

Physical Chemistry Cumulative Exam

Topic: Einstein Coefficients

April 2018

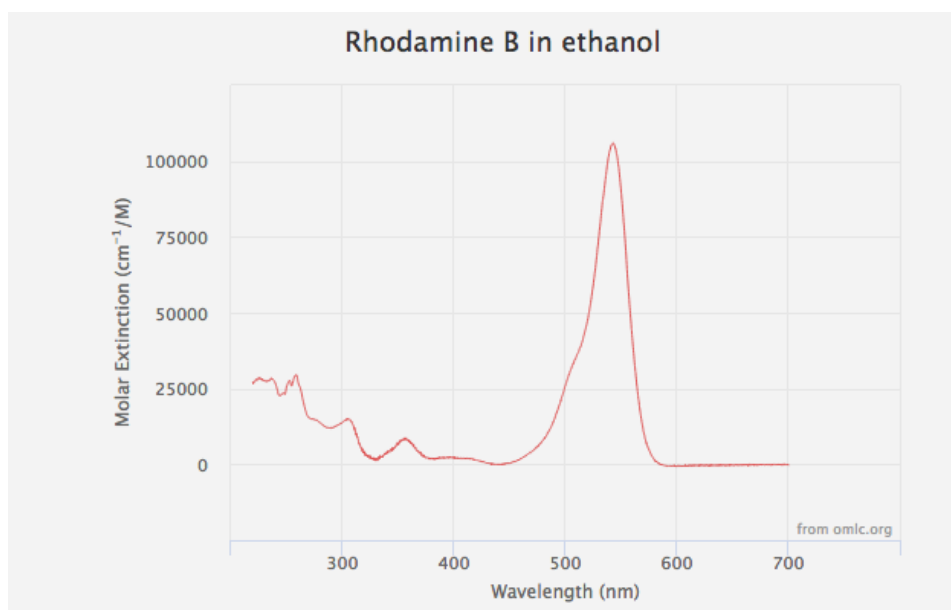
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1. (a) Derive the expression that relates the ratio of rate constants for spontaneous to stimulated emission with the frequency of emitted photons. Assume that the energy density of the radiation can be approximated using the blackbody model, as:

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

(b) Using the expression obtained in (a), explain why masers were discovered before the lasers.

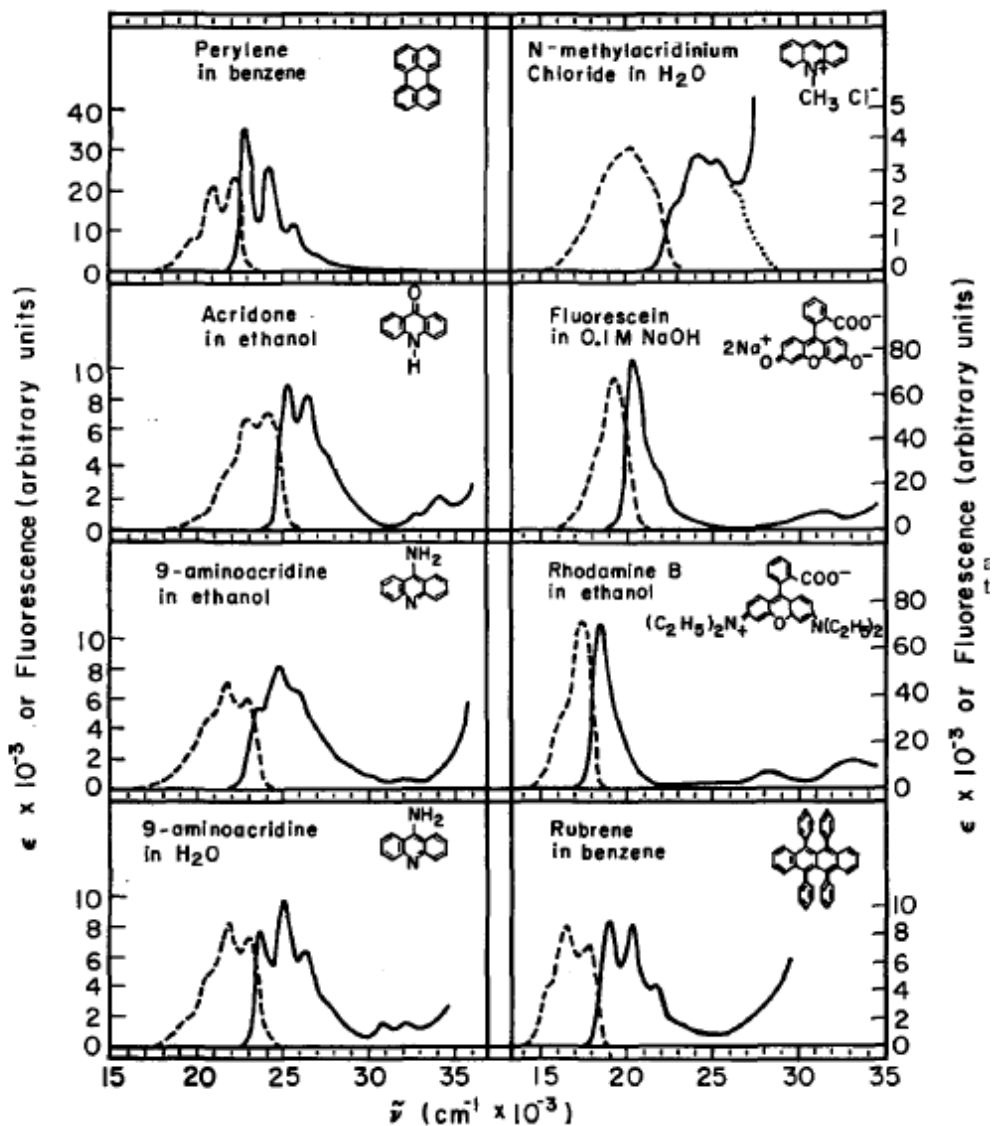
2. (a) What is transition dipole moment? Use an equation to define it.
(b) Why do we care about the transition dipole moment? What experimental value does it predict?
(c) Consider the absorption spectrum for Rhodamine B in ethanol:



Describe how you would use this data set to calculate the transition dipole moment for $S_0 \rightarrow S_1$ transition of Rhodamine B. Provide all details: how would you modify the data set, what range would you integrate, what equation would you use, etc.

3. (a) What is the difference between fluorescence lifetime and radiative lifetime? Write an equation that relates the two quantities.

- (b) What experimental method would you use to determine the fluorescence lifetime of a chromophore?
- (c) What experimental method would you use to determine the radiative lifetime of a chromophore.
- (d) The absorption spectra of eight different compounds are shown below as solid lines:



Arrange these eight compounds in the order of increasing radiative lifetime. Explain your reasoning.