Physical Chemistry and Structural Chemistry

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Introduction

Physical Chemistry

- Physical Chemistry I - Equilibrium (phase equilibrium, chemical equilibrium)
- Physical Chemistry II - Change (reaction kinetics, transport, electrochemistry)
- Physical Chemistry III - Structure (molecular structure, spectroscopy, materials science)

- Introduction
- The basics of quantum mechanics
- The structure of the hydrogen atom
- Structure of many-electron atoms
- Optical spectroscopy
- Rotational spectroscopy
- Vibrational spectroscopy
- Electronic structure of molecules

Introduction

Curriculum

- Photoelectron spectroscopy
- Lasers and laser spectroscopy
- Fundamentals of nuclear structure
- Nuclear magnetic resonance
- Mass spectrometry
- X-ray diffraction

Introduction to spectroscopy

The structure of atoms, molecules, and other particles is described by quantum mechanics.

The foundation of quantum mechanics was laid in the 1920´s.

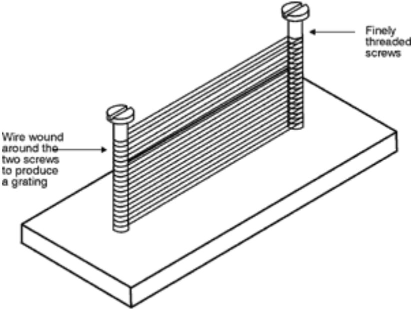
Preliminaries: some experiments which contradict the principles of classical physics

Introduction to spectroscopy

Joseph Fraunhofer's experiment, 1815

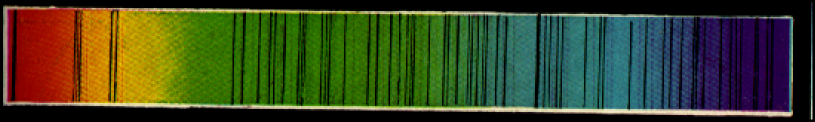
The sunlight was dispersed by a grating.

Dark lines were observed in the continuous spectrum.



Introduction to spectroscopy

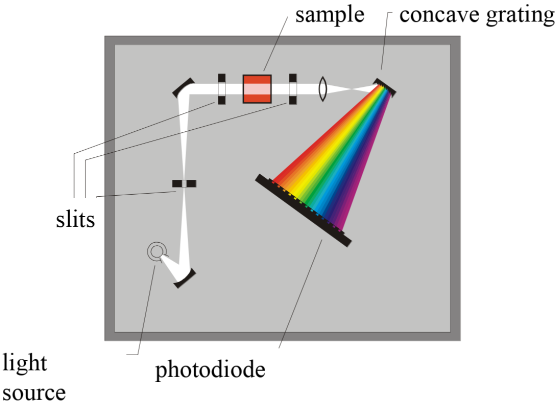
The spectrum of the sun



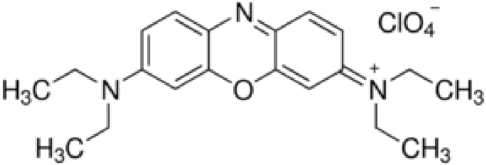
Explanation:

- the sun emits continuous radiation
- the particles of the gas surrounding the Earth and the Sun absorb only photons of particular wavelength/frequency
- particle A absorbs light of ν_{A1}, ν_{A2}, ... frequency particle B absorbs light of ν_{B1}, ν_{B2}, ... frequency, etc.
- hence the energy of particle A can be changed by quanta of $\Delta E_A = h\nu_{A1}$, $h\nu_{A2}$, ... and the energy of particle B can be changed by $\Delta E_B = h\nu_{B1}$, $h\nu_{B2}$, ...

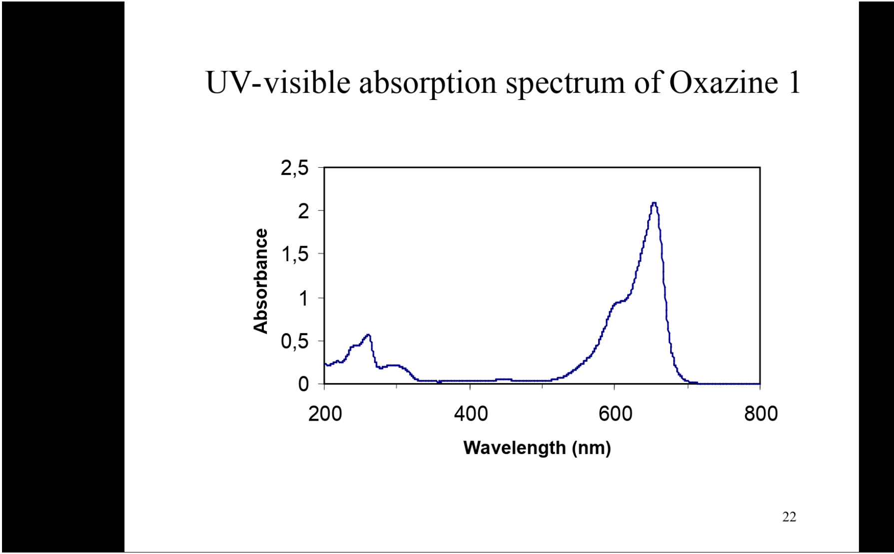
Single-beam UV-visible absorption spectrophotometer



Oxazine 1



Oxazine 1



UV-visible absorption spectrum of Oxazine 1

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Some physical properties of submicroscopic particles are quantized, that is, the corresponding physical quantities have only discrete values.

This realization is reflected by the term **quantum** mechanics

Schrödinger equation

In the non-relativistic case the submicroscopic systems can be described by the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t)=\left[-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r},t)\right]\Psi(\mathbf{r},t)$$

Let's start from the beginning. What does i stand for?

Basic concepts from mathematics

complex numbers [a]

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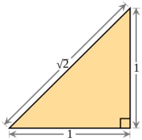
[a] P. Atkins, J. Paula, R. Friedman, Chapter 2

- Natural numbers
- negative numbers (Diophantus [200 - c.284 CE]: *The solution of the* $4 = 4x + 20$ *equation is absurd.*)
- rational numbers (Pythagorean school: *all phenomena in the universe can be reduced to whole numbers and their ratios*)

  but what is $\sqrt{2}$?



- irrational numbers (Hippasus, 5th century BC) ...

Basic concepts from mathematics

complex numbers

Real numbers form a closed set for the

$a + b, a - b, a * b, a/b$ $(a, b \in \mathcal{R})$ operations.

But what is $\sqrt{-1}$? (Cardano, 1545) real line vs. complex plane

1D vs. 2D

(x) (x, y)

$x, y \in \mathcal{R}$ (ordered pairs) $(x, y) \neq (y, x)$

Basic concepts from mathematics

complex numbers

$$\text{addition, } (a, b) + (c, d) \triangleq (a + c, b + d)$$

$$\text{subtraction, } (a, b) - (c, d) \triangleq (a - c, b - d)$$

$$\text{multiplication, } (a, b) \cdot (c, d) \triangleq (ac - bd, ad + bc)$$

real numbers have the form of $(a, 0)$ they lie on the real axis:

$$(a, 0) + (c, 0) \triangleq (a + c, 0)$$

$$(a, 0) - (c, 0) \triangleq (a - c, 0)$$

$$(a, 0) \cdot (c, 0) \triangleq (ac, 0)$$

Basic concepts from mathematics

complex numbers

imaginary numbers have the form of $(0, b)$ they lie on the imaginary axis:

$$z = (0, b)$$

$$z \cdot z = z^2$$

$$(0, b) \cdot (0, b) \triangleq (-b^2, 0)$$

$$z^2 = -b^2 \qquad z \in \mathcal{C} \quad , b \in \mathcal{R}$$

$$(0, 1) \cdot (0, 1) \triangleq (-1, 0)$$

Basic concepts from mathematics

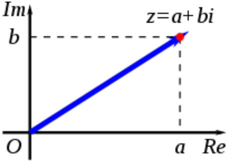
complex numbers

$z = (0, 1)$ is special, it is denoted by i, and called the imaginary unit ($i^2 = -1$) with its help $z = (a, b) = a + bi$

complex conjugate of $z = a + bi$ is denoted by a star superscript

$z^* = a - bi$

$z \cdot z^* = (a + bi) \cdot (a - bi) = a^2 + b^2 = |z|^2$



Basic concepts from mathematics

complex numbers

division by a complex number:

$$
\begin{aligned}
\frac{a+bi}{c+di} &= \frac{a+bi}{c+di} \cdot \frac{c-di}{c-di} \\
&= \frac{(a+bi)(c-di)}{c^2+d^2} \\
&= \frac{(ac+bd)}{c^2+d^2} + \frac{(bc-ad)}{c^2+d^2} i
\end{aligned}
$$

Basic concepts from mathematics

complex numbers

polar form of complex numbers

$$z = a + bi = r \cdot (\cos\varphi + i\sin\varphi)$$

$$r = \sqrt{a^2 + b^2} \quad \tan\varphi = \frac{b}{a}$$

multiplication and division in polar form:

$$z_1 = r_1(\cos\varphi_1 + i\sin\varphi_1) \qquad z_2 = r_2(\cos\varphi_2 + i\sin\varphi_2)$$

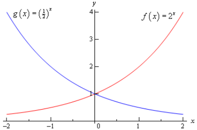
$$z_1 \cdot z_2 = r_1 \cdot r_2(\cos(\varphi_1 + \varphi_2) + i\sin(\varphi_1 + \varphi_2))$$

$$\frac{z_1}{z_2} = \frac{r_1}{r_2}(\cos(\varphi_1 - \varphi_2) + i\sin(\varphi_1 - \varphi_2))$$

Basic concepts from mathematics

Exponential functions

- $2^n = 2 \times 2 \times 2 \times \cdots \times 2$
- $2^{n/m} = \sqrt[m]{2^n}$
- $2^{-n/m} = \dfrac{1}{2^{n/m}}$



- $e = \lim_{n \to \infty} (1 + \frac{1}{n})^n = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \ldots$, where

  $e = 2.71828182845904523536028747135266249775724709369995$

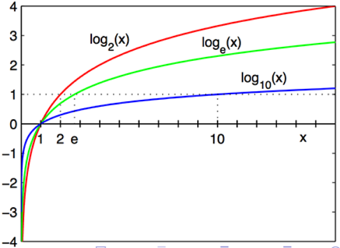
- Expression 'exponential function' generally refers to e^x

  $e^x = \lim_{n \to \infty} (1 + \frac{x}{n})^n = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots$

Basic concepts from mathematics

Logarithm

- Inverse of a function: $g(x) = f^{-1}(x)$ if $g(f(x)) = x$.
- The logarithm is the inverse operation to exponentiation, e.g., $2^{\log_2 x} = x$.
- $\log_2 8 =$ *How many 2s do we multiply to get 8?*
- Plots of logarithm functions:



Basic concepts from mathematics

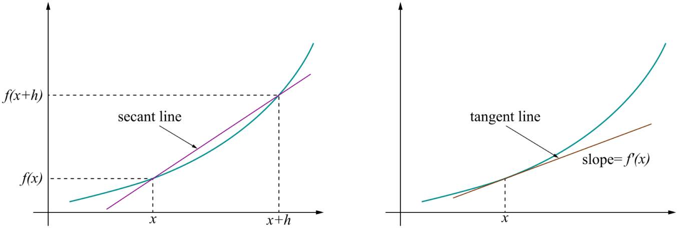
Sigma and Pi notation

- $\sum$ compactly represents summation of many similar terms: $\sum_i a_i$
- Π is frequently used for product of terms: $\Pi_i a_i$
- Examples
  - $$\sum_{i=1}^{n} \ln(a_i) = \ln(a_1) + \ln(a_2) + \cdots + \ln(a_n)$$
    $$= \ln(a_1 a_2 \dots a_n) = \ln(\prod_{i=1}^{n} a_i)$$
  - $$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$$

Basic concepts from mathematics

Derivation of single-variable functions

- The derivative of a function of a real variable measures the sensitivity to change of the function value (output value) with respect to a change in its argument (input value).
- $f'(x) = f^{(1)}(x) = \dfrac{df(x)}{dx} = \lim_{h \to 0} \dfrac{f(x+h) - f(x)}{h}$



Basic concepts from mathematics

Derivation of single-variable functions

- Derivatives of simple functions

$f(x)$	$f'(x)$	$f(x)$	$f'(x)$
$const$	0	$\ln x$	$1/x$
x^2	$2x$	$\sin x$	$\cos x$
$\sqrt{x}$	$0.5x^{-0.5}$	$\cos x$	$-\sin x$
x^n	nx^{n-1}	e^x	e^x

- Derivation of combined functions

linearity	$(af(x)+bg(x))' = af(x)' + bg(x)'$
product rule	$(f(x)g(x))' = f(x)'g(x) + f(x)g(x)'$
quotient rule	$\left(\frac{f(x)}{g(x)}\right)' = \frac{f(x)'g(x)-f(x)g(x)'}{g(x)^2}$
chain rule	$f\,(g(x))' = \frac{df(g(x))}{dg(x)}\frac{dg(x)}{dx}$

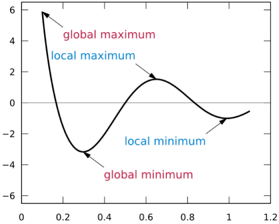
Basic concepts from mathematics

Second derivatives

- At local minima and maxima of a function the slope is zero:

  $f'(x_0) = 0$

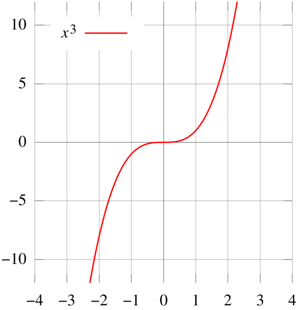
- If the second derivative, $f''(x_0) > 0$, is positive at x_0 it is a minima, if $f''(x_0) < 0$ it is a maxima. If $f''(x_0) = 0$ the higher derivatives should be investigated (e.g. $f(x) = x^4$ at $x = 0$).



Basic concepts from mathematics

Second derivatives

- In general, if $f''(x) > 0$ the tangent 'below' the function, if $f''(x) < 0$ it is 'above' the curve. If $f''(x_0) = 0$ (and $f'''(x_0) \neq 0$), x_0 can be an inflection point (e.g. $f(x) = x^3$ at $x = 0$).



Basic concepts from mathematics

Taylor-series

- Polynomial approximation of a function:

  $f(x) = f(x_0) + \frac{1}{1!} f^{(1)}(x_0)(x - x_0) + \frac{1}{2!} f^{(2)}(x_0)(x - x_0)^2 +$
  $\frac{1}{3!} f^{(3)}(x_0)(x - x_0)^3 + \frac{1}{4!} f^{(4)}(x_0)(x - x_0)^4 + \ldots$, where $f^{(n)}(x) = \frac{d^n f}{dx^n}$.

- Linear approximation: $\Delta f \approx \frac{df}{dx}|_{x=x_0} \Delta x$

  $(\Delta x = (x - x_0)$ and $\Delta f = f(x) - f(x_0))$.

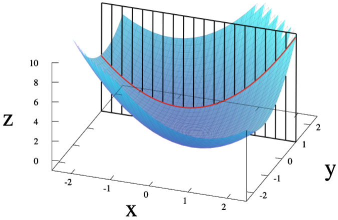
- If Δx is infinitesimal, then Δx^2 is considered to be zero, and $df = \frac{df}{dx} dx$. It is the differential of $f(x)$.

- Taylor-series: $f(x) = \displaystyle\sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(x_0)(x - x_0)^n$

Basic concepts from mathematics

Partial derivative

- $z = f = f(x, y)$ defines a surface.
- $\frac{\partial f(x,y)}{\partial x}$, $\frac{\partial f(x,y)}{\partial y}$: the task is to find the slope of a two-variable (or multi-variable) function in the directions of x and y.



- Definition: $$\left.\frac{\partial f}{\partial x}\right|_y = \lim_{h\to 0} \frac{f(x+h,y) - f(x,y)}{h},$$ $$\left.\frac{\partial f}{\partial y}\right|_x = \lim_{h\to 0} \frac{f(x,y+h) - f(x,y)}{h}$$
- For continuous, well-behaving functions: $\frac{\partial}{\partial y}\frac{\partial f}{\partial x} = \frac{\partial}{\partial x}\frac{\partial f}{\partial y}$ (Young-theorem)

Basic concepts from mathematics

Exact differential

- Linear approximation of a function of two variables:

$$\Delta f \approx \left.\frac{\partial f}{\partial x}\right|_{x,y=x_0,y_0} \Delta x + \left.\frac{\partial f}{\partial y}\right|_{x,y=x_0,y_0} \Delta y.$$

- The higher order terms contain contributions proportional to Δx^2, Δy^2, $\Delta x \Delta y$, $\Delta x \Delta y^2$ *etc.*
- If Δx and Δy are infinitesimal, then $df = \left.\frac{\partial f}{\partial x}\right|_y dx + \left.\frac{\partial f}{\partial y}\right|_x dy$.

  It is called the exact differential of $f(x, y)$.

Basic concepts from mathematics

Indefinite integral

- Reverse of differentiation: if $\frac{dF(x)}{dx} = f(x)$ then $\int f(x)dx = F(x) + C$, where $F(x)$ is the indefinite integral of $f(x)$ and C is an arbitrary constant.
- Indefinite integral of elementary functions:

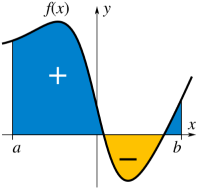
$f(x)$	$\int f(x)$	$f(x)$	$\int f(x)$
x^n	$\frac{x^{n+\mathbf{1}}}{n+1}$	$\frac{1}{x}$	$ln\|x\|$
x	$x^2/2$	$\cos x$	$\sin x$
e^{ax}	$\frac{1}{a}e^{ax}$	$\sin x$	$-\cos x$
$\ln(x)$	$x(ln(x)-1)$	c	cx

- Notation: $\int dx = \int 1dx$

Basic concepts from mathematics

Definite integral

- The signed area below (plus sign) or above (minus sign) the graph of function f in the interval bounded by a and b: $\int_a^b f(x)dx$.
- Newton-Leibnitz formula: $\int_a^b f(x)dx = [F(x)]_a^b = F(b) - F(a)$, where $F(x)$ is the indefinite integral of $f(x)$.



- To understand the N-L formula consider a short interval with length h: $hf(a) \approx \int_a^{a+h} f(x)dx = F(a+h) - F(a)$. If h goes to zero $f(a) = \frac{dF}{dx}|_{x=a}$.

Basic concepts from mathematics

Taylor-series

if $f(x)$ is infinitely differentiable at a real or complex number a then

$$
\begin{aligned}
f(x) &= f(a) + f'(a)(x-a) + \frac{1}{2}f''(a)(x-a)^2 + \frac{1}{3\cdot 2}f'''(a)(x-a)^3 + \ldots \\
&= \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!}(x-a)^n
\end{aligned}
$$

when $a = 0$ it is called a Mclaurin series

Basic concepts from mathematics

Taylor-series, $a = 0$

$$f(x) = \exp(x) = e^x$$

$$\begin{aligned} e^x &= e^0 + (e^0)'(x-0) + \frac{1}{2}(e^0)''(x-0)^2 + \frac{1}{3\cdot 2}(e^0)'''(x-0)^3 + \dots \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} x^n \end{aligned}$$

Basic concepts from mathematics

Taylor-series, $a = 0$

$$f(x) = \sin(x)$$

$$\begin{aligned}\sin x &= 0 + x + 0 - \frac{1}{3!}x^3 + 0 + \frac{1}{5!}x^5 + 0 - \frac{1}{7!}x^7 + \dots \\ &= \sum_{n=0}^{\infty} \frac{-1^n}{(2n+1)!}x^{2n+1}\end{aligned}$$

Basic concepts from mathematics

Taylor-series, $a = 0$

$f(x) = \cos(x)$

$$\begin{aligned}\cos x &= 1 + 0 - \frac{1}{2!}x^2 + 0 + \frac{1}{4!}x^4 + 0 - \frac{1}{6!}x^6 + \dots \\ &= \sum_{n=0}^{\infty} \frac{-1^n}{(2n)!} x^{2n}\end{aligned}$$

Basic concepts from mathematics

Euler's formula

$$i^0 = 1 \qquad i^1 = i$$

$$i^2 = -1 \qquad i^3 = -i$$

recall that $e^z = 1 + z + \frac{1}{2}z^2 + \frac{1}{3!}z^3 + \dots$

if $z = ix$

$$e^{ix} = 1 + ix + \frac{1}{2}i^2x^2 + \frac{1}{3!}i^3x^3 + \frac{1}{4!}i^4x^4 + \frac{1}{5!}i^5x^5 + \dots$$

Basic concepts from mathematics

Euler's formula

$$
\begin{aligned}
e^{ix} &= 1 + ix + \frac{1}{2}i^2x^2 + \frac{1}{3!}i^3x^3 + \frac{1}{4!}i^4x^4 + \frac{1}{5!}i^5x^5 + \dots \\
&= 1 + ix - \frac{1}{2}x^2 - i\frac{1}{3!}x^3 + \frac{1}{4!}x^4 + i\frac{1}{5!}x^5 + \dots \\
&= 1 - \frac{1}{2}x^2 + \frac{1}{4!}x^4 + ix - i\frac{1}{3!}x^3 + i\frac{1}{5!}x^5 + \dots \\
&= (1 - \frac{1}{2}x^2 + \frac{1}{4!}x^4 - \dots) + i(x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 - \dots) \\
&= \cos x + i \sin x
\end{aligned}
$$

Basic concepts from mathematics

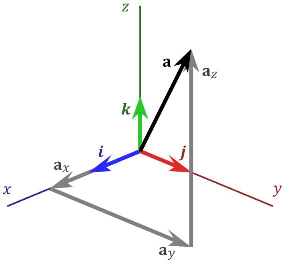
complex numbers

exponential form of complex numbers

$$\begin{aligned} z &= a + bi = r \cdot (\cos\varphi + i\sin\varphi) \quad \text{polar form} \\ e^{i\varphi} &= \cos\varphi + i\sin\varphi \\ z &= r \cdot e^{i\varphi} \quad \text{exponential form} \end{aligned}$$

Basic concepts from mathematics

vectors, Euclidean space, complex vector space



- $\mathbf{a} = a_x\mathbf{i} + a_y\mathbf{j} + a_z\mathbf{k}$
- $\mathbf{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$
- sum of two vectors (parallelogram law):

  $$\mathbf{a} + \mathbf{b} = (a_x + b_x)\mathbf{i} + (a_y + b_y)\mathbf{j} + (a_z + b_z)\mathbf{k}$$
- scalar (dot) product of two vectors:

  $$\mathbf{ab} = ab \cdot cos(\phi) = \sum_{i=x,y,z} a_i b_i$$
- dot product of two complex n dimensional vectors:

  $$\mathbf{ab} = \sum^{n} a_i^* b_i$$

Basic concepts from mathematics

vectors

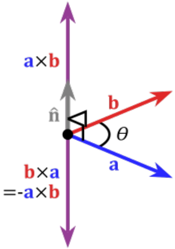
- bracket notation: $|\mathbf{b}\rangle = \begin{pmatrix} b_1 \\ b_2 \\ \dots \\ b_n \end{pmatrix}$

$$\langle\mathbf{a}| = \begin{pmatrix} a_1^* & a_2^* & \dots & a_n^* \end{pmatrix}$$

$$\langle\mathbf{a}|\mathbf{b}\rangle = \begin{pmatrix} a_1^* & a_2^* & \dots & a_n^* \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix} = \sum_{i=1}^{n} a_i^* b_i$$

Basic concepts from mathematics

vector (cross) product



$$(\mathbf{a} \times \mathbf{b})_x = a_y b_z - a_z b_y$$

$$(\mathbf{a} \times \mathbf{b})_y = a_z b_x - a_x b_z$$

$$(\mathbf{a} \times \mathbf{b})_z = a_x b_y - a_y b_x$$

$$||\mathbf{a} \times \mathbf{b}|| = ab \cdot sin\Theta$$

$\mathbf{a} \times \mathbf{b}$ is orthogonal to vectors **a** and **b** (right hand rule)

Basic concepts from classical mechanics

Newton's laws, conservation of linear momentum

- Every object in a state of uniform motion will remain in that state of motion unless an external force acts on it.
- $\mathbf{F} = m\mathbf{a}$
- For every action there is an equal and opposite reaction.
- If there is no force, $\mathbf{F} = 0$, then $m\mathbf{a} = \dot{\mathbf{p}} = 0$, i.e., $\mathbf{p}$ is constant.

