Preparatory School to the Winter Collegue on Optics: Optical Frequency Combs

Humberto Cabrera

Spectroscopy/Molecular energy levels

Molecular spectroscopy is the study of the interaction of electromagnetic (EM) radiation with matter. It is based on the analysis of EM radiation that is emitted, absorbed, or scattered by molecules, which can give information on:

- chemical analysis (finding a chemical fingerprint, so to speak)
- molecular structure (bond lengths, angles, strengths, energy levels, etc...)

Contents

Types of molecular energy

Energy can be stored either as potential energy or kinetic energy, in a variety of ways including:

- **Translational energy**: small amounts of energy stored as kinetic energy. This is unquantized (can take any value) and hence is not relevant to spectroscopy.
- **Rotational energy**: kinetic energy associated with the tumbling motion of molecules. This is quantized.
- **Vibrational energy**: the oscillatory motion of atoms or groups within a molecule (potential energy ↔ kinetic energy exchange). This is quantized.
- **Electronic energy**: energy stored as potential energy in excited electronic configurations. This is quantized.
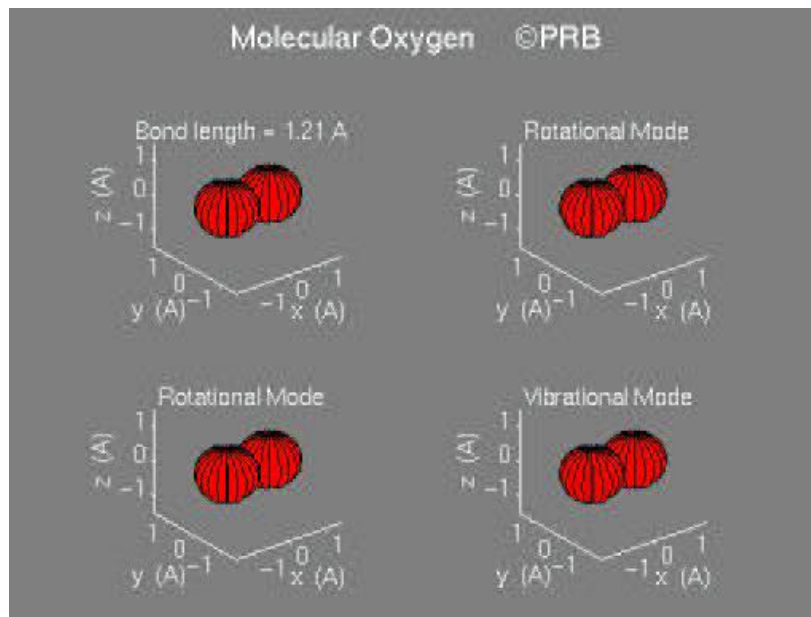
This results in a series of molecular energy levels.

