The Absorption Coefficient

$$I_\omega(s_2) \Big/ I_\omega(s_1) = e^{-k_\mathrm{v}(\omega)ds}$$

$k_v(\mathrm{v})$ is the unique *fingerprint* of molecules!

How do we calculate it?

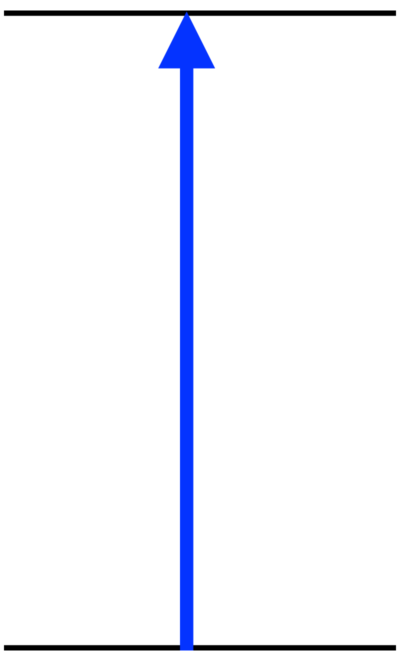
For a single transition
i.e. spectral line

$$k_v(\omega) = S\,f(\omega - \omega_0)$$

S is the intensity of the line

$f(\omega - \omega_0)$ is the line shape function

Intensity of a Line



$\omega = E' - E''$

S α population of lower state and R^2

R^2 quantum mechanical probability of the transition occurring.

The more molecules in lower state the stronger the intensity.

Line Shape function

$f(\omega - \omega_0)$ represents the broadening of the line.

γ_D Doppler broadening - due to the motion of the molecules

γ_n natural broadening - due to the natural lifetime of states

γ_L collisional broadening due to collisions of the radiating molecule with other molecules

Line Shape function

Doppler broadening

$$f_D(\omega-\omega_0)=\frac{1}{\alpha_D\sqrt{\pi}}e^{-\left(\frac{\omega-\omega_0}{\alpha_D}\right)^2}$$

where

$$\alpha_D=\frac{\omega_0}{c}\left(\frac{2kT}{m}\right)^{\frac{1}{2}}$$

is the Doppler width of the line

Line Shape function

Lorentz (collisional) broadening

$$f_L(\omega-\omega_0)=\frac{1}{\pi}\frac{\gamma}{(\omega-\omega_0-\delta)^2+\gamma^2}$$

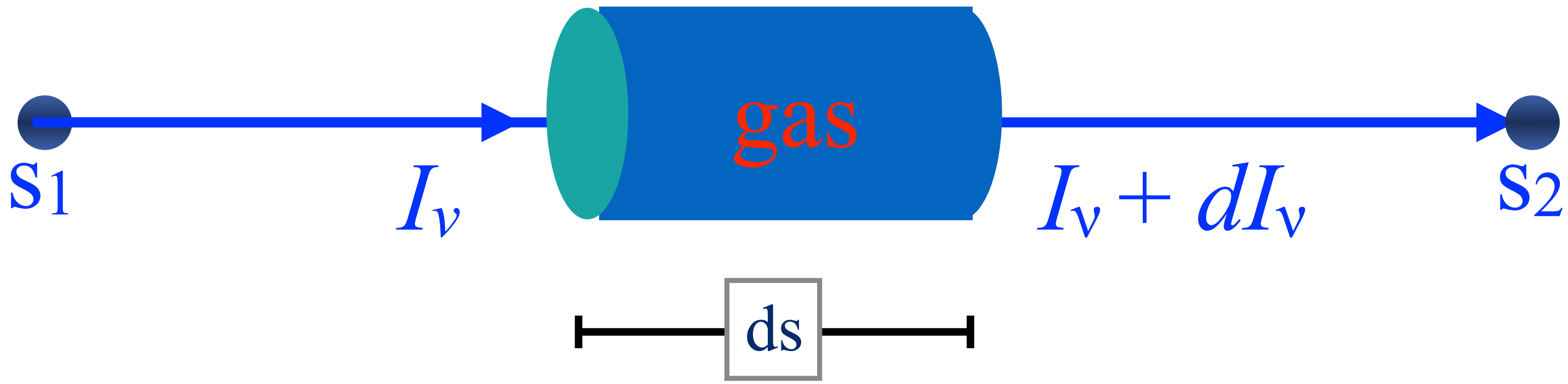
Earth's Atmosphere

Dominated by Lorentz broadening.

