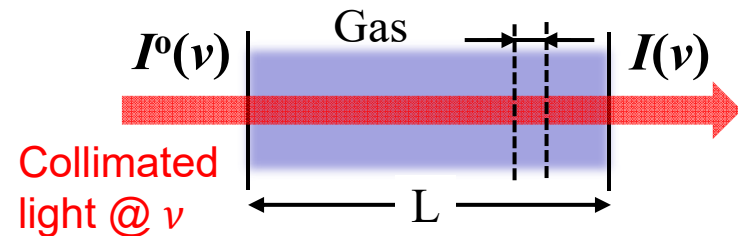# Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 5: Quantitative Emission/Absorption

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

2. Einstein theory of radiation

3. Spectral absorption coefficient

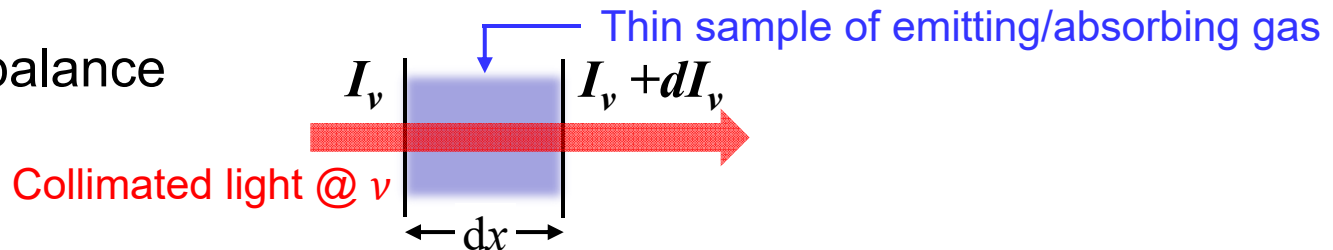4. Radiative lifetime

5. Line strengths

Light transmission through a slab of gas

Beer's Law

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

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

- Energy balance

Thin sample of emitting/absorbing gas

I_ν $I_\nu + dI_\nu$

Collimated light @ ν

$\leftarrow dx \rightarrow$

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

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

spectral absorptivity, or absorbance $\rightarrow$ $\llcorner$ spectral transmissivity

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

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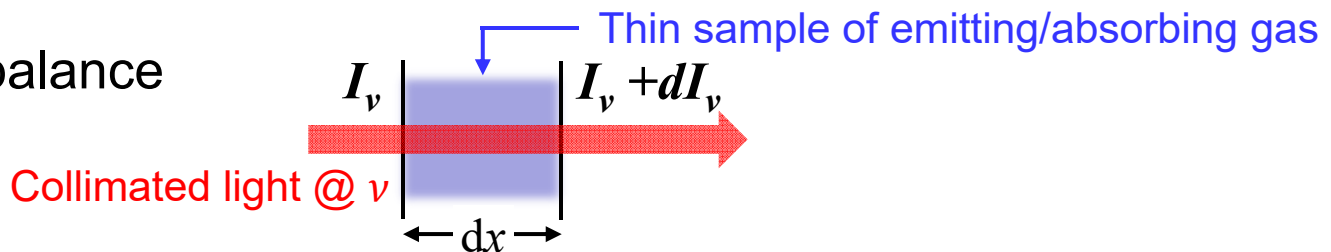
$$k_\nu \equiv -\frac{(dI_\nu / dx)}{I_\nu} [\text{cm}^{-1}]$$

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

Integrate over ν for total I

$$I[\text{W/cm}^2] = \int_\nu I_\nu d\nu$$ Also applies to I @ ν

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

- Energy balance

Thin sample of emitting/absorbing gas

I_v $I_v + dI_v$

Collimated light @ v

$\leftarrow dx \rightarrow$

Consider emission from the gas slab

➡ Spectral emissivity $\varepsilon_v = \dfrac{I_v^{em}}{I_v^{bb}} \left[\text{no units}\right] = \dfrac{I^{em}(v)}{I^{bb}(v)} \left[\text{no units}\right]$

