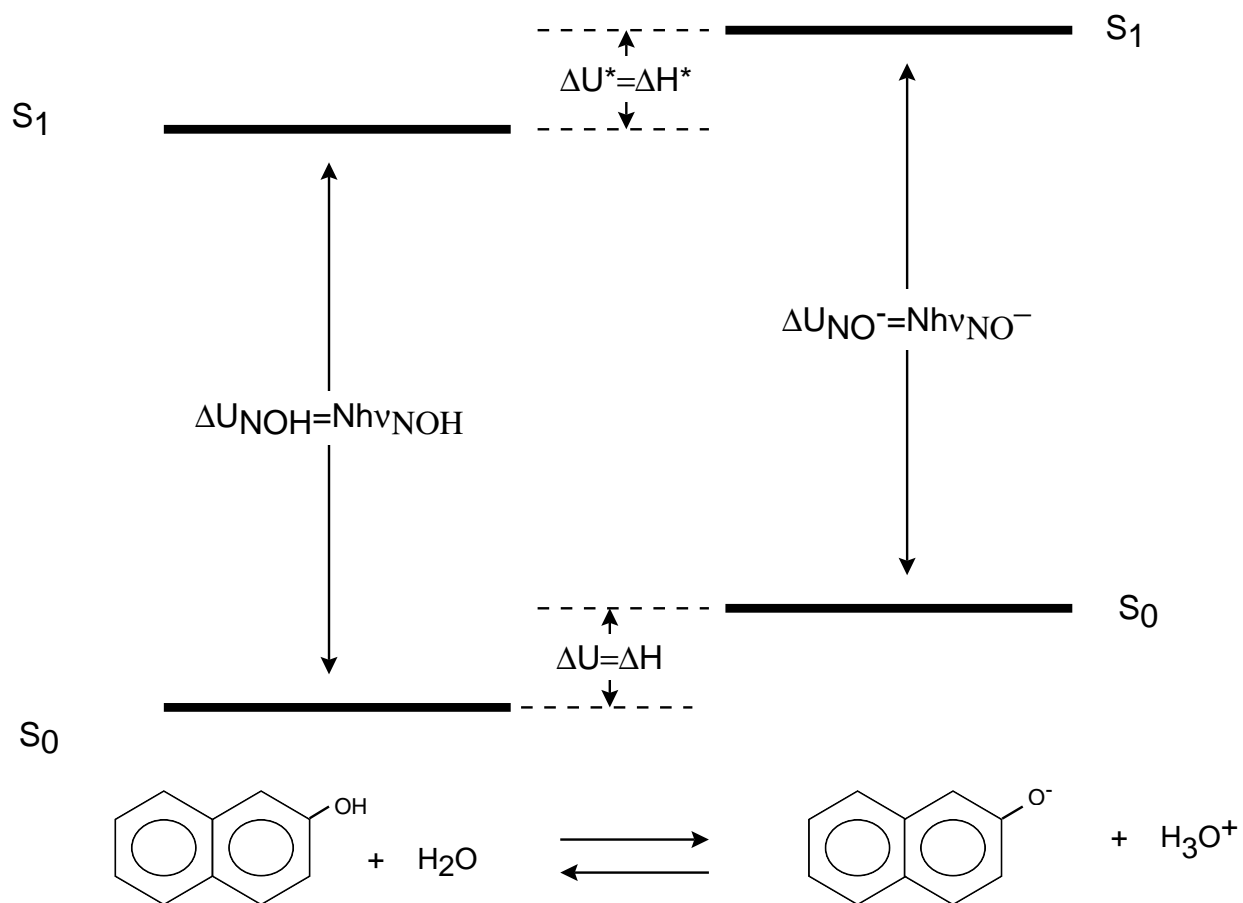


Excited State Properties of 2-Naphthol

Physical Chemistry Laboratory

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The distribution of electrons around a molecule determines many of its properties. In this experiment, we will study how the proton dissociation properties of 2-naphthol change when light is used to change the distribution of electrons in the molecule. When 2-naphthol is in solution, it can lose a proton to a nearby water molecule. The equilibrium constant for this dissociation depends on whether 2-naphthol is in the ground or the first excited state. Consider the following diagram:



At the bottom of the diagram you see the equilibrium reaction that we are considering. 2-Naphthol is in equilibrium with its base form in water. The same is true in the excited state. However, the relative energy between the base and the acid form is different in the ground and first excited states. As a result, the equilibrium constant is different in

the ground and first excited state. The first week of this experiment you will find the equilibrium constant for this reaction in the ground and first excited state. During the second week, you will find the protonation and deprotonation rates for the first excited state. In addition, you will explore the HOMO and LUMO of 2-naphthol to understand what causes the different behavior in the ground and first excited states. In the final week you'll expand this laboratory in your own direction.

