CHEM 352: Examples for chapter 5.

1. 
   a) The molar absorption coefficient of a substance dissolved in hexane is 
   \( \epsilon = 855 \text{ L mol}^{-1} \text{ cm}^{-1} \) at \( \lambda = 270 \text{ nm} \). Calculate the intensity reduction 
   in percentage when light passes through a 2.5 mm thick film of 3.25 
   mmol/L solution.

   b) Consider a 10 mmol/L solution of benzene in a non-absorbing solvent. 
   The solution was placed in a 2.0 mm thick cuvette and the transmission 
   of 256 nm light through the sample was observed to be 48 %. What 
   is the molar absorption coefficient of benzene at 256 nm? What would 
   be the transmittance when using a 4.0 mm thick cuvette at the same 
   wavelength?

   Solution:

   Recall the Lambert-Beer law: \( \log \left( \frac{I_0}{I} \right) = \epsilon [A] l \) where \( I_0 \) is the incident light 
   intensity, \( I \) is the intensity of light passing through the sample, \( \epsilon \) is the molar 
   absorption coefficient, \( [A] \) is the concentration of compount A, and \( l \) is the 
   length of the sample.

   a) \( \log \left( \frac{I_0}{I} \right) = (855 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (3.25 \times 10^{-3} \text{ mol/L}) \times (0.25 \text{ cm}) = 0.695. \)
   Now from \( \frac{I_0}{I} = 10^{0.695} = 0.20 \), which means that the intensity was reduced 
   by 80%.

   b) Recall that \( T = \frac{I}{I_0} \). Now \( \epsilon = \frac{1}{[A]l} \log \left( \frac{I_0}{I} \right) = \frac{1}{(0.010 \text{ mol/L})(0.20 \text{ cm})} \log(2.08) = 
   159 \text{ L mol}^{-1} \text{ cm}^{-1}. \) This gives \( T = \frac{I}{I_0} = 10^{-159 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1} \times 0.010 \text{ mol/L} \times 0.40 \text{ cm}} = 0.23. \) This corresponds to 23%.

2. Compare the ratio \( A/B \) between the Einstein spontaneous and stimulated 
   emission coefficients for the following wavelengths: a) \( \lambda = 70.8 \text{ pm} \) (X-ray), 
   b) \( \lambda = 500 \text{ nm} \) (visible light), c) \( \tilde{\nu} = 3000 \text{ cm}^{-1} \) (IR), d) \( \lambda = 3 \text{ cm} \) (microwaves), e) \( \nu = 500 \text{ MHz} \) (radiowaves). What does this tell you about the 
   significance of the spontaneous emission at different energies?

   Solution:

   The ration between the two coefficients is given by:
\[
\frac{A}{B} = \frac{8\pi \hbar \nu^3}{c^3} \text{ where } \nu = \frac{c}{\lambda} = \frac{c}{\tilde{\nu}}
\]

a) X-ray: \( \nu = \frac{2.9979 \times 10^8 \text{ ms}^{-1}}{7.08 \times 10^{-11} \text{ m}} = 4.23 \times 10^{18} \text{ s}^{-1}. \) \( A/B = 46.9 \times 10^{-3}. \)

b) Visible: \( \nu = \frac{2.9979 \times 10^8 \text{ m s}^{-1}}{5.00 \times 10^{-7} \text{ m}} = 6.00 \times 10^{14} \text{ s}^{-1}. \) The ratio \( \text{“visible / X-ray”} = \frac{\nu_{\text{vis}}}{\nu_{\text{X-ray}}} = 2.84 \times 10^{-12}. \)

c) IR: \( \nu = (2.9979 \times 10^{10} \text{ cm s}^{-1})(3000 \text{ cm}^{-1}) = 8.99 \times 10^{13} \text{ s}^{-1}. \) The “IR / X-ray” ratio is now \( 9.58 \times 10^{-15}. \)

d) Microwaves: \( \nu = \frac{2.9979 \times 10^8 \text{ m s}^{-1}}{3.00 \times 10^{-2} \text{ m}} = 9.99 \times 10^{9} \text{ s}^{-1}. \) The ratio is \( 13.1 \times 10^{-27}. \)

e) Radiowaves: \( \nu = 500 \text{ MHz} = 500 \times 10^6 \text{ s}^{-1}. \) The ratio is \( 1.65 \times 10^{-30}. \)

In X-ray region the spontaneous emission contributes to about 4.7%. This contribution decreases rapidly as the photon energy decreases.

3.

a) Calculate the relative Doppler broadening for gaseous ICl molecules at 25 °C. What are the linewidths \( \delta \nu_{\text{rot}} \) (kHz) and \( \delta \nu_{\text{vib}} \) (cm\(^{-1}\)) when the rotational constant \( B = 0.1142 \text{ cm}^{-1} \) and the vibrational frequency is \( \nu = 384 \text{ cm}^{-1}. \)

\[ \frac{\delta \lambda}{\lambda} = \frac{2}{c} \sqrt{\frac{2kT \ln(2)}{m}} \]

\[ = \frac{2}{2.998 \times 10^8 \text{ m/s} \sqrt{2 \left(1.381 \times 10^{-23} \text{ JK}^{-1}\right) \left(298 \text{ K}\right) \ln(2)}}_{162 \text{ u} \times 1.6605 \times 10^{-27} \text{ kg/u}} \]

b) If the excited state has a lifetime of 100 ps, what is the lifetime broadening caused by this?