Blackbody spectral radiancy

<u>Kirchhoff's Law</u> – "emissivity equals absorptivity"

$$\varepsilon_v = \alpha_v$$

$\text{emission} = \varepsilon_v I_v^{bb}$

$\text{absorption} = \alpha_v I_v$

$dI_v = \text{emission} - \text{absorption}$

$= \varepsilon_v I_v^{bb} - \alpha_v I_v = \alpha_v \left(I_v^{bb} - I_v\right)$

➡ Differential form of the eqn. of radiative transfer

$$\boxed{dI_v = k_v dx \left(I_v^{bb} - I_v\right)}$$

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

- **Energy balance**
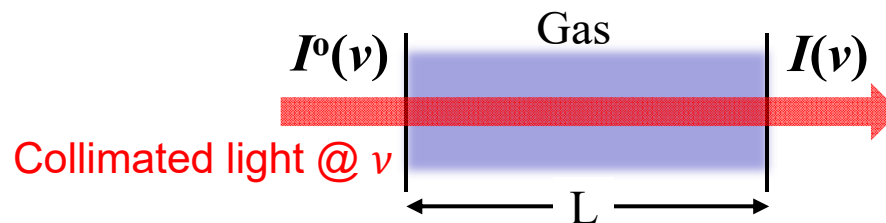
Differential form of the eqn. of radiative transfer

$$dI_v = k_v dx \left(I_v^{bb} - I_v \right)$$

⬇ Integrate over L

Integrated form of the eqn. of radiative transfer

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

Optical depth

$I^o(v)$ Gas $I(v)$

Collimated light @ v

L

Consider two interesting cases: Emission, Absorption

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

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

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

Spectral radiancy: $I_\nu(L) = I_\nu^{bb}[1 - \exp(-k_\nu L)]$

Spectral emissivity: $\varepsilon_\nu(k_\nu, L) = \dfrac{I_\nu(L)}{I_\nu^{bb}} = 1 - \exp(-k_\nu L)$

Integrate over ν

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

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

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

Note: $I^{bb} = \int_0^\infty I_\nu^{bb}d\nu = \sigma T^4$

Stefan-Boltzmann constant

$\sigma = 5.67 \times 10^{-5}[\mathrm{erg \cdot cm^{-2} \cdot s^{-1} \cdot K^{-4}}]$

Optical depth: Optically thick: $k_\nu L \gg 1$, $\qquad I_\nu(L) \to I_\nu^{bb}$

Optically thin: $k_\nu L \ll 1$, $\qquad I_\nu(L) \to (k_\nu L)I_\nu^{bb}, \varepsilon_\nu = k_\nu L$

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

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

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

$\alpha = $ absorbance

$$\boxed{I_\nu(L) = I_\nu^0 \exp(-k_\nu L)} = I_\nu^0 \exp(-\alpha_\nu)$$
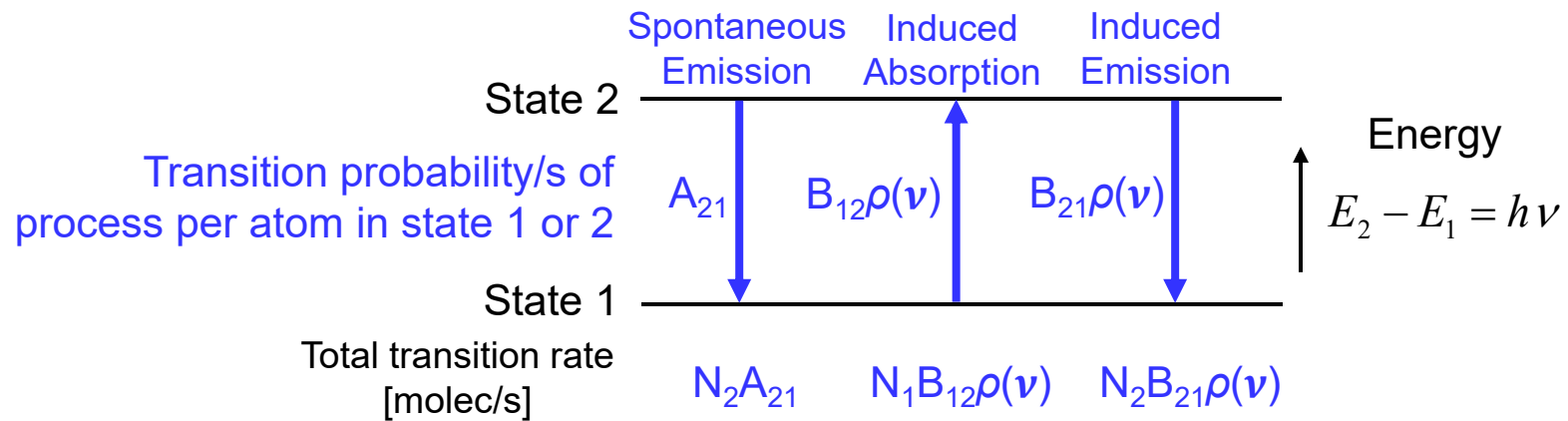
Beer's Law / Beer-Lambert Law

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

- Observations:
  1. The same equation would apply to the transmission of a pulse of laser excitation, with energy E_ν [J/cm^2/cm^{-1}], i.e., $T_\nu = E_\nu / E_\nu^0$
  2. The fundamental parameter controlling absorption over length L is the spectral absorption coefficient, k_ν.

