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Fluorescence and Phosphorescence

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Abstract

In this experiment, the intensity of light re-emited by three different organic crystals upon their optical excitation is measured. To evaluate the data, the experimenter must consider the processes and kinetics taking place in the excited molecule. The goal of this experiment is to determine the predominant process or processes leading to light emission and estimate the triplet lifetime of the crystals.

Contents

1 Introduction

Luminescence can be described as the spontaneous emission of radiation by an electronically excited molecule [5]. The two types of luminescence that are observed in this experiment are fluorescence and phosphorescence. The goal of this experiment is to investigate the properties of optical excitations, to understand the processes that lead to fluorescence and phosphorescence and to estimate the triplet lifetime of three different organic crystals.

2 Electronic states

To understand the processes that lead to fluorescence and phosphorescence, it is necessary to consider the different electronic states the molecule can be in. The electronic state of a molecule exhaustively describes the electron configuration of the molecule, i.e. it describes all the electrons and which orbitals of the molecule they occupy [2]. The electronic states of organic molecules can be divided into two main categories, singlet states and triplet states. A singlet state (S) is one in which all the electrons of the molecule are paired. Triplet states (T) are states in which one set of electron spins is unpaired. As will become clear later, triplet and singlet states differ considerably, both in their properties and in their energies. A triplet state always has a lower energy than the corresponding singlet state [4].

2.1 Absorption Processes

A Jablonski diagram is an easy and neat way to illustrate the electronic states, vibrational levels and their transitions in a molecule. Such a diagram is provided in figure 1. Note that each of the electronic states (ground state or excited state) is overlaid by a series of vibrational levels. The vibrational levels arise because a molecule in a particular electronic state can absorb or emit small increments of energy corresponding to the changes in vibrational modes, even though it retains the same electronic configuration [4]. By convention, in a Jablonski diagram, the singlet states should be stacked in one column, while the triplet states are stacked in another column shifted to the right of the singlet column. A photon with an energy ($E = h\nu$) equal to the energy difference between the ground state and an excited state can excite the molecule to that particular excited state (arrows pointing up in figure 1). Since, in general, there are multiple vibrational levels superimposed on the three states shown in figure 1, there are a number of wavelengths that can excite the molecule to that state. This in turn leads to the electronic absorption spectra generally appearing as broad bands rather than 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} times the probability of a singlet-singlet or triplet-triplet transition.

