Problem 1
The figure below shows internuclear configurations for cases a), b) and c). Draw the shapes of absorption spectra making the use of the Franck-Condon principle. Assume that the spectrum broadening is small (distinct, narrow vibronic bands).
Problem 2

Extinction coefficients ($\varepsilon_{500\text{nm}}$) at 500 nm for the organic dyes Rhodamine 110 and Rhodamine 6G are 70 000 M$^{-1}$ cm$^{-1}$ and 42 000 M$^{-1}$ cm$^{-1}$, respectively. You prepare an equimolar (0.10 mM total) mixture of the two dyes in ethanol. Calculate the absorbance (optical density) at 500 nm of the mixed solution in a 1 mm path length cell. Assume that the dye molecules do not interact with each other.
Problem 3.

Absorption $A_{\lambda}$ and fluorescence $I_{\text{fluor}}$ spectra for the dye DDI (1,1-diethyl-2,2-dicarbocyanine iodide, C$_{27}$H$_{27}$N$_2$I) are shown in the figure below.

(3.1) Discuss in a couple of sentences how these spectra relate to each other and what is the possible nature of the fluorescent state.

(3.2) The emission spectrum has been acquired using conventional steady-state fluorescence instrumentation. Why do you think the conventional fluorescence instrumentation has a problem to detect the fluorescence for $\lambda > 850$ nm?

(3.3) Make an estimate of the value of the fluorescence Stokes shift. Indicate the Stokes shift in the Figure.

(3.4) Estimate the vibrational spacing in the first excited singlet state ($S_1$).

(3.5) Estimate the vibrational spacing in the ground state ($S_0$).

(3.6) You completely dissolved 1.0 mg of the dye powder in 30 ml of ethanol. The measured absorbance is 1.5 at $\lambda = 710$ nm in a cell 1.0 mm thick. Evaluate the maximum extinction coefficient.
Problem 4.
The absorption spectrum and the $S_1 \rightarrow S_0$ fluorescence spectrum Rhodamine B dissolved in ethanol (refractive index, 1.35) is given on the OMLC website:
http://omlc.org/spectra/PhotochemCAD/index.html

(4.1) Find the value of the radiative time constant ($\tau_{\text{rad}}$) associated with the $S_1 \rightarrow S_0$ fluorescence.


\[
\frac{1}{\tau_{\text{rad}}} = 8 \times 2303 \pi c n^2 N_a^{-1} (\langle \nu_f^3 \rangle_{A\nu})^{-1} \times \frac{g_{S_0}}{g_{S_1}} \int \varepsilon \, d \ln \nu
\]

\[
= 2.880 \times 10^{-9} n^2 (\langle \nu_f^3 \rangle_{A\nu})^{-1} \times \frac{g_{S_0}}{g_{S_1}} \int \frac{\varepsilon}{\nu} \, d\nu
\]