Basic concepts from classical mechanics

Newton's laws, equation of motion

Equations of motion are obtained from Newton's second law:

$$\mathbf{F}(\mathbf{r}, \dot{\mathbf{r}}, t) = m\mathbf{a} = \dot{\mathbf{p}} = m\ddot{\mathbf{r}}$$

with the initial conditions:

$\mathbf{r}(t = t_A) = \mathbf{r}_A, \mathbf{v}(t = t_A) = \dot{\mathbf{r}}(t = t_A) = \mathbf{v}_A$

- Coulomb force: $\mathbf{F} = K\frac{q_1 q_2}{r_{12}^3}\mathbf{r}_{12}$
- spring force: $\mathbf{F} = -k\mathbf{r}$

Basic concepts from classical mechanics

Newton's laws, kinetic and potential energies

- Work: $\delta W = \mathbf{F} d\mathbf{r}$

  $$W = \int \delta W = \int_{\mathbf{r}_A}^{\mathbf{r}_B} \mathbf{F} d\mathbf{r} \text{ (line integral of a vector field)}$$

  $$= \int_{t_A}^{t_B} \mathbf{F}\dot{\mathbf{r}} dt = \int_{t_A}^{t_B} m\ddot{\mathbf{r}}\dot{\mathbf{r}} dt = \frac{1}{2}\int_{t_A}^{t_B} m\frac{d\left(\dot{\mathbf{r}}^2\right)}{dt} dt = \frac{1}{2} m\mathbf{v}_B^2 - \frac{1}{2} m\mathbf{v}_A^2$$

- Potential of a conservative force:

  $$\mathbf{F} = -grad(V(\mathbf{r})) = -\nabla V(\mathbf{r}) \quad \text{nabla: } \nabla\Phi = \begin{pmatrix} \frac{\partial\Phi}{\partial x} \\ \frac{\partial\Phi}{\partial y} \\ \frac{\partial\Phi}{\partial z} \end{pmatrix}$$

- Example for non-conservative force: $F_{drag} \sim v^2$

Basic concepts from classical mechanics

Kinetic and potential energies

- Work of a conservative force:

$$W = \int_{\mathbf{r}_A}^{\mathbf{r}_B} \mathbf{F} d\mathbf{r} = -\int_{\mathbf{r}_A}^{\mathbf{r}_B} grad(V) d\mathbf{r} =$$

$$-\int \frac{\partial V}{\partial x} dx + \frac{\partial V}{\partial y} dy + \frac{\partial V}{\partial z} dz = -\int_{\mathbf{r}_A}^{\mathbf{r}_B} dV = V(\mathbf{r}_A) - V(\mathbf{r}_B)$$

- Conservation of energy:

$$E = \frac{1}{2} m\mathbf{v}_B^2 + V(\mathbf{r}_B) = \frac{1}{2} m\mathbf{v}_A^2 + V(\mathbf{r}_A)$$

Basic concepts from classical mechanics

Energy, the ability to do work

- the kinetic energy ($E_{\mathrm{kin}} \mid K$) is due to motion; $E_{\mathrm{kin}} = f(\mathbf{p})$

  a moving object can do work
- the potential energy ($E_{\mathrm{pot}} \mid V$) is due to position; $E_{\mathrm{pot}} = g(\mathbf{r})$

  stored energy of an object that can do work
- $E_{\mathrm{tot}} = E_{\mathrm{kin}} + E_{\mathrm{pot}}$ or $H = K + V$
- Hamilton function: E=H=H($\mathbf{p}$, $\mathbf{q}$), where $\mathbf{p}, \mathbf{q}$ are the

  canonical coordinates.

Basic concepts from classical mechanics

Kinetic energy

recall the scalar product of vectors: $\mathbf{v} \cdot \mathbf{v} = |\mathbf{v}|^2 = v^2$

$$E_{\text{kin}} = \frac{1}{2} m v^2$$

$$\mathbf{p} = m\mathbf{v}$$

$$p^2 = m^2 v^2$$

$$E_{\text{kin}} = \frac{p^2}{2m}$$

Basic concepts from classical mechanics

Newton's laws, simple classical systems, $E_{\rm pot} = 0$

$$E_{\rm tot} = E_{\rm kin} = \frac{p^2}{2m}$$

$$\sqrt{2mE_{\rm kin}} = p = m\frac{dx}{dt}$$

$$\frac{dx}{dt} = \sqrt{\frac{2E_{\rm kin}}{m}}$$

$$\int_{x(0)}^{x(t)} dx = \sqrt{\frac{2E_{\rm kin}}{m}} \int_0^t dt$$

$$x(t) = x(0) + \sqrt{\frac{2E_{\rm kin}}{m}}t$$

$$p(t) = mv(t) = m\frac{dx}{dt} = m\sqrt{\frac{2E_{\rm kin}}{m}}$$

$$p(t) = \sqrt{2mE_{\rm kin}}$$

Basic concepts from classical mechanics

Newton's laws, simple classical systems, harmonic oscillator

Restoring force is proportional to the displacement from the equilibrium position.

The spring stores the energy as $V(x) = \frac{1}{2}kx^2 \Rightarrow F_x = -\frac{dV}{dx}$

$$\mathbf{F} = -k\mathbf{x}$$

$$m\frac{d^2x}{dt^2} = -kx$$

$$m\lambda^2 e^{\lambda t} = -ke^{\lambda t}$$

$$(m\lambda^2 + k)e^{\lambda t} = 0$$

$$\lambda^2 = -\frac{k}{m}$$

$$\lambda = \pm i\sqrt{\frac{k}{m}} = \pm i\omega$$

$$x(t) = c_1 e^{i\omega t} + c_2 e^{-i\omega t} = A\sin(\omega t + \varphi)$$

$$p(t) = m\frac{dx}{dt} = \omega A m\cos(\omega t + \varphi)$$

$$x(t) = e^{\lambda t} \Rightarrow \frac{dx}{dt} = \lambda e^{\lambda t} \Rightarrow \frac{d^2x}{dt^2} = \lambda^2 e^{\lambda t}$$

Basic concepts from classical mechanics

Angular momentum

- angular momentum: $\mathbf{L} = \mathbf{r} \times \mathbf{p}$
- time derivative of angular momentum:

  $\dot{\mathbf{L}} = \dot{\mathbf{r}} \times \mathbf{p} + \mathbf{r} \times \dot{\mathbf{p}} = \mathbf{r} \times \mathbf{F} = \mathbf{M}$
- conservation of angular momentum: if the moment of force (torque), $\mathbf{M}$ is zero then $\dot{\mathbf{L}} = 0$ and $\mathbf{L}$ is a constant vector.

Basic concepts from classical mechanics

Uniform circular motion, centripetal force, F_{cp}, and angular momentum, ℓ

$$\frac{\Delta s}{\Delta\varphi} = \frac{arc}{angle} = \frac{2\pi r}{2\pi} \Rightarrow \Delta s = r\cdot\Delta\varphi$$

$$v = \frac{ds}{dt} = \lim_{\Delta t\to 0}\frac{\Delta s}{\Delta t} = r\cdot\lim_{\Delta t\to 0}\frac{\Delta\varphi}{\Delta t}$$

$$= r\cdot\omega$$

$$\Rightarrow \Delta v = v\cdot\Delta\varphi$$

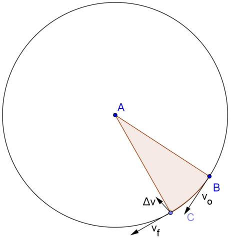
$$a = \frac{dv}{dt} = \lim_{\Delta t\to 0}\frac{\Delta v}{\Delta t} = v\cdot\lim_{\Delta t\to 0}\frac{\Delta\varphi}{\Delta t}$$

$$= v\cdot\omega = r\cdot\omega^2$$

$$F_{\mathrm{cp}} = m\cdot a = m\cdot r\omega^2 = m\cdot\frac{v^2}{r}$$

$$L = r\cdot p = r\cdot mv = mr^2\omega = I\omega$$

where I is the moment of inertia



- $E_{kin} = \frac{1}{2}mv^2 = \frac{1}{2}m(r\omega)^2 = \frac{1}{2mr^2}(mr^2\omega)^2 = \frac{L^2}{2mr^2} = \frac{L^2}{2I}$

Basic concepts from classical mechanics

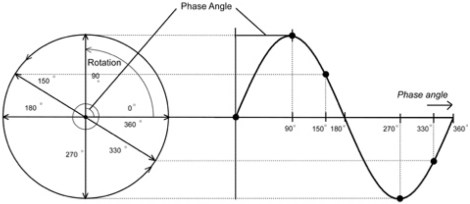
Circular motion, special case of rotational motion, **r** is fixed

$$x(t) = A\sin(\frac{2\pi}{T}t) = A\sin(\omega t)$$

$$v = r\omega$$

$$a = v\omega = r\omega^2$$

$$F = \frac{mv^2}{r}$$



Linear and angular motions

correspondences

linear momentum	$\mathbf{p}$	angular momentum	$\mathbf{L} = \mathbf{r} \times \mathbf{p} = I\omega$
velocity	$\mathbf{v}$	angular velocity	$\omega = \dfrac{\mathbf{r} \times \mathbf{v}}{r^2}$
mass	m	moment of inertia	$I = mr^2$
Kinetic energy	$\dfrac{p^2}{2m}$		$\dfrac{L^2}{2I}$

Basic concepts from classical mechanics

Conserved properties

conservation laws[a]

some measurable physical properties do not change

- mass (m) [b] and energy (E)
- electric charge (q)
- linear momentum (**p**)
- angular momentum (**L**)

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[a] There is always a symmetry behind the conservation laws: conservation of energy is connected to the time-invariance of physical systems.

[b] conservation of mass is not exact: nuclear fusions

Classical wave equation

model[a]

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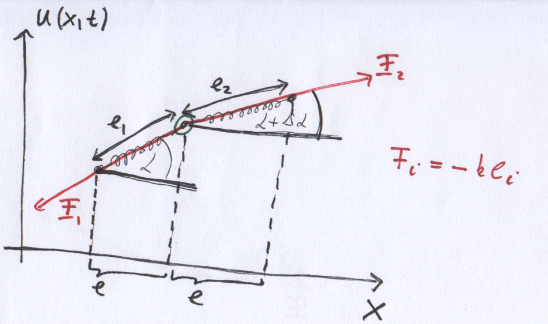
[a] see also in Wikipedia, Wave equation, Hooke's law

- elastic, homogeneous string stretched to a length of L
- endpoints are fixed
- ρ is the mass of the string per unit length
- $u(x, t)$ represents the displacement of the string at a point x at a time t from its equilibrium position
- only vertical movements are allowed (transverse wave, longitudinal waves are not considered...)

Classical wave equation

derivation



$$F_y = F_{2y} - F_{1y} = \underbrace{k\ell_2}_{T_2} sin(\alpha + \Delta\alpha) - \underbrace{k\ell_1}_{T_1} sin(\alpha)$$

no longitudinal contribution:

$$F_x = F_{2x} - F_{1x} = 0, T_2 cos(\alpha + \Delta\alpha) = T_1 cos(\alpha) = k\ell = T$$

at the end $\Delta\alpha, \ell \to 0$

Classical wave equation

derivation

$$
\begin{aligned}
T_1 \cdot \cos\alpha &= T_2 \cdot \cos(\alpha + \Delta\alpha) := T \\
T_2 \cdot \sin(\alpha + \Delta\alpha) - T_1 \cdot \sin\alpha &= m \cdot a = \rho\Delta x \cdot \frac{\partial^2 u(x,t)}{\partial t^2} \\
\frac{T_2 \cdot \sin(\alpha + \Delta\alpha)}{T_2 \cdot \cos(\alpha + \Delta\alpha)} - \frac{T_1 \cdot \sin\alpha}{T_1 \cdot \cos\alpha} &= \frac{1}{T}\rho \cdot \Delta x \cdot \frac{\partial^2 u(x,t)}{\partial t^2} \\
\tan(\alpha + \Delta\alpha) - \tan\alpha &= \frac{1}{T}\rho \cdot \Delta x \cdot \frac{\partial^2 u(x,t)}{\partial t^2} \\
\frac{\partial u_{x+\Delta x}}{\partial x} - \frac{\partial u_x}{\partial x} &= \frac{1}{T}\rho \cdot \Delta x \cdot \frac{\partial^2 u(x,t)}{\partial t^2}
\end{aligned}
$$

Classical wave equation

derivation

$$\begin{aligned}
\frac{\partial u_{x+\Delta x}}{\partial x} - \frac{\partial u_x}{\partial x} &= \frac{1}{T}\rho \cdot \Delta x \cdot \frac{\partial^2 u(x,t)}{\partial t^2} \\
\frac{\frac{\partial u_{x+\Delta x}}{\partial x} - \frac{\partial u_x}{\partial x}}{\Delta x} &= \frac{1}{T}\rho \cdot \frac{\partial^2 u(x,t)}{\partial t^2} \\
\frac{\partial^2 u(x,t)}{\partial x^2} &= \frac{1}{T/\rho} \cdot \frac{\partial^2 u(x,t)}{\partial t^2} \\
\frac{\partial^2 u(x,t)}{\partial x^2} &= \frac{1}{c^2} \cdot \frac{\partial^2 u(x,t)}{\partial t^2}
\end{aligned}$$

Classical wave equation

Solutions of the wave equation

$u(x,t) = C \cdot e^{i(kx-\omega t+\phi)}$

$\frac{\partial^2 u(x,t)}{\partial x^2} = -k^2 u(x,t),\ \frac{1}{c^2}\frac{\partial^2 u(x,t)}{\partial t^2} = -\frac{\omega^2}{c^2} u(x,t)$

$\Longrightarrow k = \frac{\omega}{c}$

real solutions: $u(x,t) = A \cdot sin(kx - \omega t + \phi)$ and

$u(x,t) = B \cdot cos(kx - \omega t + \phi)$

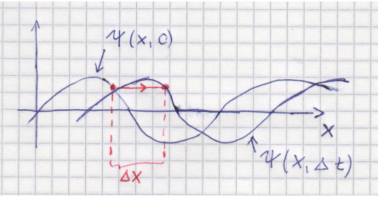
periodic solutions in time and space: $x \Longrightarrow x + \frac{2\pi}{k}$ and

$t \Longrightarrow t + \frac{2\pi}{\omega}$ transformations do not change these functions,

$k = \frac{2\pi}{\lambda}$ (wavenumber), $\omega = \frac{2\pi}{T}$ (angular velocity)

Classical wave equation

traveling, interference, and standing waves



$$\Psi(x,t) = A\cdot\sin(kx-\omega t) \Longrightarrow$$

$$\Psi(x+\Delta x, t+\Delta t) = A\cdot\sin(k(x+\Delta x)-\omega(t+\Delta t))$$

$$= A\cdot\sin(kx-\omega t) = \Psi(x,t) \Longrightarrow$$

$$k\Delta x - \omega\Delta t = 0, \qquad v_{wave} = \frac{\omega}{k} = c$$

$$\sin\alpha + \sin\beta = 2\sin(\frac{\alpha+\beta}{2})\cos(\frac{\alpha-\beta}{2})$$

$$\Psi(x,t)_{interference} = A\cdot\sin(kx-\omega t) + A\cdot\sin(kx-\omega t+\varphi) = 2A\cdot\sin(kx-\omega t+\frac{\varphi}{2})\cos(\frac{\varphi}{2})$$

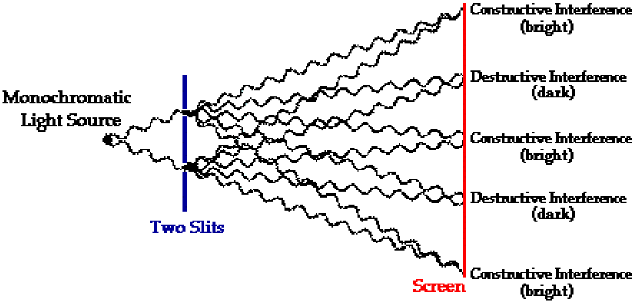
constructive $(\varphi = 0, 2\pi, 4\pi, \ldots)$ and destructive $(\varphi = \pi, 3\pi, 5\pi\ldots)$ interference

$$\Psi(x,t)_{standing} = A\cdot\sin(kx-\omega t) + A\cdot\sin(kx+\omega t) = 2A\cdot\sin(kx)\cos(\omega t)$$

$$\Psi(x,t)_{standing} = A\cdot\sin(kx-\omega t) - A\cdot\sin(kx+\omega t) = 2A\cdot\cos(kx)\sin(\omega t)$$

Classical wave equation

traveling, interference, and standing waves



A two-point source interference pattern creates an alternating pattern of bright and dark lines when it is projected onto a screen.

Classical wave equation

back to the elastic string ..., discrete Fourier series

Boundary conditions: $u(-a,0)=0,\ u(a,0)=0$

$$u_{2n}(x,t)=\frac{1}{\sqrt{a}}sin(k_{2n}x)cos(\omega_{2n}t)$$
$$\Longrightarrow k_{2n}=\frac{2n\pi}{2a},\ \omega_{2n}=k_{2n}*c\ ,\ n=1,2,...$$

$$u_{2n+1}(x,t)=\frac{1}{\sqrt{a}}cos(k_{2n+1}x)cos(\omega_{2n+1}t)$$
$$\Longrightarrow k_{2n+1}=\frac{(2n+1)\pi}{2a},\ n=0,1,2,...$$

$u(x,t)=\sum_{n=1} c_n u_n(x,t)$ (general form of standing waves)
how to get the c_n coefficients?

Classical wave equation

back to the elastic string ..., discrete Fourier series

The $u_n(x, t = 0)$ functions are "ortogonal to each other":

$$\int_{-a}^{a} u_n(x,0)u_m(x,0)dx = \delta_{nm},$$

where $\delta_{nm} = \begin{cases} 1, & \text{if } n = m \\ 0, & \text{if } n \neq m \end{cases}$ is the so-called Kronecker delta.

Any functions with the given boundary conditions can be represented as a linear combination of the above sin and cos funtions.

Classical wave equation

back to the elastic string ..., discrete Fourier series

$$u(x,0) = \sum_{n=1} c_{2n}\frac{1}{\sqrt{a}}sin(k_{2n}x) + \sum_{n=1} c_{2n+1}\frac{1}{\sqrt{a}}cos(k_{2n+1}x)$$

From the initial conditions:

$$c_n = \int_{-a}^{a} u(x,0)u_n(x,0) = \sum_m c_m \int_{-a}^{a} u_m(x,0)u_n(x,0)dx$$

The $u(x, t = 0)$ function is given in the Fourier series form.

