

Chemistry 331

Lecture 4

Introduction to Spectroscopy
Quantum Mechanics Background
Electronic states and energies
Transitions between states
Detection
Absorption and Emission

NC State University

Postulates of quantum mechanics are assumptions found to be consistent with observation

The first postulate states that the state of a system can be represented by a wavefunction $\Psi(q_1, q_2, \dots, q_{3n}, t)$. The q_i are coordinates of the particles in the system and t is time.

The wavefunction can also be time-independent or stationary, $\psi(q_1, q_2, \dots, q_{3n})$.

Postulate 2. The probability of finding a particle in a region of space is given by

$$P(a) = \int_0^a \Psi^* \Psi d\tau$$

Postulate 2. Assumptions

1. $\Psi^* \Psi$ is real (Ψ is Hermitian).
2. The wavefunction is normalized.
3. We integrate over all relevant space.

Normalization is needed so that probabilities are meaningful.

Normalization means that the integral of the square of the wavefunction (probability density) over all space is equal to one.

$$\int_{all\ space} \Psi^* \Psi d\tau = 1$$

The significance of this equation is that the probability of finding the particle somewhere in the universe is one.

Postulate 3. Every physical observable is associated with a linear Hermitian operator

Observables are energy, momentum, position, dipole moment, etc.

operator \hat{P} \rightarrow observable P

The fact that the operator is Hermitian ensures that the observable will be real.

Postulate 4. The average value of a physical property can be calculated by

$$\langle P \rangle = \frac{\int \Psi^* \hat{P} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

Normalization

Postulate 4. The calculation of a physical observable can be written as an eigenvalue equation

$$\hat{P}\Psi = P\Psi$$

This is an operator equation that returns the same wavefunction multiplied by the constant P . P is an eigenvalue. An eigenvalue is a number.

