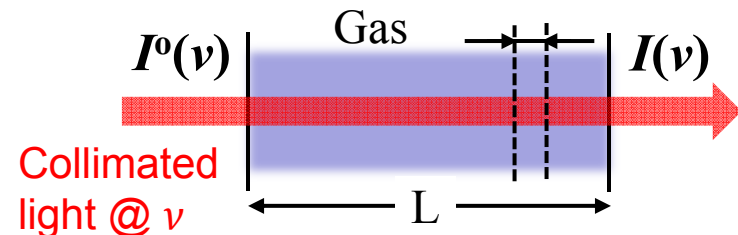


Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 5: Quantitative Emission/Absorption

1. Eqn. of radiative transfer / Beer's Law
2. Einstein theory of radiation
3. Spectral absorption coefficient
4. Radiative lifetime
5. Line strengths



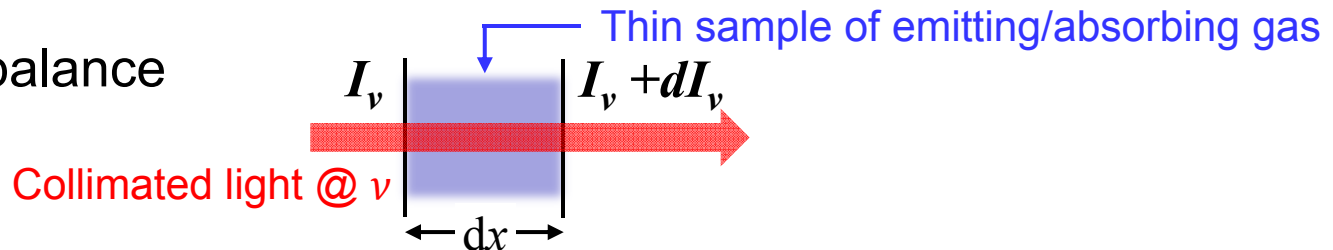
Light transmission through
a slab of gas

Beer's Law

$$I(\nu) = I^0(\nu) \exp(-k_\nu L)$$

1. Eqn. of radiative transfer / Beer's Law

- Energy balance



$$1 = \underbrace{\text{absorption}}_{\alpha_\nu} + \underbrace{\text{reflection}}_{=0} + \underbrace{\text{scattering}}_{=0} + \underbrace{\text{transmission}}_{T_\nu}$$

$$\Rightarrow \alpha_\nu + T_\nu = 1$$

spectral absorptivity, or absorbance \rightarrow \leftarrow spectral transmissivity

$$\hookrightarrow \alpha_\nu = k_\nu dx = -\frac{dI_\nu}{I_\nu} \text{ [no units]}$$

Spectral absorption coefficient (the fraction of incident light I_ν over frequency range $\nu \rightarrow \nu + d\nu$ which is absorbed per unit length dx)

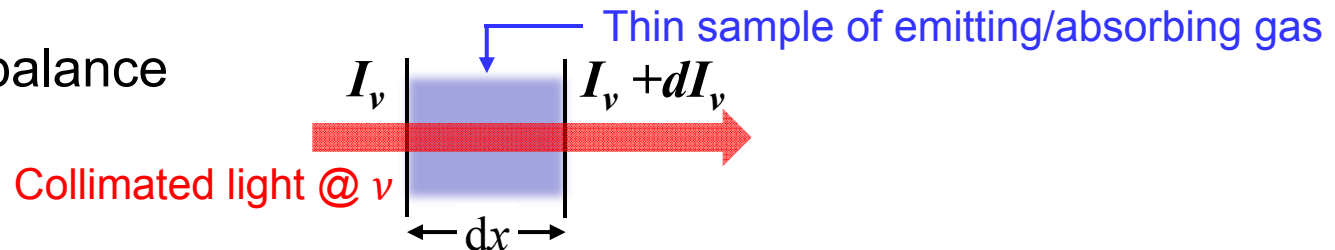
$$k_\nu \equiv -\frac{(dI_\nu / dx)}{I_\nu} \text{ [cm}^{-1}\text{]}$$

spectral intensity in $\left(\frac{\text{W/cm}^2}{\text{cm}^{-1}}\right)$ or $\left(\frac{\text{W/cm}^2}{\text{Hz}}\right)$

Integrate over ν \rightarrow for total I $I \text{ [W/cm}^2\text{]} = \int I_\nu d\nu$ Also applies to I @ ν

1. Eqn. of radiative transfer / Beer's Law

- Energy balance



Consider emission from the gas slab

➔ **Spectral emissivity** $\varepsilon_\nu = \frac{I_\nu^{em}}{I_\nu^{bb}}$ [no units] = $\frac{I^{em}(\nu)}{I^{bb}(\nu)}$ [no units]

↖ Blackbody spectral radiancy

Kirchhoff's Law – “emissivity equals absorptivity”

$$\varepsilon_\nu = \alpha_\nu$$

$$\text{emission} = \varepsilon_\nu I_\nu^{bb}$$

$$dI_\nu = \text{emission} - \text{absorption}$$

$$\text{absorption} = \alpha_\nu I_\nu$$

$$= \varepsilon_\nu I_\nu^{bb} - \alpha_\nu I_\nu = \alpha_\nu (I_\nu^{bb} - I_\nu)$$

➔ Differential form of the eqn. of radiative transfer

$$dI_\nu = k_\nu dx (I_\nu^{bb} - I_\nu)$$

1. Eqn. of radiative transfer / Beer's Law

- Energy balance

Differential form of the eqn. of radiative transfer

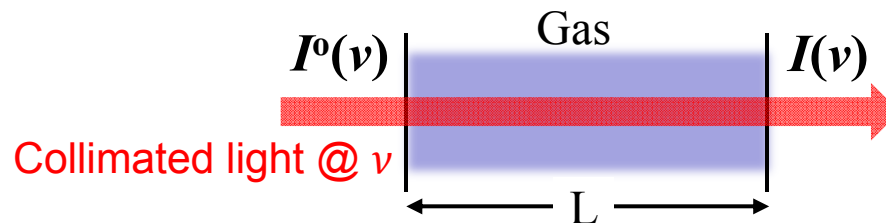
$$dI_\nu = k_\nu dx (I_\nu^{bb} - I_\nu)$$

