ATOC/ASTR 5560 Homework 2 Solutions

Due: September 28, 2001

1. *Below are two atmospheric spectra for the US standard atmosphere, one for transmission from space to 11 km and the other for transmission to sea level. Explain the large differences between the two spectra in terms of the distribution of absorbing gases.*
   Label the shortwave and longwave portions. Label on the plots as many of the absorption features listed in the lecture notes as you can (e.g. CO_2 ν_2).

Wavelen (μm)	Waveno (cm^{-1})	Species	Band type
< 0.2		O_2	electronic
0.2-0.3		O_3	electronic, Hartley
0.3-0.35		O_3	electronic, Huggins
0.5-0.7		O_3	electronic, Chappuis
0.76	13120	O_2	electronic, A band
0.94	10640	H_2O	vibration (overtone,combination)
1.1	9090	H_2O	vibration (overtone,combination)
1.38	7250	H_2O	vibration (overtone,combination)
1.87	5350	H_2O	vibration (overtone,combination)
2.7	3657,3756	H_2O	vibration (ν_1 and ν_3)
2.7	3613,3715	CO_2	vibration (combination)
3.3	3019	CH_4	vibration (ν_3)
4.3	2349	CO_2	vibration (ν_3)
6.3	1595	H_2O	vibration (ν_2)
7.6	1311	CH_4	vibration (ν_4)
7.8	1285	N_2O	vibration (ν_1)
9.6	1110, 1043	O_3	vibration (ν_1 and ν_3)
8-13		H_2O	continuum (most important here)
15	667	CO_2	vibration (ν_2)
> 20	0	H_2O	pure rotation

   The difference in transmission to space between 11 km and sea level is due to the difference in absorber amount and the pressure along the path. The path from 11 km to space has about a fifth the absorber amount that the path from sea level has for well mixed gases (CO_2, CH_4, N_2O). Water vapor is nearly all below 11 km in the atmosphere modeled, while most of the ozone is above. Thus the ozone bands are about the same in the two spectra, while the absorption from water vapor is reduced greatly from 11 km. The reduced path of CO_2 and CH_4 and the lower path pressure reduce the absorption of these bands in the 11 km spectrum.

2. *The line spacing for the regular isotope of CO_2 (ν_2 band center at $667.38\ \mathrm{cm}^{-1}$) is $1.562\ \mathrm{cm}^{-1}$. For the ^{18}O isotope of CO_2 (ν_2 band center at $662.37\ \mathrm{cm}^{-1}$) the line spacing is $0.737\ \mathrm{cm}^{-1}$. Explain this quantitatively in terms of the allowed rotational quantum numbers J and the rotational constant B.*

   First off, the ^{18}O isotope of CO_2 has a line spacing of close to half that of the regular isotope. This is easily explained by remembering that for the regular isotope only even J initial rotational states are allowed by the symmetries of the molecule ($\delta\nu = 4B$). Apparently, changing the isotope of one of the two oxygens breaks the symmetry so all J transitions are allowed ($\delta\nu = 2B$).

There is still a small difference in the rotational constants for the two isotopes:

$$B_{18O} = .3685 \text{ cm}^{-1} \quad B_{16O} = .3905 \text{ cm}^{-1} \quad \frac{B_{18O}}{B_{16O}} = 0.9437$$

This is explained by the higher moment of inertia of the heavier isotope, which causes a reduction in the rotational constant, according to $B = h/(8\pi^2 cI)$. The ratio of the moments of inertia is therefore

$$\frac{B_{18O}}{B_{16O}} = \frac{I_{16O}}{I_{18O}}$$

The moment of inertia of the symmetric isotope is $I_{16O} = 2m_O r^2$, where r is the C-O bond length. To a good approximation the moment of inertia of the ^{18}O-C-^{16}O isotope is $I_{16O} = (m_{18O} + m_{16O})r^2$. Thus the moment of inertia ratio is approximately $I_{16O}/I_{18O} = 32/34 = 0.9412$.

