3 Advanced Physical Chemistry – Exercizes

3.1 In the IR absorption spectrum of $H^{35}Cl$, the first line of the R branch lies at 2906.25 cm^{-1} and the first line of the P branch at 2865.09 cm^{-1}. A sample of HCl vapour is irradiated in a Raman spectrometer with light of 435.8 nm wavelength. At which wavelength do you expect

a) the first two Stokes lines of the rotation,

b) the first two Anti-Stokes lines of the rotation,

c) the Stokes line of the vibration of the HCl molecule?

3.2 Calculate the first two lines of the P- and the R-branch, respectively, of $H^{37}Cl$ and $D^{35}Cl$ from the spectroscopic data given in the previous exercize!

3.3 Bromine vapour is irradiated with light and electronically excited. Assume that both the ground state and the lowermost excited stated can be treated as harmonic oscillators ($\tilde{\nu} =$ 250 cm^{-1}. The mean bond length of the Br_2 molecule is about 250 pm. How does the intensity of the lowermost line of the absoprtion spectrum, which corresponds to a transition between the vibrational ground states ($v' = 0 \rightarrow v = 0$), change if if the bond length of the excited state is 250, 255, 260, 270 pm? Calculate the intensities relative to the intensity of the 250 pm case!

$$\int_{-\infty}^{+\infty} \exp\left(-\frac{(x-a)^2}{b^2}\right) \mathrm{d}x = b\sqrt{\pi}$$

$$\int_{-\infty}^{+\infty} \exp\left(-\frac{(x-a)^2}{b^2}\right) \exp\left(-\frac{(x-c)^2}{b^2}\right) \mathrm{d}x = b\sqrt{\frac{\pi}{2}} \exp\left(-\frac{(a-c)^2}{2b^2}\right)$$

3.4 List the magnetic quantum states of a proton (nuclear spin $I = \frac{1}{2}$, a deuteron ($I = 1$), and a ^{17}O nucleus ($I = \frac{5}{2}$)!

Calculate the intensity distribution of NMR signals due to spin–spin coupling for protons and deuterons!

3.5 Calculate the resonance frequency of a proton (NMR) and an electron (ESR) in a magnetic field of B = 1 T!

$g(H^+)$ = 5.586, $g(e^-)$ = 2.0023, $\mu_x = e\hbar/(2m_x)$

Is it really necessary to have a bulky and expensive magnet? What are the resonance frequencies if the magnetic field of Earth is used ($\approx 10^{-4}$ T)?