Form of the final solution:

$$u(x,t) =$$

$$\sum_{n=1} c_{2n}\frac{1}{\sqrt{a}}sin(k_{2n}x)cos(\omega_{2n}t) + \sum_{n=1} c_{2n+1}\frac{1}{\sqrt{a}}cos(k_{2n+1}x)cos(\omega_{2n+1}t)$$

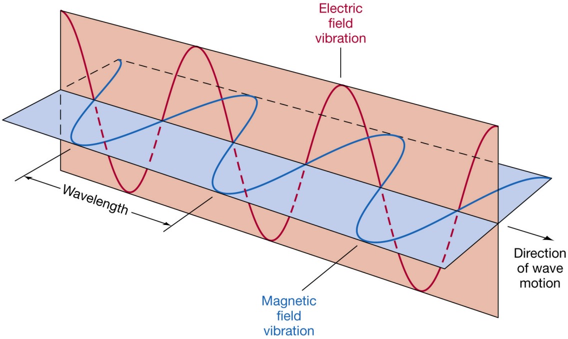
Classical wave equation

light

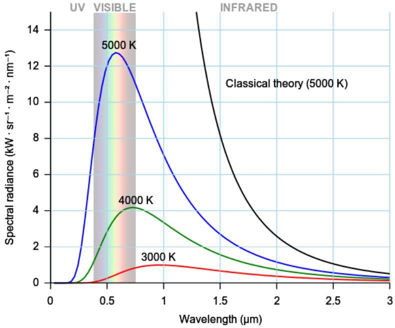
light is electromagnetic radiation: $\Psi(x,t) = A \cdot \sin(kx - \omega t) = A \cdot \sin(\frac{2\pi}{\lambda}(x - ct))$

amplitude, A, maximum displacement from the rest position

wavelength, λ, the distance between two successive maxima



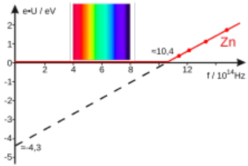
Black-body radiation (Planck, 1900)



- Insulated cave with a small hole: allows the study of the TD equilibrium of the EM radiation with matter.
- The $u(\nu, T)d\nu$ is the density of energy stored in the $d\nu$ frequency interval. For the black-body radiation it does not depend on the quality of material.
- Model: EM field consists of standing waves, $n\lambda/2 = L$, $n = 1, 2, 3, \ldots$ ED $\Longrightarrow$ number of nodes in the $d\nu$ interval: $V(\frac{8\pi}{c^3})\nu^2 d\nu$

- Classical theory: Equipartition theorem $\Longrightarrow$ each nodes has $k_B T$ energy, i.e., $Vu(\nu, T)d\nu = V(\frac{8\pi}{c^3})k_B\nu^2 T d\nu \Longrightarrow$ ultraviolet catastrophe
- Wien's displacement law: $\lambda_{max} = B/T$, where B is a constant
- Planck: Energy of EM radiation is quantized: $E_\nu = n \cdot h\nu$, $h = 6.626070040(81) \times 10^{-34} J\,s$ (Planck constatant)
- $\Longrightarrow u(\nu, T) = (\frac{8\pi}{c^3})\frac{h\nu^3}{e^{\frac{h\nu}{k_B T}} - 1}$, if $k_B T \ll h\nu$, then no EM waves with frequency ν.

- Photoelectric effect (Einstein, 1905)



- Diagram of the maximum kinetic energy as

  a function of the frequency of light on zinc.

- Emission of electrons due to EM radiation.

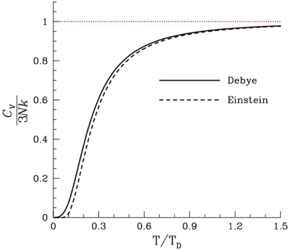
  Classically: $E_{kin.of\ e-} \sim E_{radiation}$

- Experiment: 1. increasing intensity does not increase the E_{kin} of electrons.

  2. below a certain frequency there are no emitted electrons.

- Einstein: EM radiation is a collection of photons with $n \times h\nu$ energies.

- Heat capacity of low temperature insulator crystals (Debye, 1912)



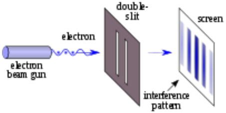
At low temperature the vibration of atomic lattice has the most significant contribution to the heat capacity of insulator crystals.

Debye: the energy of the vibration modes are quantized:

$E_{phonon} = n \cdot h\nu$

Phonones with $h\nu \gg k_B T$ are not excited $\Longrightarrow C \sim T^3$

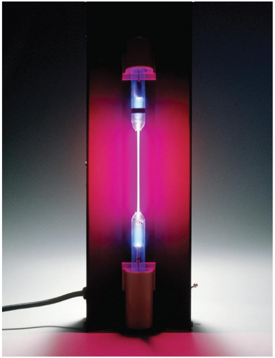
- de Broglie (1924): all matter has wave properties, $p = \frac{h}{\lambda} = \hbar k$

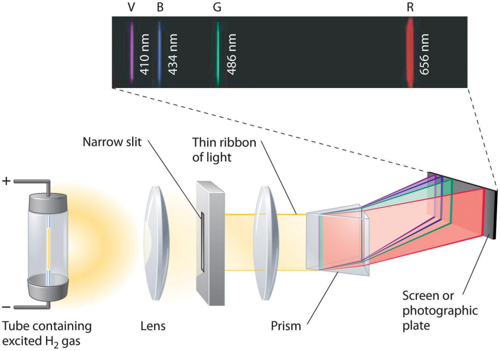


Energy levels of atoms and molecules

H emission spectrum

the experimental emission spectrum of the H-atom





Energy levels of atoms and molecules

H emission spectrum [a]

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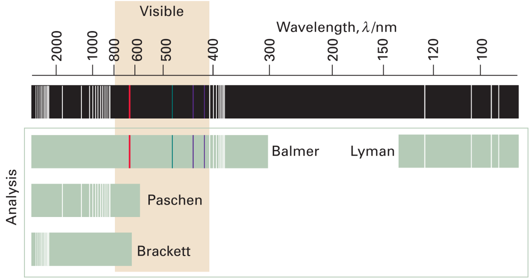
[a] wikipedia, Hydrogen spectral series



Balmer$(n \geq 3)$[1885]

$$\tilde{\nu} = 109680 \left(\frac{1}{4} - \frac{1}{n^2} \right) \mathrm{cm}^{-1}$$

Rydberg$(n_2 > n_1)$[1888]

$$\tilde{\nu} = 109680 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \mathrm{cm}^{-1}$$

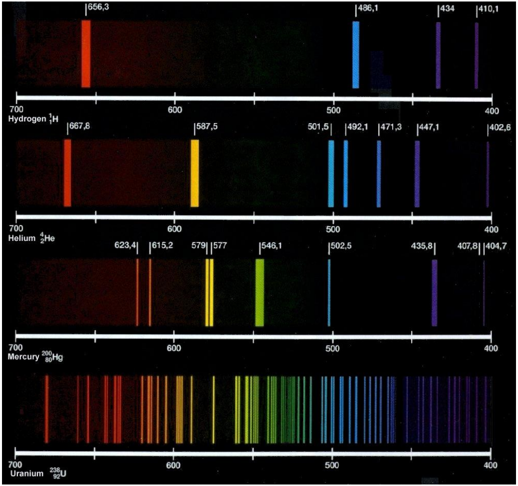
Lyman[1906 – 1914]

Ritz combination rule: spectral lines include frequencies that are either the sum or the difference of the frequencies of two other lines [$\Longleftarrow$ the wavenumber ($\tilde{\nu} = 1/\lambda$) of any spectral line is the difference of two terms

$\tilde{\nu} = term(i) - term(j)$]

Energy levels of atoms and molecules

atomic emission spectra, characteristic for the atoms



Energy levels of atoms and molecules

Bohr's theory of the H-atom (1913) [a]

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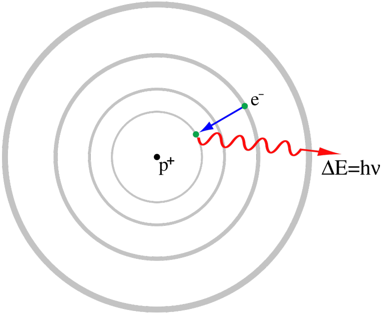
[a] wikipedia

- existence of stationary orbits (fixed nucleus and circular orbit), no electromagnetic radiation
- frequency condition: $\Delta E = h\nu$ (h is the Planck constant, $6.626 \cdot 10^{-34} \mathrm{J} \cdot \mathrm{s}$)
- angular momentum is quantized: $\ell = n\hbar$, $\hbar = h/2\pi$, where $n = 1, 2, 3, \ldots$



Energy levels of atoms and molecules

plausibility of Bohr's quantization condition, $\ell = n\hbar$

$$p_{\text{photon}} = \frac{h}{\lambda} \text{ (Einstein)}$$

$$p_{\text{particle}} = \frac{h}{\lambda} \text{ (de Broglie)}$$

$$\lambda = \frac{h}{p_{\text{particle}}}$$

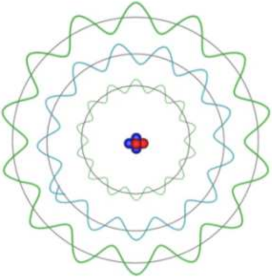
$$2r\pi = n \cdot \lambda$$

$$2r\pi = n \cdot \frac{h}{p_{\text{electron}}}$$

$$\ell = r \cdot p = n \cdot \frac{h}{2\pi}$$

constructive and destructive interference

standing wave - stationary orbit



Energy levels of atoms and molecules

Bohr's theory of the H-atom (1913)

$$F_{\text{electrostatic}} = F_{\text{centripetal}}$$

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r} \quad \text{/in SI units/}$$

$$\ell = n\hbar = r \cdot m_e v$$

$$v = \frac{n\hbar}{r \cdot m_e}$$

$$v^2 = \frac{n^2\hbar^2}{m_e^2 r^2}$$

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e \frac{n^2\hbar^2}{m_e^2 r^2}}{r}$$

$$r = \frac{n^2\hbar^2 4\pi\epsilon_0}{m_e e^2}$$

Bohr radius, $a_0 = 0.529$ Å, $(n = 1)$

vacuum permittivity $\epsilon_0 = 8.854187817620... \times 10^{-12}\mathrm{A}^2\mathrm{s}^4\mathrm{kg}^{-1}\mathrm{m}^{-3}$

electron mass $m_e = 9.10938356 \times 10^{-31}$ kg

Energy levels of atoms and molecules

Bohr's theory of the H-atom

$$\begin{aligned}
E_{\text{tot}} &= E_{\text{kin}} + E_{\text{pot}} \\
&= \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} \\
&= \frac{1}{2}\frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{1}{2}\frac{e^2}{4\pi\epsilon_0 r} \\
&= -\frac{1}{2}\frac{e^2}{4\pi\epsilon_0 \frac{n^2\hbar^2 4\pi\epsilon_0}{m_e e^2}} \\
&= -\frac{m_e e^4}{8\epsilon_0 h^2}\frac{1}{n^2}
\end{aligned}$$

$$\begin{aligned}
\frac{e^2}{4\pi\epsilon_0 r^2} &= \frac{m_e v^2}{r} \\
m_e v^2 &= \frac{r e^2}{4\pi\epsilon_0 r^2} \\
r &= \frac{n^2\hbar^2 4\pi\epsilon_0}{m_e e^2} \\
\hbar^2 &= \frac{h^2}{4\pi^2}
\end{aligned}$$

Energy levels of atoms and molecules

Bohr's theory of the H-atom

$$\Delta E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu}$$

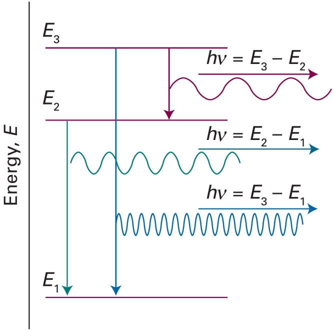
$$\Delta E = E_{n_2} - E_{n_1} = \frac{m_e e^4}{8\epsilon_0 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\tilde{\nu} = \frac{1}{hc}\frac{m_e e^4}{8\epsilon_0 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\tilde{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$R_H = \frac{1}{hc}\frac{m_e e^4}{8\epsilon_0 h^2} = 109737\mathrm{cm}^{-1}$$

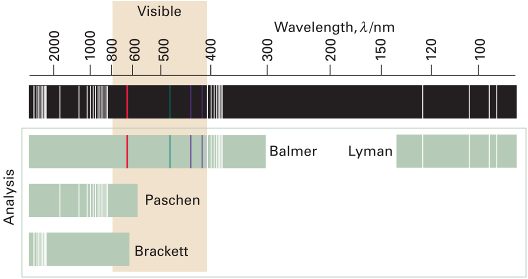
$$R_H = 109638\mathrm{cm}^{-1}\text{from experiment}$$



Energy levels of atoms and molecules

Bohr's theory of the H-atom

$$\mathrm{Bohr}(n_2 > n_1): \quad \tilde{\nu} = \frac{1}{hc}\frac{m_e e^4}{8\epsilon_0 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\mathrm{cm}^{-1}$$



$\mathrm{Lyman}(n_1 = 1)$

$\mathrm{Balmer}(n_1 = 2)$

$\mathrm{Paschen}(n_1 = 3)$

$\mathrm{Brackett}(n_1 = 4)$

1

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[1] *On December 1, 2011, it was announced that Voyager 1 detected the first Lyman-alpha radiation originating from the Milky Way galaxy. Lyman-alpha radiation had previously been detected from other galaxies, but due to interference from the Sun, the radiation from the Milky Way was not detectable. (Wikipedia)*

Energy levels of atoms and molecules

plausibility of Bohr's quantization condition, $\ell = n\hbar$

Wave-particle duality: "It seems as though we must use sometimes the one theory and sometimes the other, while at times we may use either. We are faced with a new kind of difficulty. We have two contradictory pictures of reality; separately neither of them fully explains the phenomena of light, but together they do." (Einstein)

$c = \lambda \cdot \nu$ $\qquad$ $E = h \cdot \nu$

Time-dependent Schrödinger equation

some arguments for the Schrödinger equation

of course there is no proof of it, it is a postulate

Free particle waves: $\Psi(x,t) = e^{i(kx-\omega t)}$

$\omega = E/\hbar$ (Planck)

$$\frac{\partial}{\partial t}\Psi(x,t) = -\frac{i}{\hbar}E\Psi(x,t)$$

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = E\Psi(x,t)$$

$k = p/\hbar$ (De Broglie)

$$\frac{\partial^2}{\partial x^2}\Psi(x,t) = (\frac{i}{\hbar})^2 p^2\Psi(x,t)$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) = \frac{p^2}{2m}\Psi(x,t)$$

The energy is a classical free particle:

$$E = \frac{p^2}{2m}$$

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)$$

Schrödinger equation

particle in a force field, time-independent Schrödinger equation

If the particle is not free (3D):

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t)=\left\{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})\right\}\Psi(\mathbf{r},t)$$

A particular solution of the time-dependent Schrödinger equation:

$\Psi(\mathbf{r},t)=\Phi(\mathbf{r})e^{-\frac{i}{\hbar}Et}$

$$i\hbar\frac{\partial}{\partial t}\Phi(\mathbf{r})e^{-\frac{i}{\hbar}Et}=E\Phi(\mathbf{r})e^{-\frac{i}{\hbar}Et}$$

Using the relations above we obtain the time-independent

Schrödinger equation

$$\left\{-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})\right\}\Phi(\mathbf{r})=E\Phi(\mathbf{r})$$

Energy levels of atoms and molecules

Schrödinger equation for the particle in the 1D box model [a]

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[a] Atkins, part II, chapter 8

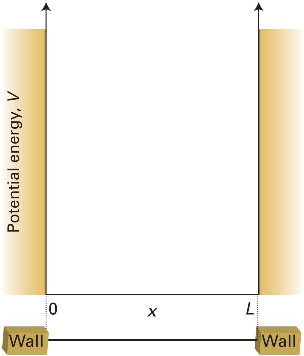
$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)$$

$$E_{\text{kin}} + E_{\text{pot}} = E_{\text{tot}}$$

$$\frac{\partial^2\Psi(x)}{\partial x^2} = \frac{-2m(E - V(x))}{\hbar^2}\Psi(x)$$

$$\frac{d^2y}{dx^2} = -k^2 \cdot y$$

$$y \in \{e^{ikx}, \sin(kx), \cos(kx)\}$$



Energy levels of atoms and molecules

Schrödinger equation for the particle in the 1D box model

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2}+V(x)\Psi(x)=E\Psi(x)$$

No particle in the infinit potential area! $\Psi(x)=0$ if $x<0$ or $x>L$.

$$\frac{\partial^2\Psi(x)}{\partial x^2}=\frac{-2mE}{\hbar^2}\Psi(x)$$

$$k=\sqrt{\frac{2mE}{\hbar^2}}$$

$$\Psi(x)=C\cos kx+D\sin kx$$

$$\left.\begin{array}{l}\Psi(0)=0\\ \Psi(L)=0\end{array}\right\}\Longleftrightarrow\left\{\begin{array}{l}C=0\\ D=0 \text{ or } \sin kL=0\end{array}\right.$$

$$kL=n\pi \quad n=(1,2,\cdots)$$

$$\Psi(x)=D\sin\frac{n\pi}{L}x$$

Energy levels of atoms and molecules

Schrödinger equation for the particle in the 1D box model

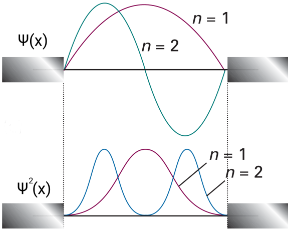
$$V(x) = \begin{cases} \infty, -\infty < x \leq 0 \\ 0, \qquad 0 < x < L \\ \infty, \qquad L \leq x < \infty \end{cases}$$

$$k = \sqrt{\frac{2mE}{\hbar^2}} \qquad = \frac{n\pi}{L}$$

$$k^2 = \frac{2mE}{\hbar^2} \qquad = \frac{n^2\pi^2}{L^2}$$

$$\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$$

$$E_n = \frac{n^2h^2}{8mL^2}$$

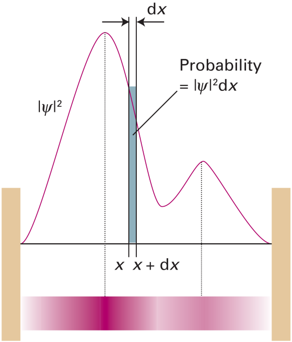


Born probability interpretation: $\int_{-\infty}^{\infty} \Psi^2(x)dx = 1$

Energy levels of atoms and molecules

properties of the solutions

- Born probability interpretation: probability of finding the particle between x and $x + dx$ is $\Psi^2(x)dx$, i.e., $\int_{-\infty}^{\infty} \Psi^2(x)dx{=}1$
- if $n \uparrow$ then E $\uparrow$
- $n = 1$, zero-point energy
- Ψ has $n - 1$ nodes in the $0 < x < L$ interval
- ground and excited states
- with increasing mass the energy gap between the levels, $E_{n+1} - E_n$, decreases



$\rho(\mathbf{r}) = \Psi^*(\mathbf{r})\Psi(\mathbf{r})$ satisfies the continuity equation, $\frac{\partial \rho}{\partial t} + div\mathbf{j} = 0$, where

$\mathbf{j}(\mathbf{r}, t) = \frac{\hbar}{2mi}\left[\Psi^*\left(\nabla\Psi\right) - \Psi\left(\nabla\Psi^*\right)\right]$ is the probability current .

Energy levels of atoms and molecules

Schrödinger equation for the particle in the 1D box model

Born probability interpretation

$$\int_{-\infty}^{\infty} \Psi^2(x)dx = 1 \Rightarrow \Psi(x) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi}{L}x)$$

$$\Psi(x) = D\sin(\frac{n\pi}{L}x)$$

$$D^2\int_{-\infty}^{\infty} \sin^2(\frac{n\pi}{L}x)dx = D^2\int_{0}^{L} \sin^2(\frac{n\pi}{L}x)dx = 1$$

$$D = \sqrt{\frac{2}{L}}$$

$$\Psi(x) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi}{L}x)$$

$$\begin{aligned} z &= \frac{n\pi}{L}x \\ dx &= \frac{L}{n\pi}dz \\ \int_0^L \sin(\frac{n\pi}{L}x)dx &= \frac{L}{n\pi}\int_0^{n\pi} \sin(z)dz \\ \sin^2 z &= \frac{\sin^2 z + \cos^2 z + \sin^2 z - \cos^2 z}{2} \\ &= \frac{1 - \cos 2z}{2} \end{aligned}$$

Energy levels of atoms and molecules

Schrödinger equation for the free particle, $V(x) = 0$, $E_{\mathrm{kin}} = E_{\mathrm{tot}}$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} = E_{\mathrm{kin}}\Psi(x)$$

$$\frac{\partial^2\Psi(x)}{\partial x^2} = \frac{-2mE_{\mathrm{kin}}}{\hbar^2}\Psi(x)$$

$$k^2 = \frac{2mE_{\mathrm{kin}}}{\hbar^2}$$

$$\Psi(x) = A \cdot \sin(kx)$$

$$\Psi(x) = A \cdot \sin(\frac{2\pi}{\lambda}x)$$

$$k = \frac{2\pi}{\lambda}$$

$$2mE_{\mathrm{kin}} = 2m \cdot \frac{1}{2}mv^2 = p^2$$

$$p^2 = k^2\hbar^2 = \left(\frac{2\pi}{\lambda}\right)^2 \cdot \left(\frac{h}{2\pi}\right)^2$$

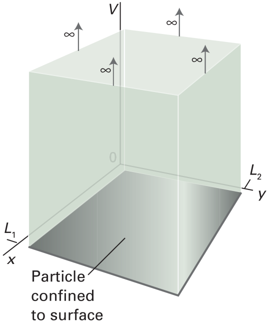
$$\lambda = \frac{h}{p}$$

Energy levels of atoms and molecules

Schrödinger equation for the particle in the 2D box model

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}\right\}+V\Psi=E\Psi$$

$$V(x,y)=\begin{cases}0, & x\in(0,L_1)\wedge y\in(0,L_2)\\ \infty, & \text{otherwise}\end{cases}$$



Energy levels of atoms and molecules

Schrödinger equation for the particle in the 2D box model

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}\right\}=E\Psi \quad \Psi(x,y)=F(x)\cdot G(y)$$

separation of variables

$$\begin{aligned}
\Psi &= F(x)\cdot G(y)\\
\frac{\partial^2\Psi}{\partial x^2} &= G(y)\frac{d^2F(x)}{dx^2}\\
\frac{\partial^2\Psi}{\partial y^2} &= F(x)\frac{d^2G(y)}{dy^2}\\
-\frac{\hbar^2}{2m}\left\{G(y)\frac{d^2F(x)}{dx^2}+F(x)\frac{d^2G(y)}{dy^2}\right\} &= EF(x)G(y)\\
-\frac{\hbar^2}{2m}\left\{\frac{1}{F(x)}\frac{d^2F(x)}{dx^2}+\frac{1}{G(y)}\frac{d^2G(y)}{dy^2}\right\} &= E
\end{aligned}$$

$$\begin{aligned}
-\frac{\hbar^2}{2m}\frac{1}{F(x)}\frac{d^2F(x)}{dx^2} &= E_x\\
-\frac{\hbar^2}{2m}\frac{1}{G(y)}\frac{d^2G(y)}{dy^2} &= E_y\\
-\frac{\hbar^2}{2m}\frac{d^2F(x)}{dx^2} &= E_xF(x)\\
-\frac{\hbar^2}{2m}\frac{d^2G(y)}{dy^2} &= E_yG(y)
\end{aligned}$$