↓ Integrate over L

Integrated form of the eqn. of radiative transfer

$$I_\nu = I_\nu^0 \exp(-k_\nu L) + I_\nu^{bb} [1 - \exp(-k_\nu L)]$$

Optical depth



Consider two interesting cases: Emission, Absorption

1. Eqn. of radiative transfer / Beer's Law

- Case I: Emission experiment $I_v^0 = 0$ (no external radiation source)

$$I_v = I_v^0 \exp(-k_v L) + I_v^{bb} [1 - \exp(-k_v L)]$$

Spectral radiancy: $I_v(L) = I_v^{bb} [1 - \exp(-k_v L)]$

Spectral emissivity: $\varepsilon_v(k_v, L) = \frac{I_v(L)}{I_v^{bb}} = 1 - \exp(-k_v L)$




Integrate over ν

$$I(L) = \int_0^\infty I_v(L) d\nu = \int_0^\infty I_v^{bb} [1 - \exp(-k_v L)] d\nu$$

$$\varepsilon(L) = \frac{I(L)}{I^{bb}} = \frac{1}{\sigma T^4} \int_0^\infty I_v^{bb} [1 - \exp(-k_v L)] d\nu$$

Emission types: Single/multiple line
Single/multiple bands
Continuum

 **Note:** $I^{bb} = \int_0^\infty I_v^{bb} d\nu = \underline{\sigma} T^4$
Stefan-Boltzmann constant
 $\sigma = 5.67 \times 10^{-5} [\text{erg} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{K}^{-4}]$

Optical depth: Optically thick: $k_v L \gg 1$, $I_v(L) \rightarrow I_v^{bb}$
Optically thin: $k_v L \ll 1$, $I_v(L) \rightarrow (k_v L) I_v^{bb}$, $\varepsilon_v = k_v L$

1. Eqn. of radiative transfer / Beer's Law

- Case II: Absorption experiment $I_\nu^0 \gg I_\nu^{bb}$

$$I_\nu = I_\nu^0 \exp(-k_\nu L) + I_\nu^{bb} [1 - \exp(-k_\nu L)]$$



$$I_\nu(L) = I_\nu^0 \exp(-k_\nu L) = I_\nu^0 \exp(-\alpha_\nu)$$

$\alpha = \text{absorbance}$
 \downarrow

Beer's Law / Beer-Lambert Law

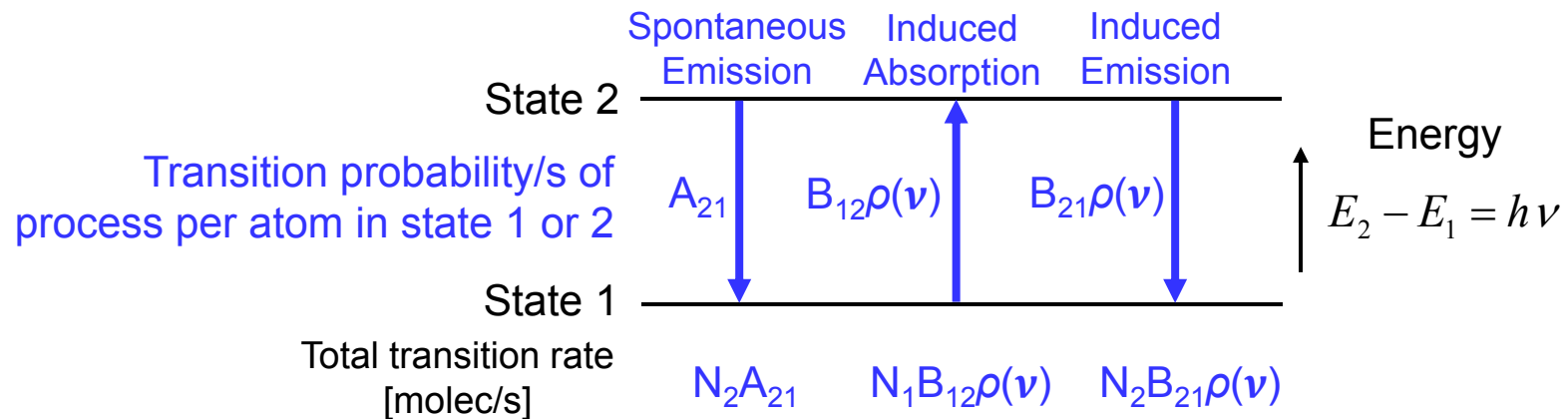
Alternate form: $T_\nu = \left(\frac{I}{I_0} \right) = \exp(-k_\nu L) = \frac{I(\nu)}{I^0(\nu)}$

- Observations:
 - The same equation would apply to the transmission of a pulse of laser excitation, with energy E_ν [J/cm²/cm⁻¹], i.e., $T_\nu = E_\nu / E_\nu^0$
 - The fundamental parameter controlling absorption over length L is the spectral absorption coefficient, k_ν .

How is k_ν related to fundamental molecular parameters?

2. Einstein theory of radiation

- Simplified theory (Milne Theory)



- Einstein coefficients of radiation

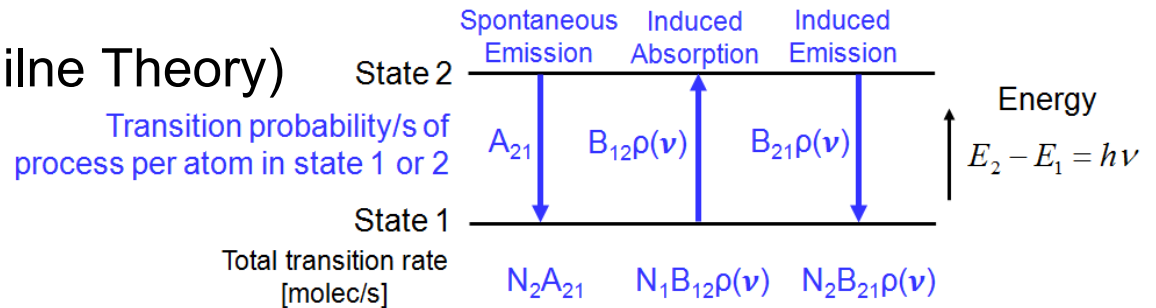
$B_{12}\rho(\nu)$ The probability/s that a molecule in state 1 exposed to radiation of spectral density $\rho(\nu)$ [$\text{J}/(\text{cm}^3\text{Hz})$] will absorb a quantum $h\nu$ and pass to state 2. The Einstein B-coefficient thus carries units of $\text{cm}^3\text{Hz}/(\text{J s})$.

