

# Basics-2

## Electromagnetic Radiation and its Interaction with Atoms and Molecules

Reference: “Spectra of Atoms and Molecules” (by P. Bernath)  
“Introduction to Modern Optics” (by G.R. Fowles)

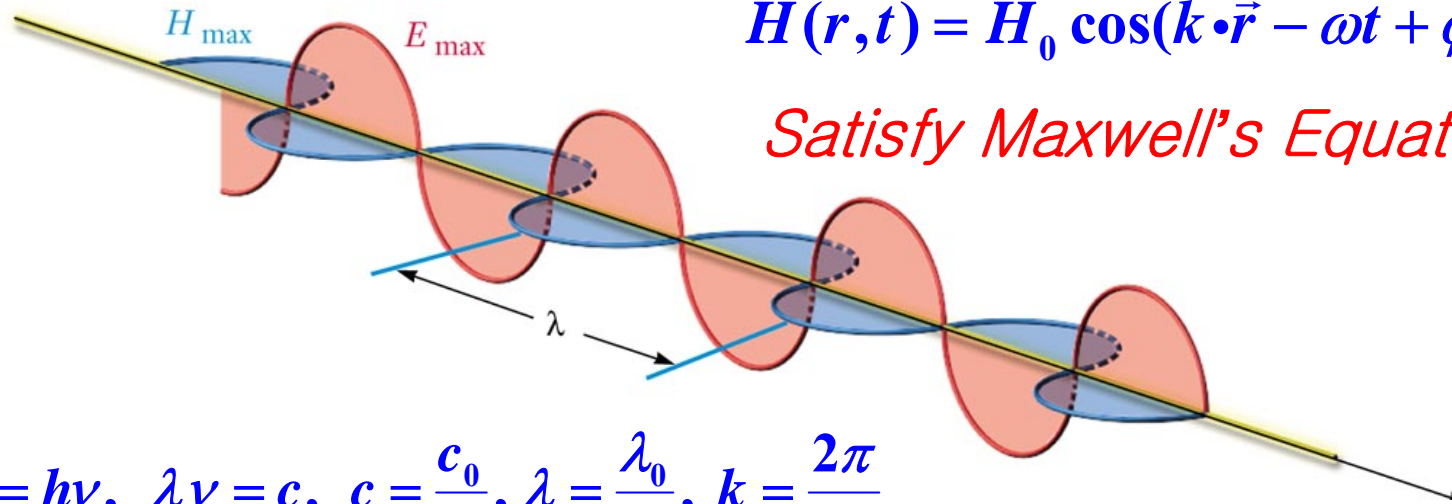
# Electromagnetic Radiation

“ Light is Electromagnetic Wave”

$$\vec{E}(r, t) = \vec{E}_0 \cos(\vec{k} \cdot \vec{r} - \omega t + \phi_0)$$

$$\vec{H}(r, t) = \vec{H}_0 \cos(\vec{k} \cdot \vec{r} - \omega t + \phi_0)$$

*Satisfy Maxwell's Equations*



$$E = h\nu, \quad \lambda\nu = c, \quad c = \frac{c_0}{n}, \quad \lambda = \frac{\lambda_0}{n}, \quad k = \frac{2\pi}{\lambda}$$

$$\text{Average Poynting Vector (energy flux)} \langle \vec{S} \rangle = \frac{1}{2} E_0 H_0 \hat{k},$$

$$\text{Irradiance (or intensity, W/m}^2\text{)} I = \frac{1}{2} E_0 H_0 \approx \frac{n}{754} E_0^2 = \frac{188}{n} H_0^2$$

$\leftarrow I(\text{W} / \text{m}^2), E(\text{V} / \text{m}), H(\text{A} / \text{m}), n : \text{refractive index}$

\* Polarization of Light (*for*  $\vec{k} // \vec{z}$ )

Linear Polarization:  $\vec{E}_0 // \vec{x}, \vec{y}, \text{ or } a\vec{x} + b\vec{y}$  i.e. constant vector

Circular Polarization:  $\vec{E} = \hat{x} E_0 \cos(kz - \omega t) \pm \hat{y} E_0 \sin(kz - \omega t)$   
(+ : *right*, - : *left*)

