Quiz 6 – Core Course 2002 Name: ______________________________

Please show your work, and your thinking, in the space provided. Be brief, but complete. Long, wandering answers typically demonstrate a lack of understanding…

$\hbar = 1.054x10^{-34}\,J\,s$

$h = 6.626x10^{-34}\,J\,s$

$m_e = 9.109x10^{-31}\,kg$

$c = 2.998x10^{8}\,m\,s^{-1}$

$k = 1.381x10^{-23}\,J\,K^{-1}$

$e = 1.602x10^{-19}\,C$

$4\pi\varepsilon_o = 1.113x10^{-10}\,J^{-1}\,C^2\,m^{-1}$

$N_0 = 6.022x10^{23}\,mol^{-1}$

$\pi = 3.14159$

Particle in a 1D box

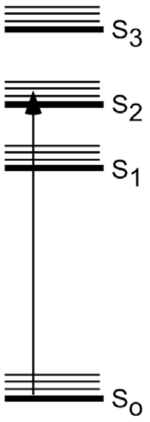
$$\psi_n = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi x}{L}\right)$$

$$E_n = \frac{n^2h^2}{8mL^2} \qquad n = 1,2,3,\ldots$$

$$H_{translational} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} \qquad p_{translational} = \frac{\hbar}{i}\frac{d}{dx} \qquad A = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$$

$$For \quad z = x + iy, \qquad z^* = x - iy$$

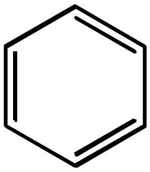
1. (20 points) You are carrying out fluorescence measurements on a molecule in solution whose electronic properties are described at right. When you go to carry out fluorescence anisotropy measurements using the S_o to S_2 transition shown, you find that the anisotropy is *negative*. What behavior would lead to negative anisotropy? Explain how this might occur.



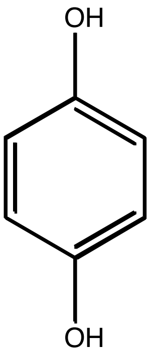
Negative anisotropy means that the fluorescence detected perpendicular to the excitation polarization is greater than that detected parallel. It is unreasonable to think that molecules would all rotate a particular way after excitation. There must be something else going on.

Rather, it is likely that molecules in the excited state S_2 relax down to state S_1 before emitting fluorescence. It may well be that whereas transitions along only x, for example, are allowed for S_o to S_2 mixing, transitions along only y are allowed for transitions between S_o and S_1. Note that the same argument involving S_3 rather than S_1 is *not* valid, since you would not expect state S_2 to relax to S_3 (higher energy).

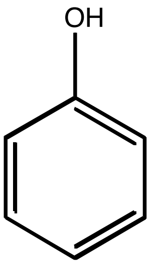
2. Consider the following molecules:



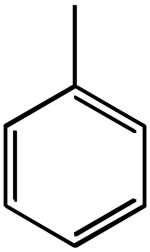
A



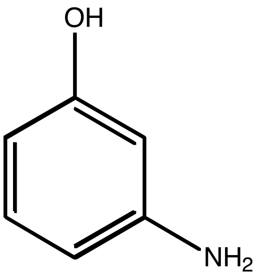
B



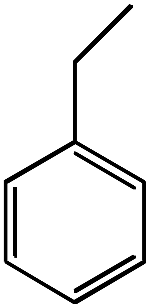
C



D



E



F

In the following, indicate ranking as follows: **C < B < (A,D) < E**
To indicate that you don't have enough information to predict a significant difference between A and D, for example. Don't pull your hair out…

a) (10 points) use simple considerations to rank them in terms of their expected extinction coefficients (lowest to highest):

(A,D,F) < (B,C) < E think "*symmetry* of the π system"
perhaps
(A,D,F) < B < C < E

b) (10 points) use simple considerations to rank them in terms of their expected wavelengths of maximal absorbance (lowest to highest):

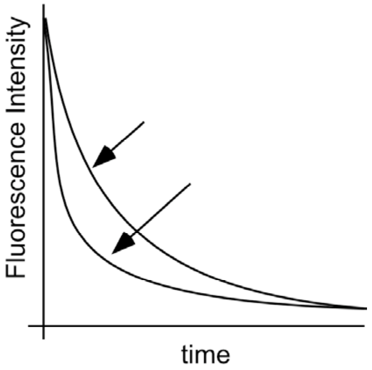
(A,D,F) < C < (B,E) think "*size* of the π system"

3. Consider fluorescence for two otherwise identical molecules you are studying.
   Molecule A has an internal conversion rate constant of **0.2 nsec^{-1}**.
   Molecule B has an internal conversion rate constant of **1.0 nsec^{-1}**.
   Assuming all else equal:

   a) (15 points) Which will have the higher fluorescence intensity?

   A will have higher intensity. Slower k_{is} means longer excited state lifetime, so more chance for fluorescence (or, less competition from k_{is})

   b) (15 points) Consider the fluorescence decay curves shown at right. In the experiment, you excite briefly with a laser, turn it off, and then monitor fluorescence as a function of time. Assign each curve to either molecule A or B.



   Top Curve: A Lower Curve: B
   Again, lower k_{is} means decay of excited state is slower.

4. The location of an electron constrained to move on a ring is given by the angle ϕ, where $0 \le \phi \le 2\pi$. The Hamiltonian for the system is:

$$H = \frac{-\hbar^2}{2I}\frac{d^2}{d\phi^2} \qquad I = m_e r^2$$

   Given the wavefuntion: $\psi_m(\phi) = Ae^{im\phi}$ (in this case, m is a quantum number)

   a) (15 points) calculate the value of the constant A.

$$\int_0^{2\pi}\psi_m^*\psi_m(\phi)d\phi = 1$$

$$\int_0^{2\pi}\left(Ae^{-im\phi}\right)\left(Ae^{im\phi}\right)d\phi = A^2\int_0^{2\pi}e^0 d\phi = A^2(2\pi - 0) = 1 \qquad A = \sqrt{\frac{1}{2\pi}}$$

   b) (15 points) Find the energy levels for this system.

$$H\psi = \frac{-\hbar^2}{2I}\frac{d^2}{d\phi^2}\sqrt{\frac{1}{2\pi}}e^{im\phi} = \frac{-\hbar^2}{2I}\sqrt{\frac{1}{2\pi}}\frac{d^2}{d\phi^2}e^{im\phi} = \frac{-\hbar^2}{2I}\sqrt{\frac{1}{2\pi}}im\frac{d}{d\phi}e^{im\phi}$$

$$= \frac{-\hbar^2}{2I}\sqrt{\frac{1}{2\pi}}i^2m^2e^{im\phi} = \frac{\hbar^2m^2}{2I}\sqrt{\frac{1}{2\pi}}e^{im\phi} = \frac{\hbar^2m^2}{2I}\psi = E\psi$$

$$E_m = \frac{\hbar^2m^2}{2I}$$ (remember that m is a quantum number, not a mass)

c) (Small extra credit) What molecule might this be good for?

Benzene