Postulate 5. The form of the operators is

Position

\hat{q}

q

Momentum

\hat{P}

$i\hbar \frac{\partial}{\partial q}$

Time

\hat{t}

t

Energy

\hat{H}

$i\hbar \frac{\partial}{\partial t}$

Stationary State Wave Equation

Quantum Mechanical Description

Hamiltonian
Energy Operator

Eigenvalue
Energy value

$$\hat{H}_0 \Psi = E_0 \Psi$$

Wavefunction

The Hamiltonian and wavefunction are time-independent

The wavefunction is composed of electronic and nuclear parts

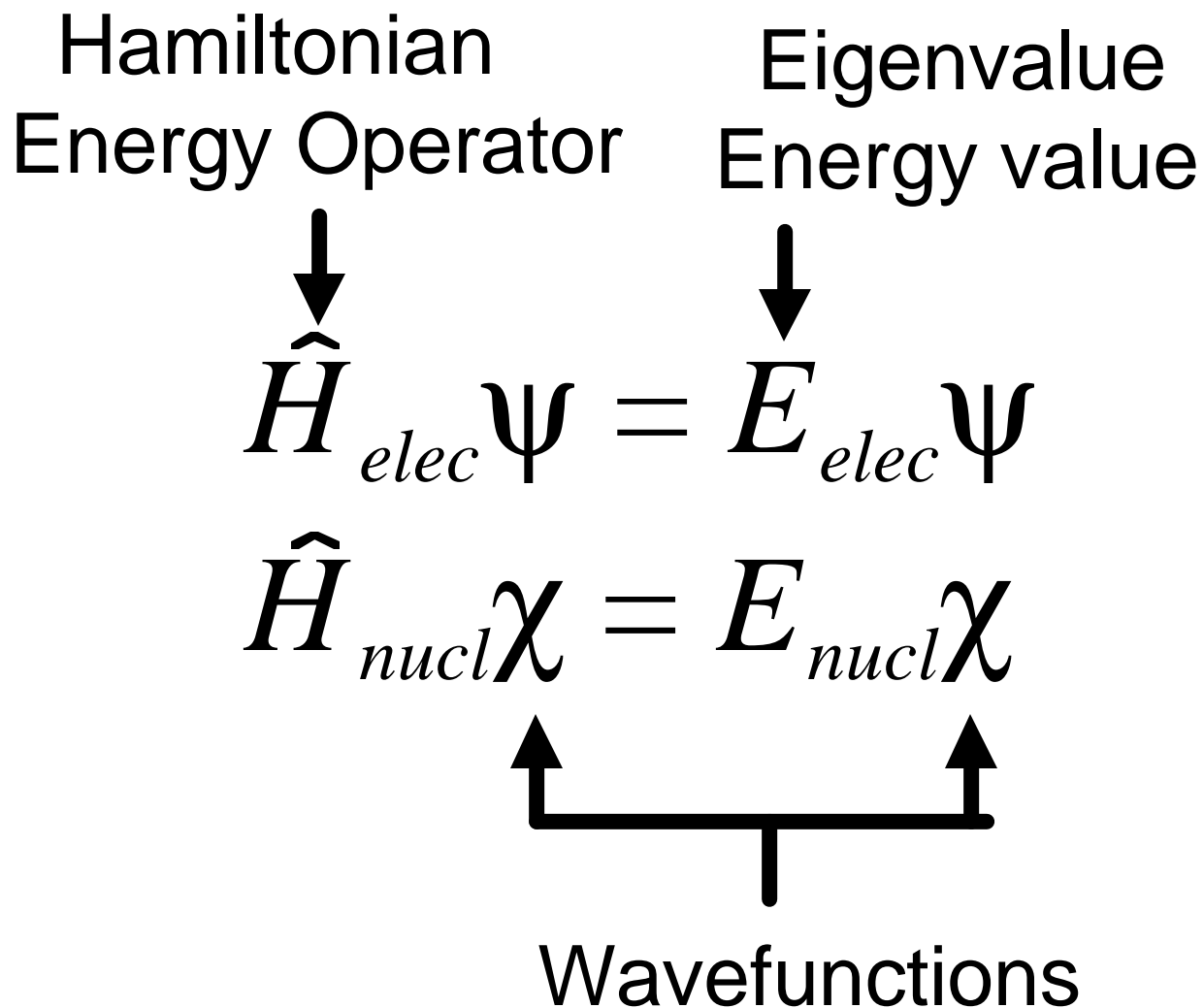
$$\Psi = \Psi_{\text{electronic}} \chi_{\text{nuclear}}$$

↑ ↑ ↑

Total Electronic Nuclear

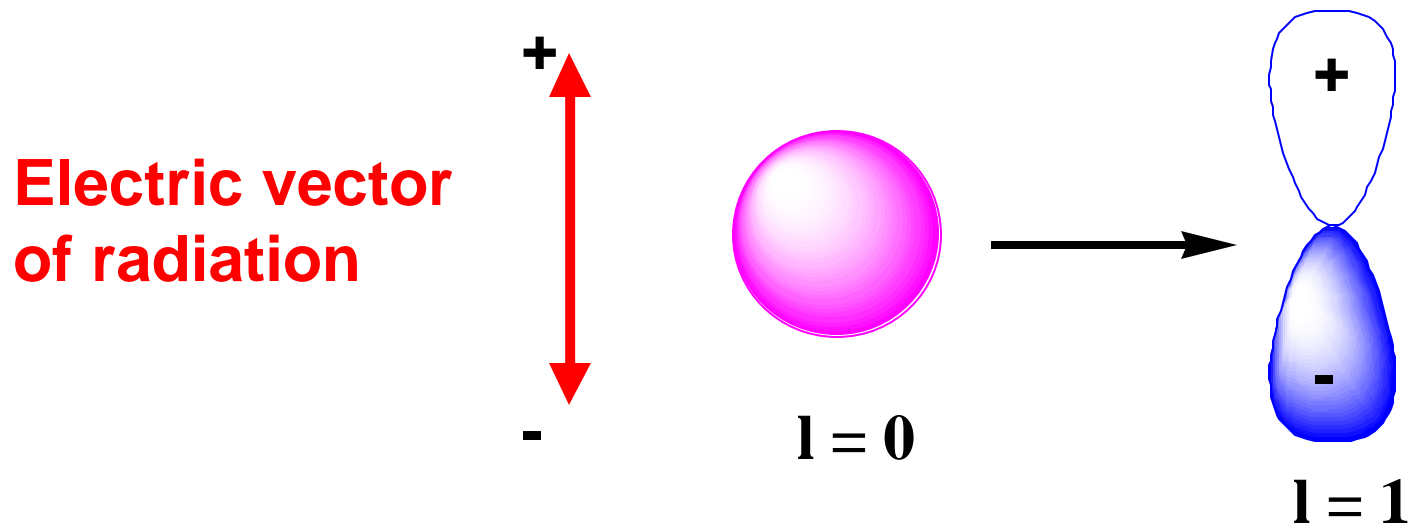
The wavefunction represents the probability amplitude of electrons and nuclei.

