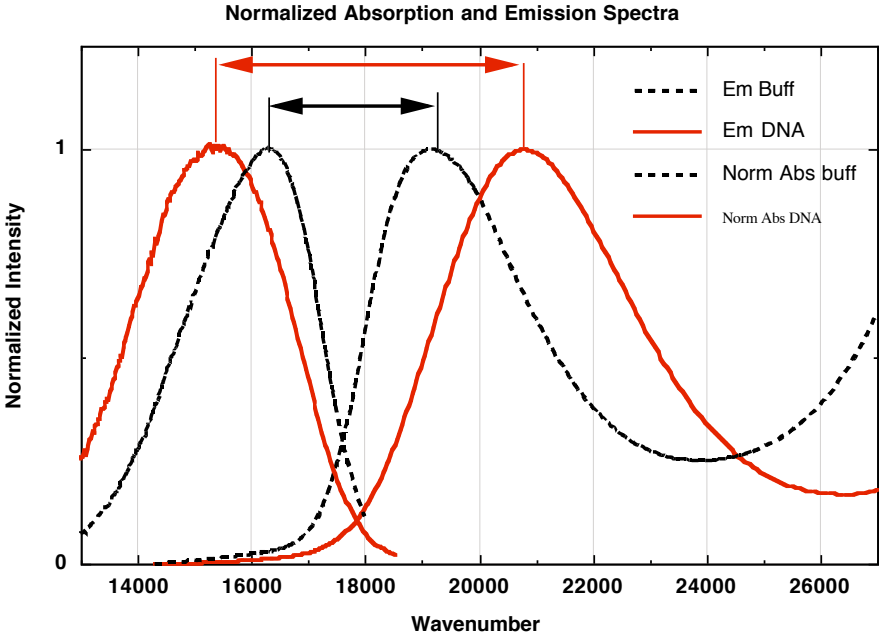
CHM 598, Photochemistry, Spring 2005, Homework 4, my answers!

Stokes Shift (DNA) = 20790 - 15400 cm-1 = 5390 cm-1 = 0.67 eV = 15.4 kcal/mol

Stokes Shift (Buff) = 19130 - 16290 cm-1 = 2840 cm-1 = 0.35 eV = 8.1 kcal/mol

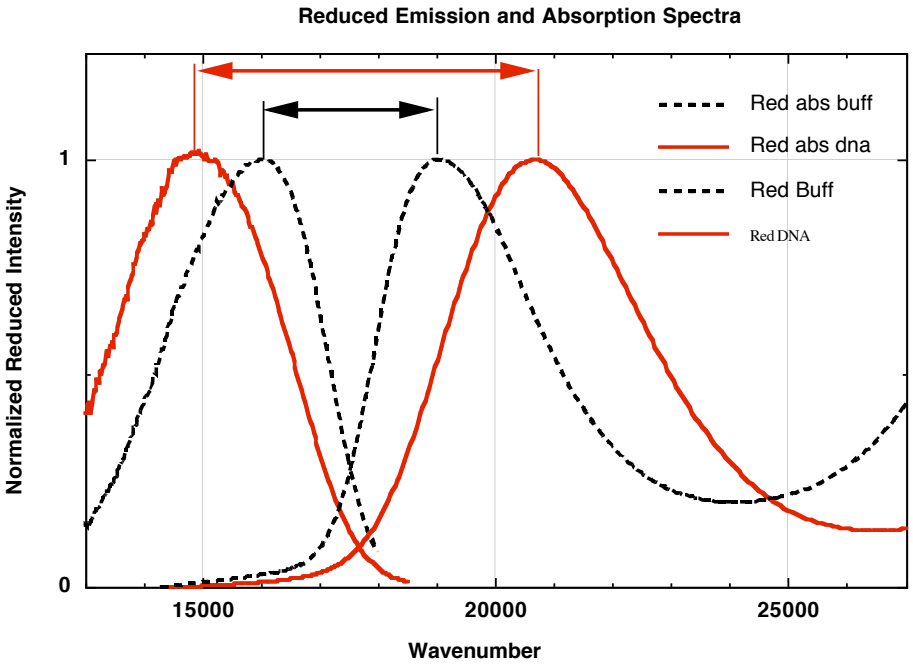


Total λ (DNA) = 20700 - 14850 cm-1 = 5850 cm-1 = 0.73 eV = 16.7 kcal/mol

$\Delta E_{0,0}$ (DNA) = 17680 cm-1 = 2.19 eV = 50.6 kcal/mol

Total λ (Buff) = 19050 - 16050 cm-1 = 3000 cm-1 = 0.37 eV = 8.6 kcal/mol

$\Delta E_{0,0}$ (Buff) = 17520 cm-1 = 2.17 eV = 50.1 kcal/mol



Determination of average emission frequency:

Evaluation of $\int I_f(\tilde{\nu})\, d\tilde{\nu}$, for the normalized to unity emission spectrum in DNA, from 18519 to 12516 cm^{-1} = 3305.8

