The Width (Breadth) of Spectrum Lines

Many spectrum lines have an observable breadth → independent of any optical system used to observe them.

Many cases → Narrow and broad lines observed simultaneously in the same spectrum.

Ex. Sharp and diffuse series of each of the alkali

General cause?

Theoretical calculations for the observed breadth of spectrum lines.

Known causes and types of spectrum-line breadths;

1. Doppler effect
2. Natural breadth
3. External effects:
   a. Collisional damping
   b. Aysmmetry and pressure shift
   c. Stark effect

Doppler effect → The distribution of frequencies observed from many atoms moving at random as they do according to the kinetic theory of gases. This is simplest of all broadening.

Natural breadth → An inherent property of the atom, independent of all external effects. Q.M. shows that the energy levels of an isolated atom are not sharp → but have a finite natural width.

The third and the least understood cause for the broadening of spectral lines includes all external effects produced by
(1) collision between atoms and (2) field of neighboring atoms and molecules

Doppler effect → one of the most classical of all atomic phenomena → as it applies to the observed frequency of a radiated line.
Shown by different stellar spectra and by the solar spectrum as observed from the limbs of the sun.
The velocities of the stars and their emitting gases are high w.r.t. observer → The observed shifts of the spectrum lines are ~~high~~ large.

Similar effects in → gaseous discharge where due to thermal agitation, the atoms emitting light have relatively high velocities.
The random motion of the atoms or molecules in a gas → produce a net broadening of the line with no apparent shift of its central maximum. This broadening is found experimentally to (1) increase with temperature and (2) decrease with increasing atomic weight.

For an appreciable Doppler effect → The atom must have an appreciable velocity at the time of radiation.

If $v \rightarrow$ velocity of the atom and θ is the angle between v and the direction of observation, the frequency of the light will be changed by an amount $\Delta\nu$, given by classical ~~rel~~ relation

$$\frac{\Delta\nu}{\nu_0} = \frac{\nu-\nu_0}{\nu_0} = \frac{v\cos\theta}{c} = \frac{u}{c} \quad -(1)$$

$\nu_0 \rightarrow$ frequency of the line for $v=0$

$\nu \rightarrow$ observed frequency

$$u = v\cos\theta \quad -(2)$$

the component of the velocity v in the direction of observation, and c the velocity of light.

Assuming a Maxwellian distribution of the velocities the probability that the velocity will lie between u and $u+du$ is given by

$$dw = \sqrt{\frac{\beta}{\pi}}\, e^{-\beta u^2}\, du \quad -(3)$$

$$\text{where } \beta = \frac{\mu}{2RT} \quad -(4)$$

$\mu \rightarrow$ Molecular weight

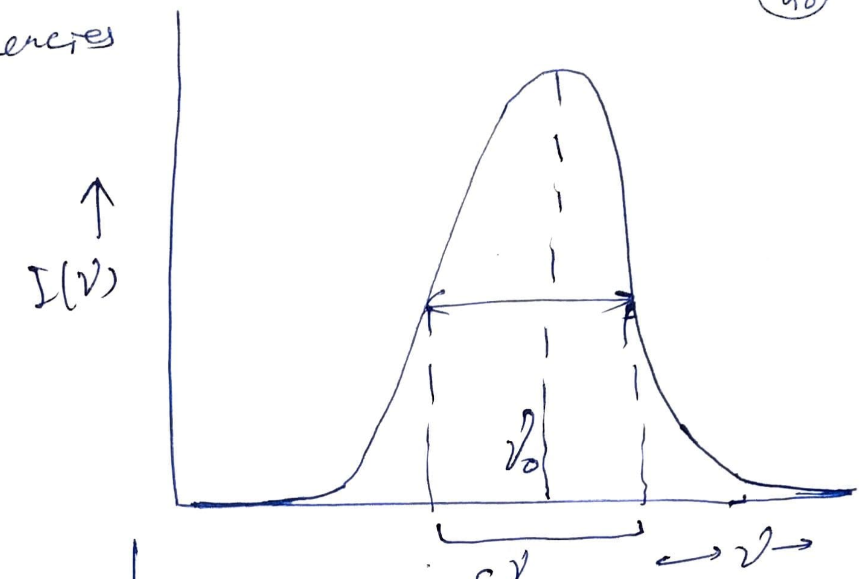
$R \rightarrow$ universal gas constant

$T \rightarrow$ absolute temperature.

Substituting the value of u from eqn (1), we get the relative intensity I as a function of the frequency ν,

$$I(\nu) = \text{constant } e^{-\beta\frac{c^2}{\nu^2}(\nu-\nu_0)^2} \quad -(5)$$

To find the two frequencies at which the intensity drops to half its maximum value, the exponential term in eq^n (5) is set equal to one-half.



Intensity - frequency plot for the Doppler broadening of a spectrum line.

Solving this for $\nu - \nu_0$ and multiplying by two we get for the half intensity breadth, in absolute frequency units

$$\delta_d^\nu = 2\frac{\nu_0}{c}\sqrt{\frac{2RT}{\mu}\ln 2} = 1.67\frac{\nu_0}{c}\sqrt{\frac{2RT}{\mu}} \quad \text{--- (6)}$$

From eq^n (6), the Doppler broadening is
(1) Proportional to the square root of temperature.
(2) Proportional to the frequency ν_0.
(3) Inversely proportional to the square root of the molecular weight.

from $\frac{\Delta\nu}{\nu} = \frac{\Delta\lambda}{\lambda}$, the half intensity breadth in terms of absolute wave-length units is

$$\delta_d^\lambda = 2\frac{\lambda_0}{c}\sqrt{\frac{2RT}{\mu}\ln 2}$$

$$= 1.67\frac{\lambda_0}{c}\sqrt{\frac{2RT}{\mu}} \quad \text{--- (7)}$$

Ex. Consider the sodium D lines at $\lambda = 5893 \mathring{A}$.
for a temperature $T = 500^\circ$ abs.

Eqn (6) gives a half ~~width~~ intensity breadth of $0.056\ cm^{-1}$ or $0.02\ \mathring{A}$, a value 200 times as large as the natural half-intensity breadth.

Natural Breadths from Classical Theory

According to the classical e.m. theory a vibrating electric charge is continually damped by the radiation of energy.

The energy of such an oscillator decreases exponentially by

$$E = E_0 e^{-\gamma t} \quad \text{——} (8)$$

and amplitude by

$$A = A_0 e^{-\frac{\gamma}{2} t}, \quad \text{——} (9)$$

$E_0 \rightarrow$ initial energy at time 't' $= 0$

$E \rightarrow$ energy at any later time 't'

$A, A_0 \rightarrow$ corresponding amplitudes

$$\gamma = \frac{2}{3} \cdot \frac{e^2}{mc^3} \omega_0^2 = \frac{8\pi^2 e^2 \nu_0^2}{3mc^3} \quad \text{——} (10)$$

The displacement x of the oscillator at any time 't' is given by

$$x = A_0 e^{-\frac{\gamma}{2} t} \cos(\omega_0 t + \phi) \quad \text{——} (11)$$