Absorption or emission of electromagnetic radiation results in a **permanent energy transfer** from the emitting object or to the absorbing medium.

This permanent energy transfer can be explained considering light to be a stream of discrete particles (**photons**, light quanta).

Quantum theory states that individual matter entities such as atoms, ions or molecules may only exist in discrete states (**quantized states**).

⇒ Absorption or emission changing the state of the species is thus explained as the uptake or release of well-defined, discrete amounts of energy, corresponding precisely to the energy difference between these states.
The energy of emitted or absorbed electromagnetic radiation is described by:

\[ E = h \nu \]

with \( h = 6.6254 \times 10^{-34} \) [Js] (Planck's constant).

Using \( \nu = \frac{c}{\lambda} \) we get

\[ E = h \frac{c}{\lambda} \]

The energy states of atoms, ions or molecules are called electronic states, which are accompanied by equally discrete vibrational and rotational states. Vibrational states correspond to the energy of interatomic or intermolecular vibrations, whereas rotational states result from the rotation of species around their center of gravity.
Emission of Radiation 1

- **Emission** is the release of electromagnetic radiation emitted as photons by the relaxation of excited species (E*), such as atoms, ions or molecules respectively aggregates of those, to lower energy levels.

  \[ E^* = E + h^*\nu (\Delta E = h^*\nu) \]

- **Continuum spectra:**
  Thermal radiation emitted by solids (to be more precise – the entity of atomic or molecular species oscillating due to thermal stimulation) heated to incandescence corresponds to the emission of a continuum spectrum, also called black body radiation.

  ![Figure 6-18 Blackbody radiation curves.](image-url)
Band spectra:
Considering small molecules in the gas phase, usually band spectra are observed consisting of a series of closely spaced emission lines. These bands are resulting from numerous quantized vibrational levels superimposed on the ground state electronic level of the molecules (Fig. 6-17b).

Figure 6-17  Energy-level diagrams for (a) a sodium atom showing the source of a line spectrum and (b) a simple molecule showing the source of a band spectrum.
Line spectra:
Considering well separated, individual atomic particles in the gas phase, line spectra are observed in the UV/Vis spectral range. These spectra consist of a series of sharp lines (Figure 6-17a).
If light is propagating through a gaseous, liquid or solid medium containing particles such as atoms, ions, molecules or respective aggregates of these, either no energy transfer occurs (transmission), or absorption, if the transmitted frequency corresponds to the resonance frequency of an absorption line/band of the species present.

\[ E + h*\nu = E^* \ (\Delta E = h*\nu) \]

The energy difference between the various energy levels is usually substance specific. Hence, recording the amount of absorption (decrease in radiant power), called absorbance (A) of a certain species, as a function of the frequency, results in a unique absorption pattern (absorption spectrum), which allows the characterization and identification of a sample.

\[ A = -\log_{10} T \]

If the amount of particles in the probed volume correlates to the absorbed amount of energy, quantification is possible.
Atomic absorption:

Passage of polychromatic UV or Vis radiation through a medium consisting of monoatomic particles. Few well-defined frequencies are absorbed. (Fig. 6-19a)

\[ E = E_{\text{electron}} \]
Molecular absorption:

Absorption spectra of polyatomic species particularly in the condensed phase are more complex due to the high number of energy states.

\[ E = E_{\text{electron}} + E_{\text{rotation}} + E_{\text{vibration}} \]

The number \( N \) of excitable states/energy levels allocated to a molecule can be ranked as

\[ N_{\text{rotation}} > N_{\text{vibration}} > N_{\text{electron}} \]
Relaxation Processes

- **Lifetime of the excited molecules/atoms:**

  Lifetime excited
  - vibrational state: $\approx 10^{-15}$ s
  Lifetime excited
  - electronic state: $\approx 10^{-8}$ s

  Generally, short lifetime, because several processes of relaxation are possible:

  - Non-radiative relaxation
  - Fluorescence ($\leq 10^{-5}$ s) (resonant/non-resonant)
  - Phosphorescence ($> 10^{-5}$ s up to min., Triplet-State)

*Figure 6-20 Partial energy-level diagrams for a fluorescent organic molecule.*