Line shape function

- Natural line width
- Pressure broadening
- Doppler broadening

Natural line width

So far:

$$h\nu = E_f - E_i$$

So absorption (and emission) would happen at exactly one frequency. (The line shape would be a delta-function.)

There is a fundamental Q.M. principle that prevents this from being true!

Heisenberg's uncertainty principle

$$\Delta x \, \Delta p \approx \frac{\hbar}{\cancel{2}}$$

~~Ich kann~~

I cannot know position and momentum simultaneously.

Another manifestation

$$\Delta E \, \Delta t \approx \frac{\hbar}{\cancel{2}} = 10^{-34} \frac{J}{s}$$

The shorter the lifetime of a state, the more uncertain its energy.

Groundstate:

$$\Delta t = \infty \longrightarrow \Delta E = 0$$

First excited electronic state:

$$\Delta t = 10^{-8}\,s \longrightarrow \Delta E = \frac{10^{-34}}{10^{-8}} = 10^{-26}\,J$$

$$\Delta \nu = \frac{\Delta E}{h} = \frac{10^{-26}\,J}{6.6 \cdot 10^{-34}\,J \cdot s} \approx 10^{8}\,Hz$$

Seems a large number at first sight, but the typical frequency of electronic transitions is 10^{14} - 10^{16} Hz

$\Rightarrow$ In this case natural line width can be considered as small.

Actual shape of the line

Finite lifetime of upper state means:

$$\frac{dn(t)}{dt} = -A\,n(t)$$

A: Einstein A coefficient

Solution:

$$n(t) = n(0)\,e^{-At} = n(0)\,e^{-\frac{t}{\tau}}$$

τ: lifetime

But:

The rate of spontaneously emitted photons is also given by $\frac{dn(t)}{dt}$! (whenever a state decays, a photon is emitted.)

Thus we can write for the radiation flux L:

$$L(t) = L(0)\, e^{-At}$$

If a signal amplitude is not constant in time, it cannot be monochromatic.

~~There is a Fourier pair:~~

Frequency spectrum is given by the Fourier transform:

$$\Rightarrow F_L(\nu) = \frac{1}{\pi} \frac{A/4\pi}{(\nu-\nu_0)^2 + (A/4\pi)^2}$$

$$= \frac{1}{\pi} \frac{\gamma_N}{(\nu-\nu_0)^2 + \gamma_N^2}$$

6

Lorentz Function

F_L is called a Lorentz-Function (also Cauchy distribution or Breit-Wigner distribution).

γ_N is the natural line width parameter.

Doppler Broadening

... is conceptually simpler than natural broadening. It is due to the thermal motion of the molecules, which Doppler-shifts the frequency.

Maxwell-distribution for velocity:
(valid for LTE)

$$p(u) = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mu^2}{2kT}\right)$$

u: velocity

Doppler shift

Non-relativistic Doppler-shift is given by:

$$\nu - \nu_0 = \frac{\nu_0 \cdot u}{c}$$

Combining this with the Maxwell velocity distribution gives

$$F_D(\nu) = \frac{1}{\gamma_D \sqrt{\pi}} \exp\left[-\left(\frac{\nu-\nu_0}{\gamma_D}\right)^2\right]$$

with $\gamma_D = \frac{\nu}{c}\sqrt{\frac{2kT}{m}}$ „Doppler width"

$\leftarrow$ mass of the molecule!

Note: This is a Gaussian!

Pressure Broadening

Collisions between molecules also limit the lifetime of energy states ("collissional broadening").

If one assumes that collissions themselves take no time, that there is no interaction between collissions, and that collissions completely "reset" the state, then the resulting shape is again a Lorentzian.

$$F_c = \frac{1}{\pi} \frac{\gamma_c}{(\nu - \nu_0)^2 + \gamma_c^2}$$

The rate of collision is proportional to pressure.

Empirically:

$$\gamma_c = p \cdot AGAM \cdot \left(\frac{T_{ref}}{T}\right)^{NAIR}$$

where AGAM and NAIR are in the spectral line catalogue. (In reality some more parameters.)

What do we use in reallity?

We neglect natural broadening, but have to use Thermal and collisional broadening (γ_C and γ_D).

The shape then is a convolution of Lorentz and Gauss shape, called „Voigt-Function".

There is no analytical form, only numerical approximations.

The exercise

In the exercise, you will find out, which effect of broadening dominates when.