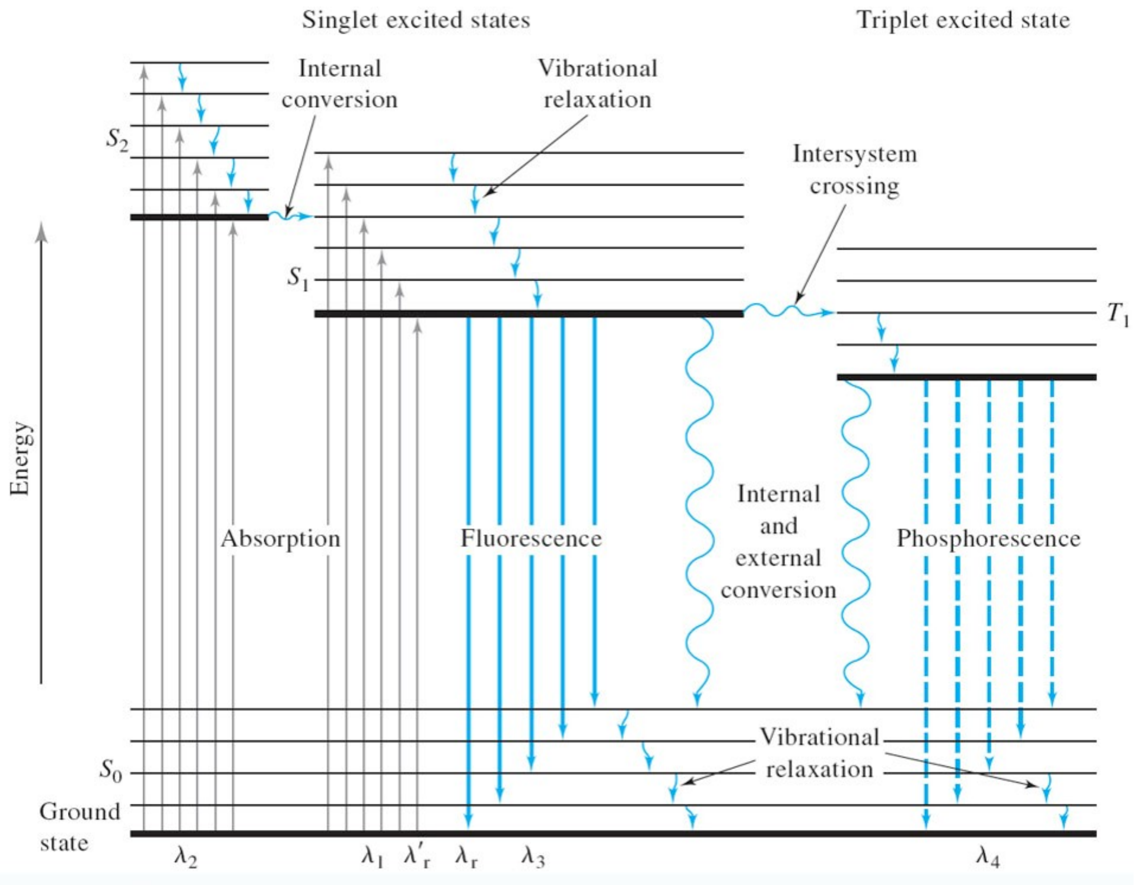

Figure 1: Jablonksi Diagram showing excitations and de-excitation pathways between the ground state (S_0) and the first and second excited singlet states (S_1 & S_2) and the triplet (T_1) state. [1].

3 Luminescence Processes

Luminescence processes can be interpreted 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 and subsequent re-emission of a photon to give luminescence seems to be quite straightforward, there are non-radiative processes which precede and/or compete with photon emission. In the following section, mean lifetimes of all processes will be lined out as they are important for determining the luminescence behaviour 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}

s. 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 [4]. In this situation it can do one of two things:

1. emit a photon from the same vibrational level to which it was excited initially
2. 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} s [4]. 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^{-6} s and therefore the decay time of fluorescence is of the same order of magnitude [4]. 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 upon de-excitation (see chapter 4). It should be noted that even though a quantum of radiation is emitted in fluorescence this quantum will be lower in energy on 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 shift 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. This 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 de-excitation in most molecules. This is particularly true in aromatic hydrocarbons, which we use in this experiment. So far, the discussion was limited to the $S_0 \to S_1$ transitions, and the question might arise as to the nature of exited state processes if a molecule is excited to a higher singlet state e.g. S_2. In such cases, the molecule will undergo vibrational relaxation as discussed before. The fate of the molecule as it reaches the zero$^{\text{th}}$ vibrational level of S_2 depends on 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 zero$^{\text{th}}$ 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 theS_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 zero$^{\text{th}}$ vibrational level (i.e. 10^{-14} to 10^{-11} s) [4]. 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. 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} s, the time required for a spin-forbidden vibrational process would be approximately 10^{-8} to 10^{-7} s, 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 zero$^{\text{th}}$ vibrational level of an excited singlet state but cannot compete with vibrational deactivation from higher vibrational level of a singlet state [4]. Once intersystem crossing has occurred the molecule undergoes the usual internal conversion process

