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: $\log \left( \frac{I}{I_0} \right) = \epsilon [A] l$ 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 compound A, and $l$ is the length of the sample.

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

b) Recall that $T = \frac{I}{I_0}$. Now $\epsilon = \frac{1}{[A] l} \log \left( \frac{I}{I_0} \right) = \frac{1}{(0.010 \text{ mol/L})(0.20 \text{ cm})} \log(2.08) = 159 \text{ L mol}^{-1} \text{ cm}^{-1}$. This gives $T = \frac{I}{I_0} = 10^{(-159 \text{ mol L}^{-1} \text{ cm}^{-1} \times 0.010 \text{ mol/L} \times 0.40 \text{ cm})} = 0.23$. 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) $\nu = 3000 \text{ cm}^{-1}$ (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:
\[
\frac{A}{B} = \frac{8\pi \hbar \nu^3}{c^3} \text{ where } \nu = \frac{c}{\lambda} = c\tilde{\nu}
\]

a) X-ray: \( \nu = \frac{2.9979 \times 10^8 \text{ ms}^{-1}}{7.68 \times 10^{-11} \text{ m}} = 4.23 \times 10^{18} \text{ s}^{-1} \). \( A/B = 46.9 \times 10^{-3} \).

b) Visible: \( \nu = \frac{2.9979 \times 10^8 \text{ ms}^{-1}}{5.00 \times 10^{-7} \text{ m}} = 6.00 \times 10^{14} \text{ s}^{-1} \). \( A/B = 1.33 \times 10^{-13} \). The ratio “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: \( \nu = \frac{2.9979 \times 10^8 \text{ ms}^{-1}}{3.00 \times 10^{-2} \text{ m}} = 9.99 \times 10^9 \text{ s}^{-1} \). 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 \( \nu = 384 \text{ cm}^{-1} \).

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, \( m = 162 \text{ u} \):

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

\[
= \frac{2}{2.998 \times 10^8 \text{ m/s}} \sqrt{\frac{2 \left(1.381 \times 10^{-23} \text{ JK}^{-1}\right) (298 \text{ K}) \ln(2)}{162 \text{ u} \times 1.6605 \times 10^{-27} \text{ kg/u}}}
\]
Doppler broadening for the rotational line: \( \nu = \tilde{\nu}c = 2Bc = 2 \times 0.1142 \text{ cm}^{-1} \times 2.998 \text{ cm/s} = 6.8 \times 10^9 \text{ Hz} \) and therefore \( \delta \tilde{\nu} = \nu \times 9.7 \times 10^{-7} = 6.6 \text{ kHz} \). 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 \text{ cm}^{-1} spacings. What is the bond length of this molecule?

Solution:

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

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

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

5. Consider \(\text{NH}_3\) molecule (non-planar geometry; symmetric top).

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°.
Solution:

a) \( \text{NH}_3 \) 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:

\[
F(J, K) = BJ(J + 1) + (A - B)K^2
\]

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

<table>
<thead>
<tr>
<th>Initial state ( J )</th>
<th>( \Delta J = \pm 2 )</th>
<th>( \tilde{\nu} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S ) Stokes (cm(^{-1}))</td>
<td>0</td>
<td>6B</td>
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<tr>
<td>1</td>
<td>10B</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>14B</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>18B</td>
<td></td>
</tr>
<tr>
<td>( O ) anti-Stokes (cm(^{-1}))</td>
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<tr>
<td>29597.4</td>
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<td>29557.5</td>
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<tr>
<td>29517.6</td>
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<table>
<thead>
<tr>
<th>Initial state ( J )</th>
<th>( \Delta J = \pm 1 )</th>
<th>( \tilde{\nu} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R ) Stokes (cm(^{-1}))</td>
<td>0</td>
<td>2B</td>
</tr>
<tr>
<td>1</td>
<td>4B</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6B</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8B</td>
<td></td>
</tr>
<tr>
<td>( P ) anti-Stokes (cm(^{-1}))</td>
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</tr>
<tr>
<td>29657.3</td>
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<tr>
<td>29637.3</td>
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<td></td>
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<tr>
<td>29617.4</td>
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</tbody>
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Rayleigh line is at 29697.2 cm\(^{-1}\) (corresponding 336.732 nm). This must be added to the rotational energies above \( (F(J, K)) \).

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:

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

where \( m_H = 1.6735 \times 10^{-27} \) kg, \( m_N = 2.3252 \times 10^{-26} \) kg, \( m = 2.8273 \times 10^{-26} \) kg (total mass), \( R = 101.2 \) 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:

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