Ground and Excited State Equilibrium constants

Ground State Equilibrium Constant: To obtain the ground state equilibrium constant for this acid dissociation, it is useful to rearrange the definition of the equilibrium constant,

$$K_a = \frac{[H_3O^+][NO^-]}{[NOH]}.$$

In particular, take its log and rearrange the terms to obtain,

$$pH = pK_a + \log \frac{[NO^-]}{[NOH]} \quad \text{where} \quad pK_a = -\log K_a \quad \text{and} \quad pH = -\log[H_3O^+].$$

Using absorption spectroscopy, you will determine the concentrations of 2-naphthol and its conjugate base. The pH will be determined from a pH meter reading. Plotting pH versus $\log \frac{[NO^-]}{[NOH]}$ should yield a straight line with an intercept of the pKa.

Excited State Equilibrium Constant: To obtain the relationship between the ground and first excited state equilibrium constant, consider the energy level diagram. Notice that

$$\Delta U_{NOH} + \Delta U^* = \Delta U_{NO^-} + \Delta U.$$

ΔU_{NOH} in units of per mole is the energy of the photon needed to promote one molecule of 2-naphthol from the ground to the excited state times Avogadro's number. ΔU_{NO^-} is the energy of the photon needed to promote one molecule of the conjugate base from the ground to the excited state times Avogadro's number. The molar energy difference between protonated and unprotonated 2-naphthol in solution is ΔU for the system undergoing the deprotonation. $\Delta U \approx \Delta H$ since $\Delta(PV)$ is about zero for our liquid system. As a result,

$$N_A h\nu_{NOH} + \Delta H^* = N_A h\nu_{NO^-} + \Delta H.$$

Rearranging and making the approximation that the entropy difference between the protonated and unprotonated forms of 2-naphthol is the same in the ground and the

excited state, we obtain

$$N_A h(\nu_{NO^-} - \nu_{NOH}) = \Delta H^* - \Delta H = \Delta G^* - \Delta G = -RT \ln K_a^* + RT \ln K_a$$

The last equality assumes we are using standard conditions. Re-arranging this equation yields

$$-\ln K_a + \frac{N_A h(\nu_{NO^-} - \nu_{NOH})}{RT} = -\ln K_a^*$$

Converting from natural log to base 10 logs and dividing by 2.303,¹

$$pK_a^* = pK_a + \frac{N_A hc(\tilde{\nu}_{NO^-} - \tilde{\nu}_{NOH})}{2.303RT}$$

In this equation, $\tilde{\nu}$ is in units of wavenumbers (/cm). Be sure to put in the speed of light in units of cm/s.

Once we have the equilibrium constant for the ground state, we can use it to find the equilibrium constant for the excited state. The only other pieces of information that we need are the frequency of light that takes the ground 2-naphthol molecule to its excited state and the frequency of light that takes the ground conjugate base molecule to its excited state.

There are a variety of ways to obtain the frequency of light needed to excite a molecule from its ground state to the first excited state.

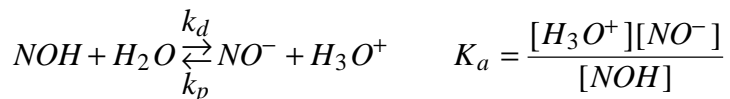
- (i) Use the frequency at the absorption maximum.
- (ii) Use the frequency at the fluorescence maximum of each species.
- (iii) Use the 0-0 energy of the molecule. This is the frequency at which emission and excitation spectra cross.

During the first week of this lab you will obtain the data needed for all of these methods. In your report, you should describe the differences.