(10^{-13} to 10^{-11} s) and falls to the zero$^{\mathrm{th}}$ vibrational level of the triplet state. If the difference in energy between the zero$^{\mathrm{th}}$ vibrational level of the triplet state and the zero$^{\mathrm{th}}$ 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^{-3} to 100 s) and therefore, loss of excitation energy by collisional transfer is generally enhanced [4]. 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^{-3} to 100 s). 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. Delayed fluorescence emerges when an intersystem crossing is followed by a reversed intersystem crossing to recover a singlet state. There are two possible paths for such a process [3]:

$$\begin{aligned} S_0 + h\nu &\rightarrow S^* \\ S^* &\rightarrow T \\ T + k_bT &\rightarrow S^* \\ S^* &\rightarrow S_0 + h\nu_f \end{aligned}$$

Here, the required energy to return from the triplet to the singlet state is provided by the thermal energy k_BT with k_B the Boltzmann constant. This process is termed thermally activated delayed fluorescence or E-type delayed fluorescence, and it is the predominant process at low triplet concentration (i.e. low chromophore concentration or low excitation intensity) [3]. On the other hand, studies of delayed fluorescence in a variety of aromatic hydrocarbons show that the intensity of delayed fluorescence can be 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:

$$\begin{array}{rcl} S_0 + h\nu & \rightarrow & S^* \\ S^* & \rightarrow & T \\ T + T & \rightarrow & S^* + S_0 \\ S^* & \rightarrow & S_0 + h\nu_f \end{array}$$

This process is termed triplet triplet annihilation delayed fluorescence or P-type delayed fluorescence and dominates at higher triplet concentrations [3].

4 Experimental System

4.1 Kinematics

In this experiment, we will investigate the processes of phosphorescence and delayed fluorescence. Regarding all considerations in section 2, we can simplify the Jablonski diagram to only include rates and transitions relevant to our discussion as is depicted in figure 2.

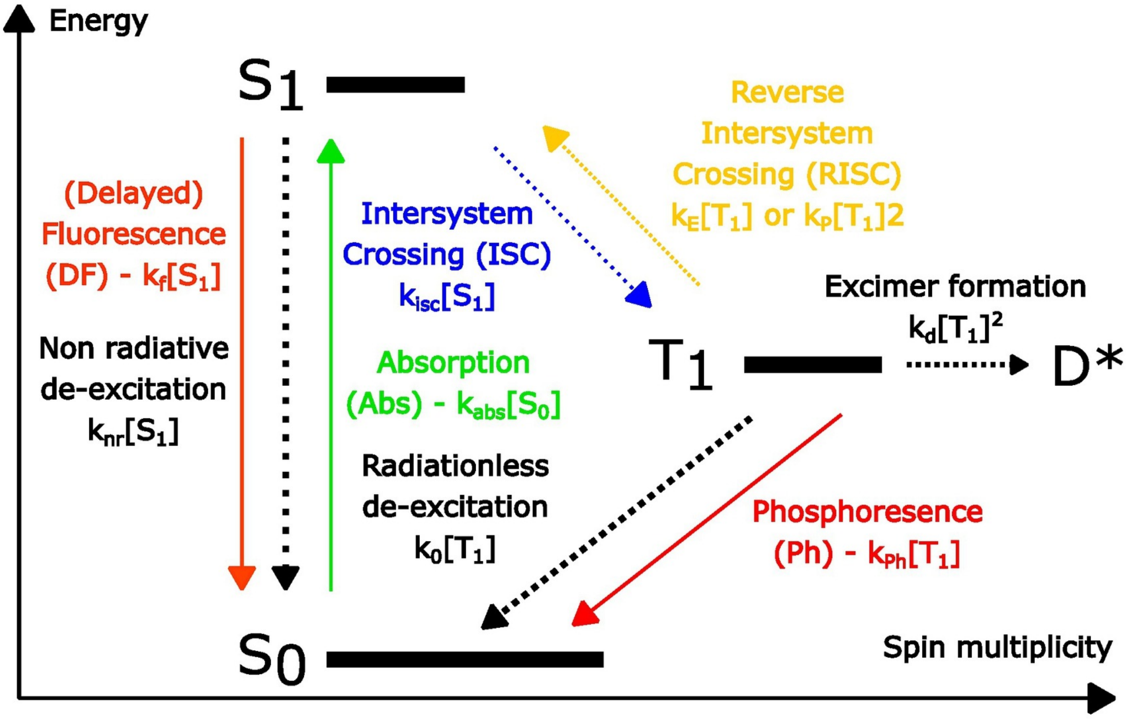

Figure 2: Simplified Jablonksi diagram showing rates and transitions between the ground state (S_0) and the first excited singlet- (S_1) and triplet (T_1) state. [3].

