

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

$$\begin{aligned} \hbar &= 1.054 \times 10^{-34} \text{ J s} \\ h &= 6.626 \times 10^{-34} \text{ J s} \\ m_e &= 9.109 \times 10^{-31} \text{ kg} \\ c &= 2.998 \times 10^8 \text{ m s}^{-1} \\ k &= 1.381 \times 10^{-23} \text{ J K}^{-1} \end{aligned}$$

$$\begin{aligned} e &= 1.602 \times 10^{-19} \text{ C} \\ 4\pi\epsilon_0 &= 1.113 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1} \\ N_0 &= 6.022 \times 10^{23} \text{ mol}^{-1} \\ \pi &= 3.14159 \end{aligned}$$

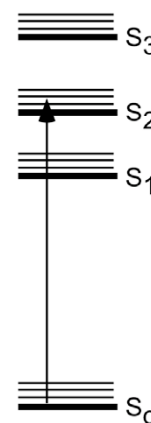
**Particle in a 1D box**

$$\begin{aligned} \psi_n &= \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \\ E_n &= \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3, \dots \end{aligned}$$

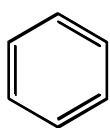
$$H_{\text{translational}} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \quad p_{\text{translational}} = \frac{\hbar}{i} \frac{d}{dx} \quad A = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$$

For  $z = x + iy$ ,  $z^* = x - iy$

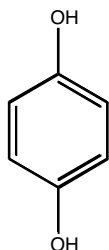
1. (20 points) You are carrying out fluorescence measurements on a molecule in solution whose electronic properties are described at right. When you go to carry out fluorescence anisotropy measurements using the  $S_0$  to  $S_2$  transition shown, you find that the anisotropy is *negative*. What behavior would lead to negative anisotropy? Explain how this might occur.



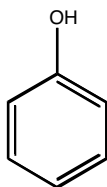
2. Consider the following molecules:



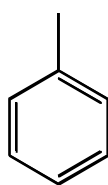
**A**



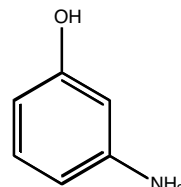
**B**



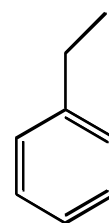
**C**



**D**



**E**



**F**

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

Don't pull your hair out on this one...

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

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

3. Consider fluorescence for two otherwise identical molecules you are studying.

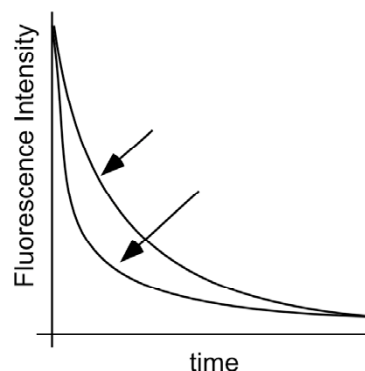
**Molecule A** has an internal conversion rate constant of **0.2 nsec<sup>-1</sup>**.

**Molecule B** has an internal conversion rate constant of **1.0 nsec<sup>-1</sup>**.

Assuming all else equal:

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

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.



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

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

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

- a) (15 points) Derive the value of the constant  $A$  (do not use a calculator)

- b) (15 points) Derive the energy levels for this system (do not use a calculator).

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