¹Here's how you convert from natural log to base 10 logs. Consider $y = \ln(x)$. This means that $x = \exp(y)$. Take the base 10 log of both sides of the equation. $\log(x) = \log(e^y) = y \log(e)$. Solving for y which is $\ln(x)$, we get

$$y = \ln(x) = \frac{\log(x)}{\log(e)} \approx 2.303 \log(x)$$

Excited State Protonation and Deprotonation Constants

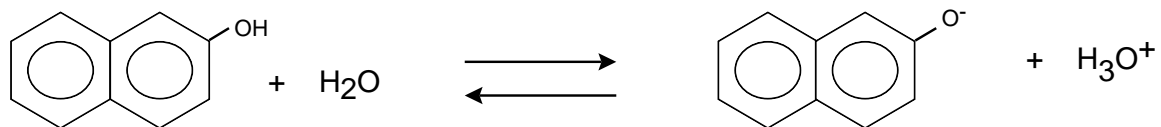
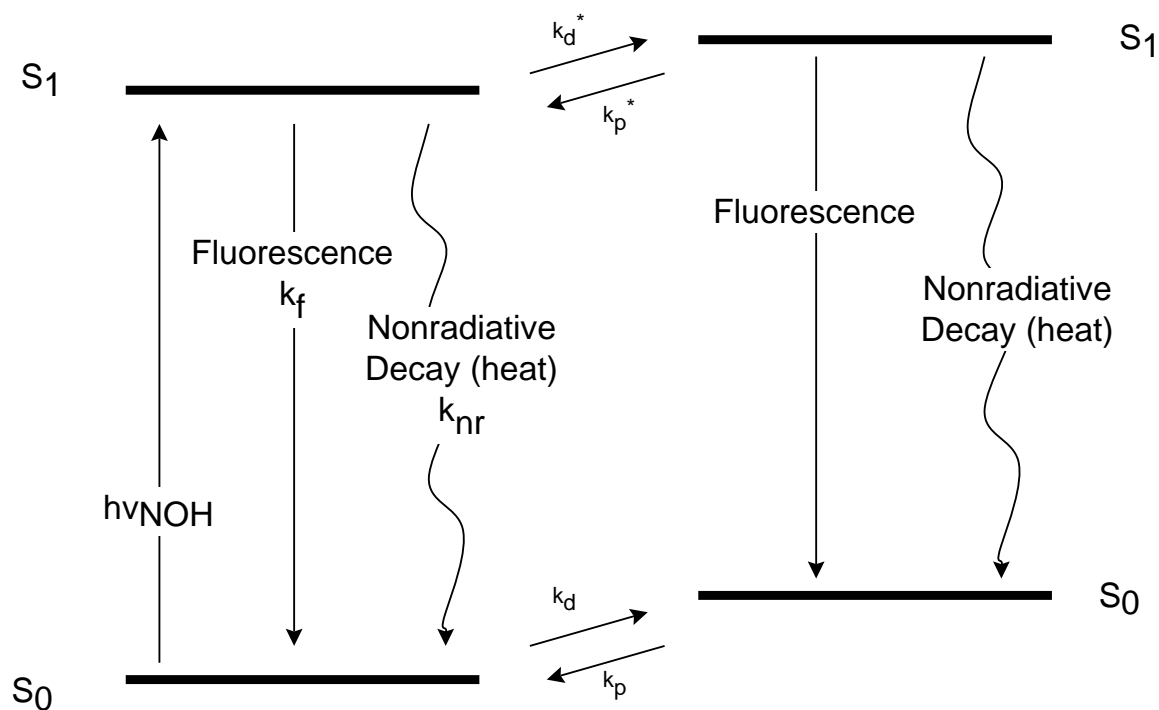


Now, we will obtain the rate of deprotonation and protonation in the excited state i.e. the forward and backward rates of the above reaction in the excited state. Notice that the $pK_a = -\log K_a$ can be rearranged to yield the following relation:

$$\log \frac{[NOH]}{[NO^-]} = pK_a - pH.$$

From this rearrangement, it's clear that if the pH is lower than the pKa, the 2-naphthol predominates. However, when the pH is higher than the pKa, the conjugate base dominates. From the first part of this experiment, you will find out that 2-naphthol is a stronger acid in its excited state i.e. its dissociation constant is larger in the excited state. The literature values for the ground and excited state acid equilibrium constants are 3.1×10^{-10} and 2.0×10^{-3} . As a result, the pKa is much lower in the excited state. This makes it possible to design an experiment in which the pH is lower than the ground state pKa but higher than the excited state pKa*. In such an experiment, 2-naphthol would predominate in the ground state. Then, it would be excited with light. In the excited state, 2-naphthol would quickly dissociate into its excited conjugate base. The excited conjugate base would decay to the ground state. It is also possible to design an experiment with the pH is lower than both of the pKas. In such a case, 2-naphthol would predominate in the ground and the excited state.