The kinetic equation of the system can now be formulated as:

$$\frac{\partial T_1}{\partial t} = k_{ISC}S_1 - (k_{ph} + k_0 + k_E)T_1 - 2(k_p + k_d)T_1^2 \tag{1}$$

$$\frac{\partial S_1}{\partial t} = k_E T_1 + k_p T_1^2 - (k_{ISC} + k_f + k_{nr})S_1 \tag{2}$$

With S_1 and T_1 the singlet and triplet densities respectively. The rate constants $k_{ISC}, k_{ph}, k_0, k_E, k_p, k_d, k_f$ and k_{nr} are defined as depicted in figure 2. Note that the absorption process is not included as the excitation beam is blanked during measurement as will become clear in section 5. Making the reasonable assumption $(k_f; k_{nr}; k_{ISC} >> k_E + k_p T_1)$, as the processes of de-excitation of singlet states happens on a timescale of ns and the processes of formation on a timescale of ms, we can apply the steady state approximation [3]:

$$\frac{\partial S_1}{\partial t} = 0 \rightarrow S_1 = \frac{1}{k_f + k_{nr} + k_{ISC}}(k_E T_1 + k_p T_1^2) \tag{3}$$

The equations 1 and 2 are now reduced to a single equation, the deactivation equation [3]:

$$\frac{\partial T_1}{\partial t} = -(k_{Ph} + k_0 + k_E)T_1 - 2(k_p + k_d)T_1^2 \tag{4}$$

$$\text{that we rewrite as} \tag{5}$$

$$\frac{\partial T_1}{\partial t} = -a \cdot T_1(t) - b \cdot T_1(t)^2 \tag{6}$$

by comprising $a = (k_{Ph} + k_0 + k_E)$ and $b = 2(k_p + k_d)$ [3].

4.2 The observables

Having established a formalism for the triplet state density $T_1(t)$ we can now turn to describe what is actually measured by the photomultiplier. Three different mechanisms (E- and P-type fluorescence and phosphorescence) contribute to the overall measured light signal. These contributions, expressed via the triplet density T_1 take the following form:

$$I_{DF}^{E} = \Phi_f k_E T_1(t) \tag{7}$$

$$I_{DF}^{P} = \Phi_f k_P T_1(t)^2 \tag{8}$$

$$I_{Ph} = k_{Ph} T_1(t) \tag{9}$$

with $\Phi_f = \frac{k_f}{k_f + k_{n_r} + k_{ISC}}$ the fluorescence quantum yield [3]. Note that these equations are just the triplet state densities multiplied by the rate constant that leads to the respective luminescence.

4.3 Different de-excitation scenarios

The only thing left now is to actually solve the deactivation equation 6. In the following, three different scenarios are considered:

- $a >> bT_1$ (first order de-excitation)
- $a << bT_1$ (second order de-excitation)
- $a \approx bT_1$ (mixed order de-excitation)

Once the deactivation equation is solved, a formula for the time dependency of the triplet density $T_1(t)$ is obtained. Inserting this solution into equations 7-9, an expression for the time dependence of the light signal is obtained. Note that for fitting, the equations 7-9 should be added up, as we measure intensity contributions from all three types of luminescence.