How is k_ν related to fundamental molecular parameters?

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2. Einstein theory of radiation

- Simplified theory (Milne Theory)

<div align="center">

	Spontaneous Emission	Induced Absorption	Induced Emission

State 2

Transition probability/s of process per atom in state 1 or 2 A_{21} $B_{12}\rho(\nu)$ $B_{21}\rho(\nu)$

Energy

$$E_2 - E_1 = h\nu$$

State 1

Total transition rate [molec/s] $N_2 A_{21}$ $N_1 B_{12}\rho(\nu)$ $N_2 B_{21}\rho(\nu)$

</div>

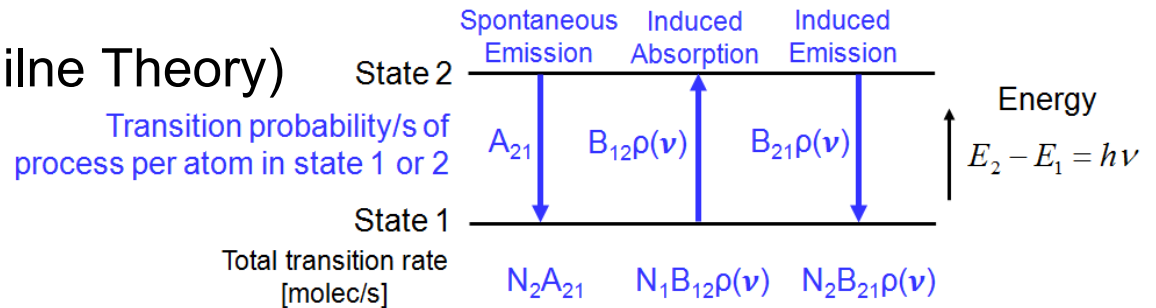- **Einstein coefficients of radiation**

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

	Spontaneous Emission	Induced Absorption	Induced Emission
State 2			
Transition probability/s of process per atom in state 1 or 2	A_{21}	$B_{12}\rho(\nu)$	$B_{21}\rho(\nu)$
State 1			
Total transition rate [molec/s]	$N_2 A_{21}$	$N_1 B_{12}\rho(\nu)$	$N_2 B_{21}\rho(\nu)$

Energy $E_2 - E_1 = h\nu$

- **Equilibrium**

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

$$\frac{N_2}{N_1} = \underbrace{\frac{B_{12}\rho(\nu)_{eq}}{A_{21} + B_{21}\rho(\nu)_{eq}}}_{\text{rad. equil.}} = \underbrace{\frac{g_2}{g_1}\exp\left(-\frac{h\nu}{kT}\right)}_{\text{statistical equil.}}$$

$$\rho(\nu)_{eq} = \frac{\left(A_{21}/B_{21}\right)}{\dfrac{g_1}{g_2}\dfrac{B_{12}}{B_{21}}\exp(h\nu/kT)-1}$$

Planck's blackbody distribution
$$\rho(\nu)_{eq} = \frac{\left(8\pi h\nu^3/c^3\right)}{\exp(+h\nu/kT)-1}$$

