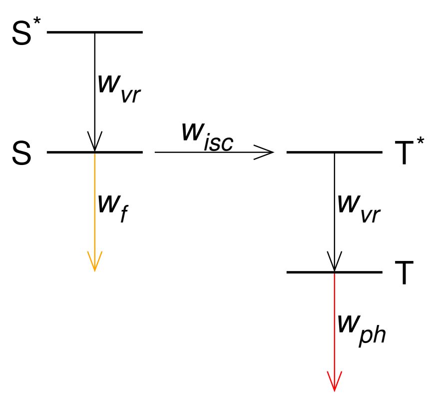
Chemistry 4000/5000/7000 Fall 2021
Assignment 4

Due: December 1st

This assignment will be submitted electronically. As usual, I will accept neatly handwritten, scanned answers. However, any figures you generate should be included with your written answers in a single document. In some questions, I will require additional files. The file names should be mentioned in your report so that I can make the correct associations between the written work and files. The report and any additional files should be sent as attachments to a single email.

Detailed solutions or answers are required. Little to no credit will be given for answers presented without your detailed reasoning. For computational problems, you must provide sufficient detail of the calculation to enable replication. Typically, this would mean the method used and basis set.

In this assignment, you will develop and briefly study a model of fluorescence and phosphorescence kinetics. The model is represented by the following diagram:



S* is an electronically and vibrationally excited singlet state, S is an electronically excited singlet state in its ground vibrational state, T* is an electronically and vibrationally excited triplet state, and T is an electronically excited triplet in its ground vibrational state. The transitions from S^* to S and from T^* to T represent vibrational relaxation, which in this context is a loss of vibrational excitation. This tends to be very fast. The transition with rate w_f is fluorescence, a relatively rapid process of emission from the excited singlet to a singlet ground state. Intersystem crossing (ISC) is a transition from an excited singlet to an excited triplet state. Because triplet states are lower in energy than the corresponding singlet states (Hund's rule), the triplet state formed by ISC will typically be vibrationally excited. For simplicity, we are assuming that vibrational relaxation occurs at the same rate for the singlet and triplet. Once the triplet has lost its vibrational excitation, it can undergo the slow emission process of phosphorescence to return to the singlet ground state.

For this assignment, assume the following transition rates:

$$
\begin{aligned}
w_{vr} &= 10^{11}\,\mathrm{s}^{-1} \\
w_f &= 10^{8}\,\mathrm{s}^{-1} \\
w_{isc} &= 10^{8}\,\mathrm{s}^{-1} \\
w_{ph} &= 10^{-2}\,\mathrm{s}^{-1}
\end{aligned}
$$

Write a population kinetic Monte Carlo simulation of this system assuming that all molecules start in the S^* state. Store the times at which each fluorescence and each phosphorescence event occurs. (These should be stored in two separate vectors, a vector of fluorescence event times, and a vector of phosphorescence event times.) The output of your program should be two separate histograms, one of the fluorescence event times, and one of the phosphorescence event times. The axes of your histograms should be appropriately labeled. Each histogram should have a title. (See below.)

The fluorescence (phosphorescence) decay time is the time it takes for the fluorescence (phosphorescence) to fall to $1/e$ of its original value. For exponential decay, which you will observe here, the decay time is equal to the average of the event times. Calculate and report the fluorescence and phosphorescence decay times.

Your report should include your Matlab code and the two histograms. You should simulate at least 1000 molecules. (As with all other things statistical, more is better.) Your code will be judged for correctness and clarity. On the latter point, some sensible comments are required. [30 marks]

In addition to the Matlab statements and functions learned in class, the following may be useful:

`close all` closes all currently open figure windows. (This is useful in order not to keep accumulating figure windows as you are developing your code.)

`figure` starts a new figure without erasing the old one.

`title('Put title here')` adds a title to a figure. Like the axis labeling functions, `title()` should be called after creating the plot and before you start a new figure.

Bonus: How are the decay times related to the rate constants? Provide a brief explanation and/or a few equations to support your answer. [4 marks]