Take-Home Examination 2 **December 6, 1996**

Chemistry 262 - 60 points **Dr. Jay H. Baltisberger**

Name: ________________________

Please answer all questions, showing all calculations

1. Suppose two molecules (A and B) dissolve in solution such that they form a complex (C) in the reaction: A + 2 B —> C. The molar absorptivities are ε_A = 325 M^{-1} cm^{-1}, ε_B = 0 M^{-1} cm^{-1}, ε_C = 15500 M^{-1} cm^{-1}. Calculate the equilibrium constant for the reaction, as well as the concentration of all species in solution, given that the absorbance of an equilibrium mixture is 1.970 in a 1 cm cell if the initial concentrations of both A and B were $5.92x10^{-3}$M. (15 points)

   You know that $[A_0] = [B_0] = 5.92x10^{-3}$ M. At equilibrium, $[A_{eq}] = 5.92x10^{-3}$ M – $[C_{eq}]$, $[B_{eq}] = 5.92x10^{-3} - 2\ [C_{eq}]$. The observed absorption will be 1.970 = l (ε_A [A] + ε_B [B] + ε_C [C]) = 1 cm (325 M^{-1} cm^{-1} ($5.92x10^{-3}$ M – $[C_{eq}]$) + 15500 M^{-1} cm^{-1} $[C_{eq}]$) = 1.924 + 15175 M^{-1} $[C_{eq}]$. This give $[C_{eq}]$ = $3.03x10^{-6}$ M, $[A_{eq}]$ = 5. $92x10^{-3}$M, $[B_{eq}]$ = $5.92x10^{-3}$M. Since K = $[C_{eq}]$ / $[A_{eq}]$ $[B_{eq}]^2$ = 14.61.

2. Suppose the fluorescence of a molecule is quenched by Na^+ ions. If the measured lifetime is 8.1 ns in the absence of Na^+ and 2.3 ns when $[Na^+]$ = 0.0005 M, calculate the the rate constant k_Q. Calculate the intensity of a solution where $[Na^+]$ = 0.0002 M given that an unquenched solution has an intensity of 100. (15 points)

   Assume that $\tau = (k_f + k_t + k_p + k_Q[Q])^{-1} = (K + k_Q[Na^+])^{-1}$. If $[Na^+]$ = 0 M and τ = 8.1 ns, then K = 1 / τ = $1.23x10^8$ s^{-1}. Now we may solve for k_Q when [Na+] = 0.0005 M, τ = 2.3 ns by inserting into the equation $\tau = 2.3x10^{-9}$ s = $(K + k_Q[Na^+])^{-1}$ = $(1.23x10^8\ s^{-1} + 0.0005\ M\ k_Q)^{-1}$. This gives k_Q = $6.23x10^{11}$ s^{-1} M^{-1}. To calculate the intensity at 0.0002 M, we only need to compare τ at this concentration to the unquenched τ = 8.1 ns. At this concentration, $\tau = (1.23x10^8\ s^{-1} + 0.0002\ M\ x\ 6.23x10^{11}\ s^{-1}\ M^{-1})^{-1}$ = 4.03 ns and thus ϕ_f = (4.03 / 8.1) x 100= 49.78.

3. Which of the following molecules will exhibit a pure rotational (microwave) spectrum? Which will exhibit a rotational raman spectrum? (15 points)

   To observe pure microwave spectrum, molecule must posess a dipole moment. To observe rotational raman spectrum, molecule must possess an anisotropic polarizability (changes upon rotation).

   SF_6 (octahedral) – *This molecule is completely symmetric and has no dipole moment, thus it exhibits neither variety of spectra.*

   CO_2 (linear) – *This molecule has no dipole moment, so no rotational spectrum, but it does has an anisotropic polarizability (bond axis differs from perpendicular axis).*

   NNO (linear) – *This molecule has a dipole moment as well as anisotropic polarizability, thus exhibiting both spectra.*

   XeF_4 (squar planar) – *This molecule has no dipole moment, but it does have anisotropic polarizability, thus like CO_2, only rotational raman spectrum.*

4. Draw your expectation of what the 1D spectrum (i.e. what are the multiplicities for each different hydrogen type) as well as the 2D-COSY spectrum (i.e. what are the COSY connectivities between various hydrogens) for 2-chloro-4-ethyl-5-methyl-3-octanone would look like, assume that all protons are fully resolved. (15 points)