As pressure get low (fewer collisions) Doppler broadening becomes important.

Voigt function - a convolution of the Doppler and Lorentz line shape functions.

Single Line



$$I_\omega(s_2) = I_\omega(s_1)\, e^{-Sf(\omega-\omega_0)\,ds}$$

What do we need to do the calculation?

ω, S, γ, E”

Where does one find such information?

HITRAN - www.cfa.harvard.edu/hitran/

~ 5 million transitions

GEISA - ether.ipsl.jussieu.fr/etherTypo/?id=950&L=0

~ 4 million transitions

JPL catalogue - spec.jpl.nasa.gov/ftp/pub/catalog/catdir.html

5 million transitions

High Temperature databases

HITEMP - www.cfa.harvard.edu/hitran/HITEMP.html >122 million transitions

AMES CO_2 - Schwenke *et al.* 2.1 billion transition

CDSD 1000 - Institute of Atmospheric Optics, Tomsk RU, Sergey Tashkun, >3 million transitions

Multiple Lines

$$I_\omega(s_2) = I_\omega(s_1)\, e^{-\sum_i S_i f(\omega - \omega_i)\, ds}$$

sum over lines that influence the absorption at wavenumber ω. Generally ± 25 cm^{-1}.

183 GHz line of $H2O$

ν_1'	ν_2'	ν_3'	ν_1"	ν_2"	ν_3"	J'	Ka'	Kc'	J"	Ka"	Kc"
0	0	0	0	0	0	3	1	3	2	2	0

$\omega = 6.114567\ \text{cm}^{-1}$, $S = 0.779\text{E}^{-22}\ \text{cm}^{-1}/\text{molec}/\text{cm}^2$,

$\gamma = .0992\ \text{cm}^{-1}/\text{atm}$, $\delta = -.002700\ \text{cm}^{-1}/\text{atm}$ $E'' = 136.1639\ \text{cm}^{-1}$

$$k_\text{v}(\omega)\,ds = S\,n\,f(\omega - \omega_0)\,ds$$

What is the absorption at 6. cm^{-1} for a 50 cm path at 286 K and 1 atm pressure

$$k_v(\omega)\,ds = S\,n\,\frac{1}{\pi}\frac{\gamma p}{(\omega-\omega_0-\delta p)^2+(\gamma p)^2}\,ds$$

where n is the number density (molec/ cm^3)

Units

S n ≡ (cm^{-1}/molec/cm^{2})*(molec/cm^{-3})

= 1/cm^{2}

γ p ≡ (cm^{-1}/atm)*atm = cm^{-1}, ω is cm^{-1}

$$\frac{1}{\pi}\frac{\gamma p}{\left(\omega-\omega_0-\delta p\right)^2+\left(\gamma p\right)^2} \qquad \text{cm}$$

ds = cm; so 1/cm^{2} *cm*cm = unitless

number density - Loschmidt's number

$$n_L(p,T) = \frac{n\,N_a}{V} = \frac{p\,N_a}{RT}$$

$$n_L(p,T) = \frac{1\,atm * 6.022\,x\,10^{23}\ molec / mole}{0.082054\,\frac{\ell\,atm}{mole\,K} * 286\,K * \frac{1000\,cm^3}{\ell}}$$

$$n_L(1\,atm, 286\,K) = 2.5661\,x\,10^{19}\ molec/cm^3$$

line shape

$$\gamma p = 0.0992 \ \frac{cm^{-1}}{atm} * 1 atm = 0.0992 \, \mathrm{cm}^{-1}$$

$$\delta p = \ \text{-}.002700 \ \frac{cm^{-1}}{atm} * 1 atm = \ \text{-}.002700 \, \mathrm{cm}^{-1}$$

$$f(\omega) = \frac{1}{\pi} \frac{\gamma p}{\left(\omega - \omega_0 - \delta p\right)^2 + \left(\gamma p\right)^2}$$