4.4 first order de-excitation

In this case, the solution to the deactivation equation is a simple exponential decay

$$T_1(t) = n_0 \exp(-t/\tau) \tag{10}$$

with $\tau = \frac{1}{a}$ the triplet lifetime. The light intensity should thus follow

$$I = (k_{ph} + \Phi_f \cdot k_e) \cdot n_0 e^{(-at)} + \Phi_f k_p n_0^2 e^{(-2at)} \tag{11}$$

with n_0 the initial triplet state density. Here, the first part corresponds to first-order delayed fluorescence (E-type) + Phosphorescence, and the second part accounting for second order delayed fluorescence by triplet–triplet annihilation (P-type).

4.5 second order de-excitation

Solving the deactivation equation for $a << bT_1$ leads to

$$T_1(t) = \frac{n_0}{1 + bn_0 t} \tag{12}$$

meaning that the measured light intensity should follow

$$I = (\Phi_f k_e + k_{ph}) \left(\frac{n_0}{(1 + bn_0 \cdot t)} \right) + \Phi_f k_p \left(\frac{n_0}{(1 + bn_0 \cdot t)} \right)^2 \tag{13}$$

With the first part again corresponding to E-type fluorescence and phosphorescence and the second part to P-type fluorescence.

4.6 mixed order de-excitation

In the case where $a \approx b$, the deactivation equation is solved by

$$T_1(t) = \frac{a}{e^{at}\left(\frac{a}{n_0} + b\right) - b} \tag{14}$$

suggesting the light signal follows

$$I = (\Phi_f k_e + k_{ph})\left(\frac{a}{e^{at}(\frac{a}{n_0} + b) - b}\right) + \Phi_f k_p \left(\frac{a}{e^{at}(\frac{a}{n_0} + b) - b}\right)^2 \tag{15}$$

Where the first part again accounts for E-type fluorescence and phosphorescence and the second part for P-type fluorescence.

5 Experimental Setup

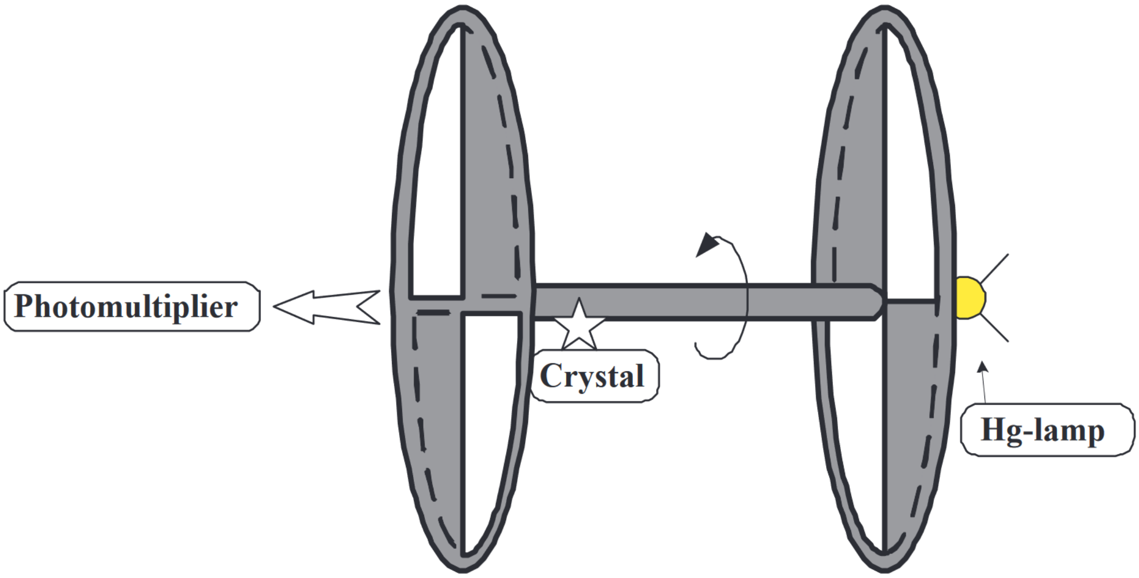

Figure 3: Experimental setup with, from right to left, a mercury lamp (Hg-lamp), rotating shutters, the crystal under investigation depicted as a star and the photomultiplier.