$B_{21}\rho(\nu)$ The probability/s that a molecule in state 2 exposed to radiation of spectral density $\rho(\nu)$ will emit a quantum $h\nu$ and pass to state 1.

A_{21} The probability/s of spontaneous transfer from state 2 to 1 with release of photon of energy $h\nu$ (without regard to the presence of $\rho(\nu)$).

2. Einstein theory of radiation

- Simplified theory (Milne Theory)



- Equilibrium

Detailed balance $(\dot{N}_2)_{rad} = \underbrace{N_1 B_{12} \rho(\nu)}_{\text{molec/s entering state 2}} - \underbrace{N_2 (A_{21} + B_{21} \rho(\nu))}_{\text{molec/s leaving state 2}} = 0$

$$\begin{aligned} \frac{N_2}{N_1} &= \frac{B_{12} \rho(\nu)_{eq}}{\underbrace{A_{21} + B_{21} \rho(\nu)_{eq}}_{\text{rad. equil.}}} = \frac{g_2}{g_1} \underbrace{\exp\left(-\frac{h\nu}{kT}\right)}_{\text{statistical equil.}} \\ \text{Planck's blackbody distribution } \rho(\nu)_{eq} &= \frac{(8\pi h \nu^3 / c^3)}{\exp(+h\nu / kT) - 1} \end{aligned} \quad \Rightarrow \quad \begin{aligned} \rho(\nu)_{eq} &= \frac{(A_{21} / B_{21})}{\frac{g_1}{g_2} \frac{B_{12}}{B_{21}} \exp(h\nu / kT) - 1} \\ &= \frac{(8\pi h \nu^3 / c^3)}{\exp(h\nu / kT) - 1} \end{aligned}$$

$$\begin{aligned} g_1 B_{12} &= g_2 B_{21} \\ A_{21} &= \left(\frac{8\pi h \nu^3}{c^3}\right) B_{21} \equiv 1/\tau_{21} \end{aligned}$$

Radiative lifetime

Note: for collimated light

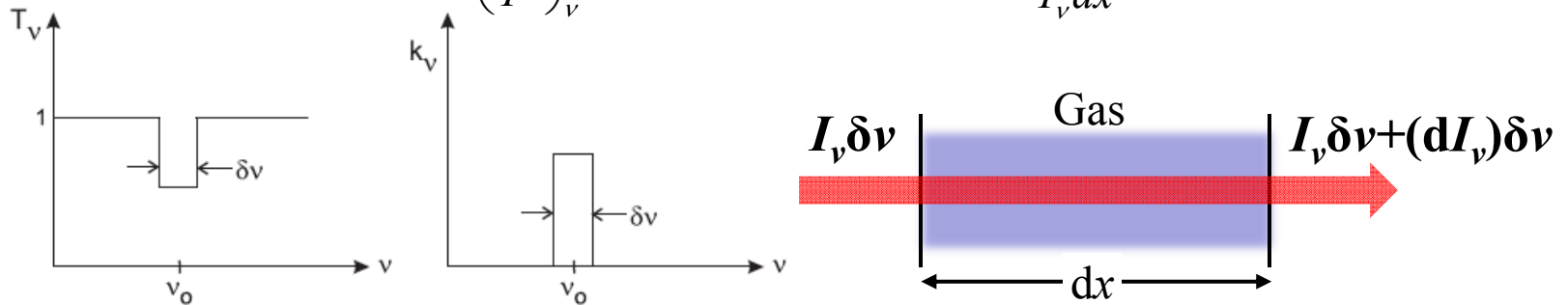
$$\begin{aligned} \rho(\nu)_{eq} &= n_p \cdot h\nu [\text{J/cm}^3 \text{s}^{-1}] \\ I_\nu &= n_p \cdot h\nu \cdot c [\text{W/cm}^2 \text{s}^{-1}] \quad \Rightarrow \quad \rho(\nu) = I_\nu / c \end{aligned}$$

Where is the link to k_ν ?

2. Einstein theory of radiation

- Find k_ν for a structureless absorption line of width $\delta\nu$

Recall Beer's Law: $T_\nu = \left(\frac{I}{I^0}\right)_\nu = \exp(-k_\nu L)$ $k_\nu \equiv -\frac{dI_\nu}{I_\nu dx}$



Absorbed power $P_{abs} = (\text{incident power over } \delta\nu) \times (\text{fraction absorbed}) \quad [\text{W/cm}^2]$

$$= (I_\nu^0 \delta\nu) \times (1 - T_\nu)$$

$$= (I_\nu^0 \delta\nu) (1 - \exp(-k_\nu L))$$

$\text{W/cm}^2\text{s}^{-1}$ s^{-1}

Optically thin limit $k_\nu dx \ll 1 \Rightarrow P_{abs} = (I_\nu^0 \delta\nu) (k_\nu dx)$

$$\frac{P_{abs}}{I_\nu^0 \delta\nu} = \text{fraction absorbed} = k_\nu dx$$

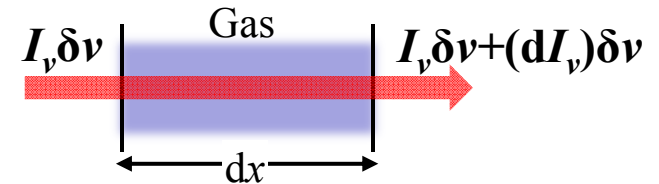
Now, let's find fraction absorbed using Einstein coefficients

