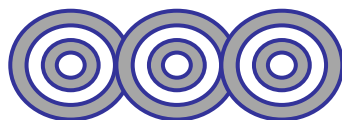




Chem 256

Spectroscopic Analytical Methods



Spectroscopy Based on Emission

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What happens to absorbed radiation

An analyte in an excited state possesses an energy, E_2 , that is greater than that when it is in a lower energy state, E_1 .

When the analyte returns, or relaxes to a lower energy state the excess energy, ΔE , must be released.

$$\Delta E = E_2 - E_1$$



Relaxation to a lower energy level or the ground state takes place with a release of the excess energy in the form of **electromagnetic radiation, heat, or perhaps both.**

Lifetime

The length of time that an analyte stays in an excited state before returning to a lower-energy state.

The **lifetime** of an analyte in the excited state, A^* , is short; typically

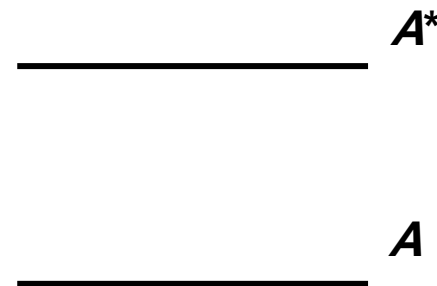
- 10^{-5} – 10^{-9} s for electronic excited states, and
- 10^{-15} s for vibrational excited states.

Relaxation

Relaxation is any process by which an analyte returns to a lower-energy state from a higher energy state.

Relaxation occurs through collisions between A^* and other species in the sample, by:

- **Photochemical reactions.**
- **Emission of photons.**

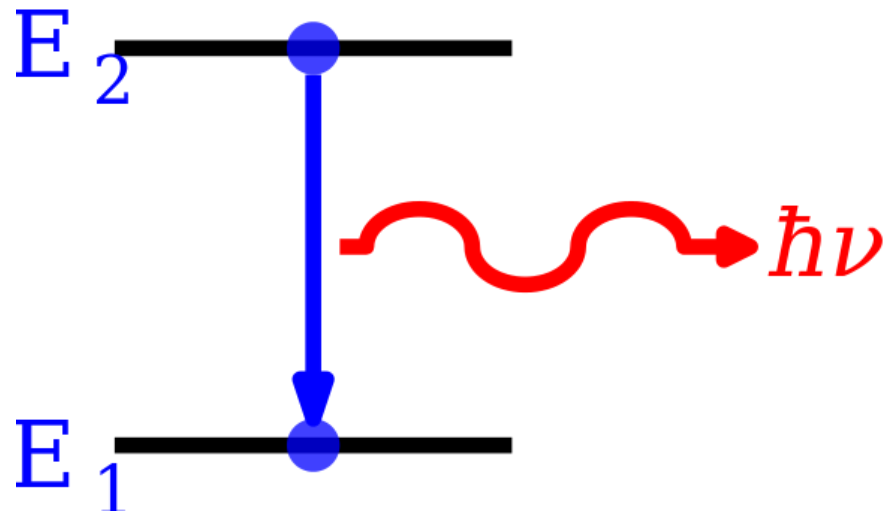


In the **photochemical reactions**, which is called **vibrational deactivation**, or **non-radiative** relaxation, the excess energy is released as **heat**; thus