Spectroscopy is the measuring of the transitions between levels.
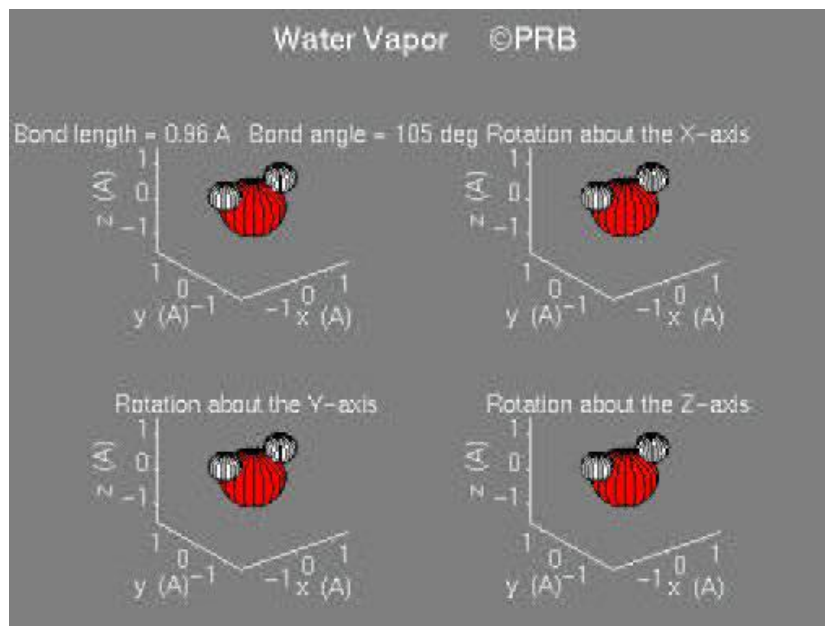
We have examined electronic transitions in molecules
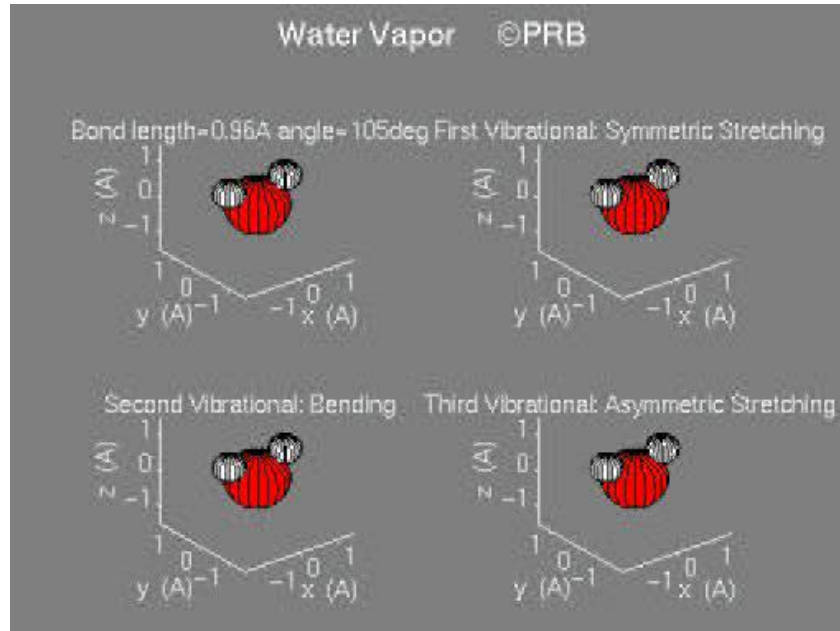– But they can also rotate and vibrate

– ex. O2

Become more complicated for more complex molecules

– ex. H2O rotational modes

ex. H2O vibrational modes

Water Vapor ©PRB

Vibrations
• Just like the electrons, molecular motion is governed by quantum mechanics
  – Energies due to rotation and vibration are quantized
• Molecular vibrations
  Chemical bond acts like a spring and can display SHM
  Have an effective spring constant k for the bond involved and effective mass $meff$
  Angular frequency

$$\omega = \sqrt{\frac{k}{m_{eff}}}$$

Energy of vibration

$$E_v = \left(v + \tfrac{1}{2}\right)\hbar\omega = \left(v + \tfrac{1}{2}\right)hf$$

$\tfrac{1}{2}\hbar\omega$ comes from quantum mechanics and represents *zero-point energy*
Characteristics

• Vibrational quantum number $v = 0,1,2,3,\ldots$
• The zero point energy $\tfrac{1}{2}\hbar\omega$ implies molecule never stops vibrating, even when its in the $v = 0$ state!
– Zero point energy cannot be harvested or extracted
– Still exists at absolute zero
• All molecules are then in $v = 0$ state

- Energy levels are equally spaced with separation $\frac{1}{2}\hbar\omega$
- Obey selection rule $\delta v = \pm 1$ *if no accompanying electronic transition*