Evaluation of $\int I_f(\tilde{\nu})\, \tilde{\nu}^{-3}\, d\tilde{\nu}$, for the normalized to unity emission spectrum in DNA, from 18519 to 12516 cm^{-1} = 9.65 x 10^{-10}

average emission frequency in DNA = (3305.8/9.65 x 10-10)^-3 = 15075 cm^{-1}
(this value really should be smaller, but we don't have the entire spectrum)

Evaluation of $\int I_f(\tilde{\nu})\, d\tilde{\nu}$, for the normalized to unity emission spectrum in Buffer, from 18519 to 12516 cm^{-1} = 2811.9

Evaluation of $\int I_f(\tilde{\nu})\, \tilde{\nu}^{-3}\, d\tilde{\nu}$, for the normalized to unity emission spectrum in Buffer, from 18519 to 12516 cm^{-1} = 7.33 x 10^{-10}

average emission frequency in Buffer = (2811.9/7.33 x 10-10)^-3 = 15654 cm^{-1}

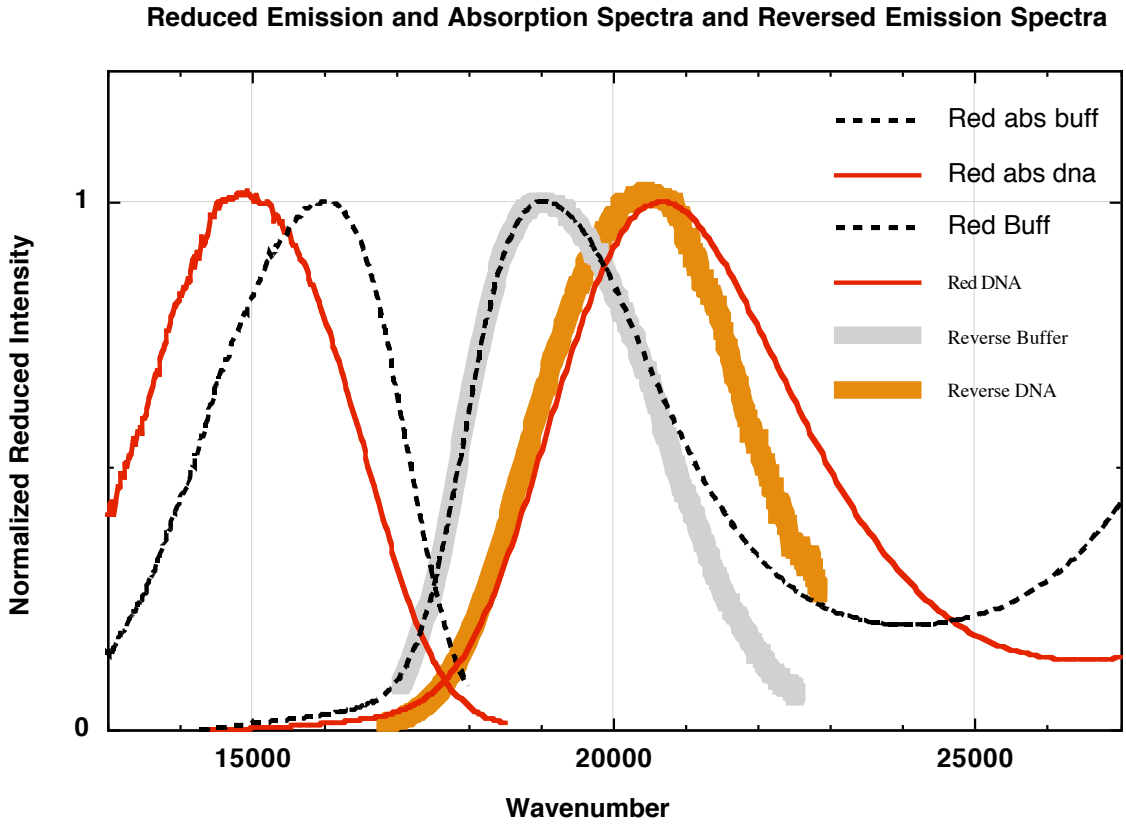
Determination of radiative rate:

Evaluation of $\int \frac{\varepsilon_{abs}(\tilde{\nu})}{\tilde{\nu}}\, d\tilde{\nu}$ from 14000 to 23500 cm^{-1} in Buffer = 1090.6

k_f = 2.881 x 10^{-9} $(1.335)^2$ $(15654)^3$ 1090.6 = **2.15 x 10^7 s^{-1}**

Evaluation of $\int \frac{\varepsilon_{abs}(\tilde{\nu})}{\tilde{\nu}}\, d\tilde{\nu}$ from 14000 to 26500 cm^{-1} in DNA = 779.7

k_f = 2.881 x 10^{-9} $(1.335)^2$ $(15075)^3$ 779.7 = **1.37 x 10^7 s^{-1}**



These plots show that the emission spectrum in buffer exhibits an good mirror image relationship with the absorption spectrum, whereas that in DNA does not