

Spectroscopic Literature

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J. J. Sakurai, Modern Quantum Mechanics

R. S. Drago, Physical Methods in Chemistry

F. A. Cotton: Chemical Applications of Group Theory

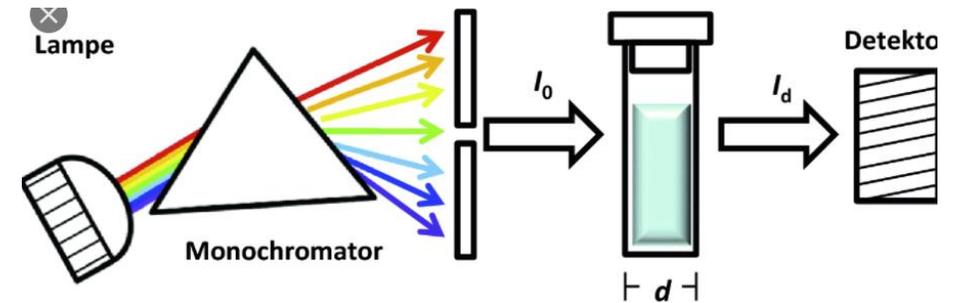
Interaction of electromagnetic waves with matter

Objective

Change electromagnetic waves:
Change matter:
Analyze matter:

