## CHEM 352: Homework 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?

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<sup>-1</sup> (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?

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<sup>-1</sup>) when the rotational constant B = 0.1142 cm<sup>-1</sup> and the vibrational frequency is  $\nu = 384$  cm<sup>-1</sup>.
- b) If the excited state has a lifetime of 100 ps, what is the lifetime broadening caused by this?

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

5. Consider NH<sub>3</sub> 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 cm<sup>-1</sup> (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°.

6. The dissociation energy  $(D_0)$  of H<sub>2</sub> is 4.46 eV with the zero-point energy being 0.26 eV. What is the value of  $D_0$  for D<sub>2</sub> molecule?

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

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

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).