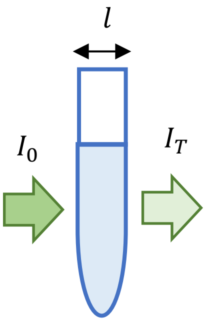
Exercise 6.1: Absorption of molecular compounds in solution.

1) The molar decadic extinction coefficient of a dye dissolved in hexane is known to be $\varepsilon_{\text{dye}} = 855\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$ at 270 nm. Calculate the percentage reduction in intensity when light of that wavelength passes through 2.5 mm of a solution of concentration 3.25 mmol dm^{-3}.

2) Calculate the cross-section of individual dye molecules at the same wavelength. How does the cross-section compare to the size of the molecule? Hint: Approximate the dye to a disk of 10 Å diameter.

Exercise 6.1 solution.

1)



The reduction of intensity is given by I_T/I_0.

According to the Beer-Lambert law the absorbance is given by

$$A = -\log \; I_T/I_0 \; = \varepsilon c l$$

where ε denotes the molar decadic extinction coefficient. Here one finds that $A = 0{,}695$. Finally, $I_T/I_0 = 10^{-A} = 20\%$.

Using the Beer-Lambert law we neglected the reflectance. In practice this is not negligible: as it was seen in previous exercises, a glass container reflects twice 4%.

Note: if you used the law of absorption $I_T/I_0 = \exp \; -\alpha l$, a typical mistake is to confuse α with εc. As demonstrated during the lecture, $\alpha = \varepsilon c \ln 10$. Make sure to not forget the $\ln \; 10$ factor.

2)

The cross-section σ is not a physical surface, but it is related to the transition dipole moment. In other words, the absorption cross-section describes the probability of an absorption process. The larger the cross-section is, the higher the probability of transition will be.

$$\varepsilon = \frac{\sigma \cdot N_A}{\ln 10} \Rightarrow \sigma = \frac{\varepsilon \ln 10}{N_A}$$

$$N_A = 6.02 \cdot 10^{23}\ \text{mol}^{-1}$$

One finds $\sigma = 3{,}27 \cdot 10^{-18}\ \text{cm}^2/\text{molecule}$.

The area of the dye molecule approximated with a disk of 10 Å : $\pi r^2 = 7{,}85 \cdot 10^{-15}\ \text{cm}^2$. The cross section is much smaller than the molecule size. In this example, the small cross-section is directly related to a small ε_{dye}. "Good" dyes have ε_{dye} values in the $10^5 - 10^6$ range.

Note: at first sight it may be intuitive to describe the probability of light absorption by the size of the molecule. But note that the cross section is not related to the molecule's size: for the lowest energy transition, a small molecule can have large cross-section, and inversely.

You can think about the absorption cross-section as the "seeming surface" of the molecule with respect to the absorption process. When the molecules interact weakly with the light (low probability of interaction), it is as if the incident light sees small molecule surfaces.

Exercise 6.2: Estimation of fluorescence and phosphorescence quantum yields.

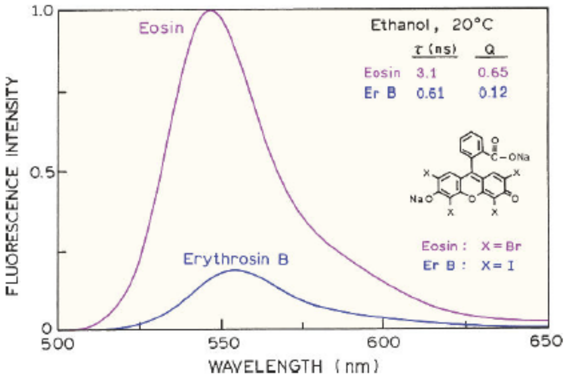


Figure 1 : Emission spectra of eosin and erythrosin B

Eosine is a red dye used to stain proteins, muscle fibers and collagen. It was also used in paintings (notably by Van Gogh!). Erythrosin-B is a red-pink dye used for food coloring and as dental plaque disclosing agent. Emission spectra, lifetimes (τ) and quantum yields (Q) for eosin and erythrosin B (ErB) are shown in Figure 1.