2. Einstein theory of radiation

- Find k_ν for a structureless absorption line of width $\delta\nu$

Energy balance

$$(dI_\nu)\delta\nu = \left(\underbrace{\text{induced emission}}_{\text{for collimated light}} + \underbrace{\text{spontaneous emission}}_{=0} \right) - \underbrace{\text{induced absorption}}$$



$$\text{Induced emission} = \underbrace{(n_2 dx)}_{\text{molec/cm}^2 \text{ in state 2}} \times \underbrace{B_{21} \rho(\nu)}_{\text{prob/s of emission}} \times \underbrace{h\nu}_{\text{energy per photon}}$$

$$\text{Induced absorption} = \underbrace{(n_1 dx)}_{\text{molec/cm}^2 \text{ in state 1}} \times \underbrace{B_{12} \rho(\nu)}_{\text{prob/s of emission}} \times \underbrace{h\nu}_{\text{energy per photon}}$$

Recall:
 $\rho(\nu) = I_\nu / c$

$$\Rightarrow (dI_\nu)\delta\nu = [n_2 B_{21} - n_1 B_{12}] \frac{h\nu}{c} I_\nu dx$$

$$\Rightarrow \frac{dI_\nu}{I_\nu dx} \equiv k_\nu = \frac{h\nu}{c} \frac{1}{\delta\nu} [n_2 B_{21} - n_1 B_{12}]$$

$$\Rightarrow k_\nu [\text{cm}^{-1}] = \frac{h\nu}{c} \frac{1}{\delta\nu} n_1 B_{12} (1 - \exp(-h\nu / kT))$$

- Since k_ν is a function of $\delta\nu$, we conclude depends on linewidths + hence shape; next, repeat with realistic lineshape

Where are we headed next?

Improved Einstein Theory, Radiative Lifetime, Line Strength

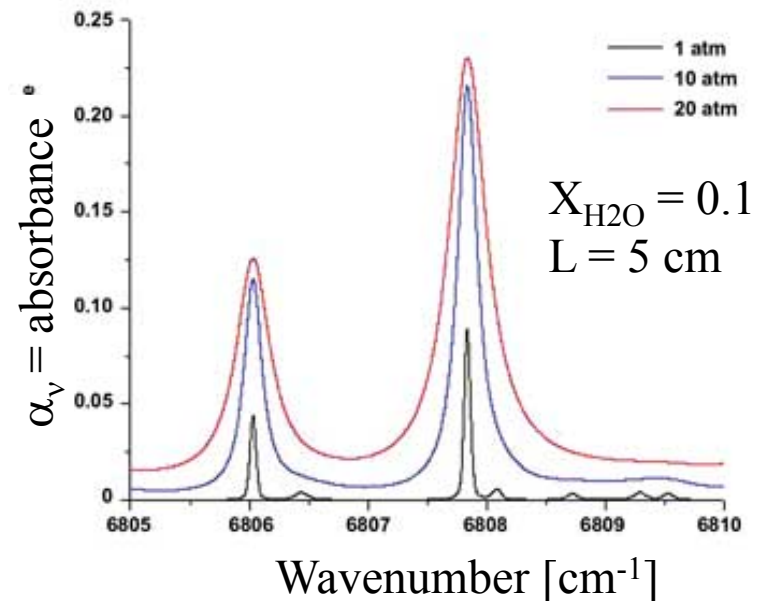
3. Spectral absorption coefficient

- with proper lineshape

4. Radiative lifetime

5. Line strengths

- Temperature dependence
- Band strength

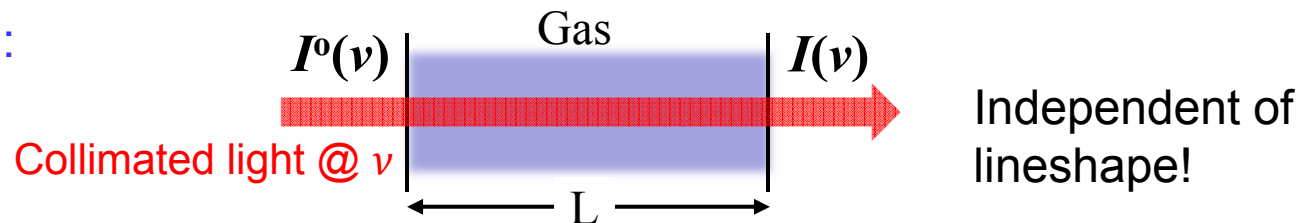


Water vapor absorption spectrum
simulated from HITRAN

1. Spectral absorption coefficient

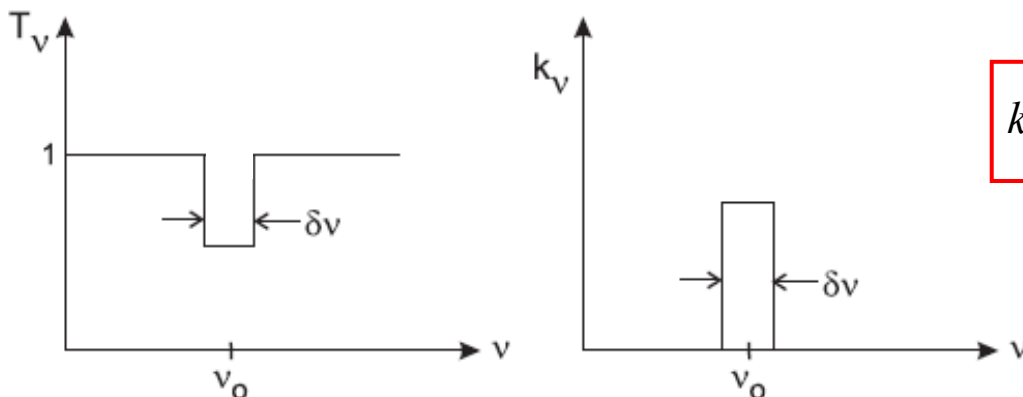
- Eqn. of radiative transfer

Recall:



$$I_\nu = I_\nu^0 \exp(-k_\nu L) + I_\nu^{bb} [1 - \exp(-k_\nu L)] \quad k_\nu \equiv -\frac{dI_\nu}{I_\nu dx}, \text{cm}^{-1}$$

