Introduction to Atomic Optical Spectroscopy (Chapter 8)

Sample is atomized (atoms/ions)

absorption or emission measured

Energy Level Diagrams

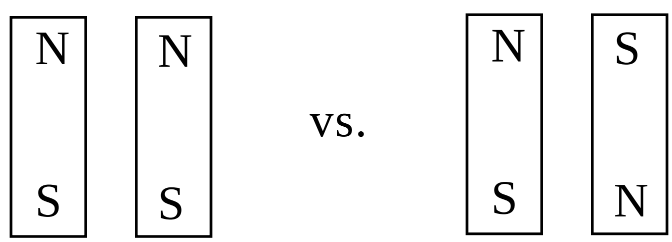
Every elements has unique set of atomic orbitals

p,d,f... levels split by spin-orbit coupling

Spin (s) and orbital (l) motion create magnetic fields that perturb each other (couple)

if fields parallel - slightly higher energy

if fields antiparallel - slightly lower energy



Define SO coupling by J (total angular momentum)

$$J=L+S \quad (L = \sum l \quad S = \sum s) \text{ (positive values only)}$$

Example:

s electron (l=0, s=+1/2 or -1/2) J=0+1/2=1/2

p electron (l=1, s=+1/2 or -1/2) J=1+1/2=3/2 (higher energy) or

1-1/2=1/2 (lower energy)

Electronic Term Symbol

$^{2S+1}L_J$ L written as letter (S, P, D...) instead of number!