research field

optical physics
photochemistry
spectroscopy



Keyword: electromagnetic waves

$$\mathcal{E} = \mathcal{E}_0 \exp i(kz - \omega t + \phi)$$

$$\mathcal{B} = \mathcal{B}_0 \exp i(kz - \omega t + \phi)$$

\mathcal{E}_0 : Amplitude,

k: wave vector = $2\pi/\lambda$

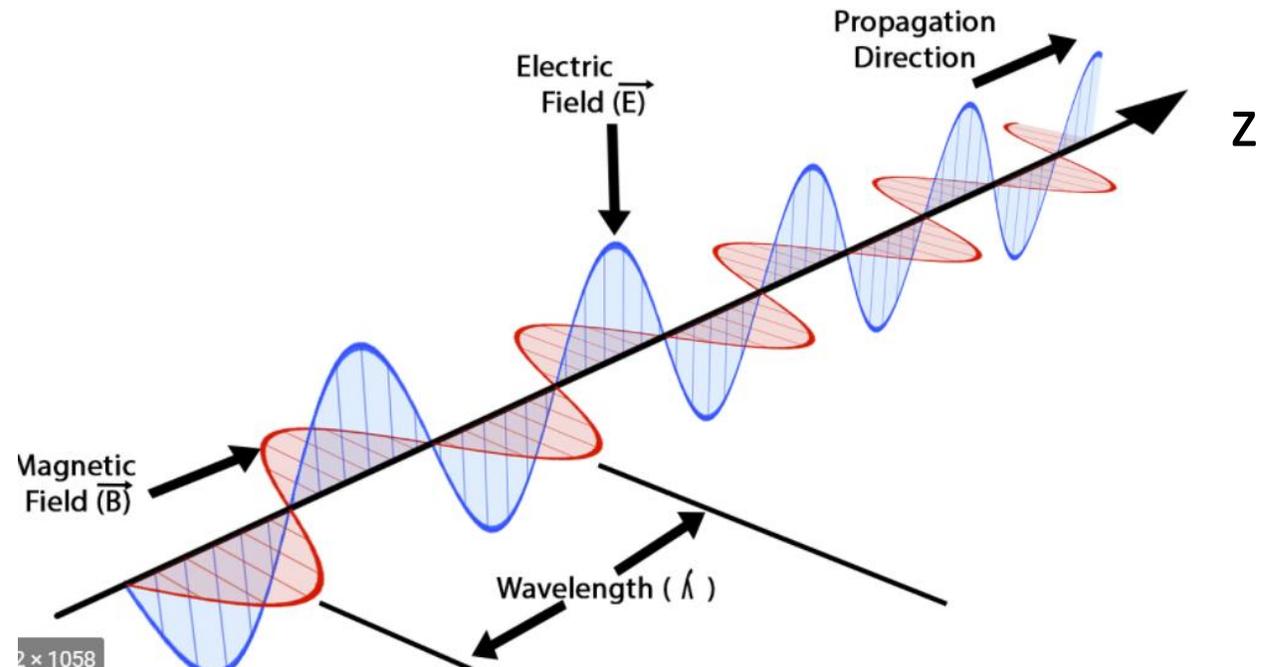
$\omega = 2\pi\nu =$ frequency

$\phi =$ phase

$v = c/n = v\lambda$

propagation velocity

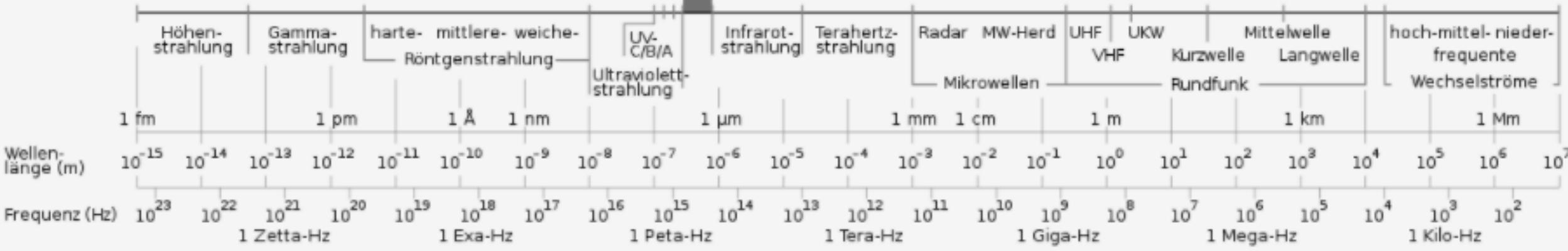
$$E = h\nu = \hbar\omega$$



2×10^{58}

The Electromagnetic Spectrum

Das für den Menschen sichtbare Spektrum (Licht)

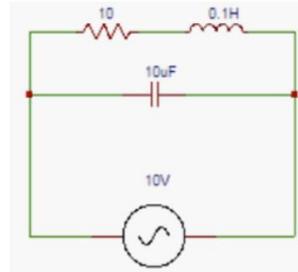


Generation of electromagnetic wavesand detection

General principle: oscillation of charges -> emission of electromagnetic waves $m\ddot{x} + f_x = 0$ ->

$$x = x_0 \exp(i\omega_0 t) \text{ with } \omega_0 = \sqrt{f/m}$$

Radiowaves:
Tank circuits



$$\omega_0 = 1/\sqrt{LC}$$

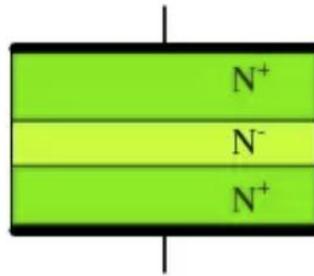
$$C = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{A}{d}$$

$$L = \mu_0\mu_r S \frac{n^2}{l}$$

Tank circuits

Electromagnetic induction -> U

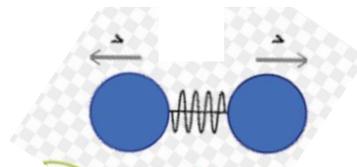
Microwaves



velocity modulated electron ensembles

Rectification -> Q
Heat transfer -> T

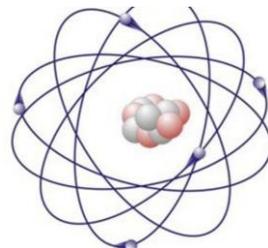
Infrared



Molecular oscillators
Black-body (thermal) radiators
Electron relaxation (lasers)

Heat transfer -> T
Photoel. effect -> U
(doped PbTe, CdTe)

Ultraviolet



Electron relaxation (following ionization)
Cyclotrons (Synchrotron)

Photoel. effect -> U
Direct or indirect
(Photostimulated Detectors)