- For structureless absorption line of width $\delta\nu$ (Hz), we found



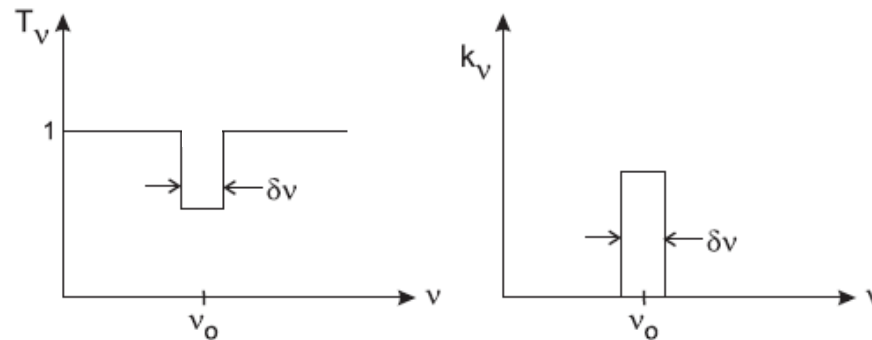
$$k_\nu [\text{cm}^{-1}] = \frac{h\nu}{c} \frac{1}{\delta\nu} n_1 B_{12} (1 - \exp(-h\nu/kT))$$

Note $k_\nu \propto n_1, B_{12},$ and $1/\delta\nu$

Next: use realistic lineshape to replace $1/\delta\nu$

1. Spectral absorption coefficient

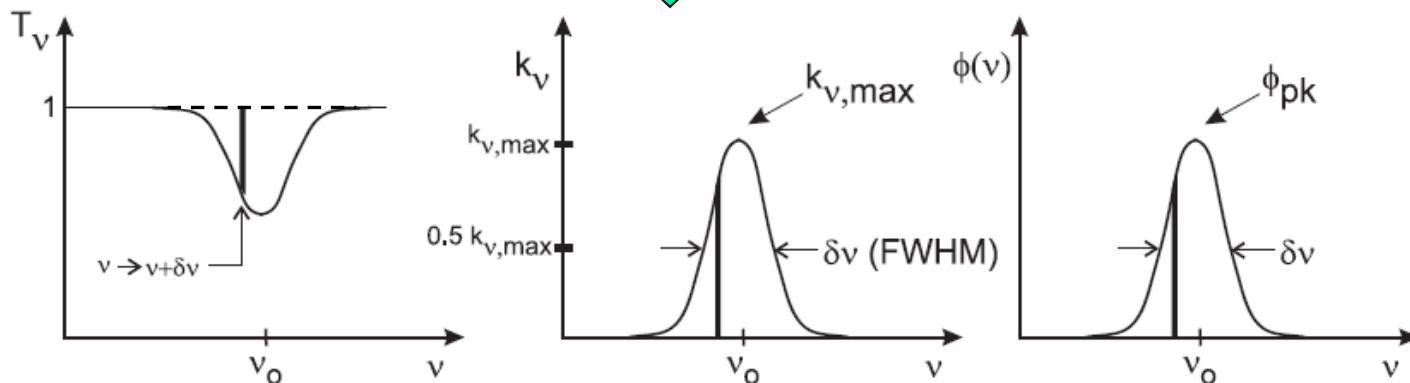
- Repeat derivation of k_ν using an improved lineshape model



Structureless absorption line of width $\delta\nu$



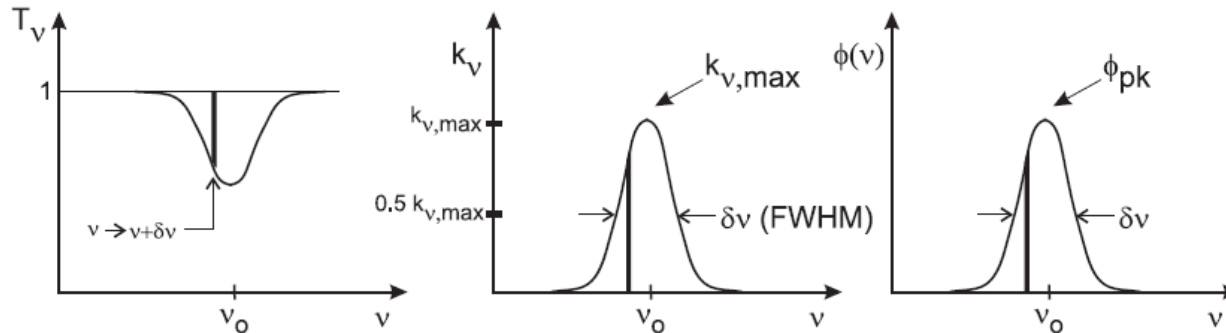
Replace with realistic lineshape



A typical absorption line with typical structure

3. Spectral absorption coefficient

■ k_ν



Recall Beer's Law: $T_\nu = \left(\frac{I}{I^0}\right)_\nu = \exp(-k_\nu L) \Rightarrow k_\nu \equiv -\frac{1}{L} \ln T_\nu$

Define: **Normalized lineshape function**

$$\phi \equiv \frac{k_\nu}{\int_{line} k_\nu d\nu} \quad \text{[cm] or [s]}, \quad \int_{line} \phi d\nu = 1$$

↑
Inverse frequency

Note: $\int k_\nu d\nu \approx k_{\nu,max} \delta\nu$
 ↑ Average width

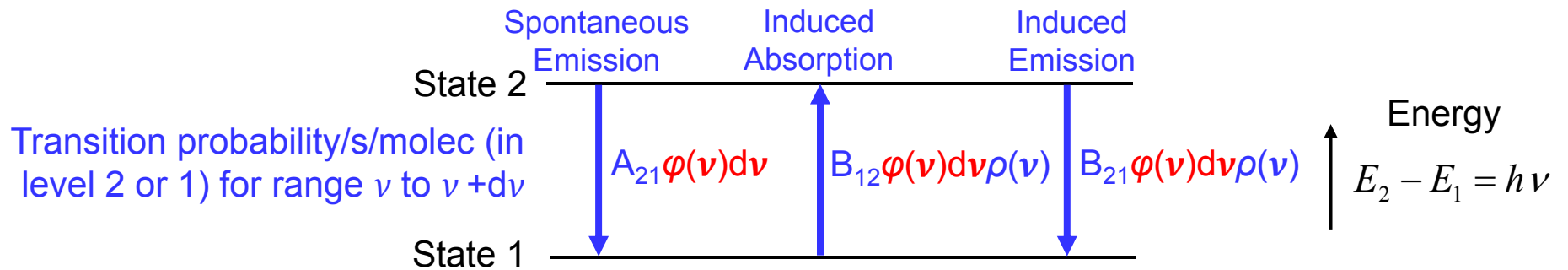
$\Rightarrow \phi_{pk} = \frac{k_{\nu,max}}{\int k_\nu d\nu} \approx \frac{1}{\delta\nu}$