$Li = 1s^2 2s^1$ $L = 0, S = \pm 1/2$ $^2S_{1/2}$

$Li^* = 1s^2 2p^1$ $L = 1, S = \pm 1/2$ $^2P_{3/2,1/2}$

$Be = 1s^2 2s^2$ $L = 0, S = 0$ $^1S_0$

$Be^* = 1s^2 2s^1 2p^1$ $L = 1, S = 1, 0$ $^3P_2, {}^1P_0$

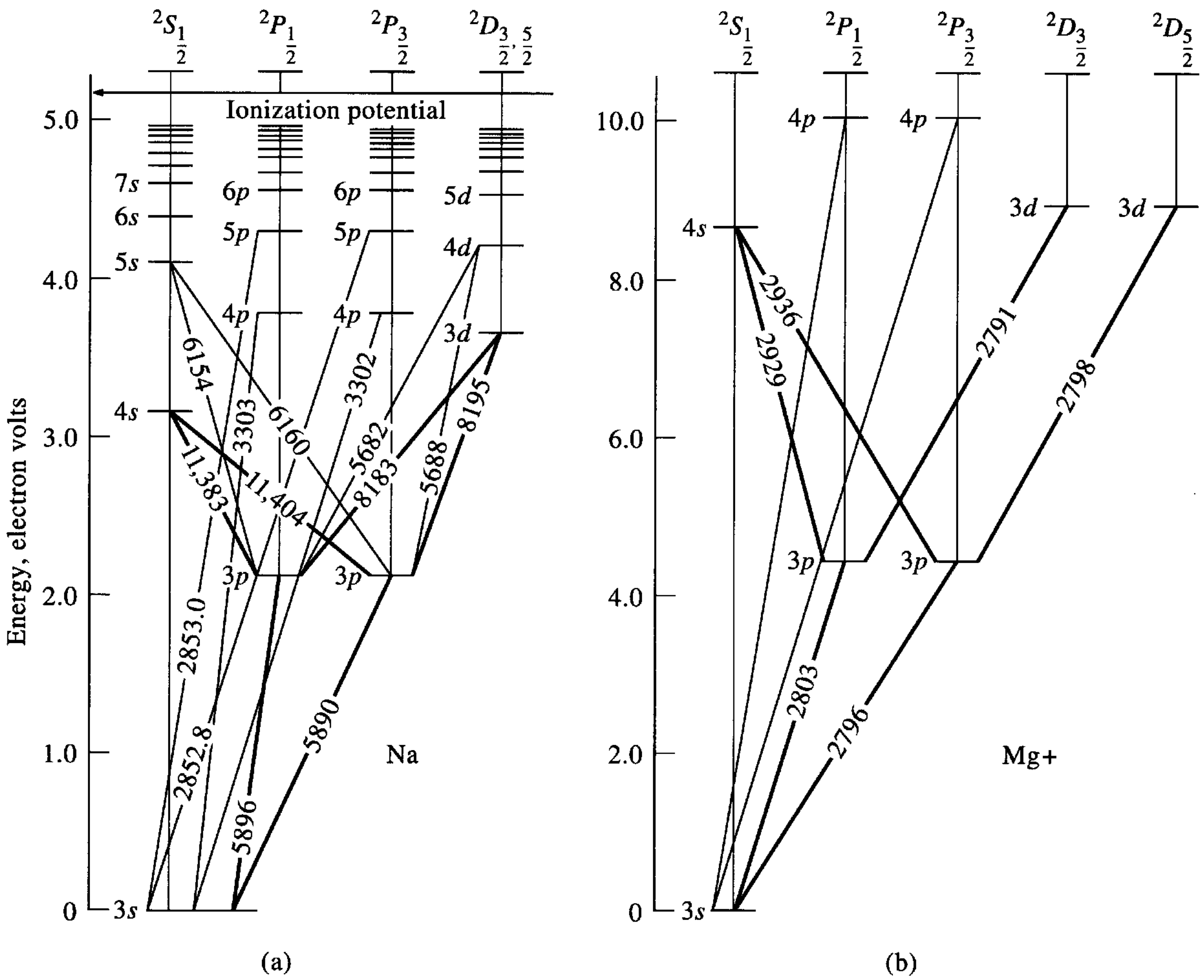


Fig 8-1

- Similar pattern between atoms but different spacing
- Spectrum of ion different to atom
- Separations measured in electronvolts (eV)

$$1\text{eV} = 1.602\text{x}10^{-19}\text{C} \times 1\text{ V}(\text{J/C}) = 1.602\text{x}10^{-19}\text{ J}$$

$$= 96.484\text{ kJ mol}^{-1}$$

- As # of electrons increases, # of levels increases

  Emission spectra become more complex

Li 30 lines, Cs 645 lines, Cr 2277 lines

Desire narrow lines for accurate identification

Broadened by

(i) uncertainty principle

(ii) pressure broadening

(iii) Doppler effect

(iv) (electric and magnetic fields)

Atomic line widths:

(i) Uncertainty Principle:

Quantum mechanical idea states must measure for some minimum time to tell two frequencies apart

$$\Delta t \quad \Delta E \geq h$$

$$\underbrace{\Delta t}_{\substack{\text{minimum}\\ \text{time for}\\ \text{measurement}}} \quad \underbrace{\Delta \nu}_{\substack{\text{minimum}\\ \text{detectable}\\ \text{difference in}\\ \text{frequencies}}} \geq 1$$

Shows up in lifetime of excited state

- if lifetime infinitely long, ΔE infinitely narrow
- if lifetime short, ΔE is broadened

Example

Lifetime of Hg*=2x10^{-8} s. What is uncertainty broadening for 254 nm line?

$$\Delta t \; \Delta\nu = 1 \qquad \Delta\nu = \frac{1}{\Delta t} = \frac{1}{2\text{x}10^{-8}\ \text{s}} = 5\text{x}10^{7}\ \text{Hz}$$

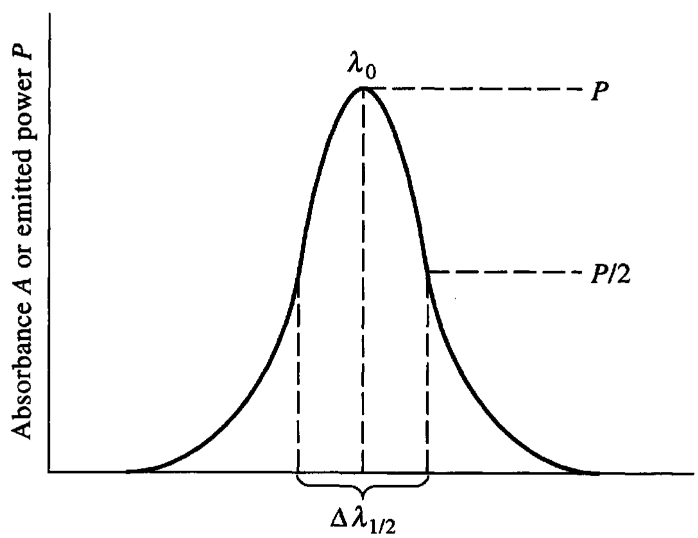
$$\nu = c \; \lambda^{-1}$$

Differentiating wrt to frequency

$$d\nu = -c\lambda^{-2}d\lambda \qquad d\nu \approx \Delta\nu \text{ and } d\lambda \approx \Delta\lambda$$