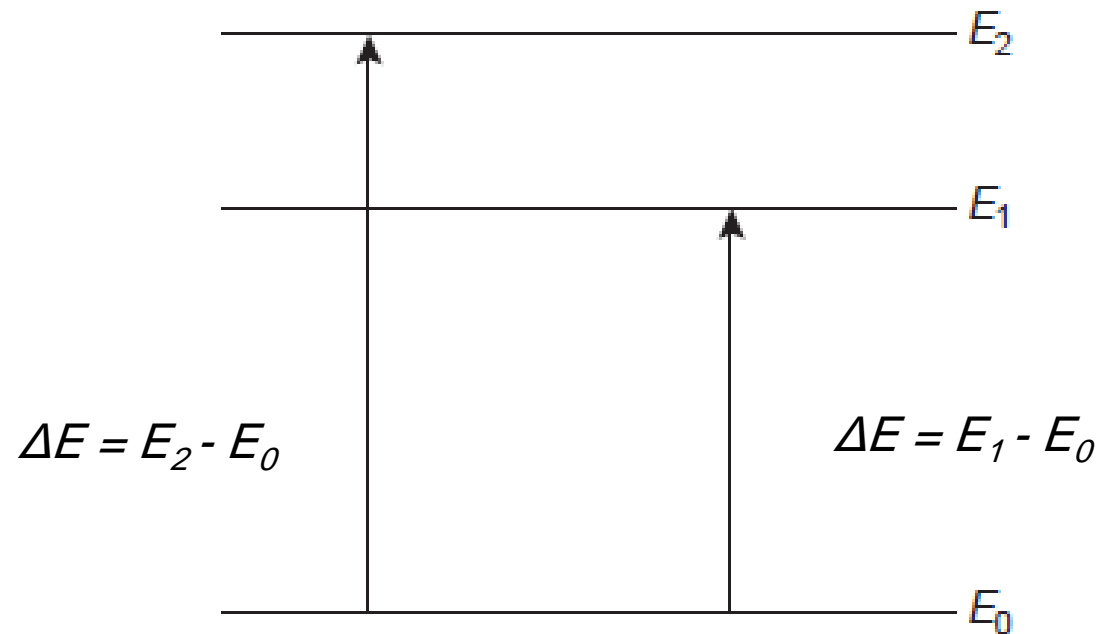
Relaxation by a photochemical reaction may involve a decomposition reaction in which A^* splits apart or a reaction between A^* and another species. In either case the excess energy is used up in the chemical reaction or released as **heat**.

In the second mechanism excess energy is released as a photon of **electromagnetic radiation**.