Relevant transition probabilities have the same spectral dependence (shape) as k_ν and $\phi(\nu)$

And we can anticipate that $1/\delta\nu$ will be replaced by ϕ in k_ν equation

3. Spectral absorption coefficient

- Modified model



- Einstein coefficients of radiation

$A_{21} \phi(\nu) d\nu$ The probability/s of a molecule undergoing spontaneous emission, in the range $\nu \rightarrow \nu + d\nu$.
 [Note that the integral of this quantity over the range of allowed is just $A_{21} [s^{-1}]$, i.e., $\int A_{21} \phi(\nu) d\nu = A_{21}$.]

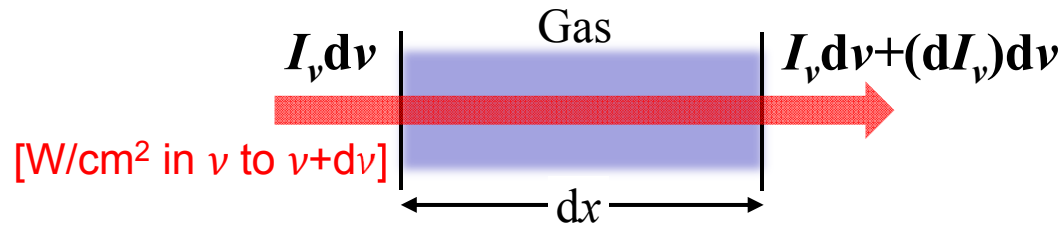
$B_{12} \phi(\nu) d\nu \rho(\nu)$ The probability/s of a molecule undergoing a transition from $1 \rightarrow 2$, in the range $\nu \rightarrow \nu + d\nu$.

$B_{21} \phi(\nu) d\nu \rho(\nu)$ The probability/s of a molecule undergoing a transition from $2 \rightarrow 1$, in the range $\nu \rightarrow \nu + d\nu$.

Recall: $\rho(\nu) = I_\nu / c$

3. Spectral absorption coefficient

- Energy balance



$dI_\nu d\nu = \text{emission in } d\nu - \text{absorption in } d\nu$

$$= \underbrace{\overbrace{n_2}^{\text{\#/cc}} dx}_{\text{molec/cm}^2} \times \underbrace{[B_{21}\phi(\nu)d\nu I_\nu / c]}_{\text{prob/s molec for } d\nu} \times \underbrace{h\nu_0}_{\text{energy/photon}} - n_1 dx \times [B_{12}\phi(\nu)d\nu I_\nu / c] \times h\nu_0$$

$$\Rightarrow -\frac{dI_\nu}{I_\nu dx} \equiv k_\nu = \frac{h\nu}{c} [n_1 B_{12} - n_2 B_{21}] \phi(\nu)$$

$$\Rightarrow k_\nu = \frac{h\nu}{c} n_1 B_{12} (1 - \exp(-h\nu / kT)) \phi(\nu)$$

Integrated absorption
/ Line strength

$$S_{12} \equiv \int_{\text{line}} k_\nu d\nu \quad [\text{cm}^{-1}\text{s}^{-1}] \Rightarrow S_{12} = \frac{h\nu}{c} n_1 B_{12} (1 - \exp(-h\nu / kT))$$

3. Spectral absorption coefficient

- Line strength – alternate forms

Line strength does not depend on lineshape, but is a function of n_1 , T , B_{12}

$$S_{12} = \frac{\lambda^2}{8\pi} n_1 A_{21} \frac{g_2}{g_1} (1 - \exp(-h\nu/kT)) \quad [\text{cm}^{-1}\text{s}^{-1}]$$

$$S_{12} = \left(\frac{\pi e^2}{m_e c} \right) n_1 f_{12} (1 - \exp(-h\nu/kT)) \quad [\text{cm}^{-1}\text{s}^{-1}]$$

Oscillator strength $f_{12} = \frac{S_{12,actual}}{S_{12,classical} (1 - \exp(-h\nu/kT))} \quad f_{21} = \left(\frac{g_1}{g_2} \right) f_{12}$

where $S_{12,classical} = \left(\frac{\pi e^2}{m_e c} \right) n_1, \left(\frac{\pi e^2}{m_e c} \right) = 0.0265 \text{cm}^2 \text{Hz}$

→ $S_{12,actual} = (0.0265 \text{cm}^2 \text{Hz}) n_1 f_{12} (1 - \exp(-h\nu/kT)) \quad n_1 = \frac{p_1}{kT}$

@ STP, $n_1 = n = 2.7 \times 10^{19} \text{cm}^{-3}$, $\exp(-h\nu_{12}/kT) \ll 1 \quad S_{12} [\text{cm}^{-2} / \text{atm}] = 2.380 \times 10^7 f_{12}$

3. Spectral absorption coefficient

- Important observations

1. From the original definition of k_ν and S_{12} we have

$$k_\nu = S_{12}\phi(\nu)$$

2. When

$h\nu / kT \gg 1$ as is common for electronic state transitions

$$S_{12} [\text{cm}^{-1}\text{Hz}] = \left(\frac{\pi e^2}{m_e c} \right) n_1 f_{12}$$

$$= (0.0265 \text{cm}^2 \text{Hz}) n_1 f_{12} \left. \vphantom{\frac{\pi e^2}{m_e c}} \right\}$$

$$= \frac{\lambda^2}{8\pi} n_1 A_{21} \frac{g_2}{g_1}$$

Aside:

@ $\lambda=1440\text{nm}$, $h\nu/k=10^4\text{K}$

@ $\lambda=720\text{nm}$, $h\nu/k=2 \times 10^4\text{K}$

@ $\lambda=360\text{nm}$, $h\nu/k=4 \times 10^4\text{K}$

$$1 - \exp(-h\nu / kT) \approx 1$$

$$\Rightarrow f_{12} / A_{12} = f_{12} \tau_{21} = 1.51 \frac{g_2}{g_1} (\lambda[\text{cm}])^2$$

Radiative lifetime of the 2→1 transition $\tau_{21} = 1 / A_{21}$

3. Spectral absorption coefficient

- Example: "Resonance Transition"

Resonance transition – one that couples the ground state to the first excited state

Electronic transition of a sodium atom $Na \left(\begin{array}{cc} \text{lower (L)} & \text{upper (U)} \\ \overbrace{3^2 S_{1/2}} & - \overbrace{3^2 P_{1/2}} \end{array} \right)$

$$\frac{g_2}{g_1} = 1, \quad \lambda = 589\text{nm} = 5.89 \times 10^{-5} \text{ cm}$$

Conventions:

atoms: (L-U)

molecules: (U↔L), arrow denotes absorption or emission

f_{ij} : i denotes initial state, j denotes final

$$f_{12} \tau_{589\text{nm}} = 1.51 \frac{g_2}{g_1} (\lambda[\text{cm}])^2 = 5.24 \times 10^{-9} \text{ s}$$

Measured: $\tau = 16.1 \times 10^{-9} \text{ s} \Leftrightarrow A = 0.62 \times 10^8 \text{ s}^{-1}$

➡ $f \approx 0.325$ ➡ Strong atomic transition: single electron
 Much smaller for molecular transitions: $\sim 10^{-2}$ - 10^{-4}

3. Spectral absorption coefficient

- Oscillator strength

Transitions	f_{21}	λ [nm]
$3^2S_{1/2} - 3^2P_{1/2}$	0.33	589.6
$3^2S_{1/2} - 3^2P_{3/2}$	0.67	589.0
$3^2S - 4^2P$	0.04	330.2

Oscillator strengths of selected sodium transitions

Molecule	$v' \leftarrow v''$	Electronic Transition	Band center [cm ⁻¹]	f_{12}
CO	1←0	-	2143	1.09x10 ⁻⁵
	2←0	-	4260	7.5x10 ⁻⁸
OH	1←0	-	3568	4.0x10 ⁻⁶
	0←0	$^2\Sigma \leftarrow ^2\Pi$	32600	1.2x10 ⁻³
CN	0←0	$^2\Pi \leftarrow ^2\Sigma$	9117	2.0x10 ⁻²

Absorption oscillator strengths of selected vibrational and vibronic bands of a few molecules

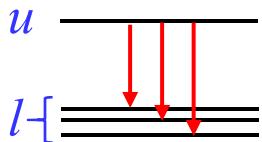
4. Radiative lifetime

- Radiative and non-radiative lifetimes

- Rate equation for radiative decay

$$\frac{dn_u}{dt} = -n_u \sum_l A_{u \rightarrow l} \quad (\text{spontaneous emission only}) \Rightarrow n_u(t) = n_u(0) \exp\left[-t \sum_l A_{u \rightarrow l}\right]$$

Upper level u \uparrow \uparrow Lower level l \uparrow Initial number density



Radiative lifetime
(zero-pressure lifetime)

$$\tau_r = \frac{1}{\sum_l A_{u \rightarrow l}}$$

- Rate equation for non-radiative decay

$$\left(\frac{dn_u}{dt}\right)_{nr} = -k_{nr} n_u = -\frac{n_u}{\tau_{nr}}$$

Rate parameter [s⁻¹] \uparrow \uparrow Non-radiative decay time, depends on the transition considered and on the surrounding molecules

- Simultaneous presence of radiative and non-radiative transitions

$$\frac{dn_u}{dt} = -\frac{n_u}{\tau_r} - \frac{n_u}{\tau_{nr}} = -\frac{n_u}{\tau}, \quad \tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1} \leftarrow \text{Lifetime of level } u$$

5. Line strengths

■ Alternate forms – Line strengths

$$1. \quad k_{\omega} [\text{cm}^{-1}] = S_{12} [\text{cm}^{-2}] \phi_{\omega} [\text{cm}] \quad \phi_{\omega} [\text{cm}] = c [\text{cm/s}] \cdot \phi_{\nu} [\text{s}]$$

$$\omega [\text{cm}^{-1}] \equiv 1 / \lambda [\text{cm}]$$

$$d\omega [\text{cm}^{-1}] \equiv (1/c) d\nu [\text{s}^{-1}]$$

$$2. \quad S_{12} [\text{cm}^{-2}] = (1/c) S_{12} [\text{cm}^{-1}/\text{s}]$$

Number density of absorbing species i in state 1

$$3. \quad S_{12} [\text{cm}^{-2} / \text{atm}] = S_{12} [\text{cm}^{-2}] / P_i [\text{atm}] = \left(\frac{n_1}{P_i [\text{atm}]} \right) \left(\frac{c}{8\pi\nu^2} \right) A_{12} \frac{g_2}{g_1} (1 - \exp(-h\nu/kT))$$

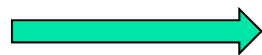
$$4. \quad S_{12} [\text{cm}^{-2} / \text{atm}] = \frac{S^* [\text{cm}^{-1} / (\text{molec} \cdot \text{cm}^{-2})] \times n [\text{molec} / \text{cc}]}{P [\text{atm}]}$$

HITRAN unit

Ideal gas law

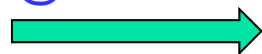
$$\rightarrow S_{12} [\text{cm}^{-2} / \text{atm}] = \frac{S^* [\text{cm}^{-1} / (\text{molec} \cdot \text{cm}^{-2})] \times 1013250 [\text{dynes} / (\text{cm}^2 \cdot \text{atm})]}{kT}$$

$$k = 1.38054 \times 10^{-16} \text{ erg/K}$$



$$S = \frac{S^* \times (7.34 \times 10^{21})}{T} [\text{cm}^{-2} \text{atm}^{-1}]$$

