

Problems

1. According to the HITRAN database, the ozone line at $1020.3189 \text{ cm}^{-1}$ has an air broadened half-width of $\alpha_0 \text{ cm}^{-1}$ at 1 atm ($p_0 = 1013.25 \text{ mb}$) and $T_0 = 296 \text{ K}$ and a temperature coefficient of n .
- a) What is the Lorentz half-width at 20 km where the pressure is 53.7 mb and the temperature is 215 K?
- b) What is the Doppler half-width at half max?

- a) Based on HITRAN 2020, $\alpha_0 = 0.0766 \text{ cm}^{-1}$, $n = 0.72$.

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

$$\alpha = \alpha_0 \left(\frac{p}{p_0} \right) \left(\frac{T_0}{T} \right)^n = (0.0766 \text{ cm}^{-1}) \left(\frac{53.7 \text{ mb}}{1013.25 \text{ mb}} \right) \left(\frac{296 \text{ K}}{215 \text{ K}} \right)^{0.72} = 0.005 \text{ cm}^{-1}$$

- b) Doppler width =

$$\alpha_D = \nu_0 \sqrt{\frac{2k_B T}{mc^2}} = (1020.3189 \text{ cm}^{-1}) \sqrt{\frac{2(1.38 \times 10^{-23} \text{ J K}^{-1})(215 \text{ K})}{(48 \times 1.66 \times 10^{-27} \text{ kg})(3 \times 10^8 \text{ m s}^{-1})^2}}$$

$$\alpha_D = 0.00093 \text{ cm}^{-1}$$

The half-width is $\alpha_D \sqrt{\ln 2} = 0.00077 \text{ cm}^{-1}$, which is about 6 times smaller than the pressure broadened width at this altitude.

2. What is the ratio of the population of states in CO₂ 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 cm⁻¹.

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 states at two temperatures is:

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

For a rigid rotator, recall that the energy levels are $E_J = hcBJ(J + 1)$, and $Q \sim \frac{k_B T}{hcB}$.

$$\frac{n_i(T = T_1)}{n_i(T = T_2)} = \frac{\exp(-hcBJ(J + 1)/k_B T_1) T_2}{\exp(-hcBJ(J + 1)/k_B T_2) T_1}$$

$$\frac{hc}{k_B} = \frac{(6.626 \times 10^{-34} \text{ J s})(299792458 \text{ m s}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1})} = 1.44 \text{ cm K}$$

For J = 4,

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

For J = 40,

$$\begin{aligned} \frac{n_i(T = 200 \text{ K})}{n_i(T = 300 \text{ K})} &= \frac{\exp(-(1.44 \text{ cm K})(0.39 \text{ cm}^{-1})(40)(41)/200 \text{ K}) 300 \text{ K}}{\exp(-(1.44 \text{ cm K})(0.39 \text{ cm}^{-1})(40)(41)/300 \text{ K}) 200 \text{ K}} = \frac{0.01}{0.046} 1.5 \\ &= 0.32 \end{aligned}$$

3. Between 691.5 cm^{-1} and 692.5 cm^{-1} , the HITRAN 2016 database contains the following parameters for lines of the relevant gases with line strengths above $10^{-21} \text{ cm/molecule}$:

23	2	691.558689	1.144E-21	8.111E-01	0.1213	1.053	43.1975	0.75
43	1	691.627250	1.066E-21	5.078E-02	0.1000	0.200	205.8231	0.75
11	1	691.767164	4.587E-21	1.024E+01	0.0976	0.396	1022.9201	0.72
2	1	691.972420	9.101E-20	9.153E-01	0.0687	0.090	362.7883	0.75
3	1	692.034820	1.140E-21	9.259E-02	0.0746	0.103	191.7092	0.78
43	1	692.125070	1.132E-21	5.151E-02	0.1000	0.200	184.4532	0.75
2	1	692.129005	4.052E-21	9.650E-01	0.0688	0.091	1007.1335	0.75
11	1	692.312700	1.013E-20	1.153E+01	0.0931	0.302	1026.6435	0.72
26	1	692.318440	1.708E-20	3.312E+00	0.0787	0.147	912.6394	0.75
2	1	692.400097	3.727E-21	9.665E-01	0.0687	0.090	1031.1292	0.75
3	1	692.468700	1.212E-21	9.278E-02	0.0755	0.103	158.1653	0.78

Compute the optical depth at a wavenumber of 692.000 cm^{-1} for a 1 km thick layer at a pressure of $p = 102 \text{ mb}$ and temperature of $T = 217 \text{ K}$. The volume mixing ratios of the radiatively active gases are $q_{\text{H}_2\text{O}} = 6.55 \times 10^{-6}$, $q_{\text{CO}_2} = 3.70 \times 10^{-4}$, and $q_{\text{O}_3} = 2.22 \times 10^{-6}$.