Energy levels of atoms and molecules

Schrödinger equation for the particle in the 2D box model

$$-\frac{\hbar^2}{2m}\frac{d^2F(x)}{dx^2} = E_x F(x)$$

$$E_x = \frac{n_1^2 h^2}{8mL_1^2}$$

$$F(x) = \sqrt{\frac{2}{L_1}}\sin\frac{n_1\pi}{L_1}x$$

$$-\frac{\hbar^2}{2m}\frac{d^2G(y)}{dy^2} = E_y G(y)$$

$$E_y = \frac{n_2^2 h^2}{8mL_2^2}$$

$$G(y) = \sqrt{\frac{2}{L_2}}\sin\frac{n_2\pi}{L_2}y$$

$$\Psi(x,y) = F(x)\cdot G(y) = \sqrt{\frac{4}{L_1L_2}}\cdot\sin\frac{n_1\pi}{L_1}x\cdot\sin\frac{n_2\pi}{L_2}y$$

$$E = E_x + E_y = \left\{\left(\frac{n_1}{L_1}\right)^2 + \left(\frac{n_2}{L_2}\right)^2\right\}\frac{h^2}{8m}$$

Energy levels of atoms and molecules

Schrödinger equation for the particle in the 2D box model

$$\Psi(x, y) = \sqrt{\frac{4}{L_1 L_2}} \cdot \sin \frac{n_1 \pi}{L_1} x \cdot \sin \frac{n_2 \pi}{L_2} y$$

$$E(n_1, n_2) = \left\{ \left(\frac{n_1}{L_1} \right)^2 + \left(\frac{n_2}{L_2} \right)^2 \right\} \frac{h^2}{8m}$$

consequence of symmetry, $L_1 = L_2 = L$

$$\Psi(x, y) = \sqrt{\frac{4}{L^2}} \cdot \sin \frac{n_1 \pi}{L} x \cdot \sin \frac{n_2 \pi}{L} y$$

$$E(n_1, n_2) = (n_1^2 + n_2^2) \frac{h^2}{8mL^2}$$

$E(1, 2) = E(2, 1)$ but the wavefunctions are different

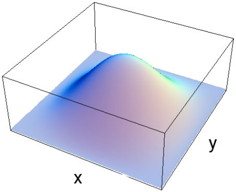
degeneracy: same energies different wavefunctions

Energy levels of atoms and molecules

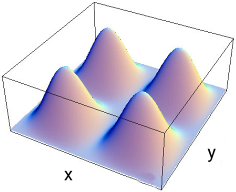
Schrödinger equation for the particle in the 2D box model

degeneracy is the consequence of symmetry

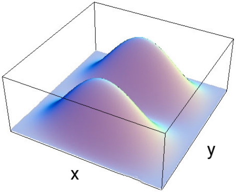
$|\psi_{11}|^2$



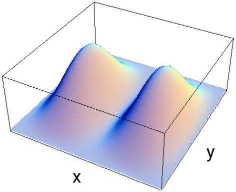
$|\psi_{22}|^2$



$|\psi_{12}|^2$



$|\psi_{21}|^2$



Energy levels of atoms and molecules

Schrödinger equation for the particle in the 3D box model

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right\}=E\Psi \quad \Psi(x,y,z)=F(x)\cdot G(y)\cdot H(z)$$

$$\Psi(x,y,z)=F(x)\cdot G(y)\cdot H(z)=\sqrt{\frac{8}{L_1L_2L_3}}\cdot\sin\frac{n_1\pi}{L_1}x\cdot\sin\frac{n_2\pi}{L_2}y\cdot\sin\frac{n_3\pi}{L_3}z$$

$$E=E_x+E_y+E_z=\left\{\left(\frac{n_1}{L_1}\right)^2+\left(\frac{n_2}{L_2}\right)^2+\left(\frac{n_3}{L_3}\right)^2\right\}\frac{h^2}{8m}$$

Energy levels of atoms and molecules

Schrödinger equation for the particle in the 3D box model

degenerate case: cube $L_1 = L_2 = L_3 = L$

$$\Psi(x, y, z) = \sqrt{\frac{8}{L^3}} \cdot \sin\frac{n_1\pi}{L}x \cdot \sin\frac{n_2\pi}{L}y \cdot \sin\frac{n_3\pi}{L}z$$

$$E(n_1, n_2, n_3) = \left(n_1^2 + n_2^2 + n_3^2\right)\frac{h^2}{8mL^2} = \left(n_1^2 + n_2^2 + n_3^2\right)\frac{h^2}{8mV^{2/3}}$$

Postulates of Quantum Mechanics [a]

postulate I

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[a] P. Atkins, J. Paula, R. Friedman, Chapter 1

The state of a quantum-mechanical system is completely specified by the so-called wavefunction, $\Psi(\mathbf{r}, t)$, that depends on the coordinates of the particles and on time. $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)dxdydz$ is the probability that the particle lies in the volume element $d\tau = dxdydz$ located at $\mathbf{r}$ at time t.

Postulates of Quantum Mechanics

postulate I

properties of $\Psi(\mathbf{r}, t)$

- continuous
- contiguously differentiable (if the $V(\mathbf{r})$ potential is realistic ...)
- finite (square integrable for bound states, i.e.,

  $\langle\Psi|\Psi\rangle = \int_{-\infty}^{\infty} |\Psi|^2 d\tau < \infty$)

Postulates of Quantum Mechanics

postulate II

To every observable in classical mechanics there exists a corresponding linear, Hermitian operator in quantum mechanics.

Operators in Quantum Mechanics

correspondences

observables		$\hat{\boldsymbol{\Omega}}$	operators
position	x	$\hat{x}$	multiplication by x
	$\mathbf{r}$	$\hat{\mathbf{r}}$	multiplication by $\mathbf{r}$
potential energy	$V(x)$	$\hat{V}(\hat{x})$	multiplication by $V(x)$
	$V(\mathbf{r})$	$\hat{V}(\hat{\mathbf{r}})$	multiplication by $V(\mathbf{r})$
momentum	p_x	$\hat{p}_x$	$-i\hbar\frac{\partial}{\partial x}$
	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar(\mathbf{e}_x\frac{\partial}{\partial x} + \mathbf{e}_y\frac{\partial}{\partial y} + \mathbf{e}_z\frac{\partial}{\partial z})$
kinetic energy	K_x	$\hat{K}_x$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
	K	$\hat{\boldsymbol{K}}$	$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$
total energy	E	$\hat{\boldsymbol{H}}$	$\hat{\boldsymbol{T}} + \hat{\boldsymbol{V}}$

Postulates of Quantum Mechanics

Bra–ket notation

- Dot product of two wavefunction: $\langle \eta | \psi \rangle = \int \eta^* \psi d\tau$
- For systems with more than one particle: $\eta = \eta(\mathbf{r}_1, \mathbf{r}_2, \ldots)$, $\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots)$, and $d\tau = dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \ldots$
- $\implies \langle \eta | \psi \rangle = \langle \psi | \eta \rangle^*$
- Operator $\hat{A}$ transforms ket function $|\psi\rangle$ to function $|\eta\rangle$: $|\eta\rangle = \hat{A}|\psi\rangle$
- Matrix element of operator $\hat{A}$: $\langle \eta | \hat{A} | \psi \rangle = \int \eta^* \hat{A} \psi d\tau = \langle \eta | \hat{A} \psi \rangle$
- $\implies \langle \hat{A}\eta | \psi \rangle = \langle \psi | \hat{A}\eta \rangle^* = \int \left(\hat{A}\eta\right)^* \psi d\tau$
- An operator is called Hermitian if $\langle \psi_i | \hat{\boldsymbol{\Omega}} | \psi_j \rangle = \langle \hat{\boldsymbol{\Omega}} \psi_i | \psi_j \rangle$.

Postulates of Quantum Mechanics

postulate III

In any measurement of the observable associated with the operator $\hat{\mathbf{\Omega}}$, the only values that will ever be observed are the eigenvalues ω_i which satisfy the eigenvalue equation $\hat{\mathbf{\Omega}}|\Psi_i\rangle = \omega_i|\Psi_i\rangle$

Operators in Quantum Mechanics

linear Hermitian operators

$$\left\{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\right\}\Psi(x)=E\Psi(x) \qquad \hat{\mathsf{H}}\Psi(x)=E\Psi(x)$$

eigenvalue equation $\hat{\mathbf{\Omega}}|\psi_i\rangle=\omega_i|\psi_i\rangle$, $i=1,2,3,\ldots$

If $\psi_i\neq\psi_j$ but $\omega_i=\omega_j$, then this eigenvalue is degenerate.

An operator is called linear if $\hat{\mathbf{\Omega}}(|\alpha\psi\rangle+\beta|\phi\rangle)=\alpha\hat{\mathbf{\Omega}}|\psi\rangle+\beta\hat{\mathbf{\Omega}}|\phi\rangle$.

$\hat{\mathbf{\Omega}}$ is Hermitian, i.e., $\langle\psi_i|\hat{\mathbf{\Omega}}|\psi_j\rangle=\int\psi_i^*\hat{\mathbf{\Omega}}\psi_j d\tau$ and

$\langle\hat{\mathbf{\Omega}}\psi_i|\psi_j\rangle=\int\left(\hat{\mathbf{\Omega}}\psi_i\right)^*\psi_j d\tau$

All eigenvalues of a Hermitian operator are real!!!

Postulates of Quantum Mechanics

postulate IV

If the state of the system is described by a normalized wavefunction Ψ, then the average value of the observable corresponding to the operator $\hat{\boldsymbol{\Omega}}$ can be calculated as $\langle \omega \rangle = \langle \Psi | \hat{\boldsymbol{\Omega}} | \Psi \rangle$

- Expectation value of operator $\hat{A}$: $\langle \psi | \hat{A} | \psi \rangle$

Postulates of Quantum Mechanics

postulate V

The wavefunction of a system evolves in time according to the time-dependent Schrödinger equation: $\hat{\mathsf{H}}\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$

Operators

required properties: measurable physical quantities are real

postulate III: $\hat{\boldsymbol{\Omega}}|\Psi_i\rangle = \omega_i|\Psi_i\rangle \quad \Rightarrow \quad \langle\Psi_i|\hat{\boldsymbol{\Omega}}|\Psi_i\rangle = \omega_i$

(we assumed that Ψ_i is normalized, $\langle\Psi_i|\Psi_i\rangle = 1$)

eigenvalue equation

$$\hat{\boldsymbol{\Omega}}\Psi = \omega\Psi$$

$$\langle\Psi|\hat{\boldsymbol{\Omega}}|\Psi\rangle = \omega\langle\Psi|\Psi\rangle$$

$$\langle\Psi|\hat{\boldsymbol{\Omega}}|\Psi\rangle = \omega$$

its complex conjugate

$$\langle\Psi|\hat{\boldsymbol{\Omega}}|\Psi\rangle^* = \omega^*$$

$$\langle\hat{\boldsymbol{\Omega}}\Psi|\Psi\rangle = \omega^*$$

$$\underbrace{\Longrightarrow}_{\hat{\Omega}\text{ is hermitian!}} \qquad \langle\Psi|\hat{\boldsymbol{\Omega}}|\Psi\rangle = \omega^*$$

ω is real if $\omega = \omega^*$.

Operators

the hamiltonian, $\hat{\boldsymbol{H}} = \hat{\boldsymbol{K}} + \hat{\boldsymbol{V}}$, is a Hermitian operator

observables		operators	
position	x	$\hat{x}$	multiplication by x
	$\mathbf{r}$	$\hat{\mathbf{r}}$	multiplication by $\mathbf{r}$
potential energy	$V(x)$	$\hat{V}(\hat{x})$	multiplication by $V(x)$
	$V(\mathbf{r})$	$\hat{V}(\hat{\mathbf{r}})$	multiplication by $V(\mathbf{r})$
momentum	p_x	$\hat{p}_x$	$-i\hbar\frac{\partial}{\partial x}$
	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar(\mathbf{e}_x\frac{\partial}{\partial x} + \mathbf{e}_y\frac{\partial}{\partial y} + \mathbf{e}_z\frac{\partial}{\partial z})$
kinetic energy	K_x	$\hat{K}_x$	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
	K	$\hat{\boldsymbol{K}}$	$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$
total energy	E	$\hat{\boldsymbol{H}}$	$\hat{\boldsymbol{T}} + \hat{\boldsymbol{V}}$

Operators

the Hamiltonian, $\hat{\boldsymbol{H}} = \hat{\boldsymbol{K}} + \hat{\boldsymbol{V}}$, is a Hermitian operator

$\hat{\boldsymbol{V}}(x, y, z)$ is hermitian; it just stands for a multiplication by the potential function

$$\begin{aligned}
\langle\eta|\hat{\boldsymbol{V}}|\Psi\rangle = \int \eta^* \hat{\boldsymbol{V}} \Psi d\tau = \int \eta^* \cdot \hat{\boldsymbol{V}} \cdot \Psi d\tau \\
= \int \eta^* \cdot \hat{\boldsymbol{V}}^* \cdot \Psi d\tau \quad (\hat{\boldsymbol{V}} = \hat{\boldsymbol{V}}^* \text{ real function}) \\
= \int \hat{\boldsymbol{V}}^* \cdot \eta^* \cdot \Psi d\tau \quad = \langle\hat{\boldsymbol{V}}\eta|\Psi\rangle \text{ (multiplication is commutative)}
\end{aligned}$$

Operators

the Hamiltonian, $\hat{\boldsymbol{H}} = \hat{\boldsymbol{K}} + \hat{\boldsymbol{V}}$, is a Hermitian operator

- $\hat{\boldsymbol{p}}_x = \frac{\hbar}{i}\frac{d}{dx}$ and the wavefunction must vanish at infinity
- recall that, $(u \cdot v)' = u' \cdot v + u \cdot v'$, therefore, $\int u \cdot v' = u \cdot v - \int u' \cdot v$

$$\langle \eta | \hat{\boldsymbol{p}}_x | \Psi \rangle =$$

$$\frac{\hbar}{i} \int\limits_{-\infty}^{\infty} \eta^* \frac{d\Psi}{dx} dx = \left[\frac{\hbar}{i} \eta^* \Psi \right]_{-\infty}^{\infty} - \frac{\hbar}{i} \int\limits_{-\infty}^{\infty} \frac{d\eta^*}{dx} \Psi dx = 0 + \int\limits_{-\infty}^{\infty} \left(\frac{\hbar}{i} \frac{d\eta}{dx} \right)^* \Psi dx$$

$$= \langle \hat{\boldsymbol{p}}_x \eta | \Psi \rangle$$

$\hat{K}_x$ is hermitian

$$\langle \eta | \hat{\boldsymbol{K}}_x | \Psi \rangle = -\frac{1}{2m} \langle \eta | \hat{\boldsymbol{p}}_x^2 | \Psi \rangle = -\frac{1}{2m} \langle \hat{\boldsymbol{p}}_x \eta | \hat{\boldsymbol{p}}_x | \Psi \rangle = -\frac{1}{2m} \langle \hat{\boldsymbol{p}}_x^2 \eta | \Psi \rangle = \langle \hat{\boldsymbol{K}}_x \eta | \Psi \rangle$$

Operators

properties of hermitian operators

If $\hat{\boldsymbol{\Omega}}$ is a Hermitian operator then the eigenfunctions with different eigenvalues are orthogonal.

$$\left.\begin{aligned}\hat{\boldsymbol{\Omega}}\Psi_i &= \omega_i\Psi_i \\ \hat{\boldsymbol{\Omega}}\Psi_j &= \omega_j\Psi_j\end{aligned}\right\} \text{/take its complex conjugate}$$

$$\left.\begin{aligned}\hat{\boldsymbol{\Omega}}^*\Psi_i^* &= \omega_i\Psi_i^* \\ \hat{\boldsymbol{\Omega}}\Psi_j &= \omega_j\Psi_j\end{aligned}\right\} \begin{aligned}\Psi_j \cdot / \quad &\text{then integrate} \\ \Psi_i^* \cdot / \quad &\text{then integrate}\end{aligned}$$

$$\left.\begin{aligned}\langle\hat{\boldsymbol{\Omega}}\Psi_i|\Psi_j\rangle &= \int \Psi_j\hat{\boldsymbol{\Omega}}^*\Psi_i^* d\tau = \omega_i \int \Psi_j\Psi_i^* d\tau \\ \langle\Psi_i|\hat{\boldsymbol{\Omega}}\Psi_j\rangle &= \int \Psi_i^*\hat{\boldsymbol{\Omega}}\Psi_j d\tau = \omega_j \int \Psi_i^*\Psi_j d\tau\end{aligned}\right\} \Rightarrow (\omega_i - \omega_j)\int \Psi_i^*\Psi_j d\tau = 0$$

$$(\omega_i \neq \omega_j \ ! \ ) \Longrightarrow \int \Psi_i^*\Psi_j d\tau = 0$$

Operators

properties of hermitian operators

If $\hat{\mathbf{\Omega}}$ is a hermitian operator then any linear combination of degenerate eigenstates/eigenfunctions is also an eigenstate/eigenfunction with the same eigenvalue.

$$\left.\begin{aligned} \hat{\mathbf{\Omega}}\Psi_i &= \omega_i\Psi_i \\ \hat{\mathbf{\Omega}}\Psi_j &= \omega_j\Psi_j \end{aligned} \text{ and } \omega_i = \omega_j = \omega \right\} \begin{aligned} \hat{\mathbf{\Omega}}\Psi_i &= \omega\Psi_i \\ \hat{\mathbf{\Omega}}\Psi_j &= \omega\Psi_j \end{aligned}$$

$$\begin{aligned} \Psi &= c_i\Psi_i + c_j\Psi_j \\ \hat{\mathbf{\Omega}}\Psi &= \hat{\mathbf{\Omega}}(c_i\Psi_i + c_j\Psi_j) && = c_i\hat{\mathbf{\Omega}}\Psi_i + c_j\hat{\mathbf{\Omega}}\Psi_j \\ &&& = c_i\omega\Psi_i + c_j\omega\Psi_j \\ &&& = \omega(c_i\Psi_i + c_j\Psi_j) \\ &&& = \omega\Psi \end{aligned}$$

Operators

properties of hermitian operators

If $\hat{\boldsymbol{\Omega}}$ is a hermitian operator then any degenerate eigenstates/eigenfunctions can be orthogonalized.

$$\left.\begin{array}{c} \hat{\boldsymbol{\Omega}}\boldsymbol{\Psi}_i = \omega_i \boldsymbol{\Psi}_i \\ \hat{\boldsymbol{\Omega}}\boldsymbol{\Psi}_j = \omega_j \boldsymbol{\Psi}_j \end{array} \text{ and } \omega_i = \omega_j = \omega \right\} \begin{array}{c} \hat{\boldsymbol{\Omega}}\boldsymbol{\Psi}_i = \omega \boldsymbol{\Psi}_i \\ \hat{\boldsymbol{\Omega}}\boldsymbol{\Psi}_j = \omega \boldsymbol{\Psi}_j \end{array}$$

$$\begin{aligned} \phi_i &= \boldsymbol{\Psi}_i \\ \phi_j &= \boldsymbol{\Psi}_j + c\boldsymbol{\Psi}_i \\ \int \phi_i^* \phi_j d\tau &= \int \boldsymbol{\Psi}_i^* (\boldsymbol{\Psi}_j + c\boldsymbol{\Psi}_i) d\tau \\ &= \int \boldsymbol{\Psi}_i^* \boldsymbol{\Psi}_j d\tau + c \end{aligned}$$

With $c = -\int \boldsymbol{\Psi}_i^* \boldsymbol{\Psi}_j d\tau$ the functions become orthogonal, i.e., $\int \phi_i^* \phi_j d\tau = 0$

Operators

postulate III and IV

- In any measurement of the observable associated with the operator $\hat{\boldsymbol{\Omega}}$, the only values that will ever be observed are the eigenvalues ω_i which satisfy the eigenvalue equation $\hat{\boldsymbol{\Omega}}\Psi_i = \omega_i\Psi_i \quad \Rightarrow \quad \int \Psi_i^* \hat{\boldsymbol{\Omega}}\Psi_i d\tau = \omega_i$
- If the state of the system is described by a normalized wavefunction Ψ, then the average value of the observable corresponding to the operator $\hat{\boldsymbol{\Omega}}$ can be calculated as $\langle\omega\rangle = \int \Psi^* \hat{\boldsymbol{\Omega}}\Psi d\tau$

Operators

postulate IV

Any state of the quantum system can be obtained as the linear combination of the eigenstates of any $\hat{\mathbf{\Omega}}$

$|\Psi\rangle = \sum_i c_i|\Psi_i\rangle$, $c_j = \langle\Psi_j|\Psi\rangle = \int \Psi_j^*\Psi d\tau$

$\hat{\mathbf{\Omega}}c_i|\Psi_i\rangle = c_i\omega_i|\Psi_i\rangle$

$$\begin{aligned}
\langle\omega\rangle &= \int \Psi^*\hat{\mathbf{\Omega}}\Psi d\tau = \int \sum_i c_i^*\Psi_i^*\hat{\mathbf{\Omega}}\sum_i c_i\Psi_i d\tau = \int \sum_i c_i^*\Psi_i^* \sum_i c_i\omega_i\Psi_i d\tau \\
&= \int \sum_i c_i^*\Psi_i^* c_i\omega_i\Psi_i d\tau + \int \sum_i \sum_{\substack{j \\ j\neq i}} c_i^*\Psi_i^* c_j\omega_j\Psi_j d\tau \\
&= \sum_i \left\{ |c_i|^2\omega_i \cdot \int \Psi_i^*\Psi_i d\tau \right\} + \sum_{\substack{i,j \\ j\neq i}} c_i^* c_j\omega_j \int \Psi_i^*\Psi_j d\tau \\
&= \sum_i |c_i|^2\omega_i + 0
\end{aligned}$$

Operators

postulate IV

$\Longrightarrow c_i^2$ is the probability to find the quantum system in state i.