– *Otherwise can be anything*

Molecular rotations

- In quantum mechanics, the rigid rotor has energy levels

$$E_J = \frac{\hbar^2}{2\Im} J(J+1)$$

where $\Im$ is the moment of inertia (PHY1080), J is the angular momentum, $J = 0,1,2,3,\ldots$

- The quantity $\frac{\hbar^2}{2\Im}$ is called the *rotational parameter*
- Moment of inertia, hence rotational parameter, can be different for each rotation axis
- Excitation energies correspond to the microwave region
- Energy scale for rotations $\ll$ vibrations
  - Each vibrational level has rotational bands built on it

- Selection rule $\delta J = \pm 1$
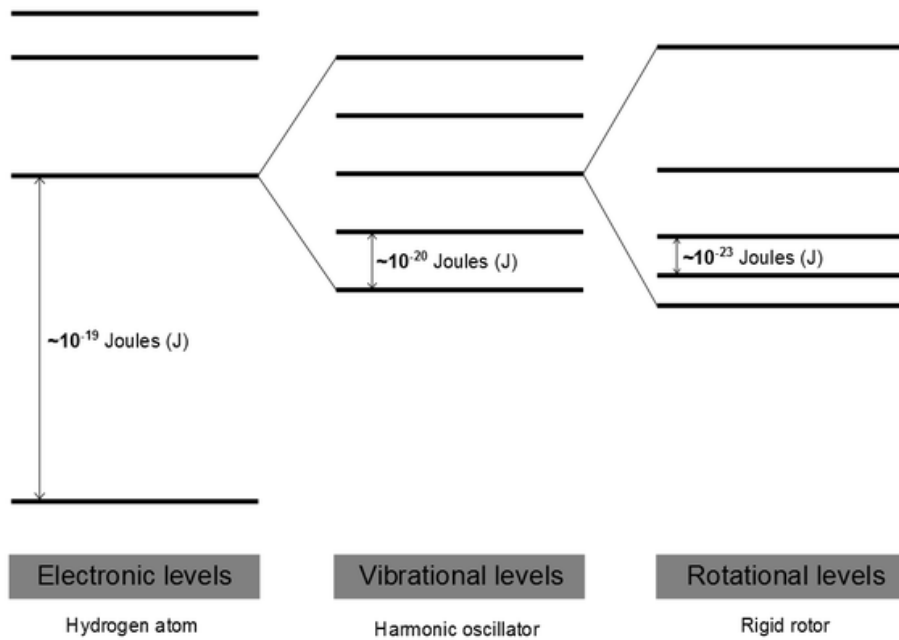
Typical values for energy level separations

- Taking rotations, vibrations, and electronic excitation into account

$$E_{n,v,J} = E_n + E_v + E_J$$

$$E_{n,v,J} = \frac{n^2 h^2}{2 m_e \ell^2} + (v + \tfrac{1}{2})\hbar\omega + \frac{\hbar^2}{2\Im} J(J+1)$$

↗ —— Ring molecule

- If the measuring instrument has very good resolution, it is possible to see the discrete transitions
- Complex molecules may have many vibrational modes, rotational modes, etc. The combination of these different modes leads to a "smearing" of the discrete spectrum (temp. effects too) so that broad bumps appear rather than discrete lines

| Electronic levels | Vibrational levels | Rotational levels |
| Hydrogen atom | Harmonic oscillator | Rigid rotor |

Energies (and wavefunctions) for these different levels are obtained from quantum mechanics by solving the Schrödinger equation. Spectroscopy is used to interrogate these different energy levels.

