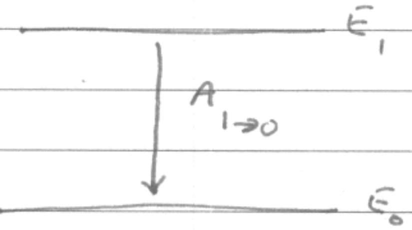
→ Line Broadening

A transition between two energy states is never seen as an infinitely sharp band corresponding to a single frequency. This happens due to several reasons:

① Instrumental limitations:
Such as slit width or the quality of the grating or monochromators.

② Natural line broadening:
Consider a two-level system as shown and an emisson (spontaneous) process is taking a place.



An important parameter called <u>relaxation time</u> or <u>lifetime</u> (τ) where

$$\tau = 1/A_{1\to 0}$$

Lifetime of X^* in the following process:

$$X \rightleftharpoons X^*$$

X: molecule or atom in the ground state
X^*: molecule or atom in the excited state

is deffined as the time taken for the concentration of X^* to fall to $1/e$ times its initial value.

The Heisenberg time-energy uncertainty principle states That

$$\Delta t \, \Delta E \geq \hbar$$

$$\tau \, \Delta E \geq \hbar$$

Heisenberg uncertainty principle implies that you can have definite excited state only when you have a very long (infinite lifetime). But experimentall, τ normally is in order of 10^{-6} to 10^{-15} seconds. This increases the uncertainty in energy difference.

Compare micro-wave spec. with femtosecond spec.

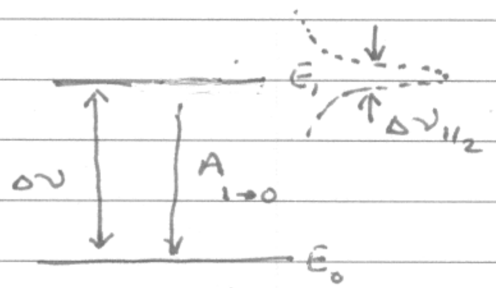
Thus, fast-decaying states have broader linewidths, while slow-decaying states have narrower linewidths.

Also, as more molecules decay, the lifetime continuosely changes.

As a result the band shape will have a property called FWHM (Full width of half maximum and given by $\Delta\nu_{1/2}$ where:

$$\Delta\nu_{1/2} \simeq \frac{1}{2\pi\tau}$$

The resultant distribution of energy causes the natural line broadening



The above relationship has a number of useful applications in calculation the lifetime of a system at an excited level from observing the linewidth associated to that transition.

Example on Natural Broadening

For lifetime excitations of 5×10^{-11} sec and of the order of 10 ns, which one is expected to have a broader line width?

Generally

$$\Delta\tau\,\Delta E \simeq \frac{h}{2\pi}$$

$$\Delta E\,(J) = hc\Delta\bar{\nu}\,(cm^{-1})$$

$$\Delta E\,(J) = h\;3\times10^{10}\ cm/sec\ \Delta\bar{\nu}\,(cm^{-1})$$

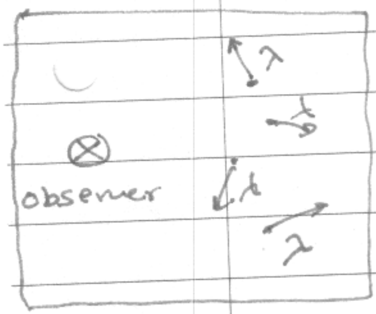
$$\therefore\ (\Delta\tau)(h)(\Delta\bar{\nu})(3\times10^{10}\ cm/sec) \simeq \frac{h}{2\pi}$$

$$\Delta\bar{\nu} \simeq \frac{5.3\times10^{-12}}{\Delta\tau}$$

Then, for $\tau = 5\times10^{-11}$ sec $\Rightarrow \Delta\bar{\nu} = 0.1\ cm^{-1}$

and for $\tau = 10\times10^{-9}$ sec $\Rightarrow \Delta\bar{\nu} = 0.0005\ cm^{-1}$

(3) Doppler broadening.



Dopple effect is the change in frequency and/or wavelength of a wave for an observer moving relative to the source of the waves. Examples include a train or a car moving by a stationary or moving observer.

For a molecule or atom moving at a velocity v away or towards the observer (detector), the measured frequency is given by:

$$\nu_{obs} = \nu_0 \left(1 \pm \frac{v}{c}\right)$$

where ν_0 is the frequency of emitted radiation at rest. The frequency (observed) will be spread out depending on the velocity of the emitting molecule with respect to the observer.

The FWHM ($\Delta\nu_{1/2}$) can be obtained from a mathematical derivation as:

$$\Delta\nu_{1/2} = 2\nu_0 \sqrt{\frac{2k_B T \ln 2}{mc^2}}$$

where T is the temperature in K, m is the mass. Then

$$\Delta\bar{\nu}_{1/2} = 7.2 \times 10^{-7}\, \bar{\nu}_0 \sqrt{\frac{T}{M}}$$

where M is the atomic mass in atomic mass unit, and $\bar{\nu}$ is in cm^{-1}

(4) Pressure Broadening.

The presence of nearby particles will affect the molecule emitting radiation. This is caused by collisions of other particles with the emitting particle. $\Delta\nu_{1/2}$ can be related to the average time between two successive collisions (t_{coll}) by:

$$\Delta\nu_{1/2} = \frac{1}{\pi t_{coll}}.$$

It is also known that t_{coll} is proportional to the reciprocal of the pressure. Therefore, one can write:

$$\Delta\nu_{1/2} = bp$$

where p is the sample pressure (for gaseous samples) and b is the pressure-broadening coefficient.

Other factors included:
- Power saturation brodening
- Wall collisions broadening
- Modulation broadening.