$\hat{\Omega} c_i \Psi_i = c_i \omega_i \Psi_i$ and $\int \Psi^* \Psi d\tau = 1 \quad \Rightarrow \sum_i |c_i|^2 = 1$

$$\begin{aligned}
1 &= \int \Psi^* \Psi d\tau = \int \sum_i c_i^* \Psi_i^* \sum_i c_i \Psi_i d\tau \\
&= \int \sum_i c_i^* \Psi_i^* c_i \Psi_i d\tau + \int \sum_{\substack{i,j \\ j \neq i}} c_i^* \Psi_i^* c_j \Psi_j d\tau \\
&= \sum_i \left\{ |c_i|^2 \cdot \int \Psi_i^* \Psi_i d\tau \right\} + \sum_{\substack{i,j \\ j \neq i}} c_i^* c_j \int \Psi_i^* \Psi_j d\tau \\
&= \sum_i |c_i|^2 + 0
\end{aligned}$$

Operators

commutator

$$\hat{A}\hat{B}\Psi = \hat{B}\hat{A}\Psi \text{ (commutative)}$$

$$\hat{A}\hat{B}\Psi \neq \hat{B}\hat{A}\Psi \text{ (non commutative)}$$

let's introduce the commutator for two operators $[\hat{A}, \hat{B}]$

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

$$[\hat{A}, \hat{B}] = 0 \text{ (}\hat{A}\text{ and }\hat{B}\text{ commute)}$$

$$[\hat{A}, \hat{B}] \neq 0 \text{ (}\hat{A}\text{ and }\hat{B}\text{ don't commute)}$$

Operators

commutator

if two operators have the same set of eigenfunctions they commute, i.e., $[\hat{\boldsymbol{A}}, \hat{\boldsymbol{B}}] = 0$

$$\begin{aligned}
\hat{\boldsymbol{A}}\Psi &= a \cdot \Psi \quad \text{and} \quad \hat{\boldsymbol{B}}\Psi = b \cdot \Psi \\
[\hat{\boldsymbol{A}}, \hat{\boldsymbol{B}}]\Psi &= \hat{\boldsymbol{A}}\hat{\boldsymbol{B}}\Psi - \hat{\boldsymbol{B}}\hat{\boldsymbol{A}}\Psi \\
&= \hat{\boldsymbol{A}}(b\Psi) - \hat{\boldsymbol{B}}(a\Psi) \\
&= b\hat{\boldsymbol{A}}\Psi - a\hat{\boldsymbol{B}}\Psi \\
&= b \cdot a\Psi - a \cdot b\Psi \\
&= (b \cdot a - a \cdot b)\Psi = 0 \cdot \Psi \quad \text{(numbers commute)}
\end{aligned}$$

Operators

commutator

- for compatible observables $[\hat{\boldsymbol{A}}, \hat{\boldsymbol{B}}] = 0$
- for incompatible observables $[\hat{\boldsymbol{A}}, \hat{\boldsymbol{B}}] \neq 0$

Heisenberg's uncertainty principle (derivation is not discussed)

$$\Delta A \cdot \Delta B \geqq \frac{1}{2}\left| \int \Psi^* [\hat{\boldsymbol{A}}, \hat{\boldsymbol{B}}] \Psi d\tau \right|$$

$$\Delta A \cdot \Delta B = \sigma_A \cdot \sigma_B$$

standard deviation:

$$\sigma_x = \sqrt{\langle x - \langle x \rangle \rangle^2} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

Operators

commutator

- The eigenfunction of momentum is completely delocalized (periodic boundary conditions): $\phi_1(x) = \frac{1}{\sqrt{L}} \cdot e^{ikx}$

  probability of finding the particle between x and $x + dx$

  $$\phi_1^*(x) \cdot \phi_1(x)dx = \frac{1}{L}dx$$

- The eigenfunction of position operator is completely localized, but has indefinite momentum: $\phi(x) = \delta(x - a)$

  A possible representation of the Dirac-delta:

  $$\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ik(x-a)}dk,$$

  where k is proportional to the momentum: $k = p/\hbar$

  $$\hat{\mathbf{x}}\phi(x) = a\phi(x)$$

Operators

commutator

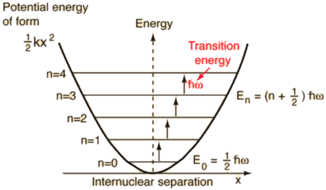
$$\hat{\boldsymbol{p}}_x = -i\hbar\frac{d}{dx} \quad \text{and} \quad \hat{\boldsymbol{x}} = x \text{ (multiply by } x\text{)}$$

$$\begin{aligned}
[\hat{\boldsymbol{p}}_x, \hat{\boldsymbol{x}}]\Psi(x) &= \hat{\boldsymbol{p}}_x\hat{\boldsymbol{x}}\Psi(x) - \hat{\boldsymbol{x}}\hat{\boldsymbol{p}}_x\Psi(x) \\
&= -i\hbar\frac{d[x\Psi(x)]}{dx} + xi\hbar\frac{d\Psi(x)}{dx} \\
&= -i\hbar\Psi(x) - i\hbar x\frac{d\Psi(x)}{dx} + i\hbar x\frac{d\Psi(x)}{dx} \\
&= -i\hbar\Psi(x) \\
[\hat{\boldsymbol{p}}_x, \hat{\boldsymbol{x}}] &= -i\hbar\hat{\boldsymbol{I}} \quad (\hat{\boldsymbol{I}} \text{ is the identity operator})
\end{aligned}$$

$$\Delta p_x \cdot \Delta x \geqq \frac{1}{2}\left|\int \Psi^*[\hat{\boldsymbol{p}}_x, \hat{\boldsymbol{x}}]\Psi d\tau\right| = \frac{1}{2}\left|\int \Psi^*\left(-i\hbar\hat{\boldsymbol{I}}\right)\Psi d\tau\right| = \frac{1}{2}\hbar|-i|\left|\int \Psi^*\Psi d\tau\right| = \frac{1}{2}\hbar$$

Heisenberg's uncertainty principle: more precisely the position of some particle is determined, the less precisely its momentum can be known.

The quantum harmonic oscillator



Potential energies are frequently approximated around the minimum by a quadratic term: e.g., in most of the cases the vibration motion of two atoms of a diatomic molecule can be well-described by a harmonic oscillator,

$V(R) \approx V(R_e) + \frac{1}{2}\frac{\partial^2 V}{\partial R^2}|_{R=R_e}(R - R_e)^2$.

Here R_e is the equilibrium distance, $k = \frac{\partial^2 V}{\partial R^2}|_{R=R_e}$ is the spring constant, and $R - R_e = x$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} + \frac{1}{2}kx^2\Psi(x) = E\Psi(x)$$

$$\frac{d^2\Psi}{dx^2} + \frac{2mE}{\hbar^2}\Psi - \frac{mk}{\hbar^2}x^2\Psi = 0$$

$$\frac{d^2\Psi}{dx^2} + (\lambda - \alpha^2 x^2)\Psi = 0$$

$$\lambda = \frac{2mE}{\hbar^2}$$

$$\alpha^2 = \frac{mk}{\hbar^2}$$

Let's try to find an asymptotic solution when $x \to \infty$

The quantum harmonic oscillator

asymptotic solution, $x \to \infty$

$$\frac{d^2\Psi}{dx^2} + (\lambda - \alpha^2 x^2)\Psi = 0$$

$$\begin{aligned}
\lambda &\ll \alpha^2 x^2 \\
\frac{d^2\Psi_\infty}{dx^2} &= \alpha^2 x^2 \Psi \\
\Psi_\infty &= e^{-\frac{\alpha x^2}{2}} \\
\frac{d\Psi_\infty}{dx} &= -\alpha x \cdot e^{-\frac{\alpha x^2}{2}} \\
\frac{d^2\Psi_\infty}{dx^2} &= -\alpha e^{-\frac{\alpha x^2}{2}} + (-\alpha x) \cdot (-\alpha x e^{-\frac{\alpha x^2}{2}}) \\
&= e^{-\frac{\alpha x^2}{2}} (\alpha^2 x^2 - \alpha) \approx \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}}
\end{aligned}$$

The quantum harmonic oscillator

$\Psi_\infty\times$ (a power series P), (Sommerfeld's polynomial method)

$$
\begin{aligned}
\psi &= e^{-\frac{\alpha x^2}{2}} \sum_{j=0}^{\infty} a_j x^j = \Psi_\infty P \\
\frac{d^2\Psi}{dx^2} &= \frac{d^2\Psi_\infty}{dx^2} P + 2\frac{d\Psi_\infty}{dx}\frac{dP}{dx} + \Psi_\infty \frac{d^2P}{dx^2} \\
\frac{d\Psi_\infty}{dx} &= -\alpha x e^{-\frac{\alpha x^2}{2}} \\
\frac{d^2\Psi_\infty}{dx^2} &= \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}} - \alpha e^{-\frac{\alpha x^2}{2}} \\
\frac{d^2\Psi}{dx^2} &= e^{-\frac{\alpha x^2}{2}} \left\{ \cancel{\alpha^2 x^2} P - \alpha P - 2\alpha x \frac{dP}{dx} + \frac{d^2P}{dx^2} \right\} \\
\frac{d^2\Psi}{dx^2} + (\lambda - \cancel{\alpha^2 x^2})\Psi &= e^{-\frac{\alpha x^2}{2}} \left\{ (\lambda - \alpha)P - 2\alpha x \frac{dP}{dx} + \frac{d^2P}{dx^2} \right\} = 0
\end{aligned}
$$

The quantum harmonic oscillator

$\Psi_\infty \times$ (a power series P)

$$\frac{d^2\Psi}{dx^2} + (\lambda - \alpha^2 x^2)\Psi = \left\{ (\lambda - \alpha)\ P - 2\alpha x \frac{dP}{dx} + \frac{d^2 P}{dx^2} \right\} e^{-\frac{\alpha x^2}{2}} = 0$$

$$P = \sum_{j=0}^{\infty} a_j x^j$$

$$\frac{dP}{dx} = \sum_{j=0}^{\infty} j a_j x^{j-1}$$

$$\frac{d^2 P}{dx^2} = \sum_{j=0}^{\infty} j(j-1) a_j x^{j-2} = \sum_{j=0}^{\infty} (j+1) j a_{j+1} x^{j-1} = \sum_{j=0}^{\infty} (j+2)(j+1) a_{j+2} x^j$$

$$\frac{d^2\Psi}{dx^2} + (\lambda - \alpha^2 x^2)\Psi =$$

$$\sum_{j=0}^{\infty} \left\{ (\lambda - \alpha)\, a_j - 2\alpha j a_j + (j+1)(j+2) a_{j+2} \right\} x^j e^{-\frac{\alpha x^2}{2}} = 0$$

The quantum harmonic oscillator

the power series solution

$$0 = \sum_{j=0}^{\infty} \left[(j+1)(j+2)a_{j+2} - \alpha(2j+1)a_j + \lambda a_j \right] x^j$$

to hold for all values of x, the coefficients must be zero

$$\begin{aligned} 0 &= (j+1)(j+2)a_{j+2} - \alpha(2j+1)a_j + \lambda a_j \\ a_{j+2} &= \frac{\alpha(2j+1) - \lambda}{(j+1)(j+2)} a_j \end{aligned}$$

The quantum harmonic oscillator

the power series solution

Because $\Psi = e^{-\frac{\alpha x^2}{2}} \sum_{j=0}^{\infty} a_j x^j \rightarrow \infty$ as $x \rightarrow \infty$

one must terminate the power series

let's terminate at $j = v + 2$,

$$a_{v+2} = 0$$

$$a_{v+2} = 0 = \frac{\alpha(2v+1) - \lambda}{(v+1)(v+2)} a_v$$

$$\lambda = \alpha(2v+1)$$

higher order terms will be zero as well

$$\lambda = \frac{2mE}{\hbar^2}$$

$$\alpha = \frac{\sqrt{mk}}{\hbar}$$

$$\frac{2mE}{\hbar^2} = \frac{\sqrt{mk}}{\hbar}(2v+1)$$

$$E = \frac{1}{2}\sqrt{\frac{k}{m}}\hbar(2v+1)$$

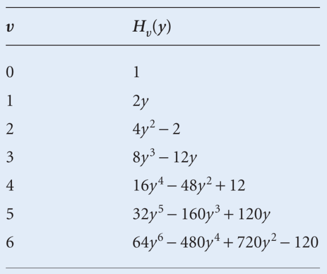
$$E = \hbar\omega(v + \frac{1}{2}), \quad v = 0, 1, 2, \ldots$$

The quantum harmonic oscillator

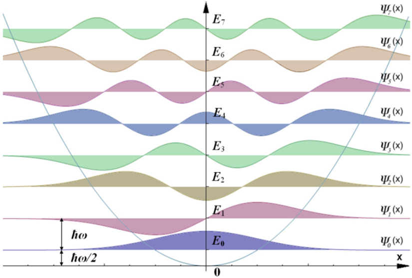
Hermite polynomials

$$\Psi(x) = N_v \cdot H_v(y) \cdot e^{\frac{-y^2}{2}}$$

- N_v is a normalization factor
- $H_v(y)$ is a Hermite polynomial
- $y = \sqrt{\alpha}x$
- recursion, $H_{v+1} - 2yH_v + 2vH_{v-1} = 0$;

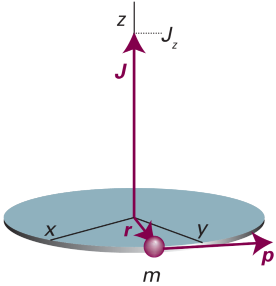


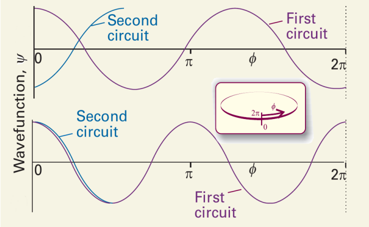
v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$



Particle on the ring problem

de Broglie + classical physics





z component of angular momentum:

$$J_z = rp$$

$$E_{rot} = \frac{J_z^2}{2I}, \quad I = mr^2$$

$$p = \frac{h}{\lambda} \quad J_z = r\frac{h}{\lambda}$$

$$2\pi r = m_\ell \cdot \lambda \quad m_\ell \in 0, \pm 1, \pm 2, \ldots$$

$$J_z = \frac{m_\ell \cancel{\lambda} h}{2\pi \cancel{\lambda}} = m_\ell \hbar$$

$$E_{rot} = \frac{m_\ell^2 \hbar^2}{2I}$$

Particle on the ring problem

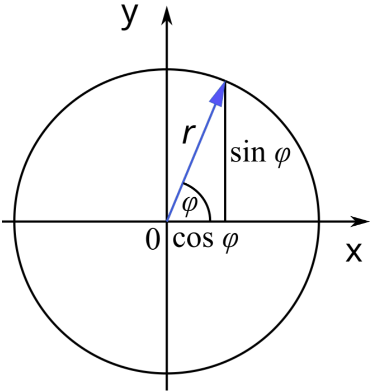
Schrödinger equation, $\hat{V} = 0$

$\hat{\mathrm{H}}\Psi(x) = E\Psi(x)$

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2}\right\} = E\Psi$$

Particle on the ring problem

polar coordinates; plane, constant radius



$$x = r \cdot \cos\varphi$$

$$y = r \cdot \sin\varphi$$

$$r^2 = x^2 + y^2$$

$$\varphi = \tan^{-1}\frac{y}{x}$$

$$(\tan^{-1} x)' = \frac{1}{1+x^2}$$

$$f(r,\varphi) = f(r(x,y), \varphi(x,y))$$

Particle on the ring problem

polar coordinates; plane, constant radius

$$f(r,\varphi) = f(r(x,y),\varphi(x,y))$$
$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial f}{\partial \varphi}\frac{\partial \varphi}{\partial x}$$
$$\frac{\partial f}{\partial y} = \frac{\partial f}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial f}{\partial \varphi}\frac{\partial \varphi}{\partial y}$$

if r =const then $\frac{\partial r}{\partial x} = \frac{\partial r}{\partial y} = 0$

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial \varphi}\frac{\partial \varphi}{\partial x}$$
$$\frac{\partial f}{\partial y} = \frac{\partial f}{\partial \varphi}\frac{\partial \varphi}{\partial y}$$

$$\frac{\partial \varphi}{\partial x} = \frac{1}{1+(y/x)^2}\cdot\frac{-y}{x^2} = \frac{-y}{r^2} = \frac{-\sin\varphi}{r}$$
$$\frac{\partial \varphi}{\partial y} = \frac{1}{1+(y/x)^2}\cdot\frac{1}{x} = \frac{x}{r^2} = \frac{\cos\varphi}{r}$$

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial \varphi}\frac{-\sin\varphi}{r}$$
$$\frac{\partial f}{\partial y} = \frac{\partial f}{\partial \varphi}\frac{\cos\varphi}{r}$$

Particle on the ring problem

polar coordinates; plane, constant radius

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial \varphi}\frac{-\sin\varphi}{r} = g(r(x,y),\varphi(x,y))$$

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial \frac{\partial f}{\partial x}}{\partial x} = \frac{\partial \frac{\partial f}{\partial x}}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial \frac{\partial f}{\partial x}}{\partial \varphi}\cdot\frac{\partial\varphi}{\partial x}$$

$$= \frac{\partial \frac{\partial f}{\partial x}}{\partial \varphi}\cdot\frac{\partial\varphi}{\partial x} = \frac{\partial \frac{\partial f}{\partial\varphi}\cdot\frac{-\sin\varphi}{r}}{\partial\varphi}\cdot\frac{\partial\varphi}{\partial x}$$

$$= (-\frac{\partial^2 f}{\partial\varphi^2}\cdot\frac{\sin\varphi}{r} + \frac{\partial f}{\partial\varphi}\cdot\frac{-1}{r}\frac{\partial\sin\varphi}{\partial\varphi})(-\frac{\sin\varphi}{r})$$

$$= \frac{\sin^2\varphi}{r^2}\frac{\partial^2 f}{{\partial\varphi^2}^2} + \frac{1}{r^2}\cos\varphi\sin\varphi\frac{\partial f}{\partial\varphi}$$

$$\frac{\partial f}{\partial y} = \frac{\partial f}{\partial \varphi}\frac{\cos\varphi}{r} = h(r(x,y),\varphi(x,y))$$

$$\frac{\partial^2 f}{\partial y^2} = \frac{\partial \frac{\partial f}{\partial y}}{\partial y} = \frac{\partial \frac{\partial f}{\partial y}}{\partial r}\frac{\partial r}{\partial y} + \frac{\partial \frac{\partial f}{\partial y}}{\partial \varphi}\cdot\frac{\partial\varphi}{\partial y}$$

$$= \frac{\partial \frac{\partial f}{\partial y}}{\partial \varphi}\frac{\partial\varphi}{\partial y} = \frac{\partial \frac{\partial f}{\partial\varphi}\cdot\frac{\cos\varphi}{r}}{\partial\varphi}\cdot\frac{\partial\varphi}{\partial y}$$

$$= (-\frac{\partial^2 f}{\partial\varphi^2}\cdot\frac{\cos\varphi}{r} + \frac{\partial f}{\partial\varphi}\cdot\frac{1}{r}\frac{\partial\cos\varphi}{\partial\varphi})(\frac{\cos\varphi}{r})$$

$$= \frac{\cos^2\varphi}{r^2}\frac{\partial^2 f}{{\partial\varphi^2}^2} + \frac{1}{r^2}(-\sin\varphi)\cos\varphi\frac{\partial f}{\partial\varphi}$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}$$

Particle on the ring problem

polar coordinates; plane, constant radius

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}\right\}=E\Psi$$

$$\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}=\frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}$$

$$-\frac{\hbar^2}{2mr^2}\frac{d^2\Psi(\varphi)}{d\varphi^2}=E\Psi(\varphi)$$

$$\frac{d^2\Psi(\varphi)}{d\varphi^2}=-\frac{2IE}{\hbar^2}\Psi(\varphi)$$

$$\Psi(\varphi)=Ae^{im_\ell\varphi}$$

$$\frac{d^2\Psi(\varphi)}{d\varphi^2}=-m_\ell^2\cancel{A}e^{im_\ell\varphi}=-\frac{2IE}{\hbar^2}\cancel{A}e^{im_\ell\varphi}$$

$$m_\ell^2=\frac{2IE}{\hbar^2}$$

$$E=\frac{m_\ell^2\hbar^2}{2I}$$

Particle on the ring problem

polar coordinates; plane, constant radius

$$\Psi(\varphi) = Ae^{im_\ell \varphi}$$

Born's interpretation

$$\int_{-\infty}^{\infty} \Psi^*(\varphi)\Psi(\varphi)d\varphi = 1$$

$$\int_0^{2\pi} Ae^{-im_\ell \varphi}Ae^{im_\ell \varphi}d\varphi = A^2 2\pi = 1$$

$$\Psi(\varphi) = \frac{1}{\sqrt{2\pi}}e^{im_\ell \varphi}$$

cyclic boundary condition:

$$\Psi(\varphi + 2\pi) = \Psi(\varphi)$$

$$\begin{aligned}\Psi(\varphi + 2\pi) &= \frac{1}{\sqrt{2\pi}}e^{im_\ell(\varphi+2\pi)}\\ &= \frac{1}{\sqrt{2\pi}}e^{im_\ell(\varphi)}e^{(i\pi)2m_\ell}\\ &= \Psi(\varphi)(-1)^{2m_\ell}\end{aligned}$$

$$1 = (-1)^{2m_\ell} \Leftrightarrow m_\ell = 0, \pm 1, \pm 2, \ldots$$

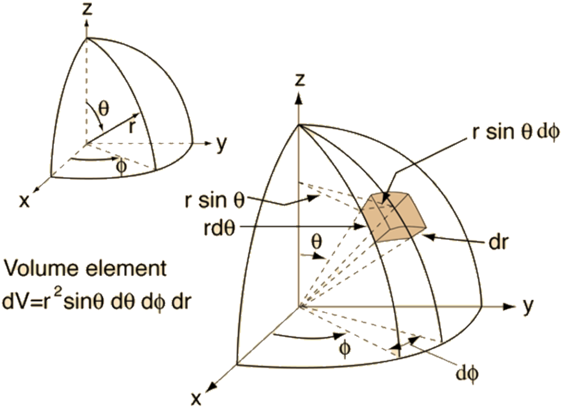
$$E = \frac{m_\ell^2 \hbar^2}{2I}$$

Spherical coordinates

$$x = r \sin\vartheta \cos\varphi \qquad r = \sqrt{x^2 + y^2 + z^2}$$

$$y = r \sin\vartheta \sin\varphi \qquad \vartheta = \cos^{-1}\frac{z}{r}$$

$$z = r \cos\vartheta \qquad \varphi = \tan^{-1}\frac{y}{x}$$



Volume element
$dV = r^2 \sin\theta\, d\theta\, d\phi\, dr$

Spherical coordinates

the Hamiltonian in Cartesian coordinates

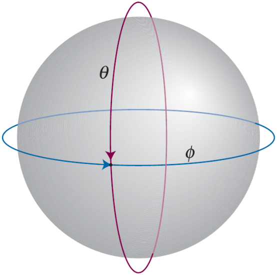
$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{V}$$

$$\nabla^2 = \nabla \cdot \nabla = \Delta \quad \text{laplacian}$$

$$\nabla = \mathbf{e}_x \frac{\partial}{\partial x} + \mathbf{e}_y \frac{\partial}{\partial y} + \mathbf{e}_z \frac{\partial}{\partial z}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}(\nabla^2) + \hat{V}$$