The wave equation can be separated into electronic and nuclear parts



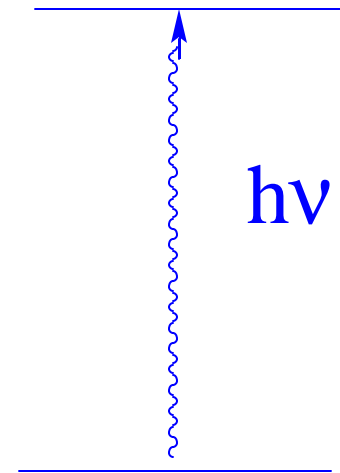
The interaction of electromagnetic radiation with a transition moment

The electromagnetic wave has an angular momentum of 1. Therefore, an atom or molecule must have a change of 1 in its orbital angular momentum to conserve this quantity. This can be seen for hydrogen atom:



Spectroscopy

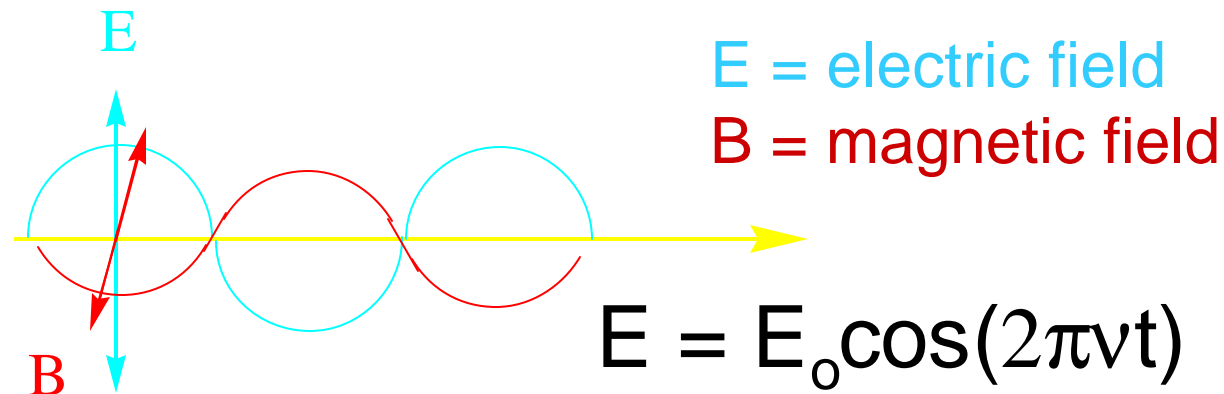
- Electromagnetic radiation
- Dipole moment
- Transition moment
- Selection rules
- Experimental techniques
- Intensities



The origin of spectral lines in molecular spectroscopy is the emission or absorption of a photon when the energy of a molecule changes.