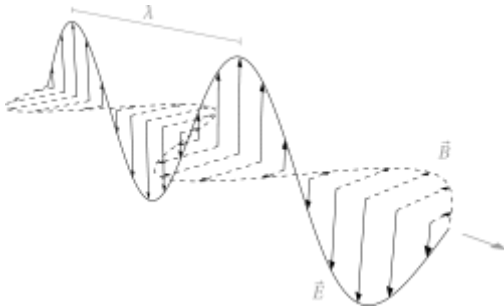Vibrational-rotational IR spectrum

• HCl
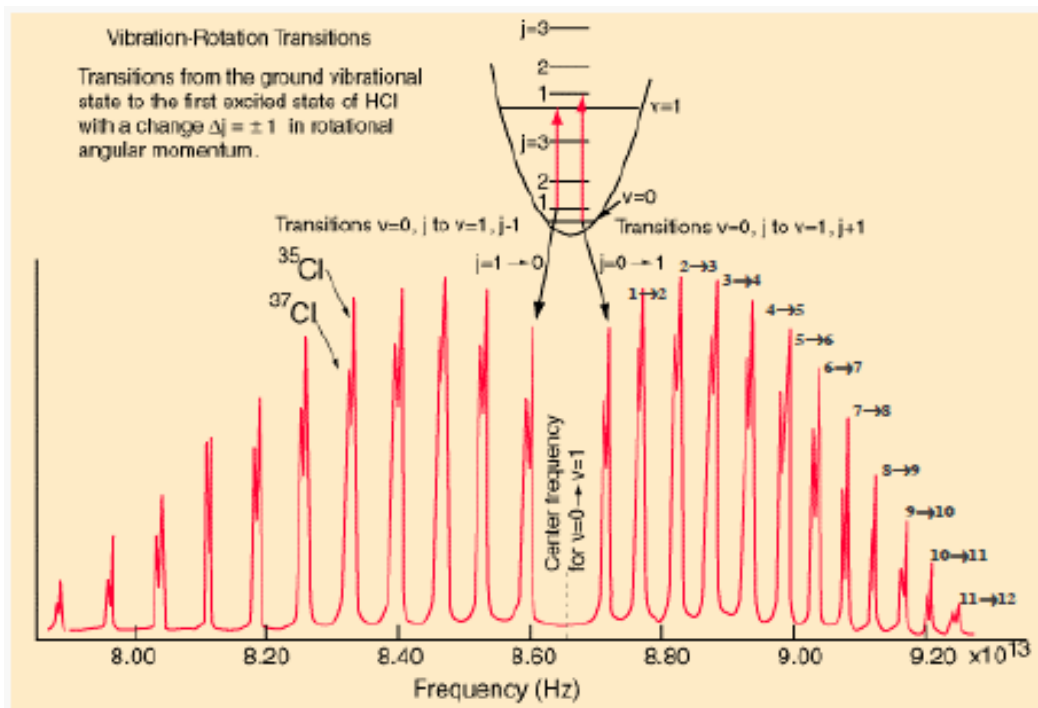
Water absorption spectrum
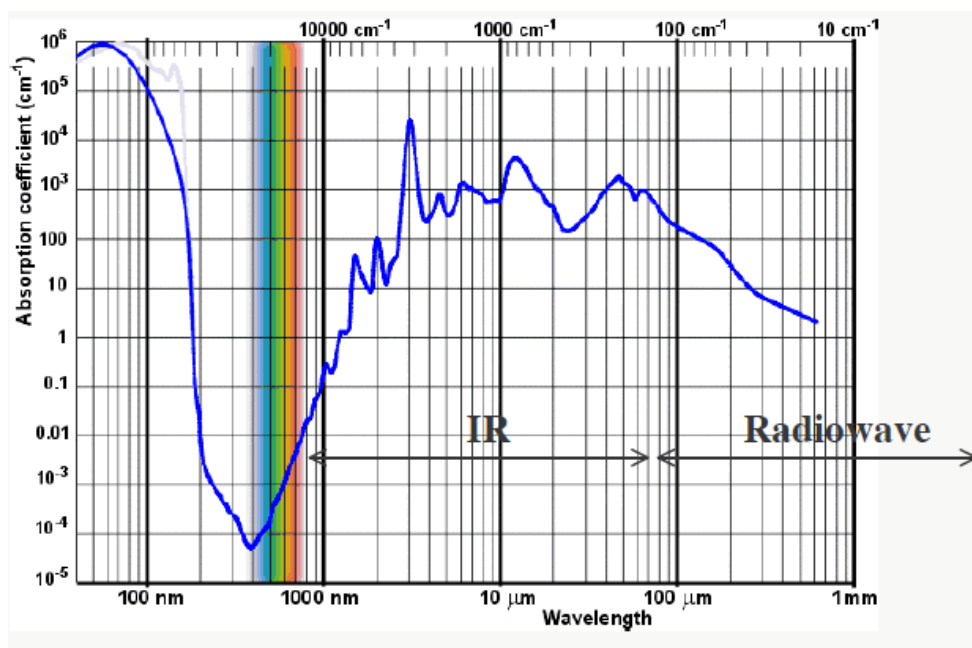
Electromagnetic radiation