Elliptical Polarization:  $\vec{E} = \hat{x} E_{0,x} \cos(kz - \omega t) \pm \hat{y} E_{0,y} \sin(kz - \omega t)$   
( $E_{0,x} \neq E_{0,y}$ )

\* Particle Nature of Light

*Energy of Single Photon*  $E = h\nu = \hbar\omega = hc\bar{\nu}$

*Momentum of Single Photon*  $p = \hbar k \leftarrow \frac{h}{\lambda}$

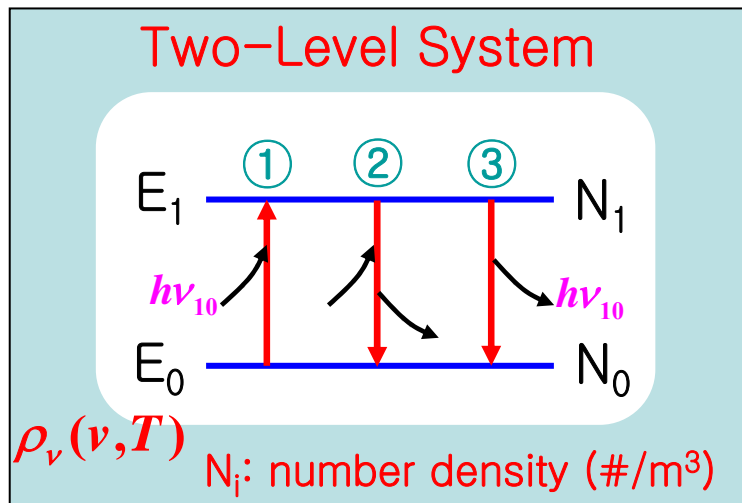
# Absorption and Emission

\* Blackbody Radiation (@Temp T):

Radiation density  $\rho = \int_0^\infty \rho_\nu(T) d\nu$  (in  $J / m^3$ )

Spectral density  $\rho_\nu(\nu, T) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1}$  (in  $J \cdot \text{sec} / m^3$ )

\* Einstein A, B Coefficients:



- ① Absorption
- ② Stimulated Emission
- ③ Spontaneous Emission

$$\frac{dN_1}{dt} = B_{01}\rho_\nu(\nu_{10})N_0 - B_{10}\rho_\nu(\nu_{10})N_1 - A_{10}N_1$$

@ Steady State,  $\frac{dN_1}{dt} = 0 \rightarrow \frac{N_1}{N_0} = \frac{B_{01}\rho_\nu(\nu_{10})}{B_{10}\rho_\nu(\nu_{10}) + A_{10}}$

Boltzmann Distribution:  $\frac{N_1}{N_0} = e^{-h\nu_{10}/kT}$

$$\therefore \rho_\nu(\nu_{10}) = \frac{\left(\frac{A_{10}}{B_{10}}\right)}{\left(\frac{B_{01}}{B_{10}}\right) e^{h\nu_{10}/kT} - 1}$$

$$B_{01} = B_{10} = B,$$

$$A_{10} = \frac{8\pi h\nu_{10}^3}{c^3} B = A$$

## \* Quantum Treatment for two-level system

– Electric dipole transition:  $\hat{H}_{\text{int}}(t) = -\vec{\mu}_{\text{mol}} \cdot \vec{E}_{\text{light}}(t)$

*Due to small variation in E-field for molecular size  
(Rule of thumb:  $E_{ED} \sim 130E_{EQ}$ ,  $E_{EQ} \sim E_{MD}$ )*

– Solve TI & TD Schrödinger eqns:

*Molecule :(TIS eqn)  $H\psi = E\psi \rightarrow E_n, \psi_n \rightarrow E_0, \psi_0; E_1, \psi_1$*

*Light – Molecule :(TDS eqn)  $i\hbar \frac{\partial \psi}{\partial t} = [\hat{H} + \hat{H}_{\text{int}}] \psi$*

*$\rightarrow$  if  $\hat{H}_{\text{int}} = 0$ ,  $\Psi_0 = \psi_0 e^{-iE_0 t/\hbar} = \psi_0 e^{-i\omega_0 t}$ ,  $\Psi_1 = \psi_1 e^{-iE_1 t/\hbar} = \psi_1 e^{-i\omega_1 t}$*

