Lineshape Broadening & Broadening Mechanisms

The concepts of "decay rate" and "lifetime"

Atoms in a higher energy level can undergo transitions to lower energy levels with some decay rate $\gamma$.

If the atom has a fast decay rate $\gamma$ from an energy level, it means the atom has a short lifetime $\tau$ in that energy level.

So "decay rate" and "lifetime" are inversely proportional,

$$\text{decay rate} = \frac{1}{\text{lifetime}}$$

fast decay rate $\leftrightarrow$ short lifetime

slow decay rate $\leftrightarrow$ long lifetime

Atoms can decay to lower energy levels by various mechanisms.

For example, if atoms in a higher energy level decay by "A" process with decay rate $\gamma_A$ "B" process with decay rate $\gamma_B$ "C" process with decay rate $\gamma_C$

Then, overall decay rate is

$$\gamma = \gamma_A + \gamma_B + \gamma_C = \frac{1}{\tau_A} + \frac{1}{\tau_B} + \frac{1}{\tau_C} = \frac{1}{\tau} \quad \text{lifetime considering all processes}$$

lifetime only due to "A" process

lifetime only due to "B" process

lifetime only due to "C" process
Example.
Consider a system with three energy levels.

Atoms can decay from an energy level by spontaneous emission (radiative) process → decay rate described by "A".
Atoms can also decay by nonradiative process → decay rate described by "K".
Assume there is no external radiation field (absorption and stimulated emission are neglected.)

Write down the rate equations for each energy level.
By the uncertainty principle, the energy uncertainty and the lifetime of an energy level can be related by

$$\Delta E \cdot \tau_{\text{lifetime}} = \text{constant}$$

Thus, atoms decay faster means shorter lifetime

means bigger $\Delta E$ (energy uncertainty)

means wider lineshape broadening

**Homogeneous Broadening**

If all atoms contribute to the decay process equally (i.e., all atoms contribute equally to the lineshape broadening), we call it "homogeneous broadening."

There are mainly three decay processes for atoms:

1. Spontaneous emission (radiative) process
   \[ \rightarrow \text{decay rate described by } "A" \text{ (Einstein A coefficient)} \]
2. Nonradiative process \[ \rightarrow \text{decay rate described by } "K" \]
3. Collision (in a gas)

Atoms that decay by these processes and result in lineshape broadening are indistinguishable. So these mechanisms are in the category of homogeneous broadening where

broadening due to 1 and 2 is called "lifetime broadening" and
broadening due to 3 is called "collision broadening".
The line shape due to these processes has a Lorentzian profile:

\[ g(x) = \frac{\Delta \nu}{2\pi (x-x_0)^2 + (\Delta \nu)^2} \]

where \( x_0 = \frac{E_2 - E_1}{h} \) and \( \Delta \nu \) is the FWHM.

This is called Lorentzian lineshape. "\( \Delta \nu \)" relates to the spectral uncertainty, which corresponds to an energy uncertainty \( \Delta E = h\Delta \nu = \frac{h}{2\pi \tau} \) where \( \tau \) is the lifetime of the atom in an energy level.

Therefore, if the energy uncertainty of level 1 and 2 are \( \Delta E_1 = \frac{h}{2\pi \tau_1} \) and \( \Delta E_2 = \frac{h}{2\pi \tau_2} \), the total energy uncertainty is

\[ \Delta E = \Delta E_1 + \Delta E_2 = \frac{h}{2\pi} (\frac{1}{\tau_1} + \frac{1}{\tau_2}) = \frac{h}{2\pi} \frac{1}{\tau} = h\Delta \nu \]

If atoms decay only due to (1) spontaneous emission (radiative) process, then

\[ \frac{1}{\tau_1} = A_1, \quad \frac{1}{\tau_2} = A_2 \]

If atoms decay due to both (1) spontaneous emission (radiative) process and (2) nonradiative process, then

\[ \frac{1}{\tau_1} = A_1 + K_1, \quad \frac{1}{\tau_2} = A_2 + K_2 \]
As we just mentioned, atoms can also decay by collision process. This is an important decay mechanism for atoms in a gas.

Due to collision between atoms, the overall effect is that atoms decay faster. The decay rate $\gamma_{\text{collision}}$ due to collisions depends on the average number of collisions per second (collision frequency) $\nu_{\text{col}}$. Since there are two atoms involved in one collision, the effective total decay rate is doubled as

$$\gamma_{\text{collision}} = 2 \nu_{\text{col}}.$$  

(* Since the average number of collisions in a gas depends on the temperature and pressure, we can expect that $\gamma_{\text{collision}}$ is a function of temperature and pressure.)