Eletromagnetic wave

Electromagnetic (EM) radiation consists of photons (elementary particles) which behave as both particles and waves.

The image to the right shows the wave-like character associated with a single photon of EM radiation.

- In the x,z plane there is an oscillating electric field (E)
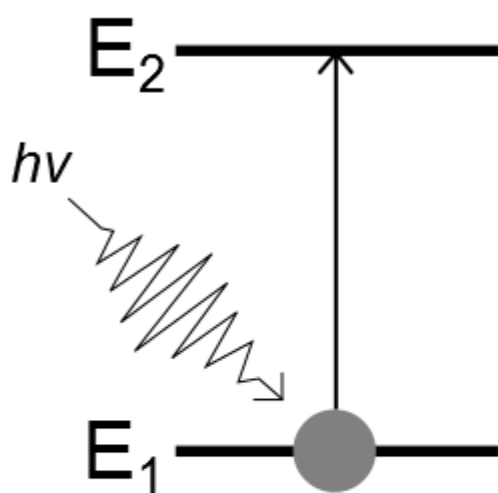- In the y,z plane there is an oscillating magnetic field (B)

Both are in phase but perpendicular to each other.

Key equations

$$\nu = \frac{c}{\lambda} \qquad\qquad \bar{\nu} = \frac{1}{\lambda}$$

- c = speed of light (2.998×10^8 ms^{-1})
- λ = wavelength (m)
- ν = frequency (s^{-1})
- $\bar{\nu}$ = wavenumber (m^{-1})

Transitions between energy levels

- Absorption spectroscopy: a photon is **absorbed** ("lost") as the molecule is raised to a higher energy level.
- Emission spectroscopy: a photon is **emitted** ("created") as the molecule falls back to a lower energy level.