X-Ray

Gamma Ray

Nuclear relaxation

Scint. Counter NaI(Tl)
Photo-electrons

Keyword: Matter

From spectroscopist's viewpoint: A sum of Hamiltonians

$$\mathcal{H} = \mathcal{H}_{rot} + \mathcal{H}_{vib} + \mathcal{H}_{el} + \mathcal{H}_{nucl} + \mathcal{H}_Z$$

For each Hamiltonian there are exact solutions of the Schrödinger equation, yielding eigenfunctions and energy eigenvalues for relatively simple model systems and approximate energies for more complex systems:

Rotation: 3D-rigid free rotor ($U = 0$)

$$E = B h J(J+1) \text{ with } B = \hbar/4\pi\Theta \text{ } (\Theta = \text{moment of inertia})$$

Vibration: harmonic oscillator $U = \frac{1}{2} f q^2$

$$E = (n_v + \frac{1}{2}) \hbar\omega_0 \text{ with } \omega_0 = \sqrt{f/m} \text{ } (m = \text{mass})$$

Electrons: H-like one-electron systems

$$E \sim 1/n^2; \text{ many-el.: } E = f(L, M_L, J) \text{ due to inter-electronic interactions}$$

Zeeman: Stern-Gerlach system

$$E = m_s \mu_B g B \text{ (EPR)} \text{-----} m_l \gamma \hbar B \text{ (NMR)} \text{ } (\mu_B = \text{Bohr magneton} = e \hbar / 2m_e)$$

Spectroscopy

Magnetic resonance

relevant quantum number

m_l (NMR) or m_s (EPR) spin orientational quantum number

Rotational spectroscopy

J (angular momentum quantum number of molecular rotation)

Vibrational spectroscopy

n_v (vibrational quantum number)

Electronic spectroscopy (VIS, UV, X-ray)

L, J, M_L, M_J, n (angular momentum or principal quantum number)

Mössbauer

I (nuclear spin quantum number)

Born-Oppenheimer Approximation.

The different parts of the Hamiltonian are independent and Schrödinger equations can be solved separately. Processes can be considered „decoupled“ -> this simplifies the theoretical analysis significantly.



Max Born
1882-1970
Göttingen, Edinburgh
Nobel Prize 1954



Robert Oppenheimer
1904-1967
UC Berkeley, Caltech
Princeton

Thermal Equilibrium

The fractional populations n_i/N of the levels having the energy ε_i and degeneracy g_i are given by the Boltzmann Distribution.

$$n_i/N = \frac{g_i \exp(-\varepsilon_i/k_B T)}{\sum_i g_i \exp(-\varepsilon_i/k_B T)}$$

Most spectroscopic experiments are conducted at thermal equilibrium. By the experiment the transitions between the energy levels take place, so that the system is transformed into a non-equilibrium state.

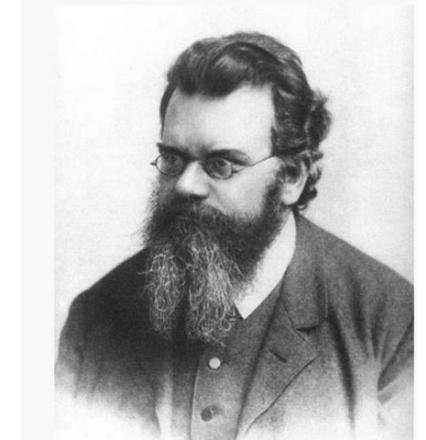
The return to thermal equilibrium is called **relaxation**

Relaxation can occur by re-emission or by transfer of energy to the lattice. The time Constant governing this return is called spin-lattice relaxation times.

Photolysis, chemical reaction, nuclear decay or cross-relaxation may create non- equilibrium states, from which return to equilibrium may occur via photon emission. (luminescence: emission spectroscopy)

Interaction with photons may create virtual states emitting electromagnetic radiation