To conclude, the broadening of the lineshape due to above processes has a Lorentzian profile:

$$g(\nu) = \frac{\Delta \nu}{2\pi} \frac{\Delta \nu}{(\nu - \nu_0)^2 + (\Delta \nu/2)^2}$$  

$\nu_0$: central transition frequency  
$\Delta \nu$: FWHM of the lineshape

If more processes are involved, which result in a faster decay rate, the spectral linewidth ($\Delta \nu$) will become broader.

Ex: If only 1 spontaneous emission (radiative) process is involved,

$$\Delta \nu_h = \frac{1}{2\pi} (A_1 + A_2)$$

If 1 spontaneous emission (radiative) process and 2 nonradiative process are involved,

$$\Delta \nu_h = \frac{1}{2\pi} \left( (A_1 + k_1) + (A_2 + k_2) \right)$$

If both 1 & 2 plus 3 collision process are involved,

$$\Delta \nu_h = \frac{1}{2\pi} \left( (A_1 + k_1) + (A_2 + k_2) + 2 \nu_{\text{col}} \right)$$
Because spontaneous emission always happens to all atoms, we can't reduce the atom decay rate below the decay rate by spontaneous emission. Therefore, the narrowest spectral linewidth that can be achieved between two states is

$$\Delta \nu_n = \frac{1}{2\pi} (A_1 + A_2)$$

where $A_{1,2}$: decay rate by spontaneous emission in state 1 and 2.

This is called "natural linewidth."
Inhomogeneous Broadening

There are certain physical mechanisms that do not affect all atoms equally, causing the transition frequencies to shift differently among different groups of atoms. The broadening of the linewidth due to these physical mechanisms is called inhomogeneous broadening.

"Doppler broadening" is one typical example that gives rise to this type of broadening. We will mainly discuss Doppler broadening in this category.

--- Doppler effect ---

If an atom emits a frequency $\nu_0$ and moves toward the observer with a velocity $\nu$, the homogeneous linewidth radiated by this atom has a Lorentzian lineshape centered at $\nu^+ = \nu_0 (1 + \frac{\nu}{c})$.

\[ \nu \rightarrow \nu_0 \rightarrow \nu^+ \]

atom \hspace{1cm} observer

\[ \Delta \nu \]

Lorentzian Lineshape

If it moves away from the observer

\[ \nu \rightarrow \nu^+ \rightarrow \nu_0 \rightarrow \nu \]

where $\nu^- = \nu_0 (1 - \frac{\nu}{c})$.

If it moves in arbitrary directions

\[ \nu \rightarrow \nu_0 \rightarrow \nu' \rightarrow \nu \]

where $\nu' = \nu_0 (1 - \frac{\nu}{c})$.
In a gas, a collection of atoms exhibits a distribution of velocities.

Because the atoms are moving, the light they emit exhibits a range of frequencies, resulting in "Doppler broadening". The overall broadening depends on the velocity distribution of the atoms in the system.

The velocity distribution is described by the Maxwell-Boltzmann distribution, which is a Gaussian function.

For example, if we consider the velocity distribution of the atoms along the $z$-axis.

Therefore, the overall lineshape will be

\[ g(v) = \sqrt{\frac{4\ln 2}{\pi}} \frac{1}{\Delta v_D} e^{-4\ln 2 \left( \frac{v-v_0}{\Delta v_D} \right)^2} \]

(Assume $\Delta v_n \ll \Delta v_D$)

where $\Delta v_D = \sqrt{\frac{8K_B T \ln 2}{MC^2}} v_0$ $M$: atomic mass

\[ g(v) = \sqrt{\frac{4\ln 2}{\pi}} \frac{1}{\Delta v_D} e^{-4\ln 2 \left( \frac{v-v_0}{\Delta v_D} \right)^2} \]
As you can see here, the overall lineshape is the total contributions from different groups of atoms with different atom characteristics. We know which group of atoms is responsible for the broadening of the lineshape at some frequency. This is called inhomogeneous broadening.

Ex: In a gas at a low pressure, the Doppler-broadening effect tends to dominate at room temperature. When the pressure is increased, frequent collisions among the gas molecules cause the homogeneous linewidth to increase. At a certain pressure, the homogeneous linewidth finally dominates the Doppler linewidth.
Numerical Example:

The 632.8nm emission of the HeNe laser is due to the radiative transitions in the Ne atoms. Using the atomic mass 20AMU for Ne and taking the gas temperature T=400K, evaluate its Doppler linewidth $\Delta \nu_D$. (1 AMU=1.67*10^{-27}kg)

If it has a homogeneous linewidth of $\Delta \nu_h=100$MHz, is the broadening of the lineshape dominated by homogeneous or inhomogeneous mechanism?