Physical Chemistry Lab II
CHEM 4644  Spring 2015  Final Exam
Name: _________

average = 10.5 / 15

5 questions at 3 points each equals 15 total points possible.

Constants:
\[ c = 3.00 \times 10^8 \text{ m/s} \]
\[ h = 6.63 \times 10^{-34} \text{ J-s} \]
\[ 1 \text{ Hartree} = 4.36 \times 10^{-18} \text{ J} = 27.21 \text{ eV} \]
\[ N_A = 6.02 \times 10^{23} \text{ /mol} \]
\[ m_e = 9.11 \times 10^{-31} \text{ kg} \]
\[ 1 \text{ nm} = 10^{-9} \text{ m} \quad 1 \text{ pm} = 10^{-12} \text{ m} \quad 1 \text{ Å} = 10^{-10} \text{ m} \]
1. Dyes.
Mamoru Fujitsuka, et al., published absorption and fluorescence spectra of hoop-shaped π-conjugated \([n]\) cycloparaphenylenes (CPP). The 8-ring \([8]\) CPP is shown at right. Absorption and fluorescence spectra of 8, 10 and 12-ring CPPs are below.  
*[Physical Chemistry Chemical Physics, 14, 1485-1488, 2012.]*

Mamoru Fujitsuka wrote that a “striking characteristic of CPPs is the smaller HOMO-LUMO gap found in smaller CPPs. This characteristic is completely in contrast to that of the linear π-conjugated systems …”

![](Image)

**a.** Explain how the absorption spectra above (all three have \(\lambda_{\text{max}} \approx 340\) nm) relate to the “HOMO-LUMO” gap. A few sentences or a sketch will suffice.

**b.** What is a striking difference between the spectra shown and those expected for linear π-conjugated molecules?

**Answer:**  
**a.** The wavelength of maximum absorption \(\lambda_{\text{max}}\) is approximately \(hc/(\Delta E)\), where \(\Delta E\) is the HOMO-LUMO gap.  

**b.** Generally, \(\Delta E\) decreases and so \(\lambda_{\text{max}}\) increases with size of a conjugated system. The absorption spectra show the same \(\lambda_{\text{max}}\) for all \(n\).

**not assigned:** For fluorescence, too, one might expect \(\lambda_{\text{max}}\) to increase with conjugation length, but the opposite trend is observed.
2. fluorescence and phosphorescence

At right are two spectra of erythrosin B in silica gel. The spectra were taken at room temperature under vacuum. One spectrum is fluorescence, the other is phosphorescence. Which is which and how do you know?

**Answer:** Phosphorescence is the longer-wavelength spectrum. That is the usual case because the excited triplet state has lower energy than the excited singlet state.

The same erythrosin sample, but exposed to varying oxygen pressures, gave the spectra at left. All spectra were taken at the same temperature, room temperature. The numbers labeling the spectra are oxygen pressures in mbar. Oxygen is quenching emission by enhancing non-luminescent transitions from the excited triplet state ($T_1$) and the excited singlet state ($S_1$) to the ground state ($S_0$).

Based on the spectra, does the presence of oxygen change the energy of the $T_1$ state relative to the $S_0$ state? Explain your conclusion.

**Answer:** The peaks near 705 nm are due to the $T_1$-to-$S_0$ transition. The peak wavelength does not change as the oxygen pressure changes, so likely the energy difference between the $T_1$ and $S_0$ states also does not change.
3. bond strength, overtones, anharmonicity

The energy of the \( \nu \)th state of a harmonic oscillator, in wavenumbers, is

\[
G(\nu) = (\nu + 1/2)\bar{\nu} - x_e \bar{\nu} (\nu + 1/2)^2
\]

To calculate the strength of the C-H bond in chloroform we measured spectral positions of the fundamental and overtones of the C-H stretching mode. Consider using anharmonicity of the C-Br vibration in methyl bromide, CH\(_3\)Br, to measure the strength of the C-Br bond. Here are four calculated vibration frequencies (DFT M06 6-31g(d,p)), with arrow depictions of the modes:

![Diagrams of modes 7, 8, 9, and 12]

a. We should measure absorption due to which mode (i.e., mode 7, 8, 9, or 12)?

b. Estimate the location in wavenumbers of the first vibrational overtone. Assume \( x_e \approx 0.02 \).

c. Based on your estimate, will that overtone be observed in the infrared spectrum, the near-infrared spectrum, or the visible spectrum?