The beauty of playing with the pH of the solution is that we can change the pathway by which 2-naphthol decays back to the ground state. Consider the diagram below. Once 2-naphthol is excited, it can deprotonate or decay back to the ground state via either fluorescence or nonradiative decay. The plan is to first consider a solution with pH much lower than both the ground and excited state pKa i.e. a solution in which excited 2-naphthol can only get back to the ground state by fluorescing or nonradiative decay. In other words, the deprotonation route is blocked. This experiment would let us extract the sum of the rate constants for fluorescence and nonradiative decay. Once we have this sum, we could consider another experiment with a pH higher than pKa* but lower than pKa. In this experiment the deprotonation channel for excited 2-naphthol is open. With the data from such an experiment and the sum of the fluorescence and nonradiative decay rate constants, we'll be able to extract the deprotonation rate constant. The protonation rate constant is then obtained by dividing the deprotonation rate constant by the Ka*.



Here is a more concrete explanation of the strategy:

1. *Extracting the sum of the fluorescence and nonradiative decay rate constants:*
 Excite 2-naphthol in a solution with pH much lower than pK_a and pK_a^{*}. Monitor the intensity of the light emitted by 2-naphthol. We don't have a fluorimeter capable of monitoring this so you will be provided with some data to analyze. The rate of depletion of excited 2-naphthol is

$$\frac{d[\text{NOH}^*]}{dt} = -(k_f + k_{nr})[\text{NOH}^*].$$

Separating concentration and time variables and integrating t from 0 to t and [NOH*] from [NOH*]₀ to [NOH*],

$$\ln \frac{[NOH^*]}{[NOH^*]_0} = -(k_f + k_{nr})t$$

Since the fluorescence intensity is proportional to the concentration, we can replace $\frac{[NOH^*]}{[NOH^*]_0}$ by I/I_0 .

$$\ln \frac{I}{I_0} = -(k_f + k_{nr})t$$

You can plot $\ln(I/I_0)$ versus time and obtain the sum of the fluorescence and nonradiative decay rate constants from the slope.

2. Extracting the deprotonation constant:

Now, we will consider a solution with pH lower than the pKa but higher than pKa*. We will obtain this pH by using an acetate buffer. Because acetate is being used, we actually add yet another channel for depletion of excited 2-naphthol. Now, there is a possible acetate assisted deprotonation. We will still be able to extract the deprotonation constant by varying the acetate concentration.

The analysis is made simpler by considering the concept of quantum yield. The quantum yield of 2-naphthol in a low pH solution is the fraction of 2-naphthol molecules that fluoresce down to the ground state.

$$\phi_0 = \frac{\text{rate of fluorescence}}{\text{rate of all decay to ground state}} = \frac{k_f [NOH^*]}{k_f [NOH^*] + k_{nr} [NOH^*]} = \frac{k_f}{k_f + k_{nr}} .$$

The quantum yield in the acetate solutions has two more terms in the denominator - a deprotonation rate and an acetate assisted deprotonation rate.

$$\phi = \frac{k_f^*}{k_f + k_{nr} + k_d^* + k_{Ac}^* [Ac^-]}$$

Notice that the acetate assisted deprotonation depends not only on the concentration of excited 2-naphthol but also the concentration of the acetate ion.

The ratio of these two quantum yields is proportional to the ratio of the fluorescence intensities and is equal to

$$\frac{\phi_0}{\phi} = \frac{I_0}{I} = 1 + \frac{k_d^*}{k_f + k_{nr}} + \frac{k_{Ac}^*}{k_f + k_{nr}} [Ac^-] .$$

We will measure all the fluorescence intensities at the same wavelength. Clearly, from a plot of I_0/I versus acetate concentration, we can obtain the deprotonation constant from the intercept and the sum of the fluorescence and nonradiative decay constants. Finally, we will obtain the protonation constant from its relationship with the acid equilibrium constant and the deprotonation rate constant.

$$K_a^* = \frac{k_d^*}{k_p^*}$$

The literature value for k_d^* is 6.0×10^7 /s. The literature value for $k_{Ac^-}^*$ is 2.3×10^9 L/mole/s.

Designing your own extension of this laboratory

Think about the 2-naphthol system and look at the references. What questions haven't been answered? How can you answer them? Pick a question for future study and in your pre-lab outline how you would answer it. You may choose questions that are discussed in the references or other literature sources. Make a list of materials needed and include it with your prelab. During down time in the first week, you and your team can discuss your ideas and make a choice on which question you want to pursue. Be sure to let me know which question and set of materials you'll need before you leave lab on the first week. On the third week of this laboratory experience, you'll try your experimental design.