Electromagnetic spectrum

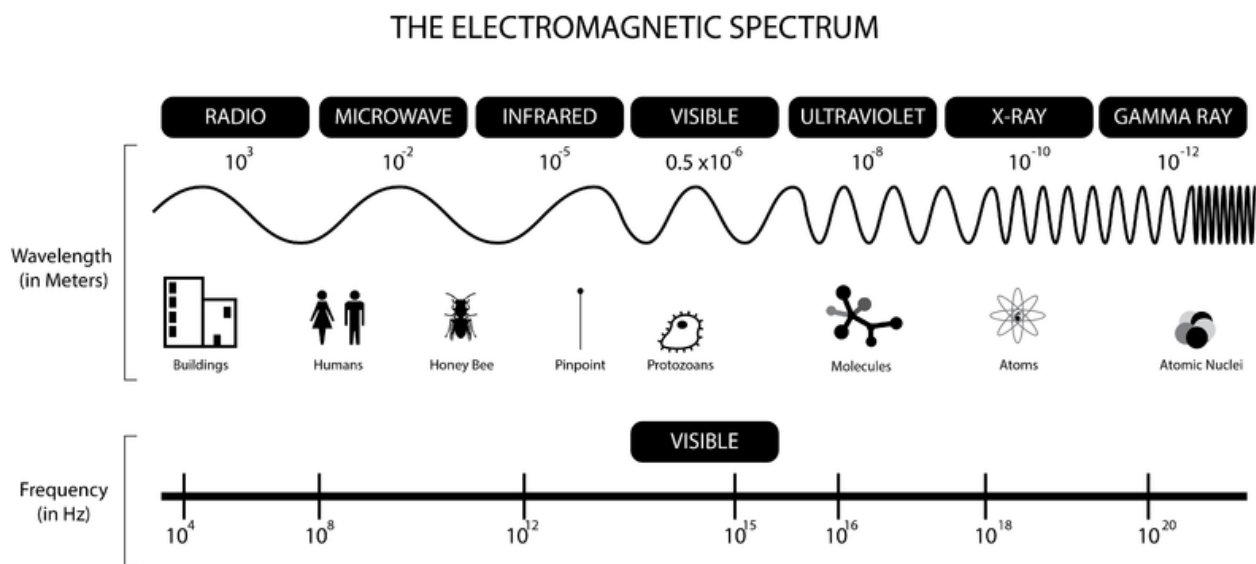Relevant regions for this course:

- Radio → nuclear spin in magnetic field
- Microwave → rotation
- Infrared → vibration
- Ultraviolet → electronic

Common units in spectroscopy

Wavelength, λ

- S.I. unit = metres (m)
- Other units = micrometer (1 μm = 10^{-6} m) ; nanometer (1 nm = 10^{-9} m) ; Angstrom (1 Å = 10^{-10} m)

Frequency, ν

- S.I. unit = Hertz (Hz) or s^{-1}
- Other units = megahertz (1 MHz = 10^{6} Hz) ; gigahertz (1 GHz = 10^{9} Hz)

Energy, E

- S.I. unit = Joules (J)
- For molar energies, multiply by Avogadro's constant (N_A) = J mol^{-1} or kJ mol^{-1}

Wavenumber, $\bar{\nu}$

- S.I. unit = m^{-1}
- Units of cm^{-1} are most commonly used in spectroscopy

- Molecular spectra are typically recorded as line intensities as a function of frequency, wavelength or wavenumber.
- Remember the importance of using correct units and being able to convert between different ones (see the formulae below).

$$E = hc\bar{\nu} \qquad\qquad \bar{\nu} = \frac{1}{\lambda}$$

Factors influencing intensity of spectral lines

1. Amount of sample

The intensity of lines on the spectrum will be affected by the amount of sample which light passes through. The intensity of this transmitted light depends on the sample concentration and path length.

- Beer-Lambert Law

2. Population of energy states

A system can undergo a transition from one level, *i*, to another level, *f*, but only if it is in the first level *i* to begin with.

- Boltzmann Distribution

3. Spectroscopic selection rules

A selection rule is a statement about which potential transitions are allowed and which are forbidden. Each spectroscopy has its own selection. Not all transitions are allowed even though energy conservation is obeyed.

1. Amount of sample

Absorbance and transmittance

Beer-Lambert Law:
$$\log \frac{I}{I_0} = -\varepsilon c L \qquad\qquad I = I_0 10^{-\varepsilon c L}$$
Absorbance (*A*)
$$A = \log \frac{I_0}{I} \rightarrow A = \varepsilon c L$$
Transmittance (*T*)
$$T = \frac{I}{I_0} \rightarrow A = -\log T$$

- ε = molar absorption coefficient

  units of ε: $conc^{-1}$ x $length^{-1}$ (usually mol^{-1} dm^3 cm-1)

- L = path length (in cm)
- ε_{max} is the maximum absorption coefficient, and is an indication of the intensity of a transition.