Characteristics of electromagnetic radiation

Electromagnetic radiation can be described as a wave with an oscillating electric field. Light can be linearly polarized along the x, y, or z axes. The electric field vector is \perp to the direction of propagation.



Basic Phenomena

Emission spectroscopy - a molecule undergoes a transition from a state of high energy E_1 to a state of lower energy E_2 and emits the excess energy as a photon.

Absorption spectroscopy – the energy of an incident photon drives a polarization from the molecular ground state to the excited state. An absorbed photon has a frequency given by the Bohr relation:

$$h\nu = E_1 - E_2$$

Definition of the Dipole Moment

The dipole moment operator is

$$\mu = e \sum_i z_i r_i$$

where $z_i e$ is the electronic charge at a nucleus and r_i is a vector from an arbitrary origin. Along the x-direction



$$\mu = e \int_0^\infty Y^* x Y dx$$

Examples of ground state dipole moments

The ground state dipole moment of hydrogen halides can be calculated from the fractional charges

1 Debye = 3.33×10^{-30} Cm

δ^+ δ^-

	δ^+	δ^-	R(pm)	$\mu(\times 10^{-30}$ Cm)
HF	0.42	0.42	91.7	$6.37 \approx 1.9$ D
HCl	0.16	0.16	127.5	$3.44 \approx 1.0$ D
HBr	0.11	0.11	141.4	$2.64 \approx 0.8$ D
HI	0.05	0.05	160.9	$1.40 \approx 0.4$ D

Definition of the transition dipole moment

The transition dipole moment results from the interaction of electromagnetic radiation with the molecule where $E = E_0 \cos(2\pi\nu t)$ and the hamiltonian for interaction is

$$H = -\mu_x E_{ox} \cos(2\pi\nu t)$$

where μ_x is the transition dipole moment

$$(\mu_x)_{ge} = e \int_0^\infty Y_g^* x Y_e dx$$

Selection Rules

A transition will be allowed only if the transition dipole moment integral is non-zero. The general rules are:

Electronic: $\Delta l = \pm 1, \Delta m = 0$

Rotational: $\Delta J = \pm 1, \Delta M = 0$

Vibrational: $\Delta v = \pm 1$

For mathematical description see the workshop on selection rules.

Sources of Radiation

- Nerst filament = infrared
- Arc lamp (Xe) = UV-vis
- Tungsten-halogen = visible near-IR
- Lasers
 - Excimer
 - Ion
 - YAG
 - Ti:sapphire

