CHEM 352: Examples for chapter 5.

1.

a) The molar absorption coefficient of a substance dissolved in hexane is $\epsilon = 855$ L mol^{-1} cm^{-1} at $\lambda = 270$ 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: $\log\left(\frac{I_0}{I}\right) = \epsilon\,[\mathrm{A}]\,l$ where I_0 is the incident light intensity, I is the intensity of light passing through the sample, ϵ is the molar absorption coefficient, [A] is the concentration of compount A, and l is the length of the sample.

a) $\log\left(\frac{I_0}{I}\right) = \left(855\text{ L mol}^{-1}\text{ cm}^{-1}\right) \times (3.25 \times^{-3}\text{ mol/L}) \times (0.25\text{ cm}) = 0.695$. 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 $\epsilon = \frac{1}{[\mathrm{A}]l}\log\left(\frac{I_0}{I}\right) = \frac{1}{(0.010\text{ mol/L})(0.20\text{ cm})}\log(2.08) = 159\text{ L mol}^{-1}\text{cm}^{-1}$. This gives $T = \frac{I}{I_0} = 10^{(-159\text{ mol L}^{-1}\text{ cm}^{-1}\times 0.010\text{ mol/L}\times 0.40\text{ cm})} = 0.23$. This corresponds to 23%.

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2. Compare the ratio A/B between the Einstein spotaneous and stimulated emission coefficients for the following wavelengths: a) $\lambda = 70.8$ pm (X-ray), b) $\lambda = 500$ nm (visible light), c) $\tilde{\nu} = 3000$ cm^{-1} (IR), d) $\lambda = 3$ cm (microwaves), e) $\nu = 500$ 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:

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3} \text{ where } \nu = \frac{c}{\lambda} = c\tilde{\nu}$$

a) X-ray: $\nu = \frac{2.9979\times10^8 \text{ ms}^{-1}}{7.08\times10^{-11} \text{ m}} = 4.23 \times 10^{18} \text{ s}^{-1}$. $A/B = 46.9 \times 10^{-3}$.

b) Visible: $\nu = \frac{2.9979\times10^8 \text{ ms}^{-1}}{5.00\times10^{-7} \text{ m}} = 6.00 \times 10^{14} \text{ s}^{-1}$. $A/B = 1.33 \times 10^{-13}$. The ratio "visible / X-ray" $= \frac{\nu_{vis}}{\nu_{X-ray}} = 2.84 \times 10^{-12}$.

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 9.58×10^{-15}.

d) Microwaves: $\nu = \frac{2.9979\times10^8 \text{ ms}^{-1}}{3.00\times10^{-2} \text{ m}} = 9.99\times10^9 \text{ s}^{-1}$. The ratio is 13.1×10^{-27}.

e) Radiowaves: $\nu = 500$ MHz $= 500 \times 10^6 \text{ s}^{-1}$. The ratio is 1.65×10^{-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 $\delta\nu_{rot}$ (kHz) and $\delta\nu_{vib}$ (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, $m = 162$ u:

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

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

$$= 9.7 \times 10^{-7} = \frac{\delta\tilde{\nu}}{\tilde{\nu}}$$

Doppler broadening for the rotational line: $\nu = \tilde{\nu}c = 2Bc = 2 \times 0.1142\ \mathrm{cm}^{-1} \times 2.998\ \mathrm{cm/s} = 6.8 \times 10^{9}$ Hz and therefore $\delta\nu = \nu \times 9.7 \times 10^{-7} = 6.6$ kHz. For the vibrational line: $\tilde{\nu} = 384\ \mathrm{cm}^{-1}$ and $\delta\tilde{\nu} = 9.7 \times 10^{-7} \times 384\ \mathrm{cm}^{-1} = 0.0004\ \mathrm{cm}^{-1}$.

b)

$$\delta\tilde{\nu} = \frac{\hbar}{\tau} = \frac{1.0546 \times 10^{-34}\ \mathrm{Js}}{100 \times 10^{-12}\ \mathrm{s}} = 1.0546 \times 10^{-24}\ \mathrm{J} = 0.05\ \mathrm{cm}^{-1}$$

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

Solution:

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

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

$$= 232.1\ \mathrm{pm} = 2.321\ \text{Å}$$

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5. Consider 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 $B = 9.977\ \mathrm{cm}^{-1}$ (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) NH_3 is a symmtric 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 ($J \to J+2$): $|\tilde{\nu}| = |F(J+2, K) - F(J, K)| = 4BJ + 6B = 2B(2J+3)$.
2. Anti-Stokes O branch ($J+2 \to J$): $|\tilde{\nu}| = 2B(2J+3)$.
3. Stokes R branch ($J \to J+1$): $|\tilde{\nu}| = |F(J+1, K) - F(J, K)| = 2BJ + 2B = 2B(J+1)$.
4. Anti-Stokes P branch ($J+1 \to J$): $|\tilde{\nu}| = 2B(J+1)$.