Procedure:

A. pKas

(i) *Preparing Solutions:* Make a pure acid, a pure base, and some intermediate solutions as suggested in the table below. Prepare these in 50.0 mL volumetrics. Be sure you record as many decimal places as your measuring device allows. Measure the pH of the buffered solutions.

Solution	1.00X10 ⁻³ M 2-naphthol	1.00 M NH ₃	1.00 M NH ₄ Cl	0.10 M H ₂ SO ₄	0.10 M NaOH
pure acid	10.0 mL	0 mL	0 mL	10.0 mL	0 mL
pure base	10.0 mL	0 mL	0 mL	0 mL	10.0 mL
1	10.0 mL	5.0 mL	5.0 mL	0 mL	0 mL

Solution	1.00X10 ⁻³ M 2-naphthol	1.00 M NH ₃	1.00 M NH ₄ Cl	0.10 M H ₂ SO ₄	0.10 M NaOH
2	10.0 mL	10.0 mL	5.0 mL	0 mL	0 mL
3	10.0 mL	5.0 mL	10.0 mL	0 mL	0 mL

(ii) Ground State pKa: Absorption Spectra

1. You will obtain the ground state equilibrium constant for this acid dissociation by using absorption spectroscopy. Be sure to make a background correction using distilled water first. Then, using the very acidic solution where only the acid form of 2-naphthol is present and the very basic solution where only the conjugate base is present, take the absorption spectrum of both species. (Suggested range: 250-400 nm. You should see a peak at about 344 nm for the conjugate base form and a peak at about 326nm for the acid.) Print both spectra and note the absorption maximum.

2. From the spectra taken in 1, you'll note that there is a region where the base is the only form to absorb. Pick a wavelength in this region. You will use the absorbance of the pure conjugate base solutions at this wavelength to find the proportionality constant between absorption and concentration for the base form. Look up Beer's law for your pre-lab to see how the absorption is related to the concentration.

3. Take the absorption spectra of the three buffered solutions. Print out a plot with all 5 spectra overlaid. What trends do you see? If you have made your solutions consistently, all the spectra should intersect at a single point, the isostilbic point. Be sure to label the spectra. Also, note the absorption of all your solutions at the wavelength chosen in step 2. From the absorption at these wavelengths and the proportionality constant found in step 2, you can find the concentration of the base form of 2-naphthol for each of the solutions. Since you know the total concentration of 2-naphthol in all forms and the concentration of 2-naphthol in base form, you can find out the concentration of 2-naphthol in the acid form.

4. Plot pH versus $\log \frac{[NO^-]}{[NOH]}$ and do a least squares fit to your data using your favorite program. What's the ground state equilibrium constant? How does it compare with the literature value for the pKa of 2-naphthol?

5. Use the absorption maxima for the acid and base forms of 2-naphthol to estimate the excited state equilibrium constant. How does it compare with the literature value?

(iii) First Excited State pKa: Fluorescence Spectra*

1. Take the fluorescence emission spectra of the pure acid and pure base forms.

- a. To do this, you will need to excite the acid at the frequency of its absorption maximum, 326nm. Then, scan the emission in the range 336-500nm. Save this spectrum. Now, take an excitation spectrum. In this case, you will watch the emission at the fluorescence maximum (354nm), and do an excitation scan from 300-344nm. This gives you a profile of the absorption on the same instrument as the emission. This avoids rescaling to compensate for different instrument signals. Overlay the emission and excitation spectra and find the frequency of the crossing point. It should be between 330 and 340 nm. This is the 0-0 frequency for the acid.
- b. Now you can take the same spectra for the base form. However, the base should be excited at its absorption maximum, 344nm. The scan of the emission should have a range of 354-500nm. When taking the excitation spectrum, you should watch the emission at the emission maximum which is around 419nm. The excitation range can be 300-409nm. Again overlay the emission and excitation spectra. The 0-0 frequency should be between 370 and 380 nm.
2. Now take the emission spectra of your intermediate pH solutions and overlay them. What pattern do you see? If you've made your solutions consistently, the spectra should intersect at a single point, the isostilbic point.
3. Now, use this 0-0 frequency to predict the excited state pKa*. How does it compare with the literature value? How does it compare with the pKa* obtained using the absorption maxima and fluorescence maxima?