Dispersion is essential

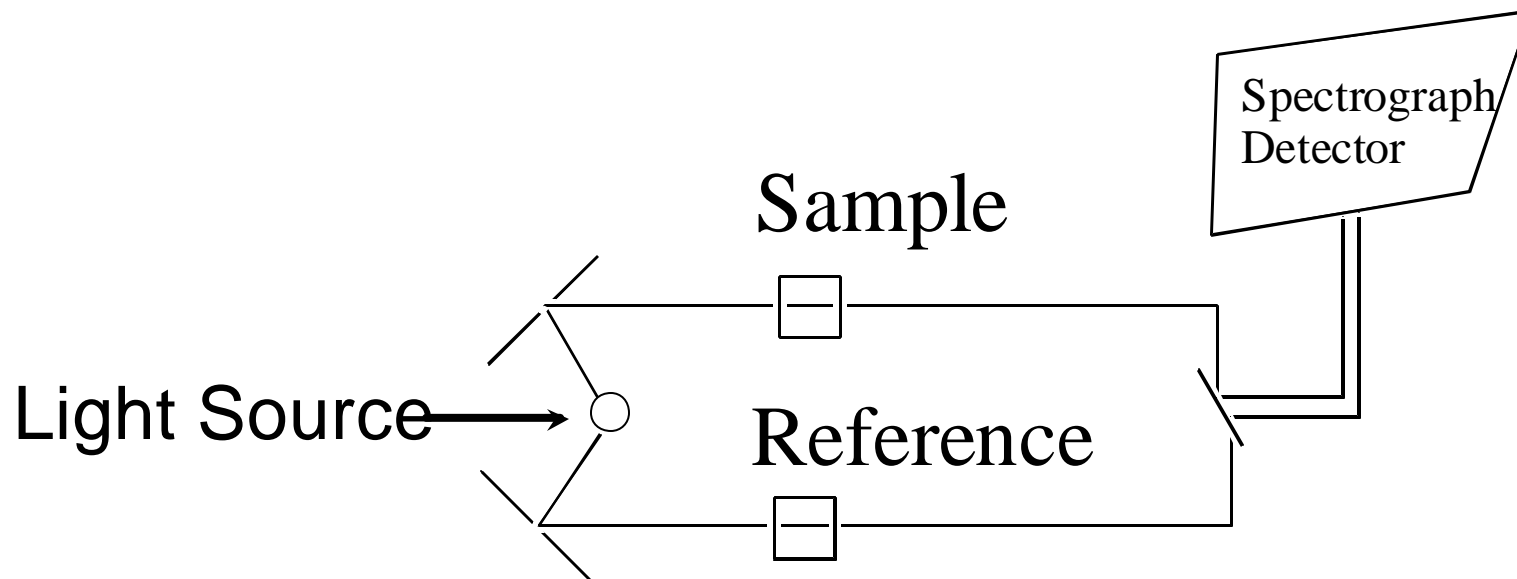
- A dispersing element separates different frequencies into different spatial directions.
- A prism separates different frequencies because of the optical beam using the variation of the index of refraction such that high-frequency radiation undergoes a greater deflection than low-frequency radiation.
- A diffraction grating consists of grooves cut ca. $1\ \mu\text{m}$ apart. Interference from reflected waves gives rise to specific angles of propagation.

Detectors

- Thermistor bolometer, far ir
- Mercury Cadmium Telluride (MCT), ir
- Germanium, near ir
- Silicon, visible
- Photomultiplier tube. Amplification by dynodes generates current for each photon hit.
- CCD detector. Array of detectors on a chip. UV coatings, efficiency, ease of use.

Absorption Spectrometer

Dispersing element is in the spectrograph



Comparison of sample and reference is essential

Intensities of Spectral Lines

- Intensity of absorption for a sample that has thickness d is given by

$$\log \frac{I}{I_0} = -\epsilon c d$$

- ϵ is the molar absorption coefficient.
- c is the concentration.
- d is the pathlength.
- I is the transmitted intensity, I_0 is the incident intensity.

