Examination 14. 04. 2010

11

a) Number of vibrational degrees of freedom:

$N_{vib} = 3N - 5 = 12 - 5 = 7$

b). Population of rotational level:

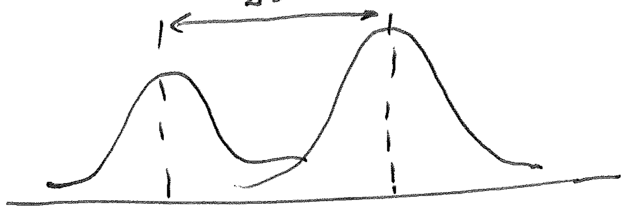
$$N(J) = \frac{(2J+1)\, e^{-\frac{BJ(J+1)}{kT}}}{Z(T)}$$

$$\frac{N(5)}{N(20)} = \frac{11}{41} \exp\left(- \frac{1.17 \cdot 1.4387}{300}(5 \cdot 6 - 20 \cdot 21)\right) =$$

$$= \frac{11}{41} \cdot \exp \cdot \left(\frac{1.17 \cdot 1.4387}{300} \cdot 390\right) = \frac{11}{41} \exp(2.188) = 2.39$$

=> Population of the level with $J = 5$ is larger

c) To resolve the lines the distance between them should be larger than their doppler width:



$$\Delta\hat{\nu}_D = 2 \frac{\hat{\nu}_0}{c} \cdot \sqrt{\frac{(2 \ln 2) RT}{M}}$$

$$\Delta\nu_D = 7.16 \cdot 10^{-7} \cdot 3400 \cdot \sqrt{\frac{300}{26}} \approx 0.00827 \text{ cm}^{-1}$$

$\Delta\nu_D < \Delta\nu$

=> It is possible to resolve the lines.

a) The wavelength of P line is

$$\tilde{\nu}_p = \tilde{\nu}_0 - 2BJ$$

Thus the distance between ~~lines~~ P(5.5) and P(6.5) lines is

$$\Delta\tilde{\nu} = 2B(J_2 - J_1) = 2B$$

$$B = \frac{\Delta\tilde{\nu}}{2} = \frac{3367.038 - 3324.577}{2} = 21.23 \text{ cm}^{-1}$$

b).
$$I = I_0 e^{-k(\nu)\cdot \ell}$$

$$\frac{I}{I_0} = e^{-k(\nu)\ell}$$

$$k(\nu) = S(\nu)\cdot \ell \cdot N_{OH} \cdot L(\nu) = S(\nu)\cdot \ell\, \frac{P}{kT} \cdot X_{OH} \cdot \frac{2}{\pi \cdot \Delta\tilde{\nu}}$$

$$\frac{I}{I_0} = \exp\left(-2.622\cdot 10^{-20} \cdot 100 \cdot \frac{1.01325\cdot 10^{6} \cdot 10^{-4}}{1.3806\cdot 10^{-16}\cdot 300}\right) = \cancel{0.9936}$$

$$\times \left. \frac{2}{3.14\cdot 0.06}\right) = 0.33$$

c) At low pressures, when Doppler broadening is dominant, the width increases with temperature.

At high pressures, the Lorentzian broadening is dominant.

$$\Delta\nu_L \sim \sigma \cdot v \cdot N$$

If σ is independent on T, we have:

$$\Delta\nu_L \sim \sqrt{T}\cdot \frac{1}{T} \sim \frac{1}{\sqrt{T}}$$

It means the spectral line width decreases with temperature

a) The intensity of scattered light is proportional to

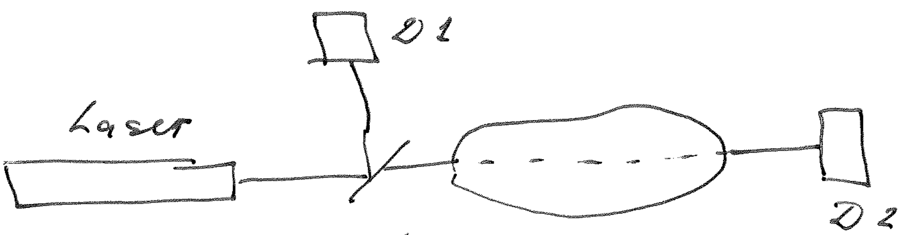
$$I_{sc} \sim \left(\frac{d}{\lambda}\right)^4 \cdot P_L$$

where d ~~and P are~~ is diameter ~~part~~ of particles and P_L is the laser power. Therefore, we have for the ratio of two signals:

$$\frac{I_1}{I_2} = \left(\frac{\lambda_2}{\lambda_1}\right)^4 \cdot \frac{P_1}{P_2} = \left(\frac{0.\cancel{7}5}{0.75}\right)^4 \cdot \frac{5}{0.1} = \left(\frac{2}{3}\right)^4 \cdot 50 = 9.87$$

Thus, the first laser gives a larger signal.

b)



$$I(L) = I_0 e^{-kL}$$

$$k(\nu) = \frac{1}{L} \ln \frac{I_0}{I}$$

$$K = \frac{\pi d_p^2}{4} Q_{ext} \cdot N$$

$$N = \frac{4K}{\pi d_p^2 \cdot Q_{ext}}$$

For small particles: $Q_{ext} \approx Q_{abs} \approx -4\left(\frac{d_p}{\cancel{\lambda}\, d_p}\right) Im\left(\frac{m^2-1}{m^2+1}\right)$

c) $$N = -\frac{K\lambda}{\pi d_p^3\, Im\left(\frac{m^2-1}{m^2+1}\right)}$$

$$\varphi = \frac{\pi d_p^3}{6} N \qquad d_p = \sqrt[3]{\frac{6\varphi}{\pi N}}$$

$$d_p = \sqrt[3]{\frac{6 \cdot 10^{-9}}{3.14 \cdot 10^{14}}} = 2.67 \cdot 10^{-7}\ m = 0.0267\ \mu m = 26.7\ nm$$

EMTGR 14-4-2011, answers on question 4

a)

12	^{12}C
13	^{13}C
14	^{14}N
15	^{15}N
16	^{16}O
17	^{17}O, (OH)
18	^{18}O, (H_2O)
22	CO_2
22.5	CO_2
23	CO_2
28	CO, (N_2)
29	CO, (N_2)
30	CO, (N_2)
32	O_2
33	O_2
34	O_2
44	CO_2
45	CO_2
46	CO_2

m/e-numbers in bold should be given, N_2 and H_2O not necessarily
H_2O and N_2 are always present in high vacuum systems.

b) besides $CO^{18}O$, $C^{17}O_2$, $^{13}CO^{17}O$ also $^{15}N_2O$, $N^{15}N^{17}O$, $N_2{}^{18}O$

c) The nuclei of ^3He and ^1H+^2H don't have exactly the same mass.
^3He: 3,0219 amu
^1H+^2H: 3,0160 amu
The difference is ~ 0,2 %, they can be separately measured in a high resolution magnetic mass spectrometer.