$$= \frac{\left(8\pi h\nu^3/c^3\right)}{\exp(h\nu/kT)-1}$$

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

Radiative lifetime

✎ Note: for collimated light
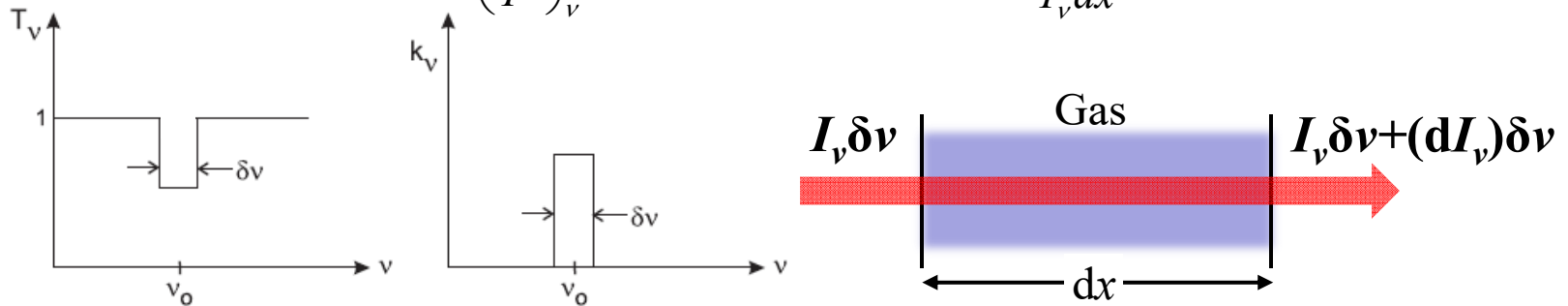$$\rho(\nu)_{eq} = n_p \cdot h\nu \left[\text{J/cm}^3\text{s}^{-1}\right]$$
$$I_\nu = n_p \cdot h\nu \cdot c \left[\text{W/cm}^2\text{s}^{-1}\right]$$

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

Where is the link to k_ν?

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2. Einstein theory of radiation

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

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

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

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

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

$W/cm^2 s^{-1}$ ⎯⬆   ⬆⎯ s^{-1}

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

$$\frac{P_{abs}}{I_\nu^0 \delta\nu} = \text{fraction absorbed} = k_\nu dx$$
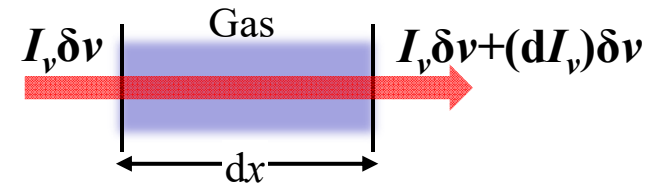
Now, let's find fraction absorbed using Einstein coefficients

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2. Einstein theory of radiation

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

$I_\nu\delta\nu$ | Gas | $I_\nu\delta\nu+(\mathbf{d}I_\nu)\delta\nu$

$\leftarrow \mathrm{d}x \rightarrow$

Energy balance

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

for collimated light

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

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

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

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

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

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

Where are we headed next?
Improved Einstein Theory, Radiative Lifetime, Line Strength
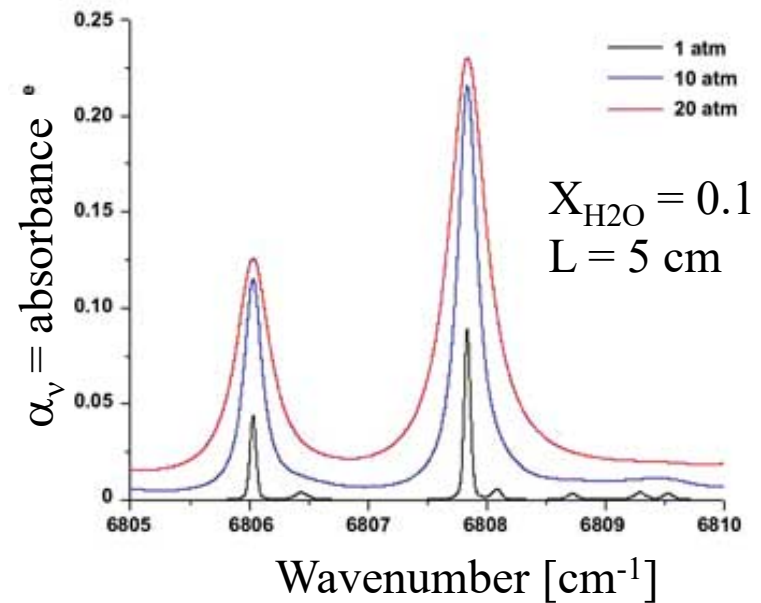
3. Spectral absorption coefficient