Beer-Lambert Law

$$I = I_0 10^{-A}$$

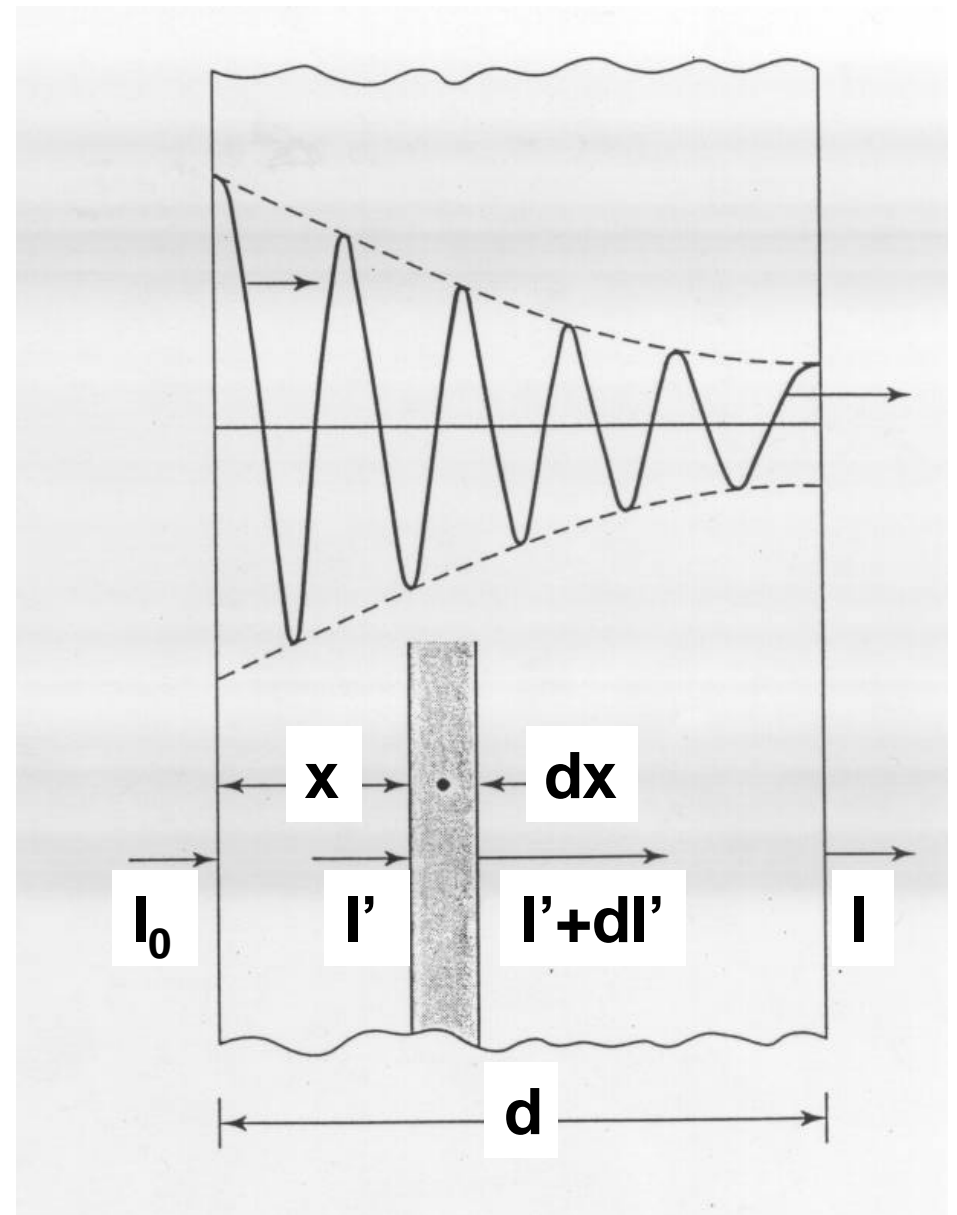
$$A = \varepsilon(\nu)cd$$

A is the absorbance.

d is the pathlength.

The exponential attenuation of the intensity is shown in the Figure.