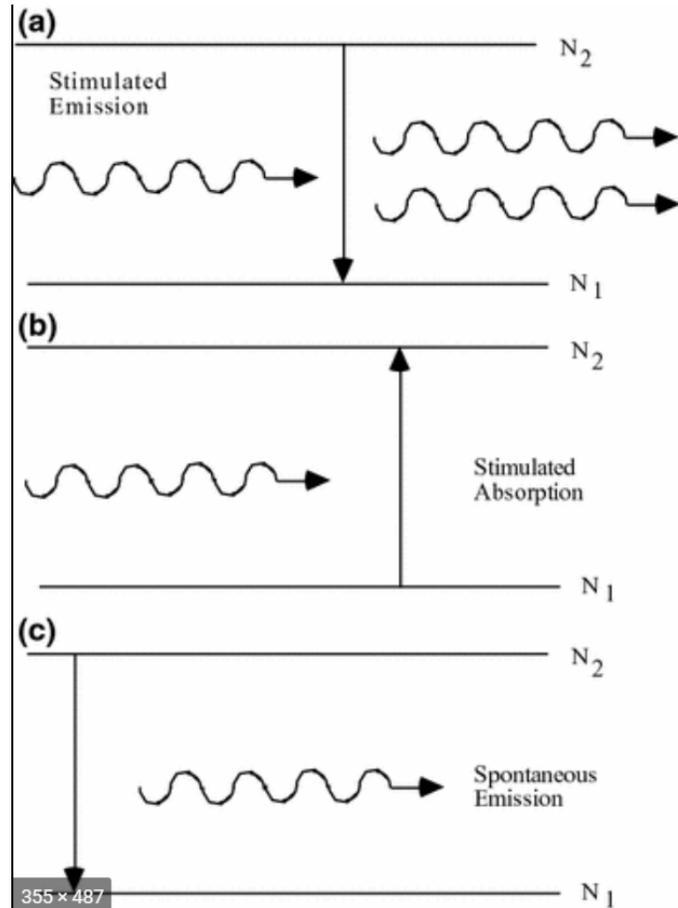
Ludwig Boltzmann



1844-1906
Universität Wien

Keyword: Interaction

Population changes in a two-level system (Einstein)



rates

$$dN_2/dt = -B_{21}N_2\rho(\nu)$$

$$dN_2/dt = B_{12}N_1\rho(\nu)$$

$$dN_2/dt = -A_{21}N_2$$

spectral energy density

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$$

Planck's radiation law

Equilibrium: Balance from all the Processes: $dN_2/dt = B_{12}N_1\rho(\nu) - B_{21}N_2\rho(\nu) - A_{21}N_2 = 0$

Simplest case: non-degenerate states

$$p_1 = N_1/N_{\text{tot}} = \frac{\exp(-\varepsilon_1/k_B T)}{\sum_i \exp(-\varepsilon_i/k_B T)} \quad p_2 = N_2/N_{\text{tot}} = \frac{\exp(-\varepsilon_2/k_B T)}{\sum_i \exp(-\varepsilon_i/k_B T)}$$

Equilibrium: Balance from all the Processes: $dN_2/dt = B_{12}N_1\rho(\nu) - B_{21}N_2\rho(\nu) - A_{21}N_2 = 0$

$$\rho(\nu) = \frac{A_{21}N_2}{B_{12}N_1 - B_{21}N_2} = \frac{A_{21} \exp(-\varepsilon_2/k_B T)}{B_{12} \exp(-\frac{\varepsilon_1}{k_B T}) - B_{21} \exp(-\frac{\varepsilon_2}{k_B T})} = \frac{A_{21}}{B_{12} \exp(\frac{\varepsilon_2 - \varepsilon_1}{k_B T}) - B_{21}} \quad \text{to be compared with}$$

$$\rho(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{\exp(\frac{h\nu}{k_B T}) - 1}$$

The result is: $A_{21} = \frac{8\pi h \nu^3}{c^3} B_{21}$ and $B_{12} = B_{21}$

-> at high frequencies spontaneous emission favored over stimulated emission

Mechanistically two conditions have to be fulfilled for energy transfer to occur:

- 1) Resonance condition: $h\nu = \varepsilon_2 - \varepsilon_1$ energy of the electromagnetic wave = energy difference between states
- 2) Coupling condition: interaction between electromagnetic wave and the wave function of the molecule (electric or magnetic dipole moment): group-theoretical criteria.