Intial state J	0	1	2	3
$(\Delta J = \pm 2)\ \lvert\tilde{\nu}\rvert$	$6B$	$10B$	$14B$	$18B$
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

Initial state J	0	1	2	3
$(\Delta J = \pm 1)\ \lvert\tilde{\nu}\rvert$	$2B$	$4B$	$6B$	$8B$
R Stokes (cm^{-1})	29677.3	29657.3	29637.3	29617.4
P anti-Stokes (cm^{-1})	29717.2	29737.1	29757.1	29777.0

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:

$$B = \frac{\hbar}{4\pi c I} \text{ with } I = m_{\mathrm{H}} R^2 \left(1 - \cos(\theta)\right) + \frac{m_{\mathrm{H}} m_{\mathrm{N}}}{m} R^2 \left(1 + 2\cos(\theta)\right)$$

where $m_{\mathrm{H}} = 1.6735 \times 10^{-27}$ kg, $m_{\mathrm{N}} = 2.3252 \times 10^{-26}$ kg, $m = 2.8273 \times 10^{-26}$ kg (total mass), $R = 101.2$ pm, and $\theta = 106.7°$. This gives the moment of inertia $I = 2.8059 \times 10^{-47}$ kg m^2. The rotational constant is then:

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

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6. The dissociation energy (D_0) of H_2 is 4.46 eV with the zero-point energy being 0.26 eV. What is the value of D_0 for D_2 molecule?

Solution:

D_0 is the energy difference between the lowest vibrational level and the dissociation limit whereas D_e is the difference between the bottom of the potential energy curve and the dissociation limit. Hence D_0 depends on the molecular masses whereas D_e does not. The expression for D_e is:

$$D_e = D_0 + \frac{1}{2}h\nu_0 = (4.46 + 0.26)\ \text{eV} = 4.72\ \text{eV}$$

Both H_2 and D_2 have the same force constants and equilibrium bond lengths. Since the zero-point energy is given, we can calculate ν_0 for H_2 (denoted by ν_{H_2} below) as 2×0.26 eV $= 0.52$ eV (from $E_0 = \frac{1}{2}h\nu_0$). Since $\nu = \frac{\sqrt{k/\mu}}{2\pi}$, the relationship between the vibrational frequencies for H_2 and D_2 is:

$$h\nu_{D_2} = \sqrt{\mu_{H_2}/\mu_{D_2}}h\nu_{H_2} = h\nu_{H_2}/\sqrt{2} = 0.37\ \text{eV}$$

This gives $D_0(D_2) = D_e - \frac{1}{2}h\nu_{D_2} = (4.72 - 0.183)$ eV $= 4.54$ eV. Check: Since H_2 is lighter and the zero-point energy is higher, its dissociation energy is smaller than for the heavier D_2.

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7. IR measurement of gaseous HCl sample yields the following Morse potential constants: $\tilde{\nu}_e = 2990.1$ cm^{-1} and $x_e = 0.01737$. What is the dissociation energy D_0? How does this compare with the known dissociation energy of HCl?

Solution:

For Morse potential the dissociation energy is related to $\tilde{\nu}_e$ and x_e as follows (see lecture notes):

$$\tilde{D}_e = \frac{\tilde{\nu}_e}{4x_e}$$

This gives $\tilde{D}_e = 43035.4\ \mathrm{cm}^{-1}$. To get $\tilde{D}_0$ we need to subtract the zero-point energy:

$$\tilde{D}_0 = \tilde{D}_e - \frac{1}{2}h\nu_e = 41540.4\ \mathrm{cm}^{-1} = 496.6\ \mathrm{kJ/mol}$$

This is much higher than the known reference value of 431 kJ/mol, which means that Morse potential is not a very accurate model for HCl near the dissociation limit.

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8. How many rotational and vibrational degrees of freedom do the following molecules have: CH_2O, C_2H_2, and C_6H_6?

Solution:

All but C_2H_2 are non-linear. Therefore both CH_2O and C_6H_6 have 3 rotational degrees of freedom whereas linear C_2H_2 has only two. The number of vibrational degrees for linear molecules is $3N - 5$ whereas for non-linear it is $3N - 6$. So for C_2H_2 this is 7, CH_2O 6, and C_6H_6 30.

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9. Which of the following molecular vibrations of benzene are IR or Raman active?

a) Vibrational mode where the aromatic ring expands and contracts (i.e., all C-C bonds elongate or contract together).

b) Evey other hydrogen moves below the molecular plane with the others going in the opposite direction (below the plane).

Solution:

a: The dipole moment does not change. However, the polarizability changes as the size of the molecule changes. Therefore this mode is not IR active but is Raman active.
b: The point group of benzene is D_{6h}. The irrep corresponding to this vibration is B_{2g}. Since the direct product with any of the IR transition dipole operators (x, y, z) or Raman (x^2, xy, etc.) do not belong to this irrep,

it is not possible to get A_g from the overall direct product. Therefore this mode is inactive in both IR and Raman.