Solution:

a) In the following, \( m \) is the ICl mass, \( m = 162 \text{ u}: \)

\[ \frac{\delta \lambda}{\lambda} = \frac{2}{c} \sqrt{\frac{2 \left(1.381 \times 10^{-23} \text{ JK}^{-1}\right) \left(298 \text{ K}\right) \ln(2)}}_{162 \text{ u} \times 1.6605 \times 10^{-27} \text{ kg/u}} \]
Doppler broadening for the rotational line: \( \nu = \tilde{\nu} c = 2Bc = 2 \times 0.1142 \text{ cm}^{-1} \times 2.998 \text{ cm/s} = 6.8 \times 10^9 \text{ Hz} = 6.6 \text{ kHz} \). For the vibrational line: \( \tilde{\nu} = 384 \text{ cm}^{-1} \) and \( \delta \tilde{\nu} = 9.7 \times 10^{-7} \times 384 \text{ cm}^{-1} = 0.0004 \text{ cm}^{-1} \).

b)

\[
\delta \tilde{\nu} = \frac{\hbar}{\tau} = \frac{1.0546 \times 10^{-34} \text{ Js}}{100 \times 10^{-13} \text{ s}} = 1.0546 \times 10^{-23} \text{ J} = 0.5 \text{ cm}^{-1}
\]

4. The rotational spectrum of \(^{127}\text{I}^{35}\text{Cl}\) shows lines with 0.2284 cm\(^{-1}\) spacings. What is the bond length of this molecule?

Solution:

The rotational transitions are \((J+1) \leftarrow J\): \( \tilde{\nu} = 2B(J+1) = 2B, 4B < 6B, \ldots \) with \( J = 0, 1, 2, \ldots \). Now \( \tilde{\nu}_{J+1} - \tilde{\nu}_J = 2B \Rightarrow B = 0.1142 \text{ cm}^{-1} \). Also \( B = \frac{\hbar}{4\pi c I} \) which gives \( I = \frac{\hbar}{4\pi c B} = \mu R^2 \) where the \( \mu \) is the reduced mass. The bond length \( R \) is now given by:

\[
R = \sqrt{\frac{1.05457 \times 10^{-34} \text{ Js}}{4\pi (27.4146 \text{ u} \times 1.66054 \times 10^{-27} \text{ kg/u}) \times (2.998 \times 10^{10} \text{ cm/s}) \times (0.1142 \text{ cm}^{-1})}}
\]

\[
= 232.1 \text{ pm} = 2.321 \text{ Å}
\]

5.

a) What are the positions of the four first Stokes and anti-Stokes rotational Raman lines when the excitation laser wavelength is 336.732 nm and the rotational constant \( B = 9.977 \text{ cm}^{-1} \) (note that you do not need the rotational constant \( A \) in this calculation since the selection rule include \( \Delta K = 0 \)).

b) Demonstrate that the above rotational constant is consistent with N-H bondlength of 101.2 pm and bond angle 106.7\(^\circ\).

Solution:
a) NH$_3$ is a symmetric top molecule, which has anisotropic polarizability and hence it is Raman active. The selection rules are: $\Delta K = 0$ and $\Delta J = -2, -1, 0, +1, +2$ giving the $O, P, Q, R, S$ branches, respectively. The energy levels are given by:

$$F(J, K) = BJ(J + 1) + (A - B)K^2$$

The Stokes $S$ branch: $|\tilde{\nu}| = F(J + 2) - F(J) = 4BJ + 6B$.
Anti-Stokes $O$ branch: $|\tilde{\nu}| = 2B(2J + 3)$.
Stokes $R$ branch: $|\tilde{\nu}| = F(J + 1, K) - F(J, K) = 2BJ + 2B$.
Anti-Stokes $P$ branch: $|\tilde{\nu}| = 2B(J + 1)$

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<tr>
<th>$J$</th>
<th>0</th>
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<tr>
<td>({$\Delta J = \pm 2$}) $</td>
<td>\tilde{\nu}</td>
<td>$</td>
<td>6B</td>
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| $S$ Stokes (cm$^{-1}$) | 29637.3 | 29597.4 | 29557.5 | 29517.6 |
| $O$ anti-Stokes (cm$^{-1}$) | 29757.1 | 29797.0 | 29836.9 | 29876.8 |

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<th>$J$</th>
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<tr>
<td>({$\Delta J = \pm 1$}) $</td>
<td>\tilde{\nu}</td>
<td>$</td>
<td>4B</td>
<td>6B</td>
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| $R$ Stokes (cm$^{-1}$) | 29657.3 | 29637.3 | 29617.4 | 29597.4 |
| $P$ anti-Stokes (cm$^{-1}$) | 29737.1 | 29757.1 | 29777.0 | 29797.0 |

b) We need to calculate the moment of inertia and show that this is equal to the given rotational constant value. The rotational constant $B$ is:

$$B = \frac{\hbar}{4\pi c I} \text{ with } I = m_H R^2 (1 - \cos(\theta)) + \frac{m_H m_N}{m} R^2 (1 + 2 \cos(\theta))$$

where $m_H = 1.6735 \times 10^{-27}$ kg, $m_N = 2.3252 \times 10^{-26}$ kg, $m = 2.8273 \times 10^{-26}$ kg, $R = 101.2$ pm, and $\theta = 106.7^\circ$. This gives the moment of inertia $I = 2.8059 \times 10^{-47}$ kg m$^2$. The rotational constant is then:

$$B = \frac{1.05457 \times 10^{-34} \text{ Js}}{4\pi \times 2.998 \times 10^8 \text{ m/s} \times 2.8059 \times 10^{-47} \text{ kg m}^2} = 997.7 \text{ m}^{-1} = 9.977 \text{ cm}^{-1}$$