Spectroscopic observables

1. Frequency of absorption/emission

2. Width

a) **natural linewidth** – Heisenberg uncertainty $\delta E \delta t > \hbar/2$

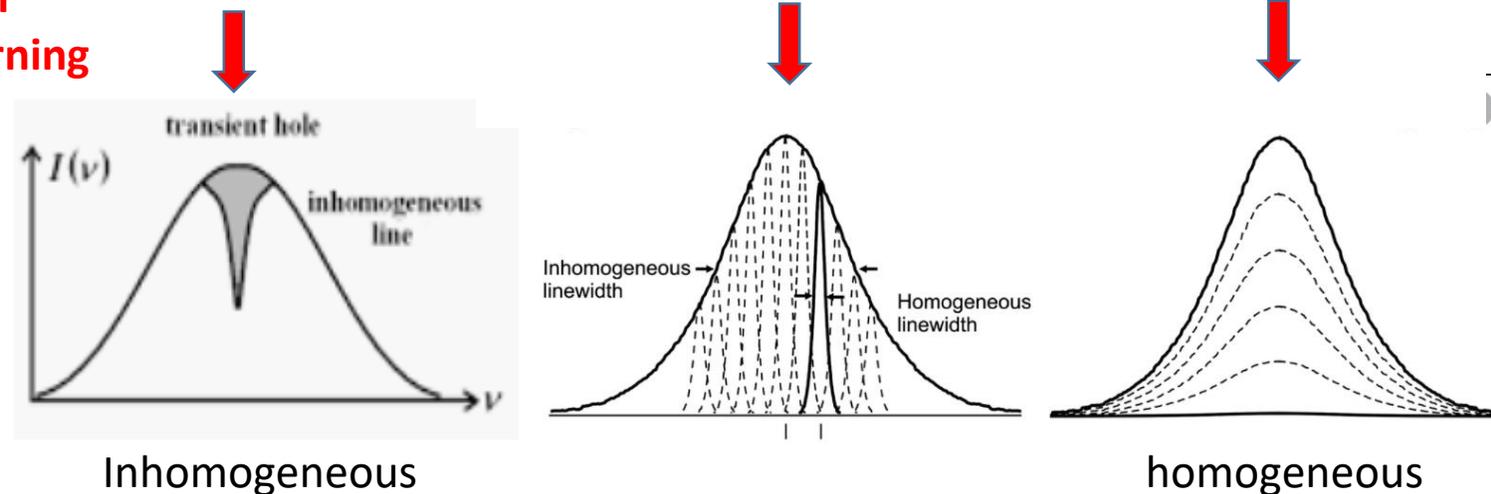
(δt = lifetime of excited state) $\delta(\hbar\omega)\delta t > \hbar/2 \rightarrow \delta\omega = 1/2\delta t$

b) **instrumental broadening** (monochromatization limits, field inhomogeneity)

c) **physical broadening**

- inhomogeneous broadening: anisotropy or distribution of energy levels
- homogeneous broadening: dynamic processes
- unresolved hyperfine structure (low-energy splitting due to weak interactions)

**Spectral
holeburning**



3. Intensities:

proportional to the rate: dN_2/dt

Remembering $dN_2/dt = B_{12}N_1\rho(\nu) - B_{21}N_2\rho(\nu) - A_{21}N_2$

Neglecting the contribution from spontaneous emission (valid at low frequencies):

$$dN_2/dt = B_{12}N_1\rho(\nu) - B_{21}N_2\rho(\nu) = B_{12} \rho(\nu)(N_1 - N_2) = B_{12} \rho(\nu)(p_1 - p_2)N_{\text{tot}}$$

Dependent on four factors:

- Population difference given by the Boltzmann law
- Intensity (wave amplitude, i.e. number of photons)
- Total number of molecules; basis of analytical applications
- Absorption coefficient B_{12} , transition probability, relating to the coupling condition

$$\text{Absorbance } A = \log \frac{T_0}{T} = \epsilon cd$$

Lambert-Beer law

T = transmission of the sample

T_0 = transmission of the sample without analyte ($c = 0$)

d = optical path length (diameter of cuvette)

c = analyte concentration (mol/dm^3)

ϵ = extinction coefficient (dm^2/mol)