$$\Delta\lambda = \frac{\Delta\nu \; \lambda^2}{c} = \frac{5\text{x}10^{7}\ \text{s}^{-1}\left(254\text{x}10^{-9}\ \text{m}\right)^2}{3\text{x}10^{8}\ \text{m}\ \text{s}^{-1}} = 1.1\text{x}10^{-4}\ \text{Å}$$

sometimes called **natural linewidth**



(ii) Pressure broadening:

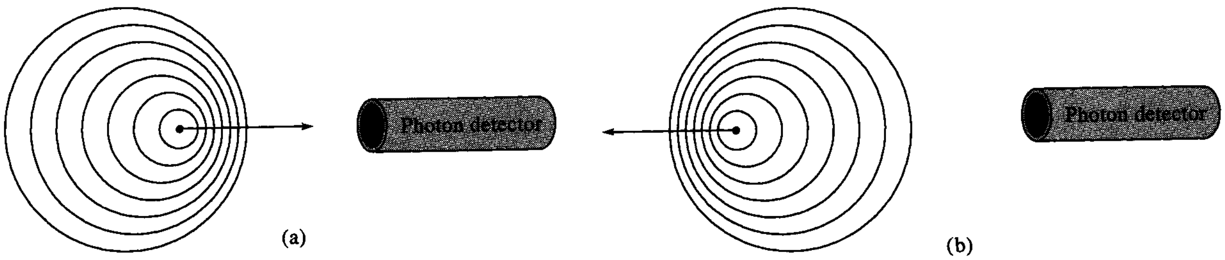
Collisions with atoms/molecules transfers small quantities of vibrational energy (heat) - ill-defined ground state energy

Effect worse at high pressures

- For low pressure hollow cathode lamps (1-10 torr) 10^{-1}-10^{-2} Å
- For high pressure Xe lamps (>10,000 torr) 100-1000 Å (turns lines into continua!)

(iii) Doppler broadening:

Change in frequency produced by **motion** relative to detector



In gas, broadens line symmetrically

Doppler broadening increases with $\sqrt{T}$

- At room T ~10^{-2}-10^{-3} Å

Total linewidth typically 0.01-0.1 Å

Other Effects of T on Atomic Spectrometry:

T changes # of atoms in ground and excited states

Boltzmann equation

$$\frac{N_1}{N_0} = \frac{P_1}{P_0}\exp\left(-\frac{\Delta E}{kT}\right)$$

atoms in level transition energy E_1-E_0

levels at each energy Boltzmann constant 1.38×10^{-23} J·K^{-1}

Important in emission measurements relying on thermal excitation

Na atoms at 2500 K, only 0.02 % atoms in first excited state!

Less important in absorption measurements - 99.98 % atoms in ground state!

Methods for Atomizing and Introducing Sample

Sample must be converted to atoms first

TABLE 8-1 Types of Atomizers Used for Atomic Spectroscopy

Type of Atomizer	Typical Atomization Temperature, °C
Flame	1700–3150
Electrothermal vaporization (ETV)	1200–3000
Inductively coupled argon plasma (ICP)	4000–6000
Direct current argon plasma (DCP)	4000–6000
Microwave-induced argon plasma (MIP)	2000–3000
Glow discharge plasma (GD)	Nonthermal
Electric arc	4000–5000
Electric spark	40,000 (?)

Must transfer sample to atomizer - easy for gases/solutions but difficult for solids

TABLE 8-2 Methods of Sample Introduction in Atomic Spectroscopy

Method	Type of Sample
Pneumatic nebulization	Solution or slurry
Ultrasonic nebulization	Solution
Electrothermal vaporization	Solid, liquid, solution
Hydride generation	Solution of certain elements
Direct insertion	Solid, powder
Laser ablation	Solid, metal
Spark or arc ablation	Conducting solid
Glow discharge sputtering	Conducting solid