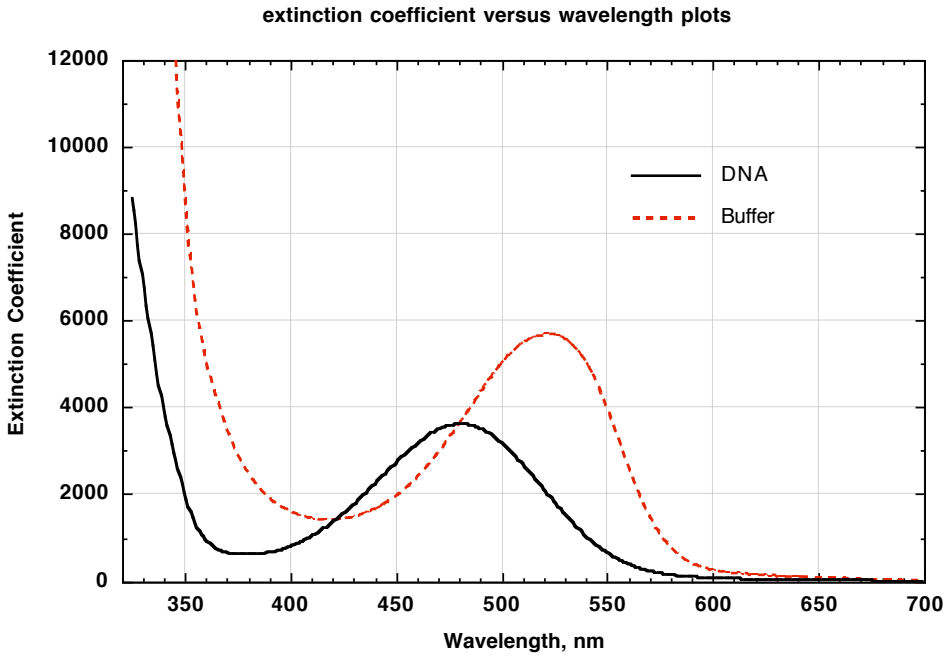
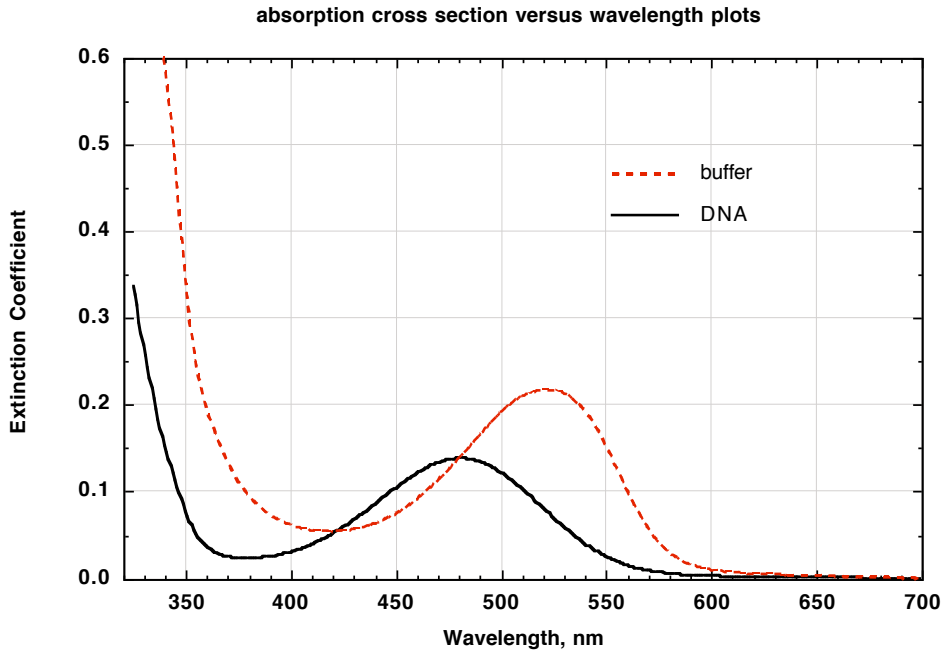
CHM 598, Photochemistry, Spring 2005, Homework 3, my answers!