Answers:

a. Mode 7 is the C-Br stretching mode

b. first overtone:

\[
G(2) - G(0) = 2\bar{\nu} - (5/2)^2 x_e \bar{\nu} e + (1/2)^2 x_e \bar{\nu} e = 2\bar{\nu} - 6 x_e \bar{\nu} e = (2 - 6 x_e)\bar{\nu} e
\]

\[
G(2) - G(0) = (2 - 6 \times 0.02) 640 = 1.88 \times 640 = 1203 \text{ cm}^{-1}
\]

c. 1203 cm\(^{-1}\) is in the infrared

For me: predicted overtones are 1203, 1766, 2304, 2816 cm\(^{-1}\), all in the IR
4. Analysis of the Fermi resonance in CO\textsubscript{2} used the following two equations:

\[
\begin{vmatrix}
E^{(0)}_{100} - E & F \\
F & E^{(0)}_{020} - E
\end{vmatrix} = 0 \quad \text{and} \quad c_1^2 + c_2^2 = 1. \quad (\text{Recall that } \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc.)
\]

In the determinant, E equals either \(E_+\) or \(E_-\), the observed Raman peak locations.

An ideal case of Fermi resonance would have \(c_1^2 = c_2^2\) and \(E^{(0)}_{100} = E^{(0)}_{020}\).

Suppose such an ideal case, and these values:

\(E_+ = 1248 \text{ cm}^{-1}\), \(E_- = 1374 \text{ cm}^{-1}\), \(E^{(0)}_{100} = E^{(0)}_{020} = 1311 \text{ cm}^{-1}\)

Calculate \(F\) (2 points) and \(c_1\) (1 point).

Answer:

\[
\begin{vmatrix}
1311 - E & F \\
F & 1311 - E
\end{vmatrix} = \begin{vmatrix} 1311 - 1248 & F \\ F & 1311 - 1248 \end{vmatrix} = (1311 - 1248)^2 - F^2 = 0
\]

\(F = 1311 - 1248 = 63 \text{ cm}^{-1}\)

Because \(c_1 = c_2\) and \(c_1^2 + c_2^2 = 1\), \(c_1 = 1/\sqrt{2} = 0.71\)
5. vibration-rotation spectra
Some possibly useful equations:

\[ B_e \equiv \frac{\hbar}{8\pi^2 \mu R_e^2} ; \quad \mu = m_A m_B / (m_A + m_B) ; \quad B_v = B_e - \alpha_e (v + \frac{1}{2}) \]

\[ E(v, J) = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + B_e J(J+1) - \alpha_e (v + \frac{1}{2}) J(J+1) - D_e J^2 (J+1)^2 \]

Vibration-rotation spectra of HBr (the bromine-79 isotope) recently were analyzed by Coxon and Hajigeorgiou [John A. Coxon, Photos G. Hajigeorgiou, *Journal of Quantitative Spectroscopy & Radiative Transfer*, 151, 133-154, 2015]. They calculated rotation constants \( B_v \) for the first eight values of the vibrational quantum number \( v \). Below is a graph of their experimental \( B_v \) versus \((v+1/2)\). Below that is Excel’s regression report for the linear trend line.

a) Based on the graphed and tabulated data, what are the values of \( \alpha_e \) and \( B_e \)? Include units.

b) A literature value of \( B_e \) is 8.46752 cm\(^{-1}\). Does that literature value differ significantly from the experiment-based value you gave in answer to question a? (Explain, do not just answer "yes" or "no.")

c) Explain why, based on bond length, the slope of the graph must be negative.

\[
\begin{array}{c|c|c|c|c}
\text{Coefficients} & \text{Standard Error} & \text{Lower 95\%} & \text{Upper 95\%} \\
\hline
\text{Intercept} & 8.471374 & 0.002971 & 8.464104 & 8.478644 \\
\text{X Variable 1} & -0.233691 & 0.000645 & -0.235268 & -0.232114 \\
\end{array}
\]

Answers:

a) \( \alpha_e \) is the negative of the slope: 0.2337 cm\(^{-1}\).

\( B_e \) is the intercept: 8.471 cm\(^{-1}\).

b) Here are three possible answers:

• The confidence interval, (8.4641, 8.4786) includes 8.46752, so the difference is not significant.
• \( B_e \pm 2\sigma = (8.471 - 2\times0.003, 8.471 + 2\times0.003) = (8.465, 8.477) \) includes 8.467, so the difference is not significant.
• \( B_e \pm \sigma = (8.471 - 0.003, 8.471 + 0.003) = (8.468, 8.474) \) does not (quite) include 8.467, so the difference may be significant.

c) As the vibrational quantum number increases, the bond length \( R_e \) increases. That causes \( B_v \) to decrease. \( B_v \) being a decreasing function of \( v \) is equivalent to a negative slope.