frac{(n_0\gamma + \beta)n(t)}{(n(t)\gamma + \beta)n_0} = -\beta t \qquad \Rightarrow \frac{n(t)}{n_0} \cdot \frac{(n_0\gamma + \beta)}{(n(t)\gamma + \beta)} = e^{-\beta t}$$

This leads to:

$$n(t) = n_0 e^{-\beta t} \left[\frac{1}{1 + \frac{\gamma n_0}{\beta}(1 - e^{-\beta t})} \right] \tag{9}$$

The term in square brackets is a deviation from the exponential behavior and represents the influence of triplet annihilation. For part of our result analysis equation 9 is used in the following form:

$$y = \ln(\frac{n(t)}{n_0}) = -\beta t - \ln\left(1 + \frac{\gamma n_0}{\beta}(1 - e^{-\beta t})\right) \tag{10}$$

As we measure intensities, we would like to link equation 9 to the intensities of phosphorescence and delayed fluorescence. For this purpose let us assume that a fraction A of the first order decay i.e. from the transition $T_0 \rightarrow S_0$ is radiative. This yields a phosphorescence intensity of

$$I_p = A\beta n = n_0 \left[\frac{A\beta}{1 + \frac{\gamma n_0}{\beta}(1 - e^{-\beta t})} \right] e^{-\beta t} \tag{11}$$

In addition we can also assume that a fraction B of the triplet-triplet annihilation results in the production of a fluorescing singlet excitation S^*, which gives the following delayed fluorescence intensity

$$I_f = \frac{1}{2}(B\gamma)n^2 = \frac{1}{2}(B\gamma)n_0 \left[\frac{1}{1 + \frac{\gamma n_0}{\beta}(1 - e^{-\beta t})} \right]^2 e^{-2\beta t} \tag{12}$$

The triplet lifetime τ_T is defined as

$$\tau_T = \frac{1}{\beta} \tag{13}$$

The lifetimes of phosphorescence and delayed fluorescence are therefore:

$$\tau_T = \tau_p = 2\tau_f \tag{14}$$

This means, that the delayed fluorescence decays here twice as fast as the phosphorescence.
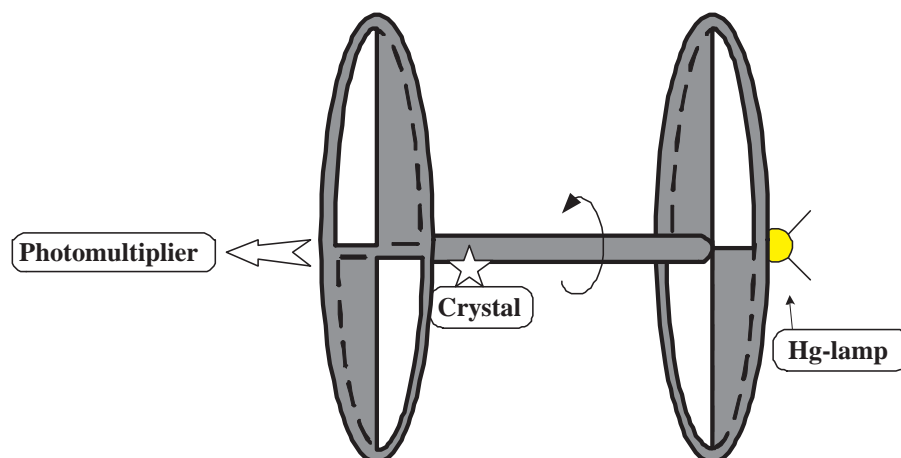
4.2 Experimental Setup

Figure 2: Experimental Setup

The side walls of the dark experimental chamber contain two wheels connected by a metal bar. Two gaps were hacked in each wheel, aligned to allow light to path only one wheel at a time, see figure 2. Using this setup the Hg-lamp (on the right) can not cause damage to the photomultiplier (on the left) by shining right at it. Furthermore, this setup ensures that the results we obtain arrive only from delayed fluorescence or phosphorescence as discussed before. The turning speed of the wheels can be controlled by a small motor that turns the metal bar. This speed should be slow enough to allow most exited molecules to decay to their ground state (suggestion: observation interval of at least three lifetimes).

As light passes the right wheel it should be focused on a crystal causing the desired excitons. While both wheels are turning the right one will now block the path of light and the left one will allow the photons from the phosphorescence and delayed fluorescence to arrive to the photomultiplier. The output from the photomultiplier has to be amplified by an current-voltage converter. Then the signal is plugged to one channel of the oscilloscope.