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 3. 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. 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. As light paths 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 at the photomultiplier. The results from the photomultiplier should be seen on channel two of the oscilloscope when the first channel is used as an external trigger. For better results it is recommended to have the oscilloscope measuring an average of 128 measurements. Figure 4 shows the schematic structure and chemical formula of the crystals used in the experiment.

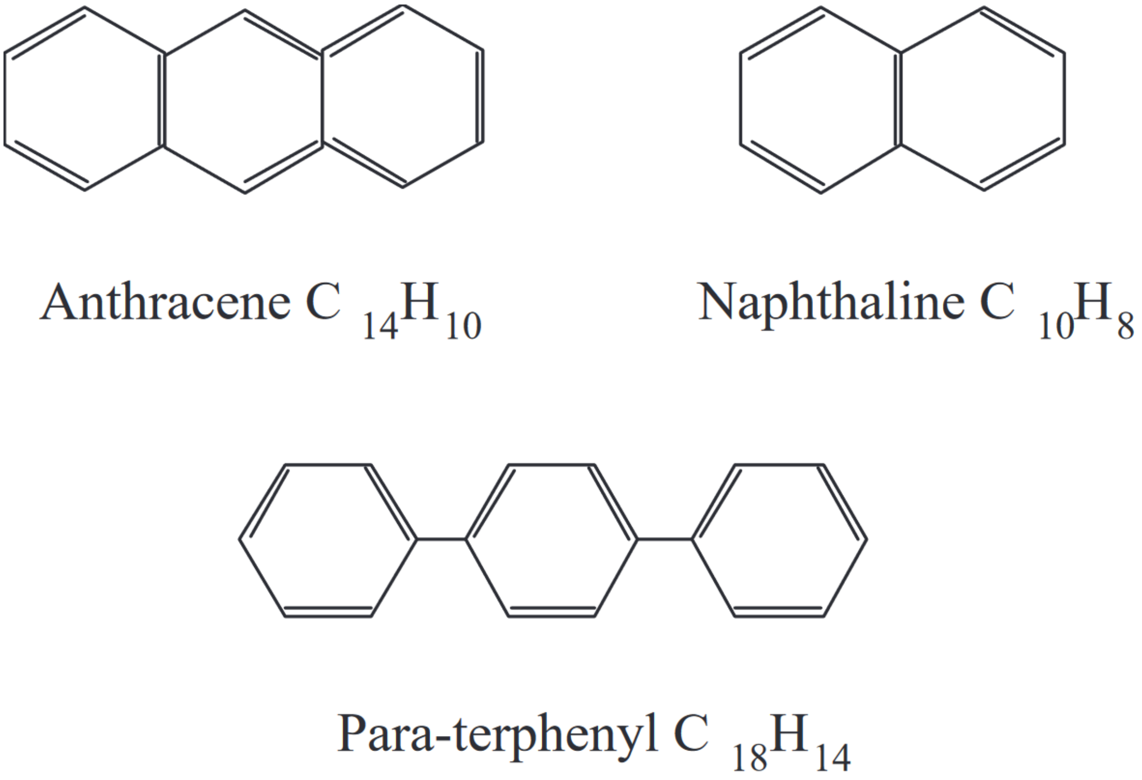

Figure 4: Chemical structure of the organic crystals investigated

6 Analysis

The measured data should be fitted with each of the three scenarios described above. From the fits, try to estimate if the de-excitation is dominated by first- or second order processes. Try to extract a value for the triplet lifetimes. Do not forget to add an offset to each fitting function to compensate for the background signal. Elaborate on your results. Does it make sense that the triplet state densities follows the determined order? What could be changed to enter a regime where de-excitation is dominated by another process? How would you improve the measurement setup?

7 Warnings

- All crystals in this experiment can sublimate at room temperature. Naphtalene is flammable, a possible carcinogen and its dust can form explosive mixture with air. All crystals are ecologically harmful and may harm your health. Be careful with these chemicals and leave the sealed vials closed.

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