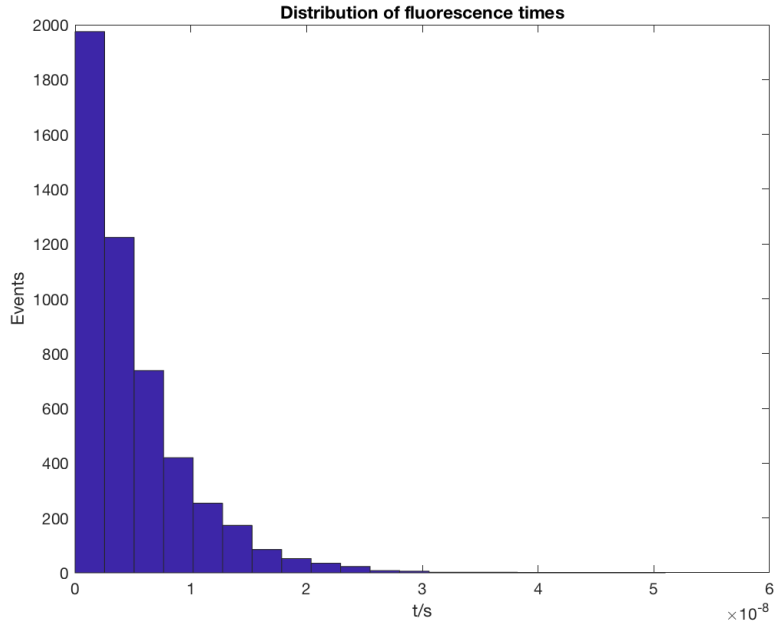
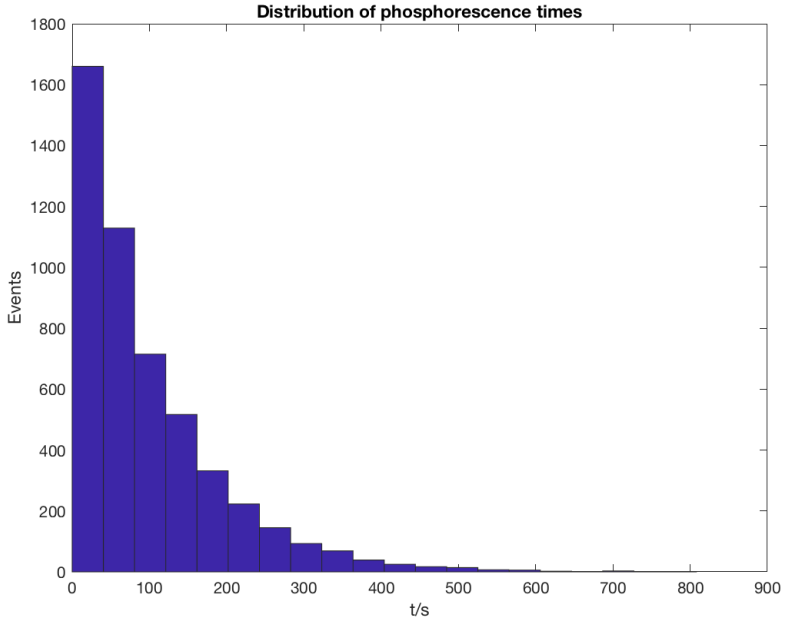
Chemistry 4000/5000/7000 Fall 2021
Assignment 4 solutions

My code is posted separately. I obtained the following histograms with 10 000 molecules:





Matlab returned the following decay times:

Fluorescence: $4.99 \times 10^{-9}\,\mathrm{s}$

Phosphorescence: $98.7\,\mathrm{s}$

Bonus For the given rate constants, vibrational relaxation is very fast, so the initial population is very rapidly transferred to the S state. Once that has happened, the S state decays by two pathways, namely ISC and fluorescence. Since the rate of fluorescence is proportional to the number of molecules of S, the decay in S controls the decay in fluorescence. In terms of the master equation, we have

$$\frac{dN_{\mathrm{S}}}{dt} = -w_{isc}N_{\mathrm{S}} - w_f N_{\mathrm{S}} = -(w_{isc} + w_f)N_{\mathrm{S}}.$$

Accordingly,

$$\tau_f = (w_{isc} + w_f)^{-1} = 5 \times 10^{-9}\,\mathrm{s}.$$

The phosphorescence process itself is extremely slow, so on the timescale of this process, ISC occurs very fast. The rate of decay of phosphorescence is therefore just controlled by the transition rate for phosphorescence itself, i.e.

$$\tau_{ph} = w_{ph}^{-1} = 100\,\mathrm{s}.$$