Particle on a sphere

the Hamiltonian in spherical coordinates, $r = \text{constant}$

without derivation:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2 \sin\vartheta}\frac{\partial}{\partial\vartheta}(\sin\vartheta\frac{\partial}{\partial\vartheta}) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$$

Supposing that $r = \text{constant}$

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\hat{\Lambda}^2\Psi(\vartheta,\varphi) = E\Psi(\vartheta,\varphi),$$

$$\text{where } \hat{\Lambda}^2 = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}(\sin\vartheta\frac{\partial}{\partial\vartheta}) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$$

$$-\frac{\hbar^2}{2I}\hat{\Lambda}^2\Psi(\vartheta,\varphi) = E\Psi(\vartheta,\varphi)$$

separation of variables: $\Psi(\vartheta,\varphi) = \Theta(\vartheta)\cdot\Phi(\varphi)$

Particle on a sphere

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}(\sin\vartheta\frac{\partial\Theta\Phi}{\partial\vartheta})+\frac{1}{\sin^2\vartheta}\frac{\partial^2\Theta\Phi}{\partial\varphi^2}=-\frac{2IE}{\hbar^2}\Theta\Phi$$

$$\frac{\Phi}{\sin\vartheta}\frac{\partial}{\partial\vartheta}(\sin\vartheta\frac{\partial\Theta}{\partial\vartheta})+\frac{\Theta}{\sin^2\vartheta}\frac{\partial^2\Phi}{\partial\varphi^2}+\frac{2IE}{\hbar^2}\Theta\Phi=0$$

multiply by $\frac{\sin^2\vartheta}{\Theta\Phi}$

$$\frac{\sin\vartheta}{\Theta}\frac{\partial}{\partial\vartheta}(\sin\vartheta\frac{\partial\Theta}{\partial\vartheta})+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}+\frac{2IE}{\hbar^2}\sin^2\vartheta=0$$

Here $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}$ must be a constant!

It is supposed to be negative to obtain a periodic solution.

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=-m_\ell^2\Longrightarrow\Phi=e^{im_\ell\varphi}$$

Particle on a sphere

$$\frac{\sin\vartheta}{\Theta}\frac{\partial}{\partial\vartheta}(\sin\vartheta\frac{\partial\Theta}{\partial\vartheta}) + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} + \frac{2IE}{\hbar^2}\sin^2\vartheta = 0$$

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = -m_\ell^2$$

$$\sin\vartheta\frac{\partial}{\partial\vartheta}(\sin\vartheta\frac{\partial\Theta}{\partial\vartheta}) - m_\ell^2\Theta + \frac{2IE}{\hbar^2}\sin^2\vartheta\Theta = 0$$

introduce $\zeta = \cos\vartheta \Rightarrow \frac{\partial}{\partial\vartheta} = \frac{\partial\zeta}{\partial\vartheta}\frac{\partial}{\partial\zeta} = -\sin\vartheta\frac{\partial}{\partial\zeta}$

please, note that $\sin^2\vartheta = 1 - \zeta^2$

$$(1-\zeta^2)\frac{\partial}{\partial\zeta}((1-\zeta^2)\frac{\partial\Theta}{\partial\zeta}) - m_\ell^2\Theta + \frac{2IE}{\hbar^2}(1-\zeta^2)\Theta = 0$$

Particle on a sphere

$$(1-\zeta^2)\left[\frac{\partial^2\Theta}{\partial\zeta^2} - 2\zeta\frac{\partial\Theta}{\partial\zeta} + \left\{\frac{2IE}{\hbar^2} - \frac{m_\ell^2}{1-\zeta^2}\right\}\Theta\right] = 0$$

This equation can be solved using the

$$\Theta(\zeta) = (1-\zeta^2)^{|m_\ell|/2}\sum_{r=0}^{\infty} c_r\zeta^r \text{ Ansatz.}$$

To obtain non-singular solutions $\frac{2IE}{\hbar^2} = \ell(\ell+1)$,

where ℓ is an integer $\ell \geq |m_\ell|$.

$$(1-\zeta^2)\left[\frac{\partial^2\Theta}{\partial\zeta^2} - 2\zeta\frac{\partial\Theta}{\partial\zeta} + \left\{\ell(\ell+1) - \frac{m_\ell^2}{1-\zeta^2}\right\}\Theta\right] = 0$$

associated Legendre differential equation

spherical harmonics $Y_{\ell,m_\ell}(\vartheta,\varphi) = \Theta_{\ell m_\ell}(\cos(\vartheta))e^{im_\ell\phi}$

Particle on a sphere

$$
\begin{aligned}
-\frac{\hbar^2}{2m}\frac{1}{r^2}\hat{\Lambda}^2 Y_{\ell,m_\ell}(\vartheta,\varphi) &= EY_{\ell,m_\ell}(\vartheta,\varphi),\\
E =& \ell(\ell+1)\frac{\hbar^2}{2I}, \quad \ell = 0,1,2,\ldots\\
m_\ell =& -\ell, -(\ell-1),\ldots,0,\ldots,\ell-1,\ell
\end{aligned}
$$

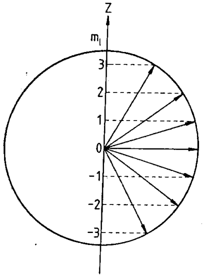
every energy level is $(2\ell+1)$-fold degenerate

ℓ - orbital angular momentum quantum number

m_ℓ - magnetic quantum number

$$-\hbar^2\hat{\Lambda}^2 Y_{\ell,m_\ell}(\vartheta,\varphi) = \hbar^2\ell(\ell+1)Y_{\ell,m_\ell}(\vartheta,\varphi)$$

Angular momentum in QM



$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \Leftrightarrow \hat{\mathbf{L}} = \frac{\hbar}{i}\hat{\mathbf{r}} \times \nabla$$

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

$$\hat{L}_z\Phi(\phi) = \frac{\hbar}{i}\frac{\partial\Phi}{\partial\phi} = \hbar m\Phi(\phi) \Rightarrow \Phi(\phi) = e^{im\phi}$$

From the periodic boundary condition:

$$\Phi(\phi + 2\pi) = \Phi(\phi), m = 0, \pm1 \pm 2, \pm3, \dots$$

$$\hat{\mathbf{L}}^{\mathbf{2}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2\left\{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}(\sin\vartheta\frac{\partial}{\partial\vartheta}) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right\} = -\hbar^2\hat{\Lambda}^2$$

$$\hat{L}^2 Y_{\ell,m_\ell}(\vartheta,\phi) = \hbar^2\ell(\ell+1)Y_{\ell,m_\ell}(\vartheta,\varphi) \Rightarrow \begin{array}{l} \ell = 0, 1, 2, \dots \\ m = -\ell, -\ell+1, \dots, (\ell-1), \ell \end{array}$$

Spherical harmonics

wavefunctions

ℓ	m_ℓ	$Y_{\ell,m_\ell}(\vartheta,\varphi)$
0	0	$\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$
1	0	$\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\vartheta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{\frac{1}{2}}\sin\vartheta e^{\pm i\varphi}$
2	0	$\left(\frac{5}{16\pi}\right)^{\frac{1}{2}}(3\cos^2\vartheta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{\frac{1}{2}}\cos\vartheta\sin\vartheta e^{\pm i\varphi}$
	±2	$\mp\left(\frac{15}{32\pi}\right)^{\frac{1}{2}}\sin^2\vartheta e^{\pm 2i\varphi}$

real combinations: $p_x=\dfrac{Y_{1,-1}-Y_{1,1}}{\sqrt{2}},\quad p_y=\dfrac{Y_{1,-1}+Y_{1,1}}{i\sqrt{2}}$

Hydrogen atom

$$\left\{-\frac{\hbar^2}{2\mu}\nabla^2 \; -\frac{e^2}{4\pi\epsilon_0 r}\right\}\Psi(r,\vartheta,\varphi) = E\Psi(r,\vartheta,\varphi)$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\vartheta}\frac{\partial}{\partial\vartheta}(\sin\vartheta\frac{\partial}{\partial\vartheta}) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{\Lambda^2}{r^2}$$

Hydrogen atom

Separation of variables: $\Psi(r,\vartheta,\varphi) = R(r)Y_{\ell,m_\ell}(\vartheta,\varphi)$

$$-\frac{\hbar^2}{2\mu r^2}\left\{Y_{\ell,m_\ell}\frac{\partial}{\partial r}(r^2\frac{\partial R}{\partial r}) + R(r)\Lambda^2 Y_{\ell,m_\ell}\right\} - \frac{e^2}{4\pi\epsilon_0 r}RY_{\ell,m_\ell} = ERY_{\ell,m_\ell}$$

$$-\frac{\hbar^2}{2\mu r^2}\left\{Y_{\ell,m_\ell}\frac{\partial}{\partial r}(r^2\frac{\partial R}{\partial r}) + R(r)\ell(\ell+1)Y_{\ell,m_\ell}\right\} - \frac{e^2}{4\pi\epsilon_0 r}RY_{\ell,m_\ell} = ERY_{\ell,m_\ell}$$

$$-\frac{\hbar^2}{2\mu r^2}\left\{\frac{\partial}{\partial r}(r^2\frac{\partial R}{\partial r}) + R(r)\ell(\ell+1)\right\} - \frac{e^2}{4\pi\epsilon_0 r}R = ER$$

The solution can be obtained using the Sommerfeld's polynomial method.

Hydrogen atom

The results:

$$R_n^\ell(r) = \frac{1}{r} e^{-r/r_0} P_n^\ell(\frac{2r}{r_0}), \text{ where } r_0 = n\frac{4\pi\epsilon_0\hbar^2}{\mu e^2}, \; 0 \leq l < n,$$

$n = 1, 2, \ldots$ and $P_n^l(x)$ are the so-called Laguerre polynomials.

$$\text{Schrödinger: } E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2}$$

$$\text{Bohr: } E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2 n^2}$$

Hydrogen atom

radial wavefunctions, Laguerre polynomials

$$\Psi(r,\vartheta,\varphi) = R_{n,\ell}(r) Y_{\ell,m_\ell}(\vartheta,\varphi)$$

n	ℓ	$R_{n,\ell}$
1	0	$2\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-\varrho/2}$
2	0	$\frac{1}{\sqrt{8}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} (2-\varrho)e^{-\varrho/2}$
2	1	$\frac{1}{\sqrt{24}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho e^{-\varrho/2}$
3	0	$\frac{1}{\sqrt{243}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} (6-6\varrho+\varrho^2)e^{-\varrho/2}$
3	1	$\frac{1}{\sqrt{486}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} (4\varrho-\varrho^2)e^{-\varrho/2}$
3	2	$\frac{1}{\sqrt{2430}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho^2 e^{-\varrho/2}$

$\varrho = \frac{2Z\mu e^2 r}{4\pi\varepsilon_0\hbar^2 n} = \frac{2Zr}{na}$, where $a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$ is the Bohr radius

Hydrogen atom

radial wavefunctions, Laguerre polynomials

hydrogenlike atomic wavefunctions: $\Psi_{n,\ell,m_\ell}(r,\vartheta,\varphi) = R_{n,\ell}(r)Y_{\ell,m_\ell}(\vartheta,\varphi)$

n	ℓ	m_ℓ	$R_{n,\ell}$	Y_{ℓ,m_ℓ}
1	0	0	$2\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-\varrho/2}$	$\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$
2	0	0	$\frac{1}{\sqrt{8}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} (2-\varrho)e^{-\varrho/2}$	$\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$
2	1	0	$\frac{1}{\sqrt{24}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho e^{-\varrho/2}$	$\left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\vartheta$
2	1	$+1$	$\frac{1}{\sqrt{24}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho e^{-\varrho/2}$	$\left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\vartheta e^{i\varphi}$
2	1	-1	$\frac{1}{\sqrt{24}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho e^{-\varrho/2}$	$\left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\vartheta e^{-i\varphi}$
3	0	0	$\frac{1}{\sqrt{243}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} (6-6\varrho+\varrho^2)e^{-\varrho/2}$	$\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$

$\varrho = \frac{2Z\mu e^2 r}{4\pi\varepsilon_0\hbar^2 n} = \frac{2Zr}{na}$, where $a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$ is the Bohr radius

Hydrogen atom

atomic units, fixed nucleus

$$\left\{-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0 r}\right\}\Psi = E\Psi$$

$$x \to \lambda x',\ y \to \lambda y',\ z \to \lambda z'$$

$$\frac{\partial^2}{\partial x^2} = \frac{1}{\lambda^2}\frac{\partial^2}{\partial x'^2}$$

$$r = \sqrt{x^2 + y^2 + z^2} \Rightarrow r \to \sqrt{(\lambda x')^2 + (\lambda y')^2 + (\lambda z')^2} = \lambda r'$$

Hydrogen atom

atomic units, fixed nucleus

$$\left\{-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0 r}\right\}\Psi = E\Psi \qquad E_a\left\{-\frac{1}{2}(\nabla_e')^2 - \frac{1}{r'}\right\}\Psi' = \mathcal{E}\Psi'$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$\left\{-\frac{\hbar^2}{2m_e\lambda^2}(\nabla_e')^2 - \frac{e^2}{4\pi\epsilon_0 r'\lambda}\right\}\Psi' = E\Psi' \qquad \left\{-\frac{1}{2}(\nabla_e')^2 - \frac{1}{r'}\right\}\Psi' = \mathcal{E}'\Psi'$$

select λ to fulfill

$$\mathcal{E}' = \frac{\mathcal{E}}{E_a}$$

$$\frac{\hbar^2}{m_e\lambda^2} = \frac{e^2}{4\pi\epsilon_0\lambda} = E_a$$

atomic units for distance and energy:

$$\Downarrow$$

$$\lambda = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0, \text{Bohr radius}$$

$$E_a\left\{-\frac{1}{2}(\nabla_e')^2 - \frac{1}{r'}\right\}\Psi' = \mathcal{E}\Psi'$$

$$E_a = \frac{\hbar^2}{m_e a_0^2}, \text{hartree}$$

Atomic orbitals

shells and subshells

atomic orbital (AO) - one electron wavefunction (Ψ_{n,ℓ,m_ℓ})

quantum numbers:

- n - principal
- ℓ - azimuthal (orbital angular momentum)
- m_ℓ - magnetic

Atomic orbitals

shells and subshells

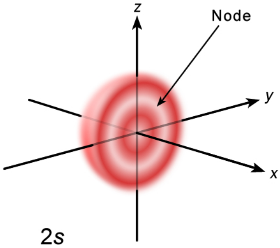
- a shell consists of AOs with the same principal quantum number n (K, L, M, N, . . .)
- subshell: orbitals with the same n and ℓ quantum numbers (s, p, d, f, g, . . . subshells)

for example: n=1,2, and 3

Atomic orbitals

s orbitals, $\ell = 0$, $m_\ell = 0$

- $\Psi_s = c \cdot \left(\frac{Z}{a}\right)^{\frac{3}{2}} P_n(\varrho) e^{-\varrho/2} \cdot \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$
- the angular wavefunction is constant, $Y_{0,0}(\vartheta, \varphi) = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$
- spherical symmetry
- the $P_n(\varrho)$s are Laguerre polynomials, and their roots give the number of nodal surfaces



Atomic orbitals

p orbitals, $\ell = 1$, $m_\ell = 0, \pm 1$

$$\Psi_{p_{\mathbf{0}}} = \frac{1}{\sqrt{24}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho e^{-\varrho/2} \cdot \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\vartheta = \varrho \cos\vartheta f(\varrho) = z f(\varrho) = \Psi_{p_z}$$

$$\Psi_{p_{+\mathbf{1}}} = \frac{1}{\sqrt{24}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho e^{-\varrho/2} \cdot \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\vartheta e^{i\varphi}$$

$$\Psi_{p_{-\mathbf{1}}} = \frac{1}{\sqrt{24}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho e^{-\varrho/2} \cdot \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\vartheta e^{-i\varphi}$$

Atomic orbitals

p orbitals, $\ell = 1,\ m_\ell = 0, \pm 1$

to get rid of the complex variable we take linear combinations of $\Psi_{p_{+\mathbf{1}}}$ and $\Psi_{p_{-\mathbf{1}}}$

$$\Psi_{p_x} = \Psi_{p_{+\mathbf{1}}} + \Psi_{p_{-\mathbf{1}}} = \frac{1}{\sqrt{24}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho e^{-\varrho/2} \cdot \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\vartheta \cdot (e^{i\varphi} + e^{-i\varphi})$$

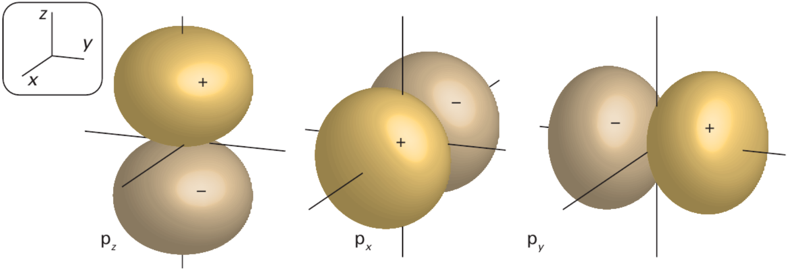
$$\Psi_{p_y} = \Psi_{p_{+\mathbf{1}}} - \Psi_{p_{-\mathbf{1}}} = \frac{1}{\sqrt{24}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \varrho e^{-\varrho/2} \cdot \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\vartheta \cdot (e^{i\varphi} - e^{-i\varphi})$$

$$\varrho \sin\vartheta \cdot (e^{i\varphi} + e^{-i\varphi}) = \varrho \sin\vartheta \cdot 2\cos\varphi \Rightarrow \Psi_{p_x} = xf(\varrho)$$

$$\varrho \sin\vartheta \cdot (e^{i\varphi} - e^{-i\varphi}) = \varrho \sin\vartheta \cdot 2i\sin\varphi \Rightarrow \Psi_{p_y} = yf(\varrho)$$

Atomic orbitals

p orbitals, $\ell = 1$



Atomic orbitals

d orbitals, $\ell = 2$

similarly to p orbitals we make linear combinations of complex WFs to get real functions

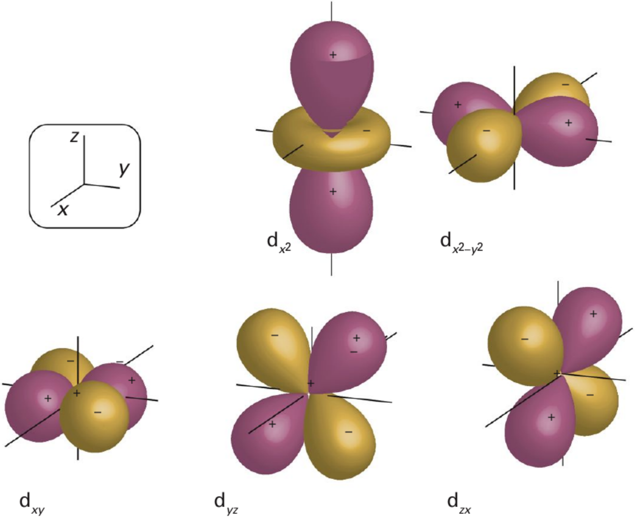
$$d_{xy} = xyf(r) \qquad d_{x^2-y^2} = \frac{1}{2}(x^2 - y^2)f(r)$$

$$d_{yz} = yzf(r) \qquad d_{z^2} = \frac{\sqrt{3}}{2}(3z^2 - r^2)f(r)$$

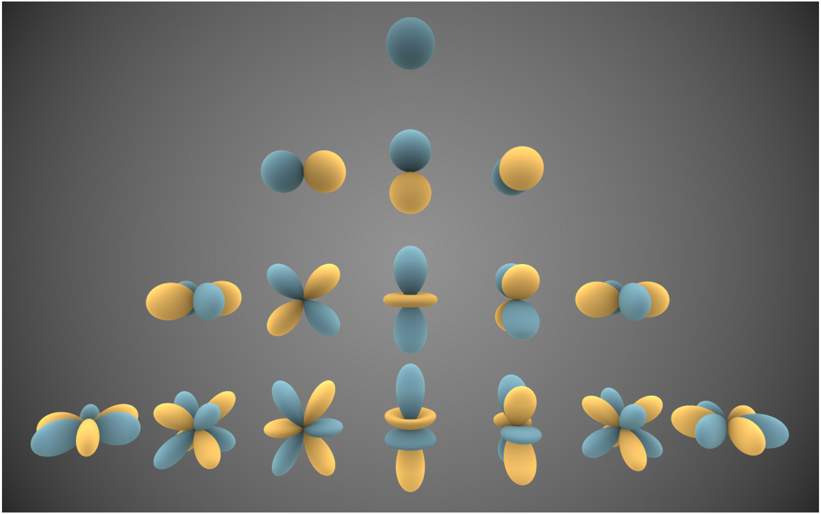
$$d_{zx} = zxf(r)$$

Atomic orbitals

d orbitals, $\ell = 2$



Spherical harmonics



Atomic orbitals

shells and subshells

atomic orbital (AO) - one electron wavefunction (Ψ_{n,ℓ,m_ℓ})