- a) Determine the single absorption line that will dominate the absorption at 692.000 cm^{-1} . Write down the molecule and wavenumber.

The important absorption line is the one at $691.97242 \text{ cm}^{-1}$ which is from the main isotope of CO_2 . The other CO_2 lines have lower strengths and are much further in terms of line half-widths from 692 cm^{-1} . The nearby ozone line is not relevant since the ozone abundance is 167 times less than CO_2 and the line strength at 296 K is about 80 times less.

- b) Calculate the Lorentz half-width for this absorption line. Self-broadening can be ignored since the mixing ratios are so small.

The half-width of the Lorentz line shape is:

$$\alpha = \alpha_0 \left(\frac{p}{p_0} \right) \left(\frac{T_0}{T} \right)^n = (0.0687 \text{ cm}^{-1}) \left(\frac{102 \text{ mb}}{1013.25 \text{ mb}} \right) \left(\frac{296 \text{ K}}{217 \text{ K}} \right)^{0.75} = 0.0087 \text{ cm}^{-1}$$

- c) Calculate the line strength for this absorption line at the temperature of this layer.
The partition functions are: $Q(217\text{ K}) = 198.4$, $Q(296\text{ K}) = 286.2$

The line strength scales as:

$$S_i(T) = S_i(T_0) \frac{\exp(-hcE_{L,i}/k_B T) Q_T(T_0) [1 - \exp(-hc\nu_{0,i}/k_B T)]}{\exp(-hcE_{L,i}/k_B T_0) Q_T(T) [1 - \exp(-hc\nu_{0,i}/k_B T_0)]}$$

$$\begin{aligned} S_i(T) &= (9.101 \times 10^{-20} \text{ cm molec}^{-1}) \\ &\cdot \frac{\exp\left[-\frac{(1.44 \text{ cm K})(362.7883 \text{ cm}^{-1})}{217 \text{ K}}\right] (286.2) \left(1 - \exp\left[-\frac{(1.44 \text{ cm K})(691.9724 \text{ cm}^{-1})}{217 \text{ K}}\right]\right)}{\exp\left[-\frac{(1.44 \text{ cm K})(362.7883 \text{ cm}^{-1})}{296 \text{ K}}\right] (198.4) \left(1 - \exp\left[-\frac{(1.44 \text{ cm K})(691.9724 \text{ cm}^{-1})}{296 \text{ K}}\right]\right)} \end{aligned}$$

$$S_i(T) = 7.080 \times 10^{-20} \text{ cm molec}^{-1}$$

- d) Calculate the absorption coefficient and optical depth of this layer at 692 cm^{-1} .

Since we are considering a single Lorentz absorption line, we use the Lorentz line shape.
For the desired wavenumber of $\nu = 692.000 \text{ cm}^{-1}$ the monochromatic absorption coefficient is

$$k_\nu = S \cdot f(\nu - \nu_0) = \frac{S \alpha / \pi}{(\nu - \nu_0)^2 + \alpha^2}$$

$$k_\nu = \frac{(7.080 \times 10^{-20} \text{ cm molec}^{-1}) \cdot (0.0087 \text{ cm}^{-1}) / \pi}{(692.000 - 691.9724 \text{ cm}^{-1})^2 + (0.0087 \text{ cm}^{-1})^2} = 2.35 \times 10^{-19} \text{ cm}^2 \text{ molec}^{-1}$$

- e) Calculate the optical depth of the layer.

The optical depth of the layer at this wavenumber is the absorber amount of CO_2 times the absorption coefficient:

The number of air molecules per cm^2 in this layer is

$$u_{\text{air}} = \frac{\Delta z N_A p}{RT} = \frac{(1000 \text{ m})(6.022 \times 10^{23} \text{ molec mol}^{-1})(10200 \text{ kg m}^{-1} \text{s}^{-2})}{(9.314 \text{ kg m}^2 \text{s}^{-2} \text{ mol}^{-1} \text{K}^{-1})(217 \text{ K})}$$

$$= 3.40 \times 10^{23} \text{ molec cm}^{-2}$$

$$\tau = k_v u_{\text{CO}_2} = k_v q_{\text{CO}_2} u_{\text{air}}$$

$$= (2.35 \times 10^{-19} \text{ cm}^2 \text{ molec}^{-1})(3.7 \times 10^{-4})(3.4 \times 10^{23} \text{ molec cm}^{-2}) = 29.57$$