* Radiative Properties of Gases

Molecules

vibration $E_n = \hbar\omega_0(n+\frac{1}{2})$

rotation $E_l = \frac{\hbar^2}{2I} l(l+1)$ $\begin{cases} l = 0, 1 \cdots \\ m \le |l| \end{cases}$

$\hbar\omega_p = E_{n+1} - E_n$ (selection rule)

$\omega_p = \omega_0$ $\quad \eta = \frac{1}{\lambda} = \frac{\omega}{c}$

$\hbar\omega_p = E_{l+1} - E_l$

$$\omega_p = \frac{\hbar}{2I}\left[(l+1)(l+2) - l(l+1)\right] = \frac{\hbar}{I}(l+1),$$

vibrational - rotational

$$E_{nl} = n\hbar(n+\tfrac{1}{2}) + \frac{\hbar^2}{2I_n} l(l+1)$$

ω_p or $\eta_p = \frac{\omega_p}{c}$

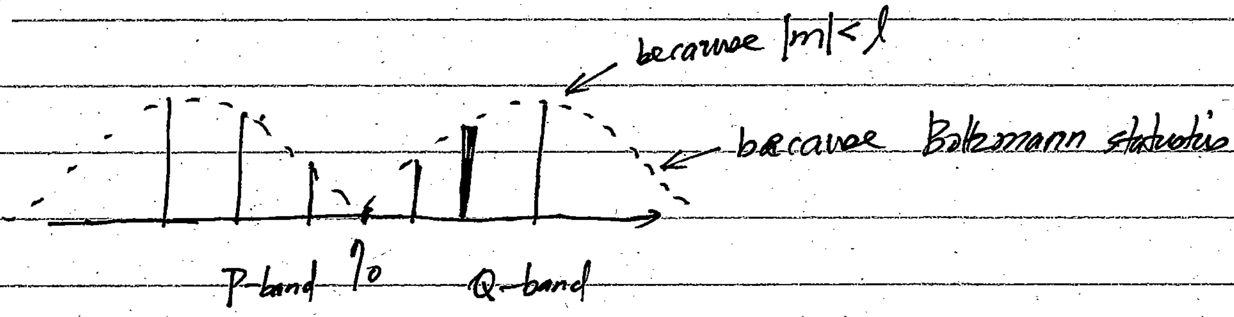
$$\eta_P = \eta_0 - (B_{n+1} + B_n)l + (B_{n+1} - B_n)l^2 \qquad \Delta l = -1$$

$l = 1, 2,$

$$\eta_Q = \eta_0 + (B_{n+1} - B_n)l + (B_{n+1} - B_n)l^2 \qquad \Delta l = 0$$

$$\eta_R = \eta_0 + 2B_{n+1} + (3B_{n+1} - B_n)l + (B_{n+1} - B_n)l^2 \qquad \Delta l = 1$$

R-band



Complications : ① for a single molecules CO_2
there can be different η_0
② Each line can be broadened.

a) natural energy uncertainty
Heisenberg uncertainty $\Delta E \cdot \Delta t \geq \frac{\hbar}{2}$.

b) molecules moving : Doppler effect

$$\eta_{ob} = \eta_{em}\left(1 + \frac{\vec{v}\cdot\vec{s}}{c}\right)$$

$$p(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2 \exp\left(-\frac{mv^2}{2kT}\right)$$

$$\Rightarrow k_\eta = \sqrt{\frac{\ln 2}{\pi}}\left(\frac{S}{b_0}\right)\exp\left[-(\ln 2)\left(\frac{\eta-\eta_0}{b_0}\right)^2\right]$$

$$b_0 = \frac{\eta_0}{c_0}\sqrt{\frac{2kT}{m}\ln 2}$$

c) Collision

$$k_\eta = \frac{S}{\pi}\,\frac{b_c}{(\eta-\eta_0)^2+b_c^2}$$

$$S = \int_{\Delta\eta} k_\eta \, d\eta$$

$$b_c = b_{c0}\left(\frac{p}{p_0}\right)\sqrt{\frac{T_0}{T}}$$

Recall Harmonic Oscillator under an electric field

$$\Delta x = x_0 e^{-i\omega t}$$

$$x_0 = \frac{E_0/m}{-\omega^2+\omega_0^2+i\gamma\omega} \quad , \quad \varepsilon = 1 + \frac{Ne^2/m}{-\omega^2+\omega_0^2+i\gamma\omega}$$

For solid, we sum N oscillators to talk about $\vec{P}$, χ & ε

For gases, $n \approx 1$ N small compared to solid.
imaginary part of interest

$$\varepsilon'' = \frac{Ne^2/m\varepsilon_0 \, (+\gamma\omega)}{(\omega_0^2-\omega_0^2)^2+(\gamma\omega)^2}$$

$$2nk = \varepsilon''$$

$$k = \frac{1}{2}\frac{Ne^2}{m\varepsilon_0}\frac{\gamma\omega}{(\omega^2-\omega_0^2)^2+(\gamma\omega)^2}$$

$$\approx \frac{1}{2}\frac{Ne^2}{m\varepsilon_0}\frac{\gamma\omega}{(\omega-\omega_0)^2\, 4\omega^2+(\gamma\omega)^2}$$

absorption coefficient

$$\alpha_j = \frac{4\pi k_j}{\lambda} = \frac{2\pi Ne^2}{m\varepsilon_0 c_0}\frac{\gamma_j}{4(\omega-\omega_{0j})^2+\gamma_j^2}$$

book use k_ω ← Lorentzian profil

EM theory. $\frac{dI_\lambda}{ds} = -\alpha_\lambda I_\lambda$

$$k_\eta = \frac{S}{\pi}\frac{b_c}{(\eta-\eta_0)^2+b_c^2}$$

b_c – line half width.