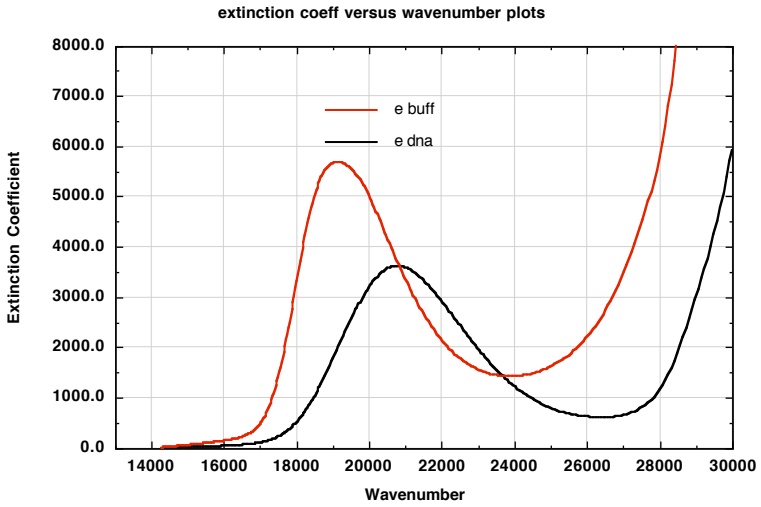
I apologize, I made 2 errors on the homework. First, the concentrations were wrong! They should have been 1.18 x 10^{-4} M for buffer, and 2.42 x 10^{-4} M for DNA. Second, the radiative frequency I gave in the formulas was ν_f, and I meant to give ν_{abs}^{max} (I was looking ahead to next weeks homework already). I have taken these errors into account when grading the homework.

Extinction coefficient calculated as Absorbance divided by Concentration (pathlength is 1 cm). The Absorption cross section as extinction coeff x 3.824 x 10^{-5} (Å^2/molecule).





Calculation of Oscillator Strengths



Using $f = 4.32 \times 10^{-9} \cdot A$

I integrated the buffer absorption band from 14,000 to 23500 wavenumber as: $A = \int \varepsilon(\tilde{\nu})\, d\tilde{\nu}$

A (buffer) = 2.17 x 10^7, f (buffer) = 0.0937

I integrated the DNA absorption band from 14,000 to 26500 wavenumber as: $A = \int \varepsilon(\tilde{\nu})\, d\tilde{\nu}$

A (DNA) =1.66 x 10^7, f (DNA) = 0.0717

Calculation of Transition Dipole Moments

Using $f = 4.70 \times 10^{-7}\ \tilde{\nu}_{abs}^{max} \cdot \mu_i^2$

μ_i = sqrt (f / 4.7 x 10^{-7} . $\tilde{\nu}_{abs}^{max}$)

I determined the absorption maximum to be 19120 cm^{-1} in buffer

μ_i = sqrt (0.0937 / 4.7 x 10^{-7} . 19120) = 3.23 D (buffer)

I determined the absorption maximum to be 20830 cm^{-1} in DNA

μ_i = sqrt (0.0717 / 4.7 x 10^{-7} . 20830) = 2.71 D (DNA)

Calculation of Effective Distance

Using:: r = μi / 4.8

r (buffer) = 0.623 Å

r (DNA) = 0.565 Å

Calculation of Radiative Rate

Using: $k_f = 2.881 \times 10^{-9}\ (\tilde{\nu}_{abs}^{max})^2\ n^2$ A

(assume the refractive index of water is OK for both systems, n = 1.335 at 500 nm)

k_f (buffer) = 2.881 x 10^{-9} $(19120)^2$ $(1.335)^2$ 2.17 x 10^7 = 4.07 x 10^7 s^{-1}

k_f (DNA) = 2.881 x 10^{-9} $(20830)^2$ $(1.335)^2$ 1.66 x 10^7 = 2.96 x 10^7 s^{-1}