B. Protonation and Deprotonation Rate Constants for the First Excited State

1. Make the following solutions in 25.0 mL volumetrics.

Solutions	1.00X10 ⁻³ M 2-Naphthol	0.50 M H ₂ SO ₄	0.200 M NH ₄ Ac	0.50 M NaOH
1	2.00 mL	5.0 mL	0.0 mL	0.0 mL
2	2.00 mL	0.0 mL	2.0 mL	0.0 mL
3	2.00 mL	0.0 mL	4.00 mL	0.0 mL
4	2.00 mL	0.0 mL	6.00 mL	0.0 mL
5	2.00 mL	0.0 mL	10.00 mL	0.0 mL
6	2.00 mL	0.0 mL	16.00 mL	0.0 mL
7	2.00 mL	0.0 mL	0.0 mL	5.00 mL

2. Obtain the emission spectra of all your solutions exciting at 320nm. Record the emission spectra in the range 336-500nm. Overlay the spectra and record the emission

at the emission maximum for 2-naphthol (~354nm). You can locate the maximum with the acid solution and use that as the monitoring wavelength in all your solutions.

Record the intensity at this wavelength for all your solutions.

3. Obtain the sum of the fluorescence and nonradiative decay constants by analysing the fluorescence lifetime data for 2-naphthol in 0.10 M sulfuric acid. We don't have an instrument fast enough to measure this so you'll use the data of Boyer et al. which is listed below. Use your favorite program.

Time (ns)	Intensity (photons emitted/time)
0.0	21753
1.0	18907
2.0	16380
3.0	14171
4.0	12432
5.0	10757
6.0	9288
7.0	8138
8.0	7083
9.0	6014
10.0	5350

4. Plot $\frac{I_0}{I}$ as a function of the acetate concentration. From this plot, obtain k_d^* and k_{Ac}^* . Find k_p^* . Remember I_0 is the intensity of the pure acid solution. Your plot should include solutions 2-6.

C. Electron density near oxygen

Use Gaussian to obtain the HOMO and LUMO for 2-naphthol with the PM3 method. Refer to the instructions given in the introduction to using Gaussian. This time instead of simply submitting the job after choosing Opt+Freq, choose an empty basis set and then add the word PM3 in the key word section. PM3 is a semi-empirical method which is sufficient for our purposes and takes less time than the ab initio methods. PM3 only considers valence electrons. You'll need to keep this in mind when selecting the HOMO and LUMO. Then, do the same analysis you did in the tutorial with formaldehyde.

Promoting an electron from the HOMO to the LUMO changes the electron density. The change in electron density is reflected in the change you see between the HOMO and the LUMO. Notice what happens. Make sure to discuss this in relation to your values for the equilibrium constants for the ground and excited states.

D. Experiment of your choice - Be sure to include the question and plan for answering it in your pre-lab. Also include a list of materials. During the first week, you'll discuss which question you choose to answer with your team and hand in the list of materials for that question at the end of the first week laboratory.

Group Strategy: Each group should do 1-4 and decide which experiment to do for D on the first week. During the second week, each team can do 5-8. Finally, on the third week 9 will be done.

Events	Group 1	Group 2	Group 3
A(i) Preparing Solutions	1	1	1
A(ii) Ground State pka: Absorption spectra and analysis.	2	4	3
A (iii), First Excited State pka*: Fluorescence Spectra	3	2	4
B 1. Preparing solutions	5	5	5
B 2 Emission Spectra	7	7	6
B 3 Getting the sum of the fluorescence and nonradiate decay constants	4	3	2
B 4 Analysis of Emission Spectra	8	8	7
C Electron Density	6	6	8
D. Your experiment	9	9	9

References:

Halpern, A. M; Reeves, J. H, *Experimental Physical Chemistry*, Scott, Foresman and Company, Boston, 1988.

Boyer, R.; Deckey, G.; Marzzacco, C.; Mulvaney, M.; Schwab, C.; Halpern, A. M. "The Photophysical Properties of 2-Naphthol: A physical chemistry experiment," *J. Chem. Ed.* **1985**, 62, 630.

van Stam, J.; Lofroth, J. "The Protolysis of Singled Excited β -naphthol. A two-day laboratory experiment to introduce photophysics," *J. Chem. Ed.* **1986**, 63, 181.

Marzzacco C.; Cooley, L. "The ground and Excited State Ionization Constants of 2-Naphthol" and "The Rate Constants for the Excited-State Deprotonation-Protonation Reaction of 2-Naphthol." Laboratory write ups from Rhode Island College.

Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.