**Examples     Week 4**

1. *According to the HITRAN database the ozone line at 1020.3189 cm*$^{-1}$ *has an air broadened halfwidth of .0706 cm*$^{-1}$ *at 1 atm (*$p_0 = 1013.25$ *mb) and* $T_0 = 296$ *K and a temperature coefficient of* $n = .76$*.*

*a) What is the Lorentz halfwidth at 20 km where the pressure is 53.7 mb and the temperature is 215 K?*

Self broadening can be ignored for ozone, so the pressure dependence is obtained from

$$\alpha = \alpha_0 \left(\frac{p}{p_0}\right)\left(\frac{T_0}{T}\right)^n$$

$$\alpha = (.0706\ \mathrm{cm}^{-1})\left(\frac{53.7\ \mathrm{mb}}{1013.25\ \mathrm{mb}}\right)\left(\frac{296\ \mathrm{K}}{215\ \mathrm{K}}\right)^{0.76}$$

$$\alpha = (.0706\ \mathrm{cm}^{-1})(0.0530)(1.275)\ = 0.0048\ \mathrm{cm}^{-1}$$

*b) What is the Doppler halfwidth at half max?*

The Doppler width is

$$\alpha_D = \nu_0\sqrt{\frac{2k_BT}{mc^2}} = \sqrt{\frac{2(1.38\times10^{-23}\ \mathrm{J/K})(215\ \mathrm{K})(6.02\times10^{26}\ \mathrm{kmol}^{-1})}{(48\ \mathrm{kg/kmol})(3\times10^8\ \mathrm{m/s})^2}}$$

$$\alpha_D = (1020.3189\ \mathrm{cm}^{-1})(9.09\times10^{-7})\ = 0.00093\ \mathrm{cm}^{-1}$$

The halfwidth is $\alpha_D\sqrt{\ln 2} = 0.00077\ \mathrm{cm}^{-1}$, which is about six times smaller than the pressure broadened width at this altitude.

2. *What is the ratio of the population of states in $CO_2$ at $T = 200$ K to that at $T = 300$ K for rotational numbers $J = 4$ and $J = 40$. Assume the rigid rotator model with $B = 0.39\,\mathrm{cm}^{-1}$.*

In LTE the population of states is determined by

$$\frac{n_i}{n_t} = \frac{g_i \exp(-E_i/k_B T)}{Q(T)}$$

The ratio of the population of states at two temperatures is

$$\frac{n_{T_1}}{n_{T_2}} = \frac{\exp(-E_i/k_B T_1) Q(T_2)}{\exp(-E_i/k_B T_2) Q(T_1)}$$

For a rigid rotator the energy levels are $E_J = hcBJ(J+1)$ and partition function is $Q_r \approx \frac{k_B T}{hcB}$. Thus the ratio of populations is

$$\frac{n_{T_1}}{n_{T_2}} = \frac{\exp[-hcBJ(J+1)/k_B T_1]}{\exp[-hcBJ(J+1)/k_B T_2]} \frac{T_2}{T_1}$$

For $J = 4$

$$\frac{n_{200}}{n_{300}} = \frac{\exp[-(1.44 \text{ cm K})(0.39 \text{ cm}^{-1})4(5)/200 \text{ K}]}{\exp[-(1.44 \text{ cm K})(0.39 \text{ cm}^{-1})4(5)/300 \text{ K}]} \frac{300 \text{ K}}{200 \text{ K}} = \frac{0.945}{0.963} 1.5 = 1.47$$

For $J = 40$

$$\frac{n_{200}}{n_{300}} = \frac{\exp[-(1.44 \text{ cm K})(0.39 \text{ cm}^{-1})40(41)/200 \text{ K}]}{\exp[-(1.44 \text{ cm K})(0.39 \text{ cm}^{-1})40(41)/300 \text{ K}]} \frac{300 \text{ K}}{200 \text{ K}} = \frac{0.010}{0.046} 1.5 = 0.32$$