Problem Set 8

14.9

The lifetime of an excited state is related to its natural linewidth via \( \Delta \nu = 1/4\pi \Delta t \).

(a) Since \( \nu = c \tilde{\nu} \),
\[ \Delta t = 1/4\pi \Delta \nu = 1/4\pi c \Delta \tilde{\nu} \]
\[ = 1/4\pi (3.00 \times 10^{10} \text{ cm s}^{-1})(1 \text{ cm}^{-1}) \]
\[ = 2.7 \times 10^{-12} \text{ s} \]

(b) \( \Delta t = 1/4\pi \Delta \nu = 1/4\pi (0.50 \text{ s}^{-1}) = 0.16 \text{ s} \)

14.10

With 86% of light absorbed, the transmittance is \( T = 1.00 - 0.86 = 0.14 \), and the absorbance is \( A = - \log T = - \log 0.14 = 0.854 \). Then using the Beer-Lambert law, \( A = \varepsilon bc \),
\[ \varepsilon = A/bc = 0.854/(1.0 \text{ cm})(0.16 \text{ M}) = 5.3 \text{ L mol}^{-1} \text{ cm}^{-1} \]

14.27

\[ \nu = (k/\mu)^{1/2} / 2\pi \]

and \( \nu = c \tilde{\nu} = (3.00 \times 10^{8} \text{ m s}^{-1})(2081.0 \text{ cm}^{-1})(100 \text{ cm/1 m}) = 6.24 \times 10^{13} \text{ s}^{-1} \)

The reduced mass for D\(^{35}\)Cl is
\[ \mu = m_{D}m_{Cl}/(m_{D} + m_{Cl}) \]
\[ = (1.66 \times 10^{-27} \text{ kg amu}^{-1})(2.01 \text{ amu})(35.0 \text{ amu})/(2.01 \text{ amu} + 35.0 \text{ amu}) \]
\[ \mu = 3.16 \times 10^{-27} \text{ kg} \]

Then using the first equation above,
\[ k = 4\pi^2 \mu \nu^2 = 4\pi^2 (3.16 \times 10^{-27} \text{ kg})(6.24 \times 10^{13} \text{ s}^{-1})^2 = 487 \text{ kg s}^{-2} = 487 \text{ N m}^{-1} \]

This is essentially the same answer as found in Example 14.2, which we would expect, since isotopic substitution does not affect the electronic configuration and thus does not affect the force constant for the bond.
Fluorescence involves the emission of photons following absorption to an excited electronic state. Phosphorescence also involves emission of light from an excited electronic state, but the state is reached by a radiationless transition following absorption. In phosphorescence, emission of a photon usually occurs with the transition from a triplet state to a singlet state, which is “spin forbidden”, meaning it occurs with small probability. The transition is weak, and it typically takes milliseconds to seconds for phosphorescence. Fluorescence has a very much shorter lifetime, on the order of nanoseconds.

The tryptophan is most likely located in the interior of the protein in a region inaccessible to the iodide ion.

We define the concentrations of A and B as $c_A$ and $c_B$, respectively. The contribution of each optical isomer toward the total specific rotation is directly proportional to the mole fraction of the isomer. Calling $x$ the mole fraction of B, so that $x = c_B / (c_A + c_B)$, then $c_A / (c_A + c_B) = 1 - x$, (the sum of the mole fractions of A and B must = 1), and

$$[\alpha_{\text{mix}}]_\lambda^T = (1-x)[\alpha_A]_\lambda^T + x[\alpha_B]_\lambda^T$$

$$16.2^\circ = (1-x)(27.6^\circ) + x(-19.5^\circ) \quad \text{so} \quad x = 0.2420$$

The equilibrium constant is $K = c_B/c_A = (c_B / (c_A + c_B)) / (c_A / (c_A + c_B)) = x/(1-x)$

so $K = 0.2420/(1-0.2420) = 0.319$

At the higher temperature, the rotation about the C-N bond becomes rapid enough to average out the chemical environment and thus the chemical shifts of the two methyl groups. Consequently, only one NMR peak for the methyl groups is seen. At 25 °C, the rotation is slower than the NMR time scale, and each peak is observed separately.