@ T=296K



$$S = S^* \times (2.4797 \times 10^{19}) [\text{cm}^{-2} \text{atm}^{-1}]$$

5. Line strengths

■ Alternate forms – Beer's Law

$$\left(\frac{I}{I^0}\right)_{\nu,\omega,\lambda} = \exp(-k_\nu L)$$

$$= \exp(-n\sigma_\nu L)$$

$$= \exp(-\beta_\omega P_i L)$$

$$= \exp(-S\phi_\nu P_i L)$$

- n = number density of the absorbing species [molecules/cm³]
- σ_ν = absorption cross-section [cm²/molec]
- S = line strength [cm⁻²atm⁻¹] or [cm⁻¹sec⁻¹/atm]
- β_ν = frequency-dependent absorption coefficient [cm⁻¹/atm]
- P_i = partial pressure of species i [atm]
- ϕ_ν = frequency-dependent lineshape function [cm] or [s]
- $\alpha_\nu = k_\nu L$ = absorbance

Common to use atmosphere and wavenumber units in IR

$$S_{12} [\text{cm}^{-2}/\text{atm}] = \int \beta_\omega d\omega$$

$$= \frac{S_{12} [\text{cm}^{-1}\text{s}^{-1}]}{cP_i [\text{atm}]}$$

$$\beta_\omega = k_\nu / P_i$$

absorption coefficient per
atmosphere of pressure

$$= 8.82 \times 10^{-13} \frac{n_1}{P_i [\text{atm}]} f_{12} (1 - \exp(-h\nu/kT))$$

$$= \frac{c}{8\pi\nu^2} \frac{n_1}{P_i} A_{21} \frac{g_2}{g_1} (1 - \exp(-h\nu/kT))$$

5. Line strengths

- Temperature dependence

Line strength in units of [cm²atm⁻¹]

$$S_i(T) = S_i(T_0) \frac{Q(T_0)}{Q(T)} \left(\frac{T_0}{T}\right) \exp\left[-\frac{hcE_i''}{k} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \\ \times \left[1 - \exp\left(-\frac{hc\nu_{0,i}}{kT}\right)\right] \left[1 - \exp\left(-\frac{hc\nu_{0,i}}{kT_0}\right)\right]^{-1}$$

Line strength in units of [cm⁻¹/(molecule·cm²)]

$$S_i^*(T) = S_i^*(T_0) \frac{Q(T_0)}{Q(T)} \exp\left[-\frac{hcE_i''}{k} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \\ \times \left[1 - \exp\left(-\frac{hc\nu_{0,i}}{kT}\right)\right] \left[1 - \exp\left(-\frac{hc\nu_{0,i}}{kT_0}\right)\right]^{-1}$$

$$\left. \begin{array}{l} S_i(T) \\ S_i^*(T) \end{array} \right\} \frac{S(T)}{S(T_0)} = \frac{S_i^*(T)}{S_i^*(T_0)} \times \frac{T_0}{T}$$

5. Line strengths

- Band strength

$$S_{band} = \sum_{band} S_{lines}$$

Example: Heteronuclear Diatomic Band Strength

$$S^{1 \leftarrow 0} = \sum_{J''}^{v'=1 \leftarrow v''=0} [S_{J' \leftarrow J''}^{1 \leftarrow 0}(P) + S_{J' \leftarrow J''}^{1 \leftarrow 0}(R)]$$

$$S_{J'J''}^{10}(R) = \frac{c}{8\pi\nu^2} \underbrace{\frac{n_{J''}}{n_i kT / 1.013 \times 10^6}}_{\frac{n_{J''}}{P_i, \text{ atm}}} \underbrace{\left[\frac{g_{J'}}{g_{J''}} = \frac{2J'+1}{2J''+1} \right]}_{\approx 1} \underbrace{\left[A_R^{10} \approx \frac{J''+1}{2J''+1} A^{10} \right]}_{A_P^{10} \approx \frac{J''}{2J''+1} A^{10}} \times (1 - \exp(-h\nu / kT))$$

➔ Based on normalized Hönl-London factor

$$\begin{cases} S^{10}(R) = \frac{(1.013 \times 10^6)}{8\pi\nu^2 kT / c} A^{10} \sum_{J''} \left[\frac{n_{J''}}{n_i} \frac{J''+1}{2J''+1} \right] \\ S^{10}(P) = \frac{(1.013 \times 10^6)}{8\pi\nu^2 kT / c} A^{10} \sum_{J''} \left[\frac{n_{J''}}{n_i} \frac{J''}{2J''+1} \right] \end{cases} \xrightarrow{\sum_{J''} (n_{J''} / n_i) = 1} S^{10}(T) = \frac{(1.013 \times 10^6) c A^{10}}{8\pi\nu^2 kT}$$

5. Line strengths

- Band strength

$$S_{band} = \sum_{band} S_{lines}$$

Example: Heteronuclear Diatomic Band Strength

$$S^{10}(T) = \frac{(1.013 \times 10^6) c A^{10}}{8\pi \nu^2 kT}$$

Band strength of CO:

$$S_{CO}^{10}(273K) = \frac{3.2 \times 10^{28} A^{10}}{\nu^2} \approx 280 \text{cm}^{-2}/\text{atm}$$

$$\omega \approx 2150 \text{cm}^{-1} \longleftrightarrow \nu \approx 6.4 \times 10^{13} \text{s}^{-1}$$

$$\rightarrow A^{10} \approx 36 \text{s}^{-1} \longleftrightarrow \tau^{10} = 0.028 \text{s}$$

Compare with previous example of $\tau_{Na} \approx 16 \text{ns}$
➔ IR transitions have much lower values of A and longer radiative lifetime than UV/Visible transitions due to their smaller changes in dipole moment



Next: Spectral Lineshapes

- ❖ Doppler, Natural, Collisional and Stark Broadening
- ❖ Voigt Profiles