1) The quantum yield for fluorescence is determined by the radiative and non-radiative decay rates. Calculate the natural lifetime of fluorescence (τ_f) and the radiative and non-radiative decay rates of eosin and ErB. What rate accounts for the lower quantum yield of ErB?

2) We now consider the phosphorescence process. Typically, the emissive rates of fluorescence and phosphorescence (k_f and k_p, respectively) vary greatly. Phosphorescence lifetimes are typically near 1-10 ms. Assume that the natural lifetime for phosphorescence emission of these compounds is 10 ms, and that the non-radiative decay rates of the two compounds are the same for the triplet state as for the singlet state. Estimate the phosphorescence quantum yields of eosin and ErB at room temperature.

Exercise 6.2 solution.

1)

As it was explained in previous lectures for the two-level system (see part on the Einstein coefficients), a decay can spontaneously emit a photon. We saw that the rate (probability per time unit) of such a transition is inversely related to the transition's lifetime. In fact, some proportion of the transitions are non-radiative, and thus do not participate in the emission of light.

The internal quantum yield Φ_f is thus defined by the ratio between radiative decay rate and the total radiative rate (including non-radiative decays):

$$\Phi_f = \frac{k_f}{k_f + k_{nr}} = \frac{1/\tau_f}{1/\tau_f + 1/\tau_{nr}} = \frac{1/\tau_f}{1/\tau}$$

So the radiative lifetime is $\tau_f = \tau/\Phi_f = 4{,}77\,ns$ and $5{,}08\,ns$ for Eosin and ErB respectively.

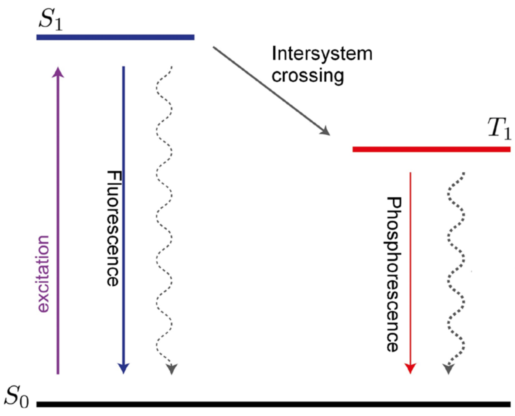
The radiative rate is $k_f = 1/\tau_f = 2 \cdot 10^8\ s^{-1}$ for both compounds.

The non-radiative rate is $k_{nr} = 1/\tau_{nr} = 1/\tau - 1/\tau_f = 1{,}12 \cdot 10^8\ s^{-1}$ for Eosin and $1{,}44 \cdot 10^9\ s^{-1}$ for ErB.

Interestingly, the two compounds have the same radiative rate, but eventually the quantum efficiency is much higher for Eosin than for ErB. The non-radiative decay rate is higher for ErB, so there are more non-radiative transitions, that do not contribute to generation of photons => this contributes to a lower quantum yield.

Additional remarks:

As shown in Figure 1, Eosin and ErB have identical structures except that Eosin contains Br atoms where ErB contains I atoms. The latter atoms being heavier, one expects that there is a stronger coupling between the S1 singlet state and the T1 triplet state. Thus, ErB have more intersystem crossing (non-radiative), which could explain why the non-radiative decay rate is higher for ErB. Note that heavier atoms generally also result in more internal conversion.



2)

Assuming that the non-radiative decay rate is the same for the triplet state and singlet state ($k_{nr,p} = k_{nr,f}$) one uses the rates calculated in question 1). Using the above definition of quantum yield,

$$\Phi_p = \frac{k_p}{k_p + k_{nr,p}} = \frac{1/10 \cdot 10^{-3}}{1/10 \cdot 10^{-3} + 1{,}12 \cdot 10^{8}} = 9 \cdot 10^{-7} \text{ for Eosin}$$

$$\Phi_p = \frac{1/10 \cdot 10^{-3}}{1/10 \cdot 10^{-3} + 1{,}44 \cdot 10^{9}} = 7 \cdot 10^{-8} \text{ for ErB}$$

Note: we find that the phosphorescence quantum yield is higher for Eosin. This is because we assumed that non radiative decay rates are equal for both compounds.

In reality, ErB will have a higher phosphorescence rate than Eosin, because of heavier atoms which facilitate the intersystem crossing.