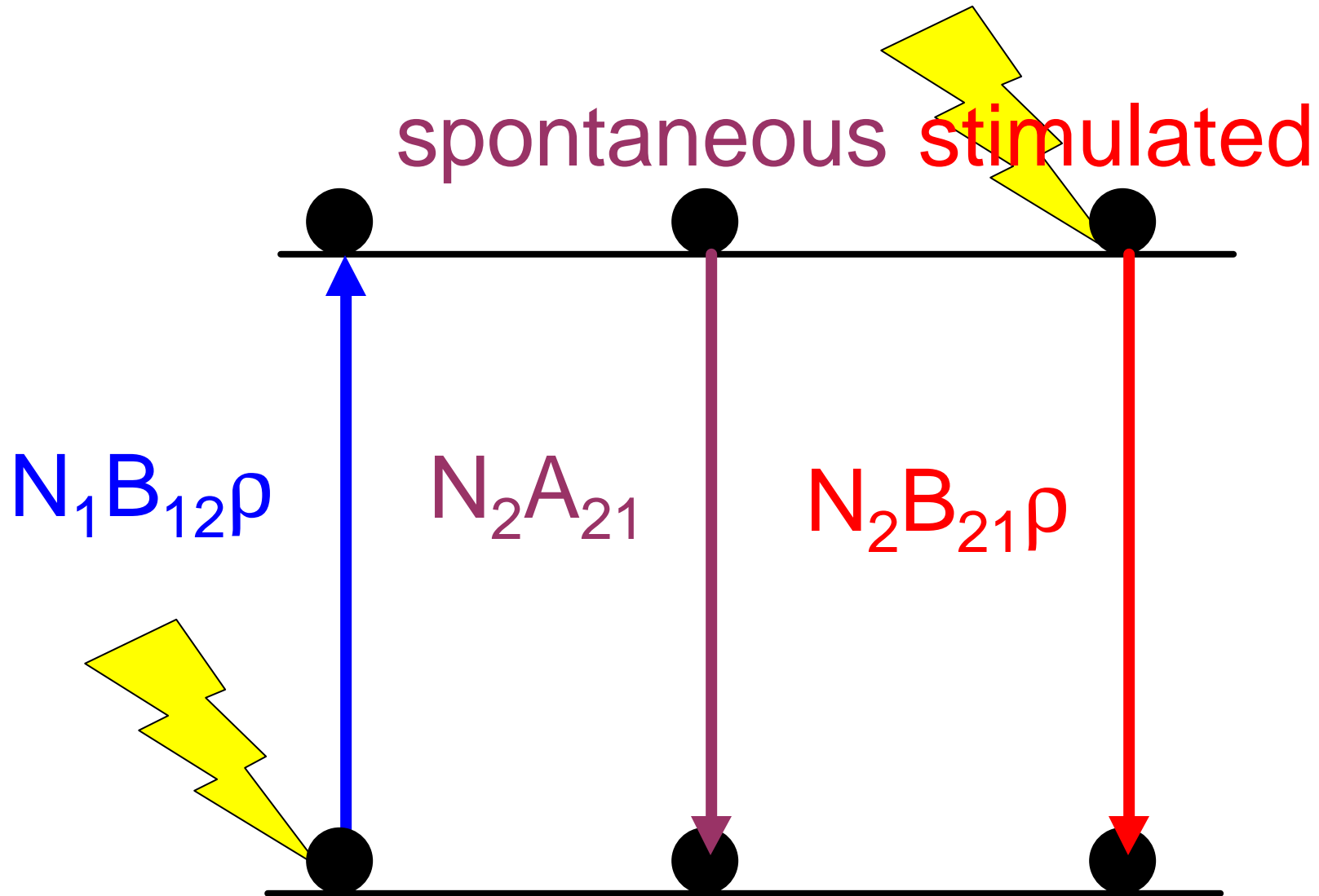
The absorption cross section for an individual molecule is σ .
 $\sigma = h\nu k_{12}$ where k_{12} is the transition rate constant.



Theory of Absorption and Emission

- Stimulated absorption - low to high driven by absorption of a photon
- Stimulated emission - high to low driven by emission of a photon
- Spontaneous emission - high to low emission independent of photon field
- Einstein coefficients:
 - B_{12} - stimulated absorption
 - B_{21} - stimulated emission
 - A_{21} - spontaneous emission