To be more precise, the center of mass of the ^{18}O isotope is no longer through the carbon atom. The general formula for the moment of inertia of a molecule is

$$I = \frac{\sum_{i,j} m_i m_j l_{ij}}{\sum_i m_i}$$

where l_{ij} is the distances between pairs of atoms. For the ^{18}O isotope the moment of inertia ratio is

$$\frac{I_{16O}}{I_{18O}} = \frac{(16)(16)(2r)^2 + (16)(12)r^2 + (16)(12)r^2}{16 + 16 + 12} \frac{18 + 16 + 12}{(18)(16)(2r)^2 + (18)(12)r^2 + (16)(12)r^2}$$

$$\frac{I_{16O}}{I_{18O}} = \frac{32}{33.913} = 0.9436$$

3. *a) Show that the ratio of the Lorentz halfwidth to the Doppler halfwidth is approximately proportional to air density. Obtain an expression for the air density at which the Lorentz and Doppler halfwidths (at half max) are equal.*

   The Doppler broadening halfwidth is proportional to wavenumber and square root of temperature:

   $$\alpha_D = \nu\sqrt{\frac{2\ln 2 k_b T}{mc^2}} = \nu\sqrt{\frac{2\ln 2 RT}{c^2}}$$

   where R is the gas constant for each type of molecule. The Lorentz halfwidth scales according to

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

   Since n is not far from 0.5 the ratio of the halfwidths goes approximately as pressure over temperature $\frac{\alpha_L}{\alpha_D} \propto \frac{p}{T}$.

To derive the air density at which the Lorentz and Doppler halfwidths are equal set $\alpha_L = \alpha_D$ and assume $n = 1/2$. Use the gas law for air density and do the algebra to get

$$\rho = \frac{p}{R_d T} = \frac{\nu}{\alpha_0} \frac{p_0}{R_d T_0} \sqrt{\frac{2 \ln 2 R T_0}{c^2}}$$

b) Calculate the density, and find the approximate height from a standard atmosphere, where the Lorentz and Doppler halfwidths are the same for water vapor absorption lines at $183.3\ \mathrm{GHz}$, $1560\ \mathrm{cm}^{-1}$, *and* $1.37\ \mu\mathrm{m}$. *For each of these lines the Lorentz halfwidth at* $T_0 = 296\ \mathrm{K}$ *and* $p = 1.013 \times 10^5\ \mathrm{Pa}$ *is about* $\alpha_0 = 0.10\ \mathrm{cm}^{-1}$.

For water vapor $R = 461\ \mathrm{J\ kg^{-1}\ K^{-1}}$ the equal halfwidth density is

$$\rho = \frac{\nu}{\alpha_0} (1.19\ \mathrm{kg/m^3})(1.45 \times 10^{-6})$$

The three frequencies give the following wavenumbers and equivalent densities:

$6.11\ \mathrm{cm}^{-1}$	$\rho = 1.06 \times 10^{-4}\ \mathrm{kg/m^3}$	70 km
$1560\ \mathrm{cm}^{-1}$	$\rho = 2.70 \times 10^{-2}\ \mathrm{kg/m^3}$	27.5 km
$7300\ \mathrm{cm}^{-1}$	$\rho = 1.26 \times 10^{-1}\ \mathrm{kg/m^3}$	18.5 km

The heights for the calculated densities come from a midlatitude summer atmosphere.

4. *a) Why does the 10 cm^{-1} resolution atmospheric transmission (such as in question 1) increase going from the band center to the band edge of an absorption feature? Explain in terms of the physics of molecular absorption. You may wish to use the 15 μm CO$_2$ band as an example.*

   The transmission from space to a given level increases as the wavenumber moves away from the vibrational band center. This implies the lines toward the band edges tend to have a smaller optical depth and thus lower mass absorption coefficient. The absorption coefficient

   $$k_{m,\nu} = \frac{S \alpha_L / \pi}{(\nu - \nu_0)^2 + \alpha_L^2}$$

   is higher in the band center because the line strength S is larger there. The line halfwidth α_L is mainly affected by pressure and the average pressure does not change with the wavenumber. The line strength decreases in the band edges, because those lines are from rotational transitions at high energy levels (large J). These large J rotational energy levels have few molecules in them because there energies are significantly above typical thermal energies in the atmosphere.

   b) The 708 to 724 cm^{-1} transmission from space to 18 km is 0.765, while from 5 to 4 km it is only 0.425, even though these two paths contain virtually the same absorber amount u of CO$_2$ ($\Delta p = 76\ \mathrm{mb}$ in each case). Explain this difference in transmission in terms of the behavior of molecular absorption lines.

   Here we have a particular wavenumber range, so we are considering the same absorption lines. However, the different height ranges correspond to average pressures of about 40 mb (for space to 18 km) and 580 mb (for 5 to 4 km). The 15 times greater pressure, causes the line widths to be 15 times wider. Although the higher pressure reduces the optical depth of the line centers, they generally remain large, so the transmission of the line centers remains zero ($\mathcal{T} = \exp(-\tau_\nu)$). The higher pressure causes the optical depth of the line wings to increase, and this effect reduces the band mean transmission.