The same time the window in the wheel is open for the Hg-lamp, there is an other one open with an photodiode behind. This gives a reference signal indicating the shutting of the Hg-lamp. It can be used for triggering. Therefore we plug it to the other channel of the oscilloscope and chose this channel as external trigger. For better results it is recommended to have the oscilloscope measuring an average of 128 measurements.

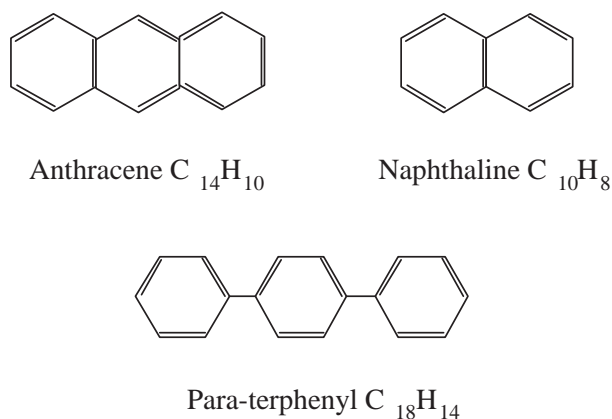Figure 3 shows the schematic structure and chemical formula of the crystals used in the experiment.

Anthracene C $_{14}$H$_{10}$ Naphthaline C $_{10}$H$_8$

Para-terphenyl C $_{18}$H$_{14}$

Figure 3: Crystals

5   Experiment

The goal of the experiment is to find the lifetime of phosphorescence and the delayed fluorescence. There are several factors that complicate this task: The system is very noisy, the resolution of the oscilloscope is limited, and due to the limited time window one can only see part of the decay. Therefore it is suggested to take a first measurement, to analyze it roughly. Then one can think about the best parameters and redo the experiment to get some better curves.

Plug the signal from the photodiode to the oscilloscope and look at this first, that's easier. Then plug the amplified signal from the photomultiplier on the second channel and trigger it by the first signal (This means you have to adjust the settings of the oscilloscope correspondingly).

If you do not average, the signal looks very noisy, it might even be hard to see it. To play with the parameters it is best to average a little bit, if you want to acquire data, you have to average by 128.

Play with the parameters of the oscilloscope and with the speed of the wheel. Changing the speed of the wheel influences the time between the shutting of the Hg-lamp and the opening of window at the photomultiplier, the time of exposure and the observation window. Estimate the background noise and try to avoid it (by working in dark).

6 Analysis

- Get out the time between the end of exposure and the begin of the observation. The end of the exposure is given by the time at which the reference signal of the photodiode goes to zero.

- Normalize the curves by the background noise level and photomultiplier offset y_0.

- Fit the curves in the two regimes where Phosphorescence and delayed Fluorescence are dominating. Therefore we have to look at the theory again: From equation 4.1 and 4.1 we get by taking the logarithm

$$\ln\left(I_p(t) - y_0\right) - \ln(n_0) = -\beta t + \ln\left(\frac{A\beta}{1 + \frac{\gamma n_0}{\beta}(1 - e^{-\beta t})}\right) \quad (15)$$

$$\ln\left(I_f(t) - y_0\right) - ln(n_0) = -2\beta t + \ln\left(\frac{B\gamma}{2}\right) - 2\ln\left(1 + \frac{\gamma n_0}{\beta}(1 - e^{-\beta t})\right) \quad (16)$$

and in the limit $t \gg \beta^{-1}$

$$\ln\left(\frac{I_p(t) - y_0}{n_0}\right) = -\beta t + \ln\left(\frac{A\beta}{1 + \frac{\gamma n_0}{\beta}}\right) \quad (17)$$

$$\ln\left(\frac{I_f(t) - y_0}{n_0}\right) = -2\beta t + \ln\left(\frac{B\gamma}{2}\right) - 2\ln\left(1 + \frac{\gamma n_0}{\beta}\right) \quad (18)$$

this means that we can use a linear fit of $\ln(n(t) - y_0)$ to extract an estimated value of β for each crystal. The value of y_0 changes in each measurement but is not difficult to extract.

- Get out a value for β for each crystal by averaging over different fits of curves of phosphorescence and delayed fluorescence.