*$\therefore \hat{H}_{\text{int}}$  mix  $\psi_n$ 's  $\rightarrow \Psi(t) = a_0(t)\psi_0 e^{-i\omega_0 t} + a_1(t)\psi_1 e^{-i\omega_1 t}$*

.....Solving ..... (see reference)

*$i\hbar \dot{a}_0 = -a_1 M_{01} E e^{-i\omega_{10} t} \cos \omega t$ ,  $i\hbar \dot{a}_1 = -a_0 M_{01} E e^{i\omega_{10} t} \cos \omega t$*

*$\leftarrow M_{01} = M_{10} = \langle \psi_1 | \hat{\mu} | \psi_0 \rangle$ ; transition dipole moment*

$$\leftarrow \omega_R = \frac{M_{10}E}{\hbar} = \text{Rabi frequency}; \quad \cos\omega t = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t})$$

$\leftarrow$  rotating wave approx :  $e^{i(\omega+\omega_{10})t}$  term average out

$\leftarrow \Delta = \omega_{10} - \omega$  : detuning frequency

$$\therefore \text{Two coupled differential eqns : } \dot{a}_0 = \frac{1}{2}i\omega_R e^{i\Delta t} a_1, \quad \dot{a}_1 = \frac{1}{2}i\omega_R e^{-i\Delta t} a_0$$

**For excitation w/ weak linearly polarized light,**

$$a_1 \approx 0, a_0 \approx 1 \rightarrow \dot{a}_1 = \frac{1}{2}i\omega_R e^{-i\Delta t} \rightarrow a_1(t) = \frac{\omega_R}{-2\Delta} (e^{-i\Delta t} - 1)$$

– Probability of being in excited state after time t:

$$P_{01}(t) = |a_1(t)|^2 = \frac{\omega_R^2}{\Delta^2} \sin^2\left(\frac{\Delta t}{2}\right) = \frac{M_{01}^2 E^2}{\hbar^2} \frac{\sin^2(\Delta t/2)}{\Delta^2}$$

*for broad band light with  $\rho = \varepsilon_0 E^2 / 2$ ,*

$$P_{01} = \frac{2M_{01}^2}{\varepsilon_0 \hbar^2} \int \rho_\nu(\omega) \frac{\sin^2((\omega - \omega_{01})t/2)}{(\omega - \omega_{01})^2} d\omega = \frac{M_{01}^2}{\varepsilon_0 \hbar^2} \rho_\nu(\omega_{01}) \pi t$$

– Transition (probability) rate:  $\frac{dP_{01}}{dt} = \frac{\pi M_{01}^2}{\varepsilon_0 \hbar^2} \rho_\nu(\omega_{01})$

– Einstein A, B Coefficients (for isotropic radiation):

*Assuming no spontaneous emission and  $N_0 \sim N$*

$$\frac{dP_{01}}{dt} = \frac{\pi M_{10}^2}{3\varepsilon_0 \hbar^2} \rho_\nu(\omega_{10}) = \frac{d(N_1 / N)}{dt} \approx B \rho_\nu(\nu_{10}) = 2\pi B \rho_\nu(\omega_{10})$$

$$\therefore B = \frac{2\pi^2}{3\varepsilon_0 \hbar^2} M_{10}^2 \rightarrow (\text{in reality}) B = \int \frac{2\pi^2}{3\varepsilon_0 \hbar^2} M_{10}^2 g(\nu - \nu_{10}) d\nu$$

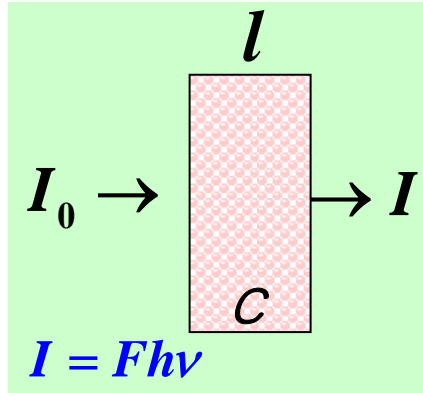
*line-shape function*

$$A = \frac{16\pi^3 \nu_{10}^3}{3\varepsilon_0 \hbar c^3} M_{10}^2 \rightarrow (\text{in reality}) A = \int \frac{16\pi^3 \nu_{10}^3}{3\varepsilon_0 \hbar c^3} M_{10}^2 g(\nu - \nu_{10}) d\nu$$

$$= 3.136 \times 10^{-7} (\tilde{\nu})^3 M_{01}^2 \text{ (in } s^{-1}) \leftarrow \tilde{\nu} (\text{in } cm^{-1}), M_{01} (\text{in Debye})$$