2. Population of energy states

The continuous thermal agitation that molecules experience at any temperature (greater than zero Kelvin) ensures that they are distributed over all possible energy levels.

- Population of a state = the average number of molecules in a state at any given time.

$T_1 = 0 \text{ K}$ $T_2 > 0 \text{ K}$ $T_3 > T_2$
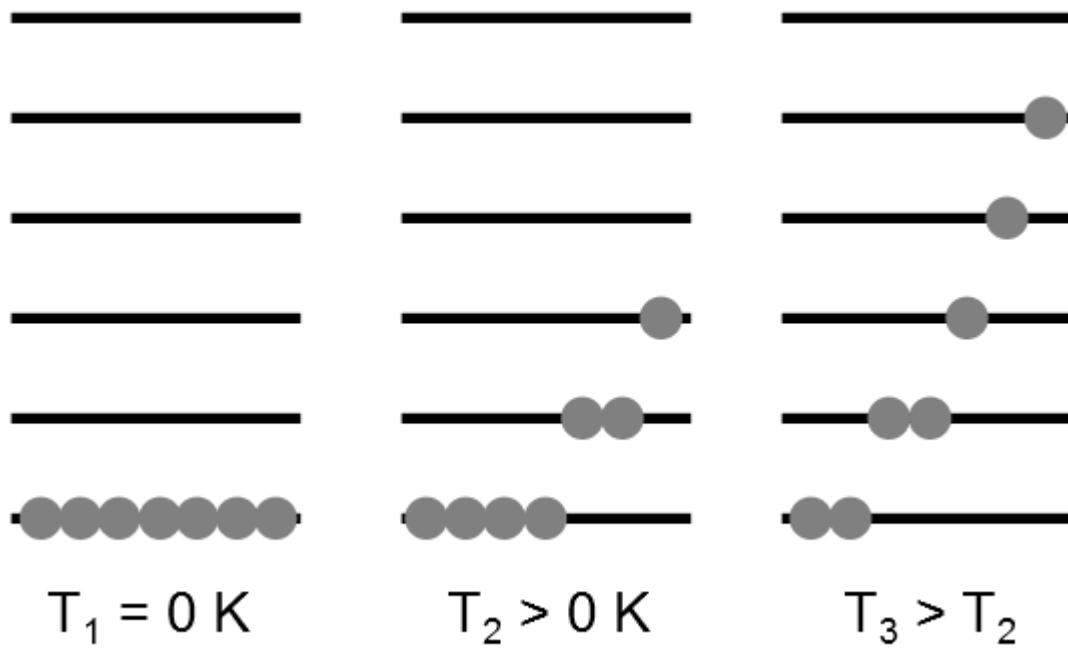
The mathematical formulation of how to calculate the population of a state was provided by Ludwig Boltzmann in the late 19th century.

The Boltzmann distribution

The Boltzmann distribution defines the relative population of energy states (usually the ratio of excited states to ground state).

