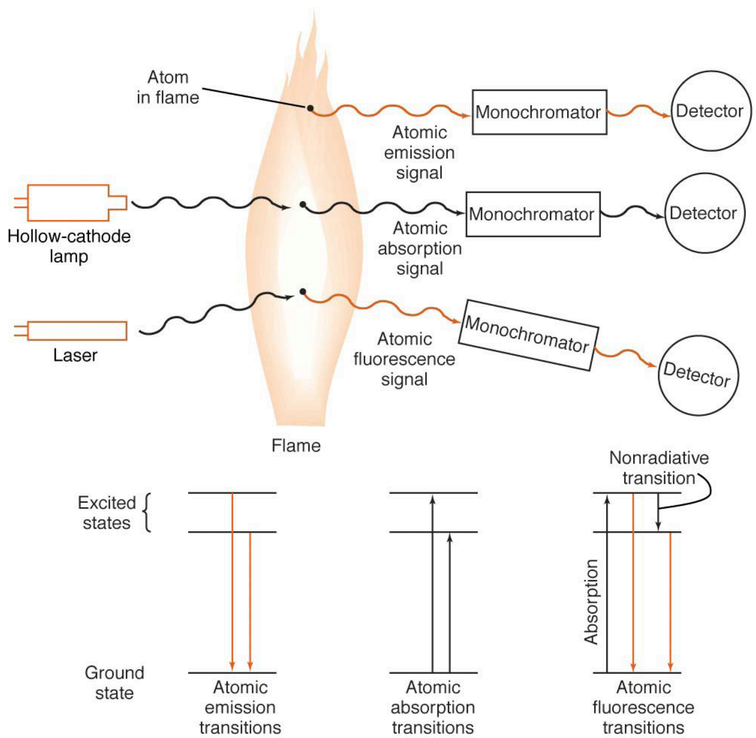
ATOMIC ADSORPTION



Atomic spectroscopy – need to convert the analyte to free, unbound atoms or ions (atomization).

Atomization

a. Flame – premix burner (fuel, oxidant and sample mixed before flame introduction)

- Drawn into pneumatic nebulizer by air (oxidant) and creates small droplets (aerosol).

b. Electrothermal – the graphite furnace

- greater sensitivity and less sample

- maintains constant temperature, reducing memory effects

c. Inductively coupled plasma (ICP), 0.001-50 ng L^{-1}

- high temperature, stability and chemically inert Ar environment

Atomization method	Temperature (K)	Measurement Type
Flame	2300-3400	Abs, emission
Electrothermal	2000-3300	Abs, emission
ICP	6000-8500	emission

Atomic Spectroscopy

- Unbound atoms, rather than molecules, are the absorbing species.

- Monochromator in atomic absorption or emission is place after the sample (remove unwanted radiation during atomization process).

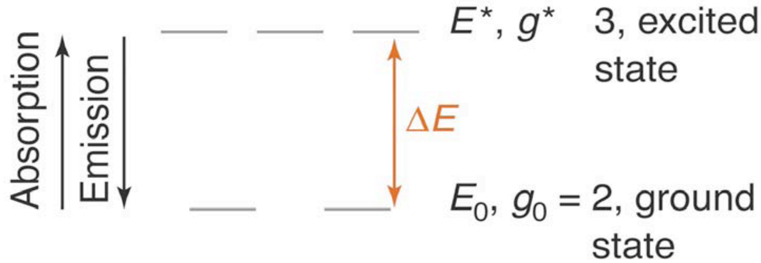
- Bandwidths are very narrow (0.002-0.005 nm), often referred to as lines.

Temperature Effects

Boltzmann Distribution – degeneration of energy states (describes the relative populations of diff. states at thermal equilibrium).

- Ground state atoms can absorb light to be promoted to the excited state.

- Excited state atoms can emit light to return to the ground state.



Boltzmann distribution:

$$\frac{N^*}{N^0} = \frac{g^*}{g^0} e^{\frac{-\Delta E}{kT}}$$

Where T is temperature (K), k is Boltzmann's constant (1.381×10^{-23} J/K)

<u>Example</u> Calculate the fraction of sodium atoms in the excited state in an acetylene-air flame at 2600 K.

- lowest excited state = 3.371×10^{-19} J/atom above ground state

- Degeneracy of excited state = 2, ground state = 1

$$\frac{N^*}{N^0} = \frac{g^*}{g^0} e^{\frac{-\Delta E}{kT}} = \frac{2}{1} e^{\frac{-(3.371 \cdot 10^{-19}\ \text{J/atom})}{(1.381 \cdot 10^{-23}\ \text{J/K}) \cdot 2600\,K}} = 1.67 \cdot 10^{-4}$$

- fewer than 0.02% of atoms are in the excited state

<u>The Effect of Temperature on Absorption and Emission</u>

- Excited state population changes by 4% when the temperature rises 10 K....therefore the emission intensity rises by 4%.

Table 21-3 Effect of energy difference and temperature on population of excited states

Wavelength difference of states (nm)	Energy difference of states (J/atom)	Excited-state fraction $(N^*/N_0)^a$	
		2 500 K	**6 000 K**
250	7.95×10^{-19}	1.0×10^{-10}	6.8×10^{-5}
500	3.97×10^{-19}	1.0×10^{-5}	8.3×10^{-3}
750	2.65×10^{-19}	4.6×10^{-4}	4.1×10^{-2}

a. Based on the equation $N^*/N_0 = (g^*/g_0)e^{-\Delta E/kT}$ in which $g^* = g_0 = 1$.