CHM 598, Photochemistry, Homework 4

On the website are two emission spectra of ethidium bromide in the form of electronic text files. Just as last week, you will need to download these files and get them into a data analysis program.

The files are "emdna.txt" and "embuffer.txt", corresponding to ethidium bromide intercalated into DNA, and simply dissolved in aqueous buffer. Each file consists of emission intensity normalized to unity versus wavelength.

You must hand in the following:

1. A plot of the absorption spectra and the emission spectra versus wavenumber for both buffer and DNA, with all spectra normalized to unity. From this plot, determine the "normal" Stokes shift, for both buffer and DNA. Print this information on your plots in units of cm^{-1}, eV and kcal/mol.
2. A plot of "reduced" emission intensity and "reduced" absorption intensity versus wavenumber for both buffer and DNA. From these plots, determine the sum of the high-frequency and low-frequency reorganization energies ($\lambda_s + \lambda_v$) and the $\Delta E_{0,0}$. Report these in cm^{-1}, eV and kcal/mol.
3. Determine a value for the "average emision frequency", $\tilde{\nu}_{av}$, in each case, using the following equation.

$$\tilde{\nu}_{av} = \left[\frac{\int I_f(\tilde{\nu})\, d\tilde{\nu}}{\int I_f(\tilde{\nu})\, \tilde{\nu}^{-3}\, d\tilde{\nu}} \right]^{-3}$$

(in these cases we do not actually have the entire emission spectra, so your average emission frequencies determined in this way will be inaccurate, but just use them anyway)

4. Determine a value for the radiative rate constant using the accurate form of the Strickler-Berg equation:

$$k_f = 2.881 \times 10^{-9}\ n^2\ \tilde{\nu}_{av}^{\ 3} \int \frac{\varepsilon_{abs}(\tilde{\nu})}{\tilde{\nu}}\, d\tilde{\nu}$$

5. To your reduced intensity plot, add plots showing how reduced emission intensity versus $\tilde{\nu}_{reverse}$ for both DNA and buffer, where $\tilde{\nu}_{reverse}$ is given by the following:

$$\tilde{\nu}_{reverse} = (\Delta E_{0,0}\ (cm^{-1}) - \tilde{\nu}_f) + \Delta E_{0,0}\ (cm^{-1})$$

State what kind of information that you think you get from such a plot versus $\tilde{\nu}_{reverse}$.

Some hints!
1. As last week, if you don't have access to a suitable computer program, come and see me before you start!

2. As last week, the absorption spectrum shows more than one absorption band. It isn't obvious where one bands ends and the other starts! Again, there is going to be more than 1 set of correct answers to this homework. In principle, you could do band shape analysis to determine where the first absorption band ends and the second begins. Maybe we will do that before the end of the semester.

3. Again, the only tricky parts are figuring out how to do the integrals properly. Again, if you need help, come and see me and we will do it together.

4. Remember, from the Einstein relations that emission intensity depends upon emission frequency cubed, and that a reduced emission spectrum consists of intensity divided by emission frequency cubed. Absorption intensity depends upon frequency, and thus a reduced absorption spectrum consists of absorption intensity divided by frequency.