Spontaneous emission is fluorescence
Stimulated emission is used for lasers

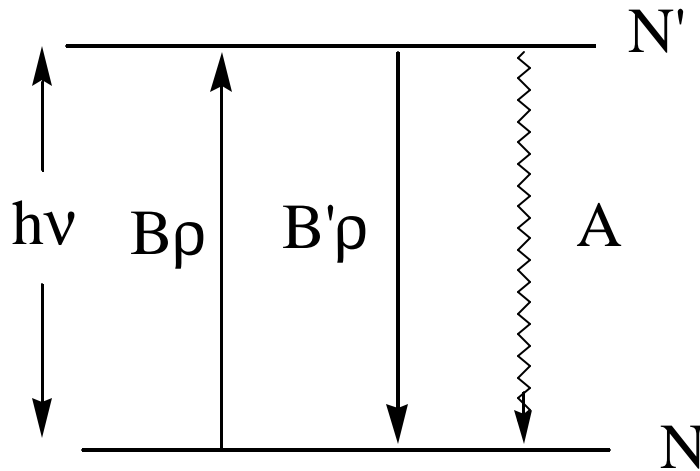


Einstein's derivation of absorption and emission coefficients

- Absorption $w_{12} = B_{12}\rho$, Emission $w_{21} = (A_{21} + B_{21}\rho)$ for individual molecules.
- The total rates of absorption and emission
 $W = N_1 w_{12}$ where N_1 is the number in the ground state
 $W' = N_2 w_{21}$ where N_2 is the number in the excited state
- Thermal equilibrium demands that
 $W = W'$ i.e. $N_1 B_{12}\rho = N_2 (A_{21} + B_{21}\rho)$
- The derivation consists of solving for ρ and noticing the similarity with Planck distribution.

Treatment of states in equilibrium

$$\rho = \frac{N_2 A_{21}}{N_1 B_{12} - N_2 B_{21}} = \left(\frac{A_{21}}{B_{12}} \right) \frac{1}{\left(\frac{N_1}{N_2} \right) - \left(\frac{B_{21}}{B_{12}} \right)}$$



$$\frac{N_2}{N_1} = e^{-h\nu/kT}$$

Comparison with Planck's blackbody distribution

The equation for the radiation density, r has the same form as the Planck distribution provided,

$$\frac{B_{12}}{B_{21}} = 1 \quad , \quad \frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3}$$

The Planck distribution is:

$$r = \frac{8\pi h\nu^3}{c^3} \left(\frac{1}{e^{h\nu/kT} - 1} \right)$$

Interpretation of Einstein Coefficients

The intrinsic coefficient for absorption B_{12} is related to $k_{12} = NB_{12}\rho$, where ρ is the energy density:

$$I = c \int \rho(\nu) d\nu$$

Einstein showed that the rate of absorption and stimulated emission are equal. The spontaneous emission rate has a definite relation to the stimulated emission rate:

$$B_{21} = B_{12}$$

$$A_{21}^{spontaneous} = \frac{8\pi h\nu^3}{c^3} B_{21}$$

The transition probability is proportional to the square of the transition moment

The absorption of radiation involves time-dependence because the field is time-varying $E_0 \sin(2\pi\nu t)$. If we solve for the transition probability we find that it is proportional to the square of transition moment.

$$B = \frac{1}{6\varepsilon_0 \hbar^2} (\mu_x)_{g,e}^2$$

Connection with experiment

Beer's law states that

$$I = I_0 10^{-\epsilon(\nu)cd}$$

$\epsilon(\nu)$ is the molar extinction coefficient.

c is the concentration.

d is the pathlength.

In differential form this is written:

$$- dl = 2.303\epsilon(\nu)cl dx$$

A comparable expression in terms of the individual transition rates is given by

$$- dl = Nh\nu k_{12} dx$$

Experimental determination of the transition moment by absorption spectroscopy

$$2.303\varepsilon(\nu)cl = Nh\nu k_{12} = \frac{Nh\nu l}{6c\varepsilon_0\hbar^2}(\mu)^2 FC L(\nu)$$

$$2.303C \int_{band} \frac{\varepsilon(\nu)}{\nu} d\nu = \frac{\pi N}{3c\varepsilon_0\hbar}(\mu)^2 \int_{band} FC L(\nu) d\nu$$

$$(\mu)^2 = \frac{6909c\varepsilon_0\hbar}{\pi N_A} \int_{band} \frac{\varepsilon(\nu)}{\nu} d\nu$$

The transition moment is related to the integrated extinction coefficient.