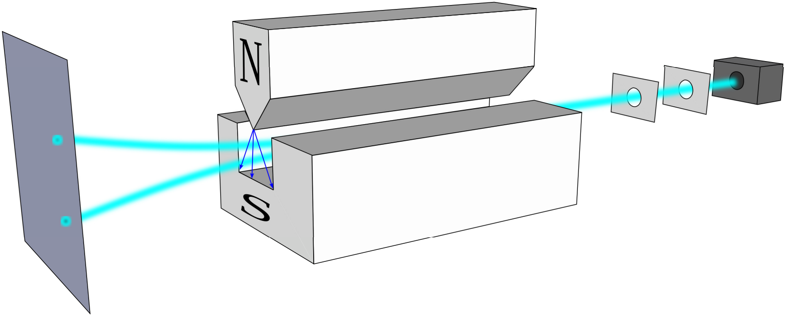
quantum numbers:

- n - principal
- ℓ - azimuthal (orbital angular momentum)
- m_ℓ - magnetic
- m_s - spin

spin

an intrinsic angular momentum of a particle

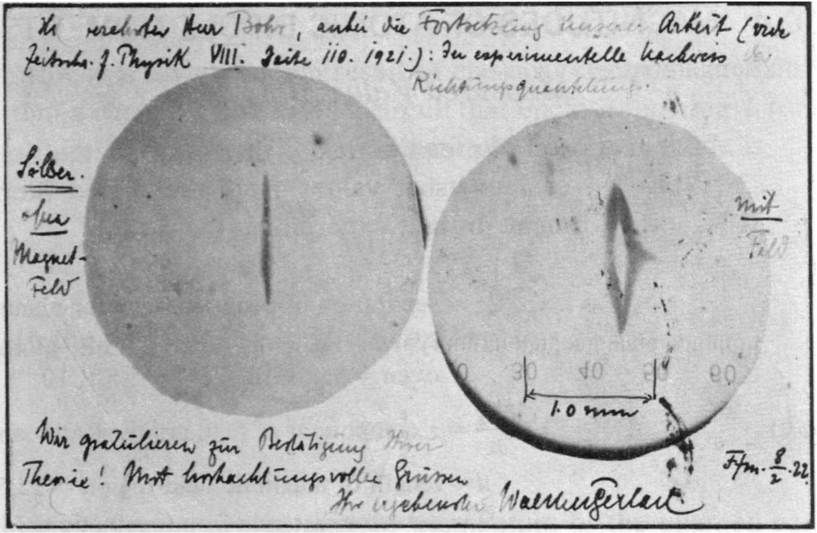
Stern - Gerlach experiment(1922)



A beam of silver atoms. Inhomogeneous magnetic field!

spin

an intrinsic angular momentum of a particle



Hochverehrter Herr Bohr, anbei die Fortsetzung unserer Arbeit (vide Zeitschr. f. Physik VIII. Seite 110. 1921): den experimentellen Nachweis der Richtungsquantelung.

Silber.
ohne
Magnet-
Feld

mit
Feld

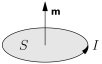
Wir gratulieren zur Bestätigung Ihrer Theorie! Mit hochachtungsvollen Grüssen
Ihr ergebenster Walther Gerlach

Ffm. $\frac{8}{2}$.22

spin

Magnetic dipole moment, relation to the angular momentum

Classical description



$\mathbf{m} = SI\mathbf{n}$, where I is the current in an electric current loop, S is the surface of the loop, and vector $\mathbf{n}$ perpendicular to the loop.

If the current is produced by a single charged particle $I = e/T$, where T is the periodic time of the motion.

$$I = \frac{2m_e\pi re}{2m_e\pi rT} = \frac{pe}{2m_e\pi r} = \frac{erp}{2m_e\pi r^2} = \frac{e\ell}{2m_e\pi r^2}$$

$$m = \frac{r^2\pi e\ell}{2m_e\pi r^2} = \frac{e\ell}{2m_e}$$

Torque (moment of force): $\mathbf{r} \times \mathbf{F} = \mathbf{m} \times \mathbf{B}$

Force on a moment : $\mathbf{F} = \nabla(\mathbf{mB})$

spin

an intrinsic angular momentum of a particle

Stern - Gerlach experiment

- to confirm the Bohr-Sommerfeld theory

  ($\oint_{E(\mathbf{p},\mathbf{r})=const.} \mathbf{p}d\mathbf{r} = nh$)

  They assumed that for Ag atoms L=1. (We know that it is zero [$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^1$].)
- If L=1 then the beam should split into three components.
- Ag atoms are in $\ell = 0$ state $\Rightarrow$ no splitting
- the spatial orientation is quantized

spin

an intrinsic angular momentum of a particle

Stern - Gerlach experiment(1922)

- Uhlenbeck and Goudsmit - spin(1925): An internal angular momentum of the electron ($\hat{S}$) produces on additional magnetic moment:$\hat{\mathbf{m}}_z = -\frac{g\mu_B}{\hbar}\hat{\mathbf{S}}_z$, where g is the g-factor, and $\mu_B = \frac{e\hbar}{2m}$ is the Bohr magneton, e is the positive unit charge.
- no spin in non-relativistic quantum mechanics
- *ad hoc* introduction by Pauli
- it occurs naturally in Dirac's relativistic QM(1928) ($g = 2$)
- correction from quantum electrodynamics (1948): $g = 2.002319$

spin

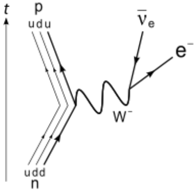
an intrinsic angular momentum of a particle

The intrinsic angular momentum (S) can be characterized by the eigenvalues of the $\hat{S}_z$ and $\hat{S}^2$ operators, where $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$.

$\hat{S}_z\sigma = \hbar s_z\sigma$

$\hat{S}^2\sigma = \hbar^2 s(s+1)\sigma$

The possible values of s are $0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots,$ while $m_s = -s, -s+1, \dots, s$



- fermions like electron, proton, neutron (half-integer spin, $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$)
- bosons like photon, W bosons, ^{4}He (integer spin, $s = 0, 1, 2, \dots$)

The eigenvalues of spin for an electron:

$\hat{S}_z\sigma = \pm\frac{\hbar}{2}\sigma$, frequently used notation: $\hat{S}_z\alpha = \frac{\hbar}{2}\alpha$, $\hat{S}_z\beta = -\frac{\hbar}{2}\beta$

spin

Wave function of the particle and the spin

The wavefunction of the electron must be extended by the spin: E.g., the wavefunction of the electron in the H atom:

$\Psi_{n,\ell,m_\ell,m_s=\frac{1}{2}}(r,\theta,\phi) = \Psi_{n,\ell,m_\ell}(r,\theta,\phi)\alpha$

Wave functions with different spins are orthogonal to each other.

Vector representation: $\Psi_{n,\ell,m_\ell}\alpha = \begin{pmatrix} \Psi_{n,\ell,m_\ell} \\ 0 \end{pmatrix}$, $\Psi_{n,\ell,m_\ell}\beta = \begin{pmatrix} 0 \\ \Psi_{n,\ell,m_\ell} \end{pmatrix}$

The x, y, z component of the total angular momentum of a particle is the sum of the orbital and spin angular momentums:
$\hat{J}_i = \hat{L}_i + \hat{S}_i, i = x, y, z,\ \hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$
In the non-relativistic case (the speed of the particles are negligible with respect to the speed of light) the $\hat{J}^2, \hat{J}_z, \hat{S}^2, \hat{S}_z, \hat{L}^2, \hat{L}_z$ operators commute with each other and with the Hamilton operator, i.e., we can find a common set of eigenfunctions for all these operators. These operators belong to the compatible measurable physical quantities.
In the relativistic case: only $\hat{J}^2, \hat{J}_z$ and $\hat{H}$ commute with each other.

spin

Magnetic dipole moment in QM

In general $\hat{\mathbf{m}}_z = -g\frac{e}{2m}\hat{\mathbf{J}}_z$

- for the orbital angular momentum of the electron: $\hat{\mathbf{m}} = -\frac{e}{2m_e}\hat{\mathbf{L}} = -\frac{\mu_B}{\hbar}\hat{\mathbf{L}}$, i.e., $g_L = 1$
- for an electron without orbital angular momentum: $\hat{\mathbf{m}} = -\frac{2\mu_B}{\hbar}\hat{\mathbf{S}}$, i.e., $g_S = 2$
- in general the Landé g_J factor should be used: $\hat{\mathbf{m}} = -\frac{g_J\mu_B}{\hbar}\hat{\mathbf{J}}$, where $g_J = g_L\frac{j(j+1)-s(s+1)+\ell(\ell+1)}{2j(j+1)} + g_S\frac{j(j+1)+s(s+1)-\ell(\ell+1)}{2j(j+1)}$
- abs. value of magnetic moment: $M = g_J\sqrt{j(j+1)}\mu_B$

- In magnetic field the Hamiltonian contains an additional term: $\hat{V}_{mag} = -\hat{\mathbf{m}}\mathbf{B}$, where **B** is the magnetic induction vector.
- Supposing that the magnetic field is oriented along the z axis, $\hat{V}_{mag} = -\hat{\mathbf{m}}_\mathbf{z}\mathbf{B}_\mathbf{z} = \frac{g_J \mu_B}{\hbar} \hat{J}_z B_z$
- Due to this term the energy levels depend on the j_z quantum numbers (Zeeman effect).

Corrections from the Dirac equation (hydrogen atom)

- total angular momentum quantum number: $j = |\ell \pm s|$, e.g.,

  $\ell = 0$, s orbital, $j = \frac{1}{2}$

  $\ell = 1$, p orbital, $j = \frac{1}{2}, \frac{3}{2}$

  $\ell = 2$, d orbital, $j = \frac{3}{2}, \frac{5}{2}$

- The energy is slightly j-dependent (fine structure of the H atom: splitting of the spectral lines of atoms due to electron spin)

  $$E_{j\,n} \approx -\frac{\mu c^2 \alpha^2}{2n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right],$$

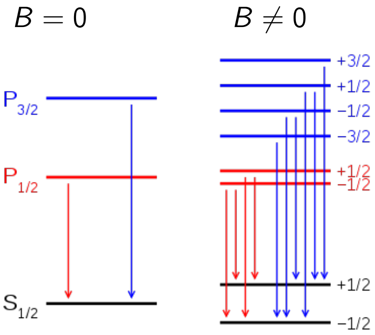
  where $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137}$ is the fine-structure constant

Corrections from the Dirac equation (hydrogen atom)

- j-dependent relativistic correction: spin-orbit splitting
- With respect the resting frame of the electron the proton is orbiting around the electron and producing a magnetic field **B**, $\mathbf{B} = -\frac{1}{c^2}\mathbf{v} \times \mathbf{E}$
- From a brief derivation (sherically symmetric pot., $V(\mathbf{r}) = V(r)$) the magnetic field is: $\mathbf{B} = \frac{1}{m_e ec^2}\frac{1}{r}\frac{\partial U(r)}{\partial r}\mathbf{L}$ ($U(r) = eV(r)$ is the pot. energy)
- As the energy shift is $\Delta E_{mag} = -m_z B_z$ and $\hat{m}_z = -\frac{2\mu_B}{\hbar}\hat{S}_z$ then $\Delta \hat{H}_{mag} = \frac{1}{2}\frac{2\mu_B}{\hbar m_e ec^2}\frac{1}{r}\frac{\partial U(r)}{\partial r}\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$, where the 'Thomas-half' is also included (Llewellyn Thomas, 1926).

spin

Lyman alpha transition in hydrogen (1215.668 and 1215.674 Å)



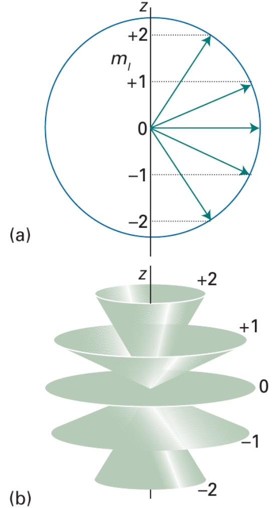
The slitting of energies according to the j values is a relativistic effect.

The Zeeman effect splits the energy levels of the H atom. As the value of g_J depends on the j, ℓ, s values the extent of the splitting is different for the energy levels.

vector model for angular momentum

cyclic permutations

$$\left[\hat{\ell}_z, \hat{\ell}_x\right] = i\hbar\hat{\ell}_y$$
$$\left[\hat{\ell}_y, \hat{\ell}_z\right] = i\hbar\hat{\ell}_x$$
$$\left[\hat{\ell}^2, \hat{\ell}_z\right] = 0, \left[\hat{\ell}_x, \hat{\ell}_y\right] \quad = i\hbar\hat{\ell}_z$$



The angular momentum can be visualized as a vector with length $\hbar\sqrt{\ell(\ell+1)}$ rotating around the z axis.

vector model for the spin

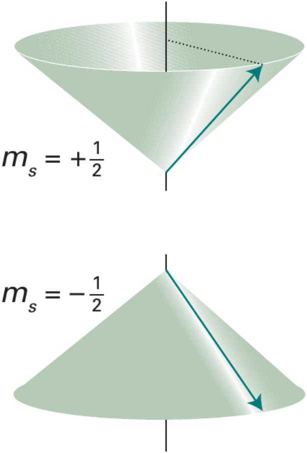
cyclic permutations

$$[\hat{s}_x, \hat{s}_y] = i\hbar\hat{s}_z$$

$$[\hat{s}_z, \hat{s}_x] = i\hbar\hat{s}_y$$

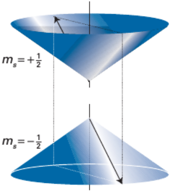
$$[\hat{s}_y, \hat{s}_z] = i\hbar\hat{s}_x$$

$$\left[\hat{s}^2, \hat{s}_z\right] = 0$$



Singlet and triplet states

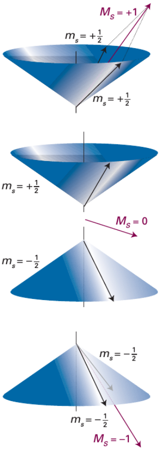
$$\hat{S}_i = \hat{S}_i^{(1)} + \hat{S}_i^{(2)}$$



singlet combination:

$$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

multiplicity: 1



triplet combinations:

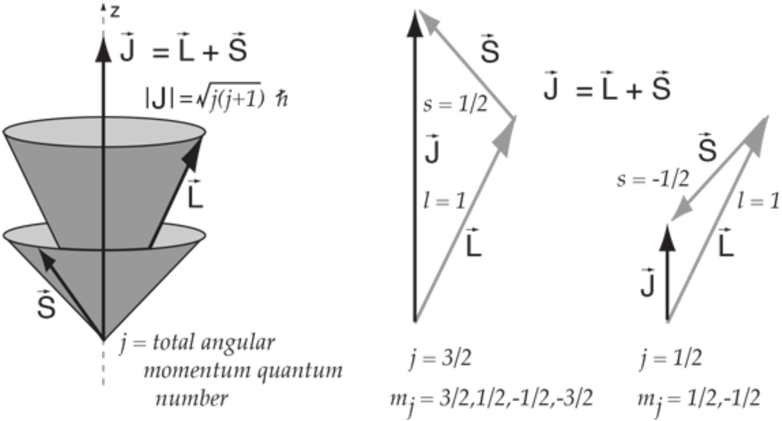
$$\alpha(1)\alpha(2)$$

$$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \alpha(2)\beta(1))$$

$$\beta(1)\beta(2)$$

multiplicity: 3

vector model for the total angular momentum



In general, if $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 \rightarrow$

$$j = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, |j_1 + j_2|$$

Selection rules

Time dependent perturbation

- Let's suppose that the stationary system is effected by a small time-dependent external force (perturbation, $K\hat{(}t)$):
  $\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} + \left(\hat{H}_0 + \hat{K}(t)\right)\Psi = 0$
- The eigenfunctions of the unperturbed Hamiltonian are Ψ_r, $\hat{H}_0\Psi_r = E_r\Psi_r$. At $t = 0$ the system is in state Ψ_i.
- Due to the perturbation at t the wavefunction is the lin. comb. of the eigenstates of $\hat{H}_0$: $\psi = \sum_r c_r(t)\Psi_r e^{-\frac{i}{\hbar}E_r t}$, where $c_r(t=0) = \delta_{ir}$, i.e., $c_i(t=0) = 1$ and $c_r(t=0) = 0$ if $r \neq i$.

Selection rules

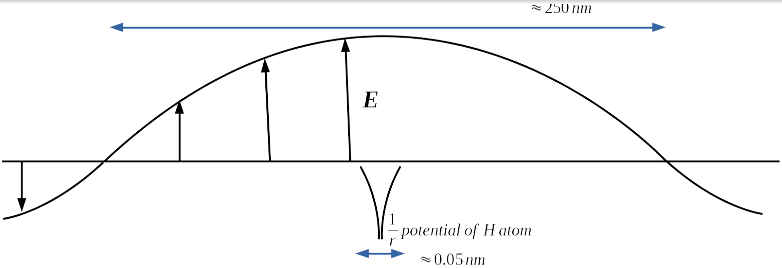
Time dependent perturbation

- One can easily show that $\frac{dc_k}{dt} = -\frac{i}{\hbar}\sum_r K_{kr} c_r e^{i\omega_{kr} t}$, where $\omega_{kr} = \frac{E_k - E_r}{\hbar}$ and $K_{kr} = \int \psi_k^* \hat{K}(t)\psi_r d\tau$.
- As a "first order" approximation at the *rhs* of the $\frac{dc_k}{dt} = -\frac{i}{\hbar}\sum_r K_{kr} c_r e^{i\omega_{kr} t}$ equation c_r is set to zero except c_i which is one.
- Integrating the $\frac{dc_k}{dt} = -\frac{i}{\hbar} K_{ki} e^{i\omega_{ki} t}$ equations with respect to time, the new $c_k^{(1)}(t) = \delta_{ki} - \frac{i}{\hbar}\int_0^t K_{ki}(\tau) e^{i\omega_{ki}\tau} d\tau$ defines the transition probability:

$$W(i \to k) = |c_k(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^t K_{ki}(\tau) e^{i\omega_{ki}\tau} d\tau\right|^2, \text{ if } i \neq k.$$

Selection rules

Electric dipole transition



H atom in visible light. **E** field is homogeneous in the scale of the H atom.

Potential energy in the electric field: $E_{pot} = \sum_i e_i \Phi(\mathbf{r}_i) = \int \rho(\mathbf{r})\Phi(\mathbf{r}) d^3r$, where ρ is the density of electric charge $E_{pot} = \int \rho(\mathbf{r})\Phi(\mathbf{r})d^3r =$
$\int \rho(\mathbf{r})(\Phi(0) + \nabla\Phi|_{\mathbf{r}=\mathbf{0}} \cdot \mathbf{r} + \frac{1}{2}\sum_{i,j}^{x,y,z} \frac{\partial^2\Phi}{\partial x_i \partial x_j}|_{\mathbf{r}=\mathbf{0}} x_i x_j + \ldots)d^3r$.

If the total charge is zero and derivatives of **E** is supposed to be small,

$E_{pot} = -\mathbf{E}|_{\mathbf{r}=\mathbf{0}} \int \rho(\mathbf{r})\mathbf{r}d^3r = -\mathbf{E}\mathbf{d}$, where **d** is the electric dipole moment.

Selection rules

Electric dipole transition

- Transitions induced by a light beam, perturbation operator:
  $\hat{K} = eE_x\hat{x}sin(\omega t) \rightarrow K_{kr} = eE_x x_{kr} sin(\omega t)$
- $W(i \rightarrow k) = \frac{e^2 E_x^2}{\hbar^2}|x_{ki}|^2 \left|\int_0^t sin(\omega t) e^{i\omega_{ki}\tau} d\tau\right|^2$, where $sin(\omega t)$ can be replaced by $\frac{1}{2i}\left(e^{i\omega t} - e^{-i\omega t}\right)$
  $W(i \rightarrow k) = \frac{e^2 E_x^2}{4\hbar^2}|x_{ki}|^2 \left|\int_0^t e^{i((\omega_{ki}+\omega)\tau} d\tau - \int_0^t e^{i((\omega_{ki}-\omega)\tau} d\tau\right|^2$
- The above transition probability large if $\omega \approx \omega_{ki}$ or $\omega \approx -\omega_{ki}$: absorption and induced emission of a photon.
- The transition probability is proportional to the square of the transition dipole moment: $ex_{ki} = \int \psi_k^* ex \psi_r d\tau$

Selection rules

Electric dipole transition

- if a x_{ki} is zero the k ⇒ i transition is called forbidden.
- As an example, investigate the $\Psi_{n=1,\ell=0,m_\ell=0,m_s=\frac{1}{2}} \Rightarrow \Psi_{n=2,\ell=0,m_\ell=0,m_s=\frac{1}{2}}$ transition! $x_{1,0,0,\frac{1}{2}\Rightarrow 2,0,0,\frac{1}{2}} = \int \Psi_{2,0,0,\frac{1}{2}} x \Psi_{1,0,0,\frac{1}{2}} d\tau$. The value of this integral is zero because of the symmetry. $\Psi_{2,0,0,\frac{1}{2}}$ and $\Psi_{1,0,0,\frac{1}{2}}$ are symmetric functions, e.g., $\Psi_{2,0,0,\frac{1}{2}}(\mathbf{r}) = \Psi_{2,0,0,\frac{1}{2}}(-\mathbf{r})$, on the other hand x is anti-symmetric.
- Similarly, s ⇒ s, p ⇒ p, d ⇒ d, ... transitions are all forbidden.
- The selection rules for the hydrogen atom:
  $\ell' = \ell \pm 1$, $m_\ell' = m_\ell, m_\ell \pm 1$, and $m_s' = m_s$

Many-electron systems

Pauli exclusion principle

Pauli exclusion principle (postulate VI of quantum mechanics):

- No more than two electrons may occupy any given orbital, and if they do so, their spins must be paired
- There cannot exist two electrons having the same set of quantum numbers
- The total wavefunction must be antisymmetric with respect to the interchange of all coordinates of two electrons (fermions)

Many-electron systems

Pauli exclusion principle

$$\Psi(x_1, x_2, \ldots, x_i, \ldots, x_j, \ldots) = -\Psi(x_1, x_2, \ldots, x_j, \ldots, x_i, \ldots),$$

where x_i is a composite notation for the spatial coordinates and the spin, $x_i = (\mathbf{r}_i, \sigma_i)$.