$$S \equiv \int_{\Delta\eta} k_\eta \, d\eta$$

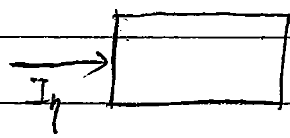
↑ line strength (line integrated abs. coeff)

We can also define mass absorpti coefficient

$$K_{a\eta} = \frac{\kappa_{\eta a}}{\rho_a}$$

└ ρ_a — partial density of specy a.

$$\boxed{\begin{array}{l} S \text{ — optical path length} \\ \rho_a S \text{ — mass based} \end{array}}$$



$$\frac{dI_\eta}{ds} = -\kappa_\eta I_\eta$$

$$I_\eta = I_\eta(0)\, e^{-\kappa_\eta S}$$

$X = S$ / $\rho_a S$ — mass path length

absorptance over S

$$A_\eta = \frac{I_\eta(0) - I_\eta(S)}{I_\eta(0)} = 1 - e^{-\kappa_\eta X}$$

Kirchoff law $= \varepsilon_\eta$

Integrated line Emissivity

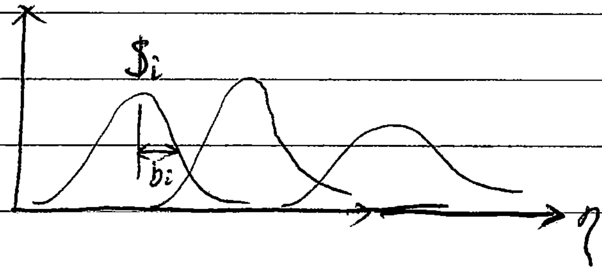
$$W = \frac{\int_0^\infty \varepsilon_\eta I_{b\eta}\, d\eta}{\int_0^\infty I_{b\eta}\, d\eta}$$

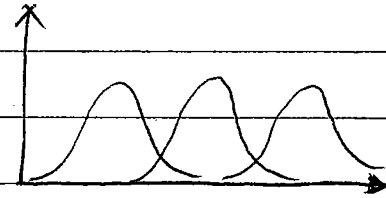
└ blackbody varies little over one line width

$$= \int_0^\infty \left(1 - e^{-\kappa_\eta X}\right) d\eta$$

$$= \begin{cases} SX & (\kappa X \ll 1,\ \text{weak line}) \\ 2\sqrt{SXb} & (\kappa X \gg 1\ \ \text{strong line}) \end{cases}$$

How to deal with overlapping lines





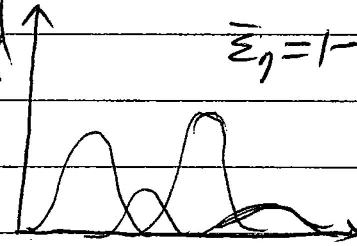
all lines are identical & equally spaced

Elsasser Model

$$\bar{\varepsilon}_\eta = 1-\exp\left[-\frac{\beta X \bar{k}_\eta}{\sqrt{1+\frac{X\bar{k}_\eta}{\beta}}}\right]$$

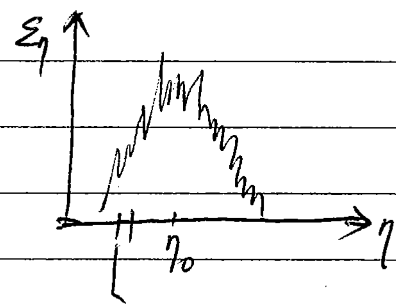
$$k_\eta = \sum_j k_{\eta j}.$$

$$\varepsilon_\eta = 1-\exp\left[-X\sum_j k_{\eta j}\right]$$



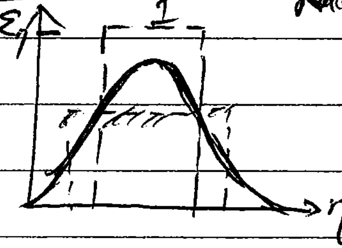
Goody model – statistical

Randomly spaced



smooth

line-by-line



$$\bar{\varepsilon} = \frac{1}{\Delta\eta}\int_{\Delta\eta} \varepsilon_\eta \, d\eta$$

The above are narrow band models.

Wide Band Model.

$$A \equiv \int_{band} \bar{\varepsilon}_\eta \, d\eta$$

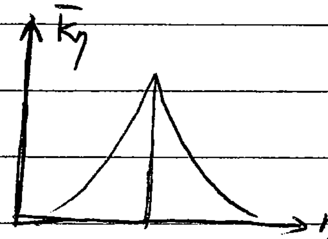
effective band width if $\varepsilon = 1$

$$\bar{\varepsilon}_\eta = 1 - e^{-\bar{k}_\eta X}$$

Construct models for $\bar{k}_\eta$ rather than $\bar{\varepsilon}_\eta$

So that no X – dependence

$$\bar{k}_\eta = \frac{\bar{S}}{d}$$



Edwards exponential.