 - with proper lineshape

4. Radiative lifetime

5. Line strengths

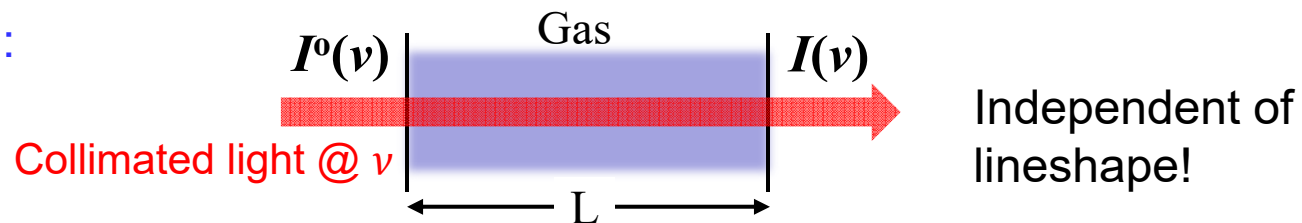 - Temperature dependence

 - Band strength

$X_{H2O} = 0.1$
$L = 5$ cm

Water vapor absorption spectrum simulated from HITRAN

1. Spectral absorption coefficient

- Eqn. of radiative transfer

Recall:

Gas

$I^0(v)$ $I(v)$

Collimated light @ v

Independent of lineshape!

L

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

$$k_v \equiv -\frac{dI_v}{I_v dx}, cm^{-1}$$

- For <u>structureless</u> absorption line of width δv (Hz), we found
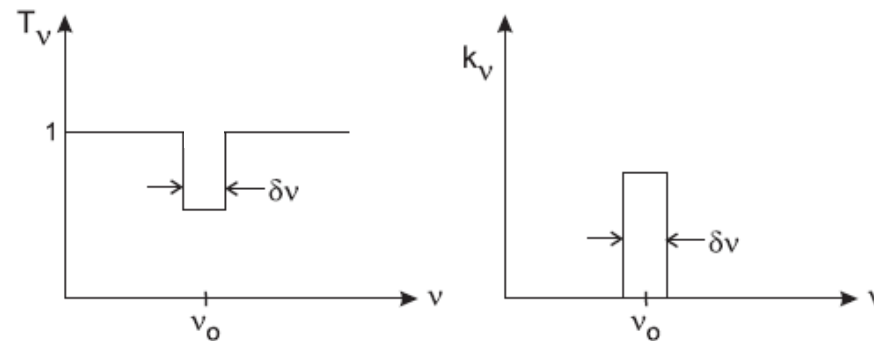
T_v

1

δv

v_0

v

k_v

δv

v_0

v

$$k_v[cm^{-1}] = \frac{hv}{c}\frac{1}{\delta v} n_1 B_{12}(1 - \exp(-hv/kT))$$
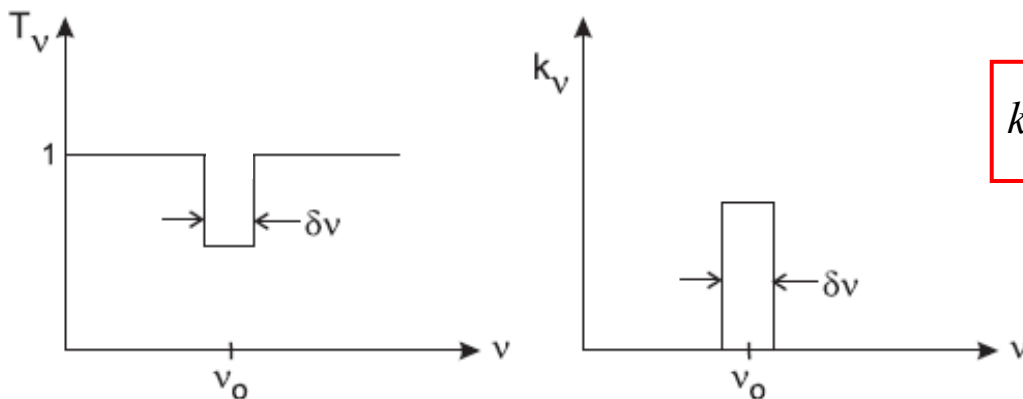
Note $k_v \propto n_1$, B_{12}, and $1/\delta v$

Next: use realistic lineshape
To replace $1/\delta v$
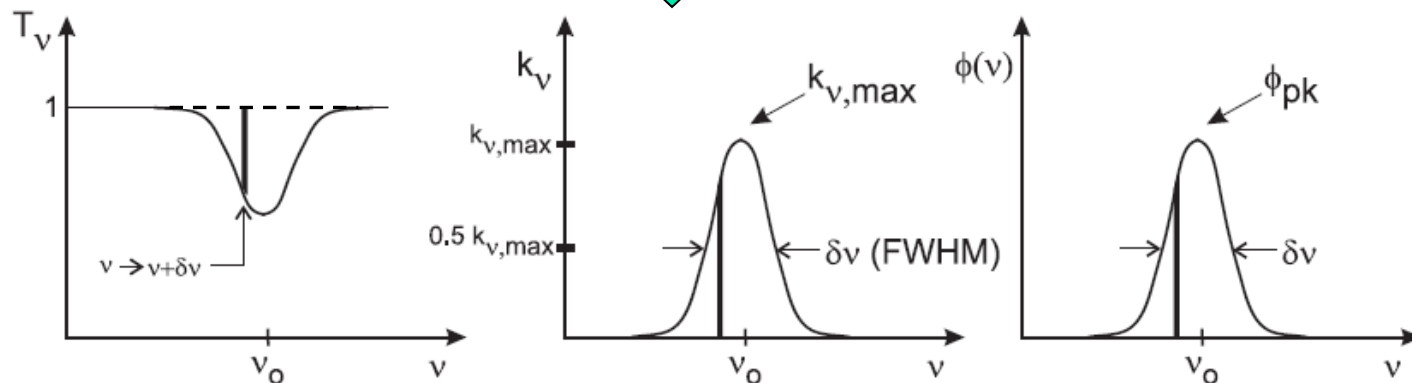
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1. Spectral absorption coefficient

- Repeat derivation of k_ν using an improved lineshape model

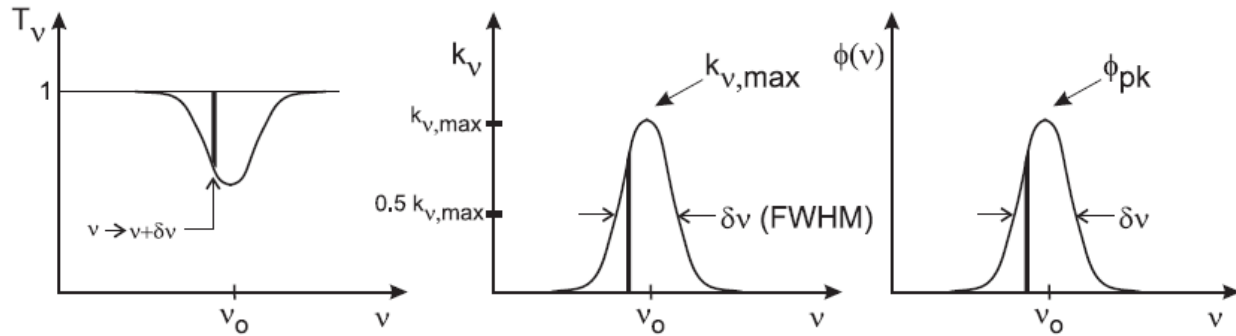Structureless absorption line of width $\delta\nu$

Replace with realistic lineshape

A typical absorption line with typical structure

3. Spectral absorption coefficient

k_ν

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

Define: **Normalized lineshape function**

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

Inverse frequency

Note: $\displaystyle\int k_\nu d\nu \approx k_{\nu,max}\,\delta\nu$

Average width

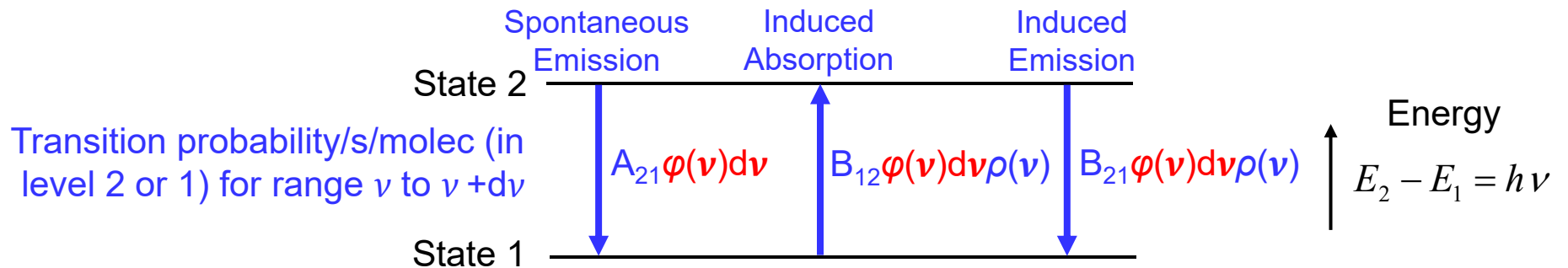$\implies \phi_{pk} = \dfrac{k_{\nu,max}}{\int k_\nu d\nu} \approx \dfrac{1}{\delta\nu}$

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

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

3. Spectral absorption coefficient

- Modified model

Spontaneous Emission   Induced Absorption   Induced Emission

State 2 ——————————————————

Transition probability/s/molec (in level 2 or 1) for range ν to $\nu +d\nu$

$A_{21}\varphi(\nu)d\nu$ $B_{12}\varphi(\nu)d\nu\rho(\nu)$ $B_{21}\varphi(\nu)d\nu\rho(\nu)$

Energy

$E_2 - E_1 = h\nu$

State 1 ——————————————————

- **Einstein coefficients of radiation**

$A_{21}\varphi(\nu)d\nu$ 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., $\int A_{21}\phi(\nu)d\nu = A_{21}$.]
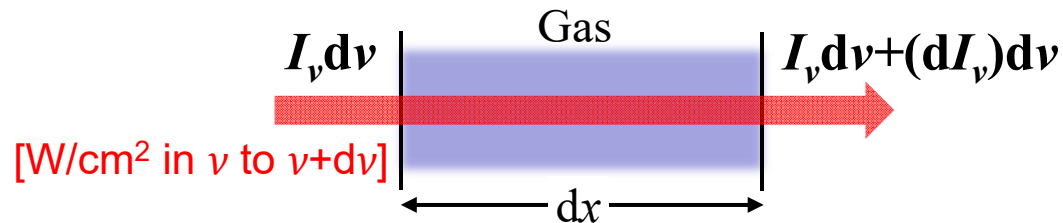
$B_{12}\varphi(\nu)d\nu\rho(\nu)$ The probability/s of a molecule undergoing a transition from $1\rightarrow2$, in the range $\nu \rightarrow \nu+d\nu$.

$B_{21}\varphi(\nu)d\nu\rho(\nu)$ The probability/s of a molecule undergoing a transition from $2\rightarrow1$, in the range $\nu \rightarrow \nu+d\nu$.

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

3. Spectral absorption coefficient

- Energy balance

$$I_\nu d\nu \boxed{\quad \text{Gas} \quad} I_\nu d\nu + (dI_\nu)d\nu$$

[W/cm² in ν to $\nu + d\nu$]

$$\longleftarrow dx \longrightarrow$$

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

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

$$\underbrace{n_2 dx}_{\text{molec/cm}^2}$$

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

$$\Longrightarrow \quad \boxed{k_\nu = \frac{h\nu}{c}n_1 B_{12}\left(1 - \exp(-h\nu / kT)\right)\phi(\nu)}$$

Integrated absorption / Line strength $\quad S_{12} \equiv \int_{line} k_\nu d\nu \ \left[\text{cm}^{-1}\text{s}^{-1}\right] \Longrightarrow \boxed{S_{12} = \frac{h\nu}{c}n_1 B_{12}\left(1 - \exp(-h\nu / kT)\right)}$

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

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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}

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

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

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

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

$$S_{12,actual} = \left(0.0265\mathrm{cm^2 Hz}\right) n_1 f_{12} \left(1 - \exp(-h\nu/kT)\right) \qquad \boxed{n_1 = \frac{p_1}{kT}}$$

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

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3. Spectral absorption coefficient

- Important observations

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

  $$\boxed{k_v = S_{12}\phi(v)}$$

  2. When

  $$hv/kT \gg 1 \text{ as is common for electronic state transitions}$$

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

  $$= \left(0.0265 cm^2 Hz\right)n_1 f_{12}$$

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

Aside:
@λ=1440nm, hv/k=10^4K
@λ=720nm, hv/k=2x10^4K
@λ=360nm, hv/k=4x10^4K

$$1 - \exp(-hv/kT) \approx 1$$

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

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

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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 $Na\left(\overbrace{3^2 S_{1/2}}^{\text{lower (L)}} - \overbrace{3^2 P_{1/2}}^{\text{upper (U)}}\right)$

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

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: ~ 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	$1 \leftarrow 0$	-	2143	1.09×10^{-5}
	$2 \leftarrow 0$	-	4260	7.5×10^{-8}
OH	$1 \leftarrow 0$	-	3568	4.0×10^{-6}
	$0 \leftarrow 0$	$^2\Sigma \leftarrow ^2\Pi$	32600	1.2×10^{-3}
CN	$0 \leftarrow 0$	$^2\Pi \leftarrow ^2\Sigma$	9117	2.0×10^{-2}

Absorption oscillator strengths of selected vibrational and vibronic bands of a few molecules
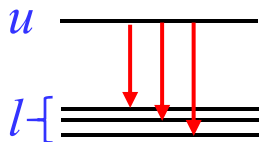
4. Radiative lifetime

- Radiative and non-radiative lifetimes

  - Rate equation for radiative decay (in the absence of replenishing n_u)

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

Upper level u ⎤ ⎡ Lower level l

Initial number density

u ——————

l ═══════

Radiative lifetime
(zero-pressure lifetime)

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

  - 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}]

Non-radiative decay time, depends on the transition considered and on the surrounding molecules

  - Simultaneous presence of radiative and non-radiative transitions

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

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5. Line strengths

- Alternate forms – Line strengths

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

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

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

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

   Number density of absorbing species i in state 1

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

   HITRAN unit

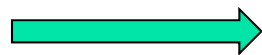4. $S_{12}[cm^{-2}/atm] = \dfrac{S^*[cm^{-1}/(molec \cdot cm^{-2})] \times n[molec/cc]}{P[atm]}$

Ideal gas law $\longrightarrow$ $S_{12}[cm^{-2}/atm] = \dfrac{S^*[cm^{-1}/(molec \cdot cm^{-2})] \times 1013250[dynes/(cm^2 \cdot atm)]}{kT}$

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

$\longrightarrow$ $S = \dfrac{S^* \times (7.34 \times 10^{21})}{T}[cm^{-2}atm^{-1}]$
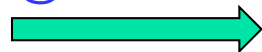
@ T=296K $\longrightarrow$ $S = S^* \times (2.4797 \times 10^{19})[cm^{-2}atm^{-1}]$

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/cm^3]
- σ_ν = absorption cross-section [cm^2/molec]
- S = line strength [cm^{-2}atm^{-1}] or [cm^{-1}sec^{-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

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

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

$$= 8.82\times10^{-13}\frac{n_1}{P_i[\text{atm}]}f_{12}\left(1-\exp(-h\nu/kT)\right)$$

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

$$\boxed{\beta_\omega = k_\nu/P_i}$$

absorption coefficient per atmosphere of pressure

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5. Line strengths

- Temperature dependence

Line strength in units of [cm^{-2}atm^{-1}]

$$S_i(T) = S_i(T_0) \frac{Q(T_0)}{Q(T)} \left(\frac{T_0}{T}\right) \exp\left[-\frac{hcE_i''}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

$$\times \left[1 - \exp\left(-\frac{hc\,v_{0,i}}{kT}\right)\right]\left[1 - \exp\left(-\frac{hc\,v_{0,i}}{kT_0}\right)\right]^{-1}$$

Line strength in units of [cm^{-1}/(molecule·cm^{-2}]

$$S_i^*(T) = S_i^*(T_0) \frac{Q(T_0)}{Q(T)} \exp\left[-\frac{hcE_i''}{k}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

$$\times \left[1 - \exp\left(-\frac{hc\,v_{0,i}}{kT}\right)\right]\left[1 - \exp\left(-\frac{hc\,v_{0,i}}{kT_0}\right)\right]^{-1}$$

$$\frac{S(T)}{S(T_0)} = \frac{S_i^*(T)}{S_i^*(T_0)} \times \frac{T_0}{T}$$

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5. Line strengths

■ Band strength

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

Example: Heteronuclear Diatomic Band Strength

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

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

➡ Based on normalized Hönl-London factor

$$\Rightarrow \begin{cases} S^{10}(R) = \dfrac{c(1.013 \times 10^6)}{8\pi v^2 kT} A^{10} \sum_{J''} \left[\dfrac{n_{J''}}{n_i} \dfrac{J''+1}{2J''+1} \right] \\[4ex] S^{10}(P) = \dfrac{c(1.013 \times 10^6)}{8\pi v^2 kT} A^{10} \sum_{J''} \left[\dfrac{n_{J''}}{n_i} \dfrac{J''}{2J''+1} \right] \end{cases}$$

$$\sum_{J''}(n_{J''}/n_i) = 1 \qquad \boxed{S^{10}(T) = \frac{(1.013 \times 10^6) c A^{10}}{8\pi v^2 kT}}$$

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5. Line strengths

- Band strength

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

Example: Heteronuclear Diatomic Band Strength

$$S^{10}(T) = \frac{(1.013 \times 10^6)cA^{10}}{8\pi v^2 kT}$$

Band strength of CO:

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

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

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

Compare with previous example of $\tau_{Na} \approx 16$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

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Next: Spectral Lineshapes

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