Many-electron systems

He ground state: $1s^2$ (fixed nucleus, independent particle approximation)

$$\hat{\boldsymbol{H}}_H = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

$$\hat{\boldsymbol{H}}_{He} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} = \hat{\boldsymbol{h}}_1 + \hat{\boldsymbol{h}}_2 + \frac{1}{r_{12}}$$

For the sake of simplicity the e^-–e^- interac. is neglected:

$$\hat{\boldsymbol{H}}_{He}^{approx} = \hat{\boldsymbol{h}}_1 + \hat{\boldsymbol{h}}_2$$

$$\Psi(1,2) = \Psi(r_1, r_2) = \phi_1(r_1)\cdot\phi_2(r_2) = \phi_1(1)\phi_2(2),$$

these are H atom-like wavefunctions (see page 146)

$$\hat{\boldsymbol{h}}_i\phi_i = E_i\phi_i$$

$E^{approx} = E_1 + E_2$, here E_1 and E_2 are the H atom-like energies (Z=2)

$$E_n = -\frac{Z^2}{2n^2}$$

Many-electron systems

He ground state: $1s^2$ (fixed nucleus, independent particle approximation)

let's label the electrons $\phi_a(1) = 1s(1)\alpha(1)$ and $\phi_b(2) = 1s(2)\beta(2)$

$$\Psi_{\mathrm{ground}}(1,2) = 1s(1)\alpha(1) \cdot 1s(2)\beta(2)$$

It is not anti-symmetric!

$\Psi^1_{\mathrm{ground}}(1,2) = \frac{1}{\sqrt{2}}\left(1s(1)\alpha(1) \cdot 1s(2)\beta(2) - 1s(2)\alpha(2) \cdot 1s(1)\beta(1)\right) =$
$1s(1)1s(2)\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right).$

It is the only possible anti-symmetric wavefunction. Ψ^1_{ground} is the eigenfunction of the $\hat{S}_z = \hat{S}_z(1) + \hat{S}_z(2)$ and $\hat{S}^2$ spin operators with $m_s = 0$ and $s = 1$ quantum numbers.

Many-electron systems

He excited states

ϕ_a and ϕ_b are the occupied atomic orbitals

Degenerate product states (e-e interaction is not considered):

$\Phi_1(1,2) = \phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2}), \quad \Phi_2(1,2) = \phi_a(\mathbf{r_2})\phi_b(\mathbf{r_1})$

These are orthogonal to each other, $\int dr_1^3 \int dr_2^3 \Phi_1(1,2)\Phi_2(1,2) = 0$, and degenerate with $E^{approx.} = E_a + E_b$ energy:

$(\hat{h}_1 + \hat{h}_2)\Phi_1 = (\hat{h}_1\phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2}) + \phi_a(\mathbf{r_1})\hat{h}_2\phi_b(\mathbf{r_2})) =$

$E_a\phi_a(\mathbf{r_1})\phi_b(\mathbf{r_2}) + \phi_a(\mathbf{r_1})E_b\phi_b(\mathbf{r_2}) = (E_a + E_b)\Phi_1$

To include the e-e interaction the wavefunction can be approximated by a linear combination: $\Psi = b_1\Phi_1 + b_2\Phi_2$

$(\hat{h}_1 + \hat{h}_2)\Psi = (E_a + E_b)\Psi \Longrightarrow (\hat{h}_1 + \hat{h}_2 + \hat{V})\Psi = (E_a + E_b + \hat{V})\Psi$

Many-electron systems

He excited states

Introducing some shorthand notations:

$$\hat{V} = \frac{1}{r_{12}}$$

$$C = \left\langle \Phi_1 | \hat{V} | \Phi_1 \right\rangle = \left\langle \Phi_2 | \hat{V} | \Phi_2 \right\rangle = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{|\phi_a(\mathbf{r_1})|^2 |\phi_b(\mathbf{r_2})|^2}{r_{12}},$$

$$K = \left\langle \Phi_1 | \hat{V} | \Phi_2 \right\rangle = \left\langle \Phi_2 | \hat{V} | \Phi_1 \right\rangle^* = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\phi_a^*(\mathbf{r_1})\phi_b^*(\mathbf{r_2})\phi_b(\mathbf{r_1})\phi_a(\mathbf{r_2})}{r_{12}} \delta_{\sigma_a\sigma_b},$$

where $\delta_{\sigma_a\sigma_b}$ is 1 if spins σ_a and σ_b are equal (α-α or β-β) and zero otherwise.

$$\Delta E = E - E_a - E_b$$

$$\left(E_a + E_b + \hat{V}\right)\Psi = E\Psi \Rightarrow (-\Delta E + \hat{V})\Psi = 0 \quad (\Psi = b_1\Phi_1 + b_2\Phi_2)$$

$$b_1\left(-\Delta E + \hat{V}\right)\Phi_1 + b_2\left(-\Delta E + \hat{V}\right)\Phi_2 = 0$$

Many-electron systems

He excited states

$$\langle\Phi_1| \ / \Rightarrow b_1\left(-\Delta E+\hat{V}\right)\Phi_1+b_2\left(-\Delta E+\hat{V}\right)\Phi_2=0$$
$$\langle\Phi_2| \ / \Rightarrow b_1\left(-\Delta E+\hat{V}\right)\Phi_1+b_2\left(-\Delta E+\hat{V}\right)\Phi_2=0$$

$$b_1\left(\left\langle\Phi_1|\hat{V}|\Phi_1\right\rangle-\Delta E\right)+b_2\left\langle\Phi_1|\hat{V}|\Phi_2\right\rangle=0$$
$$b_1\left\langle\Phi_2|\hat{V}|\Phi_1\right\rangle+b_2\left(\left\langle\Phi_2|\hat{V}|\Phi_2\right\rangle-\Delta E\right)=0$$

The result is a system of homogeneous linear equation:

$b_1\left(C-\Delta E\right)+b_2K=0$

$b_1K^*+b_2\left(C-\Delta E\right)=0$

To have a non-trivial solution the determinant of the coefficient matrix should be zero: $(C-\Delta E)^2-|K|^2=0$

Many-electron systems

He excited states, matrices

A homogeneous system of linear equations:

$$\begin{aligned}
c_{11}x_1 + c_{12}x_2 + c_{13}x_3 + \ldots \qquad & c_{1n}x_n = 0 \\
c_{21}x_1 + c_{22}x_2 + c_{23}x_3 + \ldots \qquad & c_{2n}x_n = 0 \\
\vdots \qquad & \quad \vdots \\
c_{n1}x_1 + c_{n2}x_2 + c_{n3}x_3 + \ldots \qquad & c_{nn}x_n = 0
\end{aligned}$$

Matrix notation: $\mathbf{C} \cdot \mathbf{x} = 0$, where

$$\mathbf{C} = \begin{pmatrix} c_{11} & c_{12} & \ldots & c_{1n} \\ c_{21} & c_{22} & \ldots & c_{2n} \\ \vdots & \vdots & & \vdots \\ c_{n1} & c_{n2} & \ldots & c_{nn} \end{pmatrix}, \qquad \mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}$$

Many-electron systems

He excited states, determinant of a matrix (2 by 2 and 3 by 3 case)

$$\det(\mathbf{C}) = \begin{vmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{vmatrix} = c_{11}c_{22} - c_{21}c_{12}$$

$$\det(\mathbf{C}) = \begin{vmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{vmatrix}$$

$$= c_{11}c_{22}c_{33} + c_{12}c_{23}c_{31} + c_{13}c_{21}c_{32} - c_{13}c_{22}c_{31} - c_{11}c_{23}c_{32} - c_{12}c_{21}c_{33}.$$

Many-electron systems

He excited states, adjoint of a matrix (3 by 3 case)

$$\mathrm{adj}(\mathbf{C}) = \begin{pmatrix} +\begin{vmatrix} c_{22} & c_{23} \\ c_{32} & c_{33} \end{vmatrix} & -\begin{vmatrix} c_{12} & c_{13} \\ c_{32} & c_{33} \end{vmatrix} & +\begin{vmatrix} c_{12} & c_{13} \\ c_{22} & c_{23} \end{vmatrix} \\ \\ -\begin{vmatrix} c_{21} & c_{23} \\ c_{31} & c_{33} \end{vmatrix} & +\begin{vmatrix} c_{11} & c_{13} \\ c_{31} & c_{33} \end{vmatrix} & -\begin{vmatrix} c_{11} & c_{13} \\ c_{21} & c_{23} \end{vmatrix} \\ \\ +\begin{vmatrix} c_{21} & c_{22} \\ c_{31} & c_{32} \end{vmatrix} & -\begin{vmatrix} c_{11} & c_{12} \\ c_{31} & c_{32} \end{vmatrix} & +\begin{vmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{vmatrix} \end{pmatrix}$$

Many-electron systems

He excited states, matrices, determinant

- Formal solution of a inhomogeneous system of linear equation, $\mathbf{C} \cdot \mathbf{x} = \mathbf{b}$, needs the inverse of matrix $\mathbf{C}$: $\mathbf{x} = \mathbf{C}^{-1} \cdot \mathbf{b}$
- $\mathbf{C}^{-1} = \mathrm{adj}(\mathbf{C})/\det(\mathbf{C})$ (see wikipedia page: Invertible matrix)
- To have a non-trivial solution of the homogeneous system of linear equation, the matrix $\mathbf{C}^{-1}$ should not exist. → $\det(\mathbf{C}) = 0$

$$b_1 (C - \Delta E) + b_2 K = 0$$

$$b_1 K^* + b_2 (C - \Delta E) = 0$$

To have a non-trivial solution the determinant of the coefficient matrix should be zero: $(C - \Delta E)^2 - |K|^2 = 0$

Many-electron systems

He excited states

We obtained two solutions for the energy: $\Delta E = C \pm |K|$ or

$E = E_a + E_b + C \pm |K|$

If $\Delta E = C + |K|$ then $b_1 = b_2 = \frac{1}{\sqrt{2}}$ and

$\Psi_+ = \frac{1}{\sqrt{2}} \left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) + \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1) \right) \alpha(1)\beta(2) \Rightarrow$ singlet state

If $\Delta E = C - |K|$ then $b_1 = -b_2 = \frac{1}{\sqrt{2}}$ and

$\Psi_- = \frac{1}{\sqrt{2}} \left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1) \right) \alpha(1)\beta(2) \Rightarrow$ triplet state

Pauli exclusion principle $\Rightarrow \Psi^1 = \Psi_+(\mathbf{r}_1, \mathbf{r}_2) - \Psi_+(\mathbf{r}_2, \mathbf{r}_1)$,

$\Psi^1 = \frac{1}{\sqrt{2}} \left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) + \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1) \right) \left(\alpha(1)\beta(2) - \alpha(2)\beta(1) \right)$

$\Psi^3 = \frac{1}{\sqrt{2}} \left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1) \right) \left(\alpha(1)\beta(2) + \alpha(2)\beta(1) \right)$

What are the meaning of the C and K coefficients?

$C = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{|\phi_a(\mathbf{r_1})|^2|\phi_b(\mathbf{r_2})|^2}{r_{12}}$ is the classical coulomb interaction of two charged particle. It is always a positive quantity.

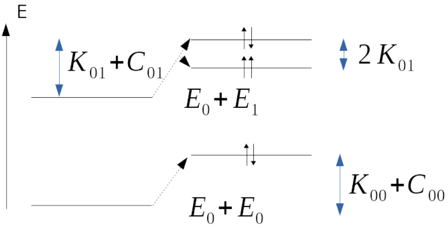
$K = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\phi_a^*(\mathbf{r_1})\phi_b^*(\mathbf{r_2})\phi_b(\mathbf{r_1})\phi_a(\mathbf{r_2})}{r_{12}}\delta_{\sigma_a\sigma_b}$ is the so-called exchange interaction, no classical analog.

For the ground state, $\phi_a = \phi_b = \phi_{n=1,\ell=0,m_\ell=0}$, only the singlet combination, Ψ^1 can appear.

For the first excited state $\phi_a = \phi_{n=1,\ell=0,m_\ell=0}$ and $\phi_b = \phi_{n=2,\ell=0,m_\ell=0}$.

Many-electron systems

He excited states



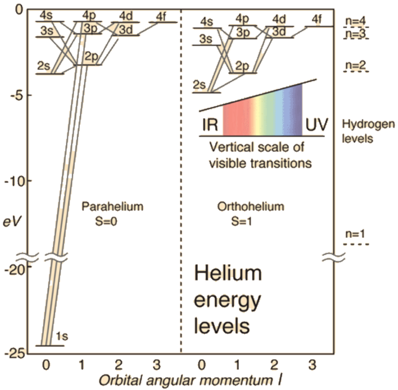
For states arising from the same configuration, the triplet state generally lies lower than the singlet state (see Hund's rule). Qualitative explanation:

$\Psi^3(\mathbf{r}_1, \mathbf{r}_1) = 0$, i.e., the two electrons can not be at the same place. $\leftrightarrow$

$\Psi^1(\mathbf{r}_1, \mathbf{r}_1) \neq 0$, i.e., large repulsive coulomb force increases the energy.

Many-electron systems

parahelium, orthohelium



Excitation of both of the electrons requires an energy larger than the ionization energy: only $1s^1nl^1$ excitations appear in the spectra

No radiative transitions between singlet and triplet states

Spectroscopically, He behaves like two distinct species, parahelium and orthohelium

the Slater determinant

the easy way to build antisymmetric wavefunctions

$$\Psi_{\text{ground}} = 1s1s[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} = 1s(1)\alpha(1)1s(2)\beta(2) - 1s(1)\beta(1)1s(2)\alpha(2)$$

$$= 1s(1)1s(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

rows → electrons

columns → spinorbitals

the Slater determinant

Determinant

A homogeneous system of linear equations:

$$\begin{array}{lr}
c_{11}x_1 + c_{12}x_2 + c_{13}x_3 + \dots & + c_{1n}x_n = 0 \\
c_{21}x_1 + c_{22}x_2 + c_{23}x_3 + \dots & + c_{2n}x_n = 0 \\
\vdots & \vdots \\
c_{n1}x_1 + c_{n2}x_2 + c_{n3}x_3 + \dots & + c_{nn}x_n = 0
\end{array}$$

Matrix notation: $\mathbf{C} \cdot \mathbf{x} = 0$, where

$$\mathbf{C} = \begin{pmatrix} c_{11} & c_{12} & \dots & c_{1n} \\ c_{21} & c_{22} & \dots & c_{2n} \\ \vdots & \vdots & & \vdots \\ c_{n1} & c_{n2} & \dots & c_{nn} \end{pmatrix}, \qquad \mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix}$$

the Slater determinant

Determinant

- Formal solution of a inhomogeneous system of linear equation, $\mathbf{C} \cdot \mathbf{x} = \mathbf{b}$, needs the inverse of matrix $\mathbf{C}$: $\mathbf{x} = \mathbf{C}^{-1} \cdot \mathbf{b}$
- $\mathbf{C}^{-1} = \mathrm{adj}(\mathbf{C})/\det(\mathbf{C})$ (see wikipedia page: Invertible matrix)
- To have a non-trivial solution of the homogeneous system of linear equation, the matrix $\mathbf{C}^{-1}$ should not exist. $\rightarrow \det(\mathbf{C}) = 0$
- $\det(\mathbf{C}) = \sum_{\{p_{\mathbf{1}}, p_{\mathbf{2}}, \ldots, p_n\}} (-1)^p c_{1p_{\mathbf{1}}} c_{2p_{\mathbf{2}}} c_{3p_{\mathbf{3}}} \ldots c_{np_n}$, where the sum runs on the whole set of permutations of numbers $1, 2, 3, \ldots, n$ and p is the parity (number of exchange of indices requiered to obtain the given permutation) of the given permutation.

the Slater determinant

Determinant

Some properties of determinants:

- $\det(\mathbf{AB}) = \det(\mathbf{A})\det(\mathbf{B})$
- $\det(\mathbf{A}^{\mathrm{T}}) = \det(\mathbf{A})$, where $\mathbf{A}^{\mathrm{T}}$ denotes the transpose of $\mathbf{A}$.
- If matrix $\mathbf{A}$ is composed from column vectors, $\mathbf{A} = ([\mathbf{a}_1], [\mathbf{a}_2], [\mathbf{a}_3], \ldots, [\mathbf{a}_n])$, and vectors $[\mathbf{a}_i]$ are linearly dependent then $\det(\mathbf{A}) = 0$.
- $\det([\mathbf{a}_1], [\mathbf{a}_2], \ldots, [\mathbf{a}_i], \ldots, [\mathbf{a}_j], \ldots, [\mathbf{a}_n]) = -\det([\mathbf{a}_1], [\mathbf{a}_2], \ldots, [\mathbf{a}_j], \ldots, [\mathbf{a}_i], \ldots, [\mathbf{a}_n])$.

the Slater determinant

Determinant

- Expansion of a determinant along a column (e.g., second column)(or a row):

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \cdots & a_{3n} \\ \vdots & \vdots & & & \\ a_{n1} & a_{n2} & a_{n3} & \cdots & a_{nn} \end{vmatrix} = (-1)^{1+2} a_{12} \cdot \begin{vmatrix} a_{21} & a_{23} & \cdots & a_{2n} \\ a_{31} & a_{33} & \cdots & a_{3n} \\ \vdots & & & \\ a_{n1} & a_{n3} & \cdots & a_{nn} \end{vmatrix}$$

$$+(-1)^{2+2} a_{22} \cdot \begin{vmatrix} a_{11} & a_{13} & \cdots & a_{1n} \\ a_{31} & a_{33} & \cdots & a_{3n} \\ \vdots & & & \\ a_{n1} & a_{n3} & \cdots & a_{nn} \end{vmatrix} + (-1)^{3+2} a_{32} \cdot \begin{vmatrix} a_{11} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{23} & \cdots & a_{2n} \\ \vdots & \vdots & & \\ a_{n1} & a_{n3} & \cdots & a_{nn} \end{vmatrix} + (-1)^{4+2} a_{42} \cdot \ldots$$

the Slater determinant

Li atom

$$\Phi_{\mathrm{Li}} = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

rows → electrons

columns → spinorbitals

the Slater determinant

Li atom

if two columns are equal - three electrons are on one spatial orbital

the Pauli exclusion principle is not fulfilled

$$
\begin{aligned}
\Phi_{\mathrm{Li}} &= \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 1s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 1s(3)\beta(3) \end{vmatrix} \\
&= 1s(1)\alpha(1) \begin{vmatrix} 1s(2)\beta(2) & 1s(2)\beta(2) \\ 1s(3)\beta(3) & 1s(3)\beta(3) \end{vmatrix} \\
&- 1s(1)\beta(1) \begin{vmatrix} 1s(2)\alpha(2) & 1s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) \end{vmatrix} \\
&+ 1s(1)\beta(1) \begin{vmatrix} 1s(2)\alpha(2) & 1s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) \end{vmatrix} \\
&= 0
\end{aligned}
$$

the Slater determinant

Li atom

if two rows are interchanged - the determinant changes sign
antisymmetric wavefunction

1st row expansion

$$\Phi_{\mathrm{Li}} = \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

$$= 1s(1)\alpha(1) \begin{vmatrix} 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

$$- 1s(1)\beta(1) \begin{vmatrix} 1s(2)\alpha(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 2s(3)\alpha(3) \end{vmatrix}$$

$$+ 2s(1)\alpha(1) \begin{vmatrix} 1s(2)\alpha(2) & 1s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) \end{vmatrix}$$

2nd row expansion

$$\Phi_{\mathrm{Li}}^{\mathbf{1}\rightarrow\mathbf{2}} = \begin{vmatrix} 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

$$= -1s(1)\alpha(1) \begin{vmatrix} 1s(2)\beta(2) & 2s(2)\alpha(2) \\ 1s(3)\beta(3) & 2s(3)\alpha(3) \end{vmatrix}$$

$$+ 1s(1)\beta(1) \begin{vmatrix} 1s(2)\alpha(2) & 2s(2)\alpha(2) \\ 1s(3)\alpha(3) & 2s(3)\alpha(3) \end{vmatrix}$$

$$- 2s(1)\alpha(1) \begin{vmatrix} 1s(2)\alpha(2) & 1s(2)\beta(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) \end{vmatrix}$$

the Slater determinant

General properties

- The electrons are indistinguishable...
- The individual one-particle orbitals have no physical meaning: the Slater determinant is invariant with respect to any orthogonality and scalar product keeping linear combination of the original orbitals.

Electronic structure of atoms

Hamiltonian

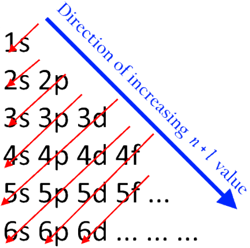
$$\hat{\mathrm{H}} = -\sum_{i}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i}^{N} \frac{Z_A}{R_{iA}} + \sum_{i}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} + \Delta H_{so}$$