$$\frac{N_f}{N_i} = \exp\left(-\frac{\Delta E}{k_B T}\right)$$
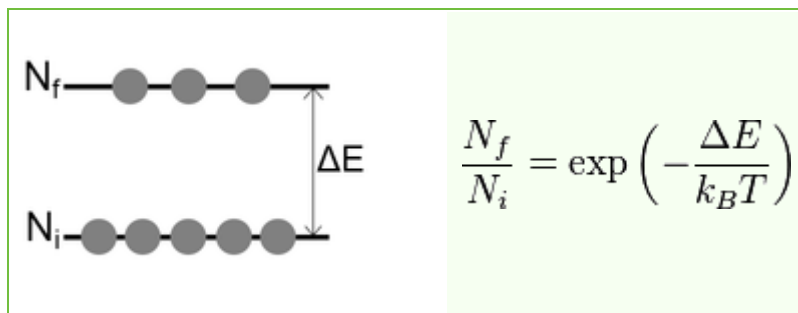
- k_B = Boltzmann constant (= R / N_A) = 1.381×10^{-23} J K^{-1}
- T = temperature (Kelvin)
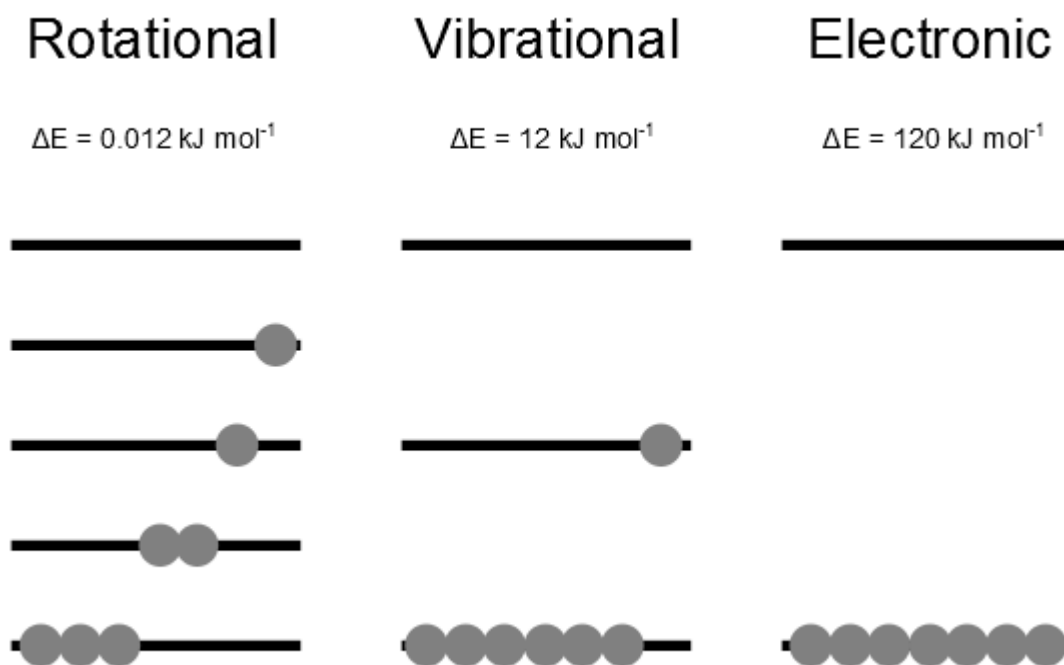
Effect of temperature

The Boltzmann distribution is a continuous function.

There is always a higher population in a state of lower energy than in one of higher energy.

At lower temperatures, the lower energy states are more greatly populated. At higher temperatures, there are more higher energy states populated, but each is populated less.

Effect of energy separation

$k_B T \sim 2.5$ kJ mol^{-1} at 300 K.

Rotational	Vibrational	Electronic
$\Delta E = 0.012$ kJ mol^{-1}	$\Delta E = 12$ kJ mol^{-1}	$\Delta E = 120$ kJ mol^{-1}

- Rotational: $\dfrac{N_1}{N_0} = \exp\left(-\dfrac{0.012}{2.5}\right) \approx 1$

- Vibrational: $\dfrac{N_1}{N_0} = \exp\left(-\dfrac{12}{2.5}\right) \approx 0.008$

- Electronic: $\dfrac{N_1}{N_0} = \exp\left(-\dfrac{120}{2.5}\right) \approx 1 \times 10^{-21} \approx 0$

Degeneracy

Degeneracy = when more than one state has the same energy.

$$\frac{N_f}{N_i} = \frac{g_f}{g_i} \exp\left(-\frac{\Delta E}{k_B T}\right)$$

- g_i and g_f = degeneracies of initial and final states

This is very important for rotational energy levels (see later). As a result, the population of an energy state is then a product of the Boltzmann distribution and the degeneracy.

- This means that the ground state may no longer be the most populated state.