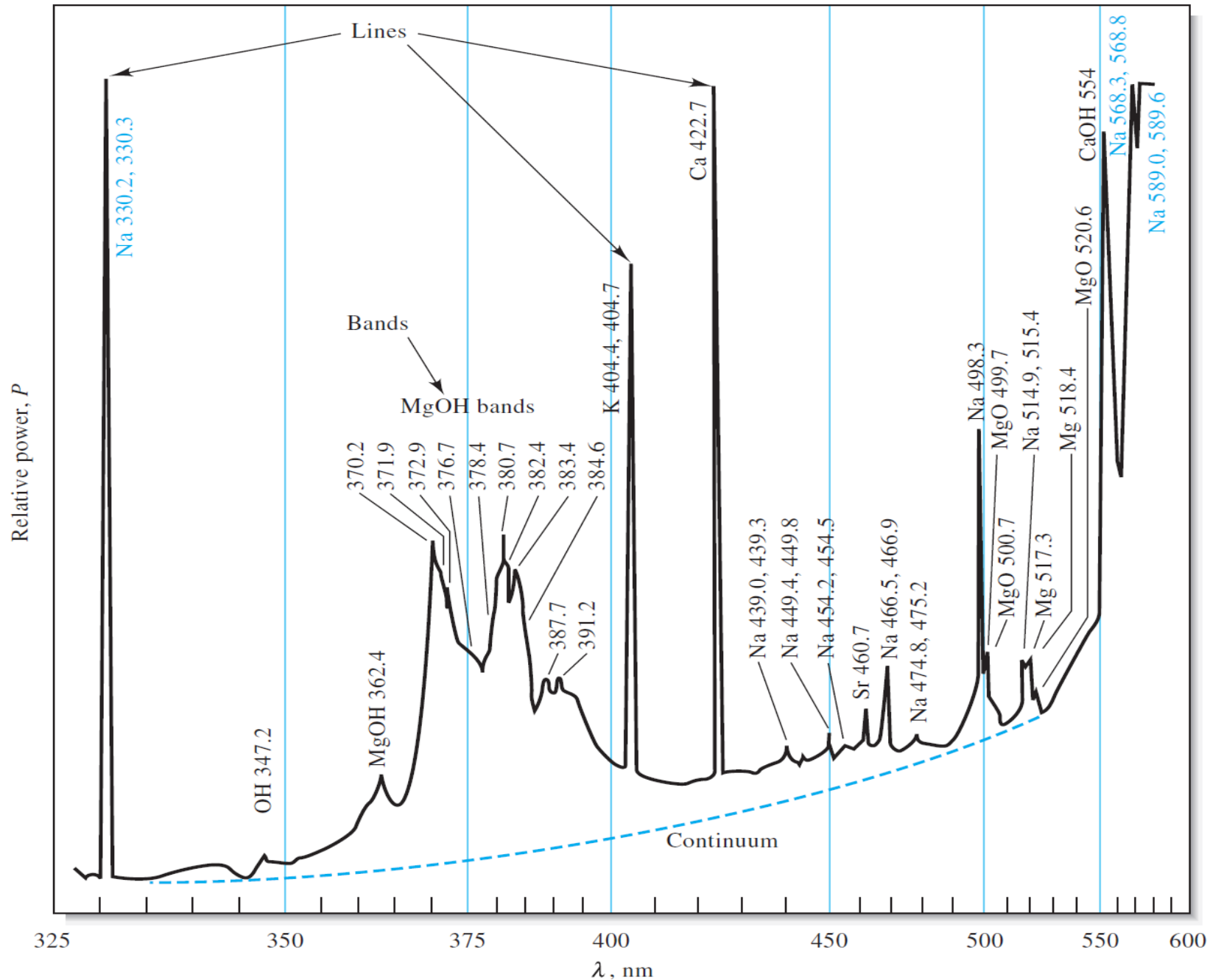


Atoms, ions, and molecules can be excited to one or more higher energy levels by any of several processes, including:

- **Bombardment** with electrons or other elementary particles.
- **Exposure** to a high-temperature plasma, flame or electric arc (thermal energy).
- **Exposure** to a source of electromagnetic radiation (photons).
- **Chemical** sources of energy (exothermic reactions, thermal energy).



- The release of a photon following **thermal** excitation is called **emission**.
- The release of a photon that following the **absorption of a photon** is called **photoluminescence**.
- The release of a photon that following the excitation results from a **chemical or biochemical reaction** is called **chemiluminescence** and **bioluminescence**, respectively.



Typical emission spectrum, which was obtained by aspirating a brine solution into an oxyhydrogen flame

Three types of spectra are superimposed in the figure: a **line spectrum**, a **band spectrum**, and a **continuum spectrum**.

Line Spectra

The line spectrum, consists of a series of sharp, well-defined spectral lines caused by excitation of individual atoms that are well separated, as in a gas. For example, lines for sodium, potassium, strontium, calcium and magnesium (in the figure).

The individual particles in a gaseous medium behave independently of one another, and the spectrum in most media consists of a series of sharp lines with widths of $0.1\text{--}0.01\text{\AA}$ ($10^{-2}\text{--}10^{-3}\text{nm}$).

The wavelengths of atomic lines are unique for each element and are often used for qualitative analysis.

Band Spectra

The band spectrum is comprised of several groups of lines so closely spaced that they are not completely resolved. The source of the bands is small molecules or radicals in the source flame.

Band spectra are often produced in spectral sources because of the presence of gaseous radicals or small molecules. For example, bands for OH, MgOH, and MgO (in the figure), which consist of a series of closely spaced lines that are not fully resolved by the instrument used to obtain the spectrum.

Bands arise from the numerous quantized vibrational levels that are superimposed on the ground state electronic energy level of a molecule.

Continuum Spectrum

A spectral continuum of radiation is produced when solids such as carbon and tungsten are heated to incandescence. Thermal radiation of this kind, which is called **blackbody radiation**, is more characteristic of the temperature of the emitting surface than of its surface material.

Blackbody radiation is produced by the innumerable atomic and molecular oscillations excited in the condensed solid by the thermal energy.

The continuum spectrum, is responsible for the increase in the background that appears above about 350 nm (in the figure). The line and band spectra are superimposed on this continuum.

Effect of Concentration on Line and Band Spectra

The radiant power P of a line or a band depends directly on the number of excited atoms or molecules, which in turn is proportional to the total concentration c of the species present in the source. Thus, we can write:

$$P = kc$$

where k is a proportionality constant. This relationship is the basis of quantitative emission spectroscopy.