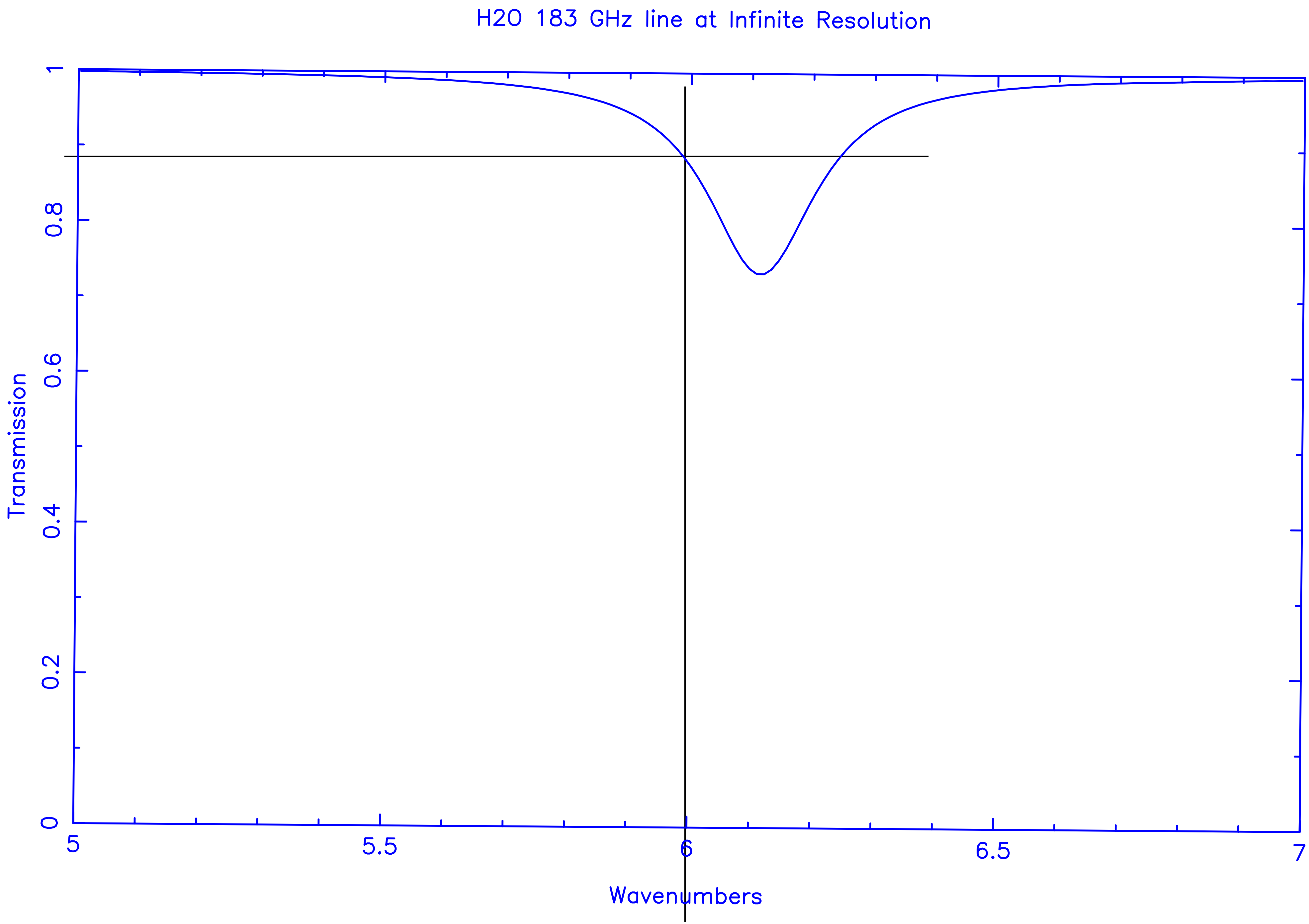
$$f(\omega) = 1.14250 \, cm$$

$$k_{\mathrm{v}}(\omega)ds = 0.779x10^{-22}\,\frac{cm^{-1}}{molec\,cm^{-2}} * 2.5661x10^{19}\,\frac{molec}{cm^{3}} *$$

$$50\,cm * 1.14250\,cm$$

$$= 0.11419$$

$$\frac{I}{I_0} = e^{-k_{\mathrm{v}}(\omega)ds} = 0.892$$



H2O 183 GHz line at Infinite Resolution
Transmission
0
0.2
0.4
0.6
0.8
1
5
5.5
6
6.5
7
Wavenumbers