*“line-shape function  $g(\nu - \nu_{10})$  consider finite lifetimes of excited state due to spontaneous emission or collisions”*

– Beer–Lambert Law:  $A = -\log_{10} T = -\log_{10} \left( \frac{I}{I_0} \right) = \epsilon c l$



$I$  (intensity) : W/m<sup>2</sup>  
 $F$  (flux) : # photons/m<sup>2</sup>sec  
 $N$  (number density): # molecules/m<sup>3</sup>  
 $\sigma$  : m<sup>2</sup>/molecule  
 $\rho = I / c = h\nu F / c$

$$\frac{dN_1}{dt} = B \rho_\nu(\nu_{10})(N_0 - N_1) = \sigma F (N_0 - N_1) \rightarrow \sigma = \frac{h\nu B}{c} = h\nu \bar{B}$$

*due to negligible contribution from spontaneous emission*

*“absorption cross section”*

\* Concept of "cross section":  $\frac{d(N_1 / N)}{dt} \simeq \sigma F$

$$\frac{\text{transition probability}}{\text{second}} = (\text{effective area}) \times \left( \frac{\text{photons}}{\text{sec} \times \text{area}} \right) = \left( \frac{\sigma}{\text{area}} \right) \times \left( \frac{\text{photons}}{\text{sec}} \right) = \frac{\sigma}{A} \times \frac{\text{power}}{h\nu}$$

$$\rightarrow \left( \frac{\sigma}{\text{beam area}} \right) = \text{probability of absorption of a photon per molecule}$$



$$\frac{dN_1}{dt} = \sigma F (N_0 - N_1) = -\frac{dF}{dl}$$

$$\int_{F_0}^F \frac{dF}{F} = -\int_0^l \sigma (N_0 - N_1) dl \rightarrow F = F_0 e^{-\sigma(N_0 - N_1)l}$$

$$\therefore I = I_0 e^{-\sigma(N_0 - N_1)l} = I_0 \cdot 10^{-\epsilon c l} = I_0 \cdot 10^{-OD}$$

$$\leftarrow c \text{ (mol} \cdot \text{L}^{-1}\text{)}, l \text{ (cm)}, \epsilon \text{ (L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}\text{)}$$

$$\therefore \epsilon = \frac{\sigma N_A}{\ln 10} = \frac{N_A h \bar{\nu} B}{\ln 10}, \text{ (in reality)} \quad \int_{\bar{\nu}_1}^{\bar{\nu}_2} \epsilon(\bar{\nu}) d\bar{\nu} = \frac{N_A h \bar{\nu}_{av} B}{\ln 10}$$

**Note:**  $\sigma N x = \epsilon c l \times \ln 10 \rightarrow \sigma [m^2] = \frac{0.2303}{N_A} \epsilon [L mol^{-1} cm^{-1}]$

$\swarrow$   $\swarrow$   $\swarrow$   $\swarrow$   
 $\# / m^3$   $m$   $\# / N_A \text{ liter}$   $cm$

e.g.) for H<sub>2</sub>-phthalocyanine dye,  $\epsilon_{PK}(690\text{nm}) = 10^5 \text{ L/mol cm}$  at room temp

$$\sigma_{PK} = 3.8 \times 10^{-20} m^2 \approx (1.96 \text{ angstrom})^2$$

– Oscillator Strength:

“... a measure of relative absorption intensity by ratio of transition intensity to intensity of an harmonically oscillating electron in three dimensions...”

$$f = \frac{|M_{01}|^2}{|M_{e^- osc}|^2} = \frac{|M_{01}|^2}{3he^2 / 8\pi^2 m_e \nu}$$
$$f = \frac{4\varepsilon_0 m_e c^2 \ln 10}{N_A e^2} \int_{\bar{\nu}_1}^{\bar{\nu}_2} \varepsilon(\bar{\nu}) d\bar{\nu} \approx 4.35 \times 10^{-10} \int_{\bar{\nu}_1}^{\bar{\nu}_2} \varepsilon(\bar{\nu}) d\bar{\nu}$$
$$\approx 1.44 \times 10^{-18} \int_{\nu_1}^{\nu_2} \varepsilon(\nu) d\nu$$

*$f \approx 1$  for ED allowed transitions,*

*$f \approx 10^{-5}$  for forbidden ( $S \rightarrow T$ ) transitions*

Ref: Am. J. Phys. 50, 982 (1982); 51, 471 (1983)

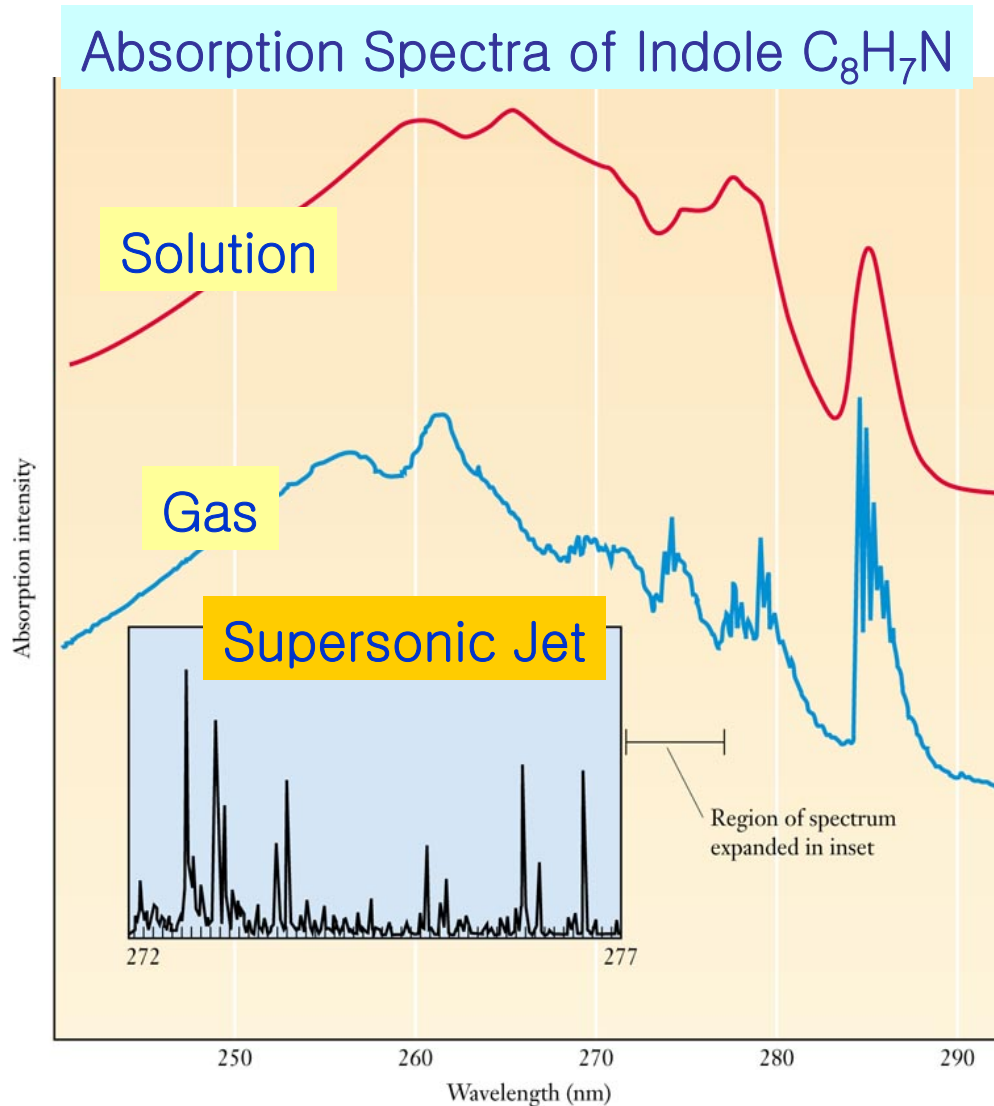
– Selection Rule of Transition:

“transition dipole moment is nonzero”

$$M_{01} = \langle \psi_1 | \hat{\mu} | \psi_0 \rangle \neq 0$$

$$\text{Absorption Intensity} \propto |M_{01}|^2 = (M_{01}^x)^2 + (M_{01}^y)^2 + (M_{01}^z)^2$$

# Line Width



## Homogeneous Broadening

*natural line broadening*  
*pressure (collision) broadening*  
*power broadening*  
*transit time broadening*  
*phonon scattering,*  
*dephasing processes*

*“Lorentzian line–shape function”*

$$g(\nu - \nu_{10}) \propto \frac{a}{b + (\nu - \nu_{10})^2}$$

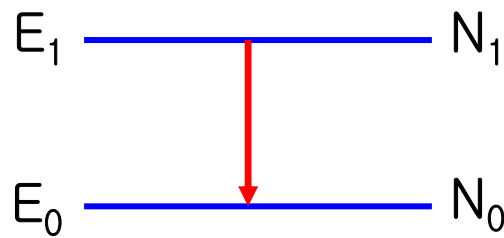
## Inhomogeneous Broadening

*Doppler broadening,*  
*Disorder in environment*  
*(strains, stress, local e–fields,*  
*solvent cage effects,...)*

*“Gaussian line–shape function”*

$$g(\nu - \nu_{10}) \propto e^{-a(\nu - \nu_{10})^2}$$

– Natural line broadening:



$$-\frac{dN_1}{dt} = kN_1 \rightarrow N_1 = N_1^0 e^{-kt}, \tau \equiv \frac{1}{k} = \frac{1}{\gamma}$$

*lifetime of excited state*

Uncertainty principle:  $\Delta E \cdot \tau \geq \hbar \rightarrow \Delta \nu \geq \frac{1}{2\pi\tau}$

Only spontaneous emission:  $k = A \rightarrow \frac{1}{\tau} = A = \frac{16\pi^3 \nu_{10}^3}{3\epsilon_0 hc^3} M_{10}^2$

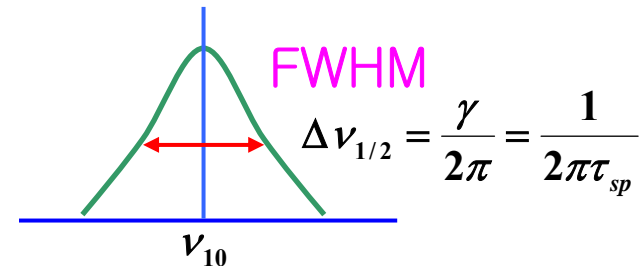
$$\therefore \Delta \nu \geq \frac{1}{2\pi\tau} = \frac{8\pi^2 \nu_{10}^3}{3\epsilon_0 hc^3} M_{10}^2$$

*~ 10 MHz (electronic state)*  
*~ 10<sup>-4</sup> Hz (rotational state)*

Damped oscillating dipole moment in superposition state

(see Bernath):  $\vec{M} = \vec{M}_0 e^{-\gamma t/2} \cos(\omega_{01} t)$

$$g(\nu - \nu_{10}) = \frac{\Delta \nu_{1/2} / 2\pi}{(\Delta \nu_{1/2} / 2)^2 + (\nu - \nu_{10})^2}$$



$$g(\omega - \omega_{10}) = \frac{\Delta\omega_{1/2} / 2\pi}{(\Delta\omega_{1/2} / 2)^2 + (\omega - \omega_{10})^2}, \quad \Delta\omega_{1/2} = \gamma = 2\pi\Delta\nu$$

$$g(\tilde{\nu} - \tilde{\nu}_{10}) = \frac{\Delta\tilde{\nu}_{1/2} / 2\pi}{(\Delta\tilde{\nu}_{1/2} / 2)^2 + (\tilde{\nu} - \tilde{\nu}_{10})^2}$$

– Dephasing processes:

*“... processes that interrupt the phase of the oscillating dipole moment due to collisions or phonon scattering...”*

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2} \leftarrow T_2 : \text{average time between phase interruptions}$$

– Pressure broadening:

*“... Collisions induce phase shifts to an oscillating dipole or collision-induced energy exchange broaden energy levels...”*

$$\begin{aligned} \Delta\nu_{1/2} &= \frac{1}{\pi T_2} \leftarrow T(\text{mean collision time}) \propto \frac{1}{P} \\ &= bP \leftarrow b(\text{pressure broadening coeff}) \approx 10\text{MHz/torr} \end{aligned}$$

## – Phonon scattering

- Elastic phonon scattering interrupts phase of oscillation
- Responsible for 1,000 – 10,000 fold narrowing as 300K to 1K
- Complex Temp dependence: depends upon density of phonons (T)

## – Power (or saturation) broadening:

*“For intense laser radiation,  $N_1/N_0$  approach 1.*

*Then, maximum absorption intensity decrease*

*→ Central part of spectral line flattens and wings increase in intensity (i.e. saturation) → Spectral line broadens”*

✳ **Rabi Oscillation:** *coherent population oscillation due to strong E-field of light shortens lifetime of excited state.*

$$\text{Rabi frequency } \omega_R = \frac{M_{10} E}{\hbar}, \therefore \Delta E \cdot \tau_R \geq \hbar \rightarrow \Delta \nu \geq \frac{1}{2\pi\tau_R} = \frac{\omega_R^2}{4\pi^2}$$

– Doppler broadening:

Doppler effect:  $\nu = \nu_0 \left( 1 \pm \frac{v}{c} \right)$  ← + : *forward* / - : *backward*

Resonance frequency:  $\nu_0 = \frac{\nu_{10}}{1 \pm \frac{v}{c}}$

Line-shape:  $g_D(\nu - \nu_{10}) = \frac{2}{\Delta \nu_D} \left( \frac{\ln 2}{\pi} \right)^{1/2} e^{-4 \ln 2 \left( \frac{\nu - \nu_{10}}{\Delta \nu_D} \right)^2}$

Total lineshape:  $g(\nu - \nu_{10}) = \int_{-\infty}^{+\infty} g_I(\nu_0 - \nu_{10}) g_H(\nu - \nu_0) d\nu_0$   
“Voigt lineshape”

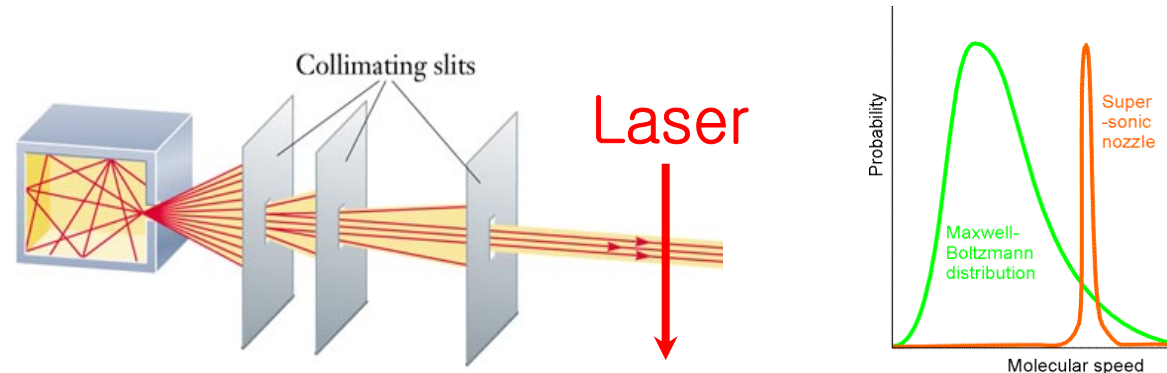
Linewidth:  $\Delta \nu_D = 2\nu_{10} \left( \frac{2k_B T \ln 2}{mc^2} \right)^{1/2}$ ,  $\Delta \bar{\nu}_D = 7.1 \times 10^{-7} \bar{\nu}_{10} \left( \frac{T}{M} \right)^{1/2}$   
T(K), M(amu)

e.g.) Na atoms in heat pipe cell at 300K:

$$\Delta \nu_D = 0.044 \text{ cm}^{-1} = 1317 \text{ MHz}$$

– Removal of line broadening: two examples

Effusive (supersonic) atomic or molecular beam:



*"No collisions and Doppler-free"*

Lamb dip spectroscopy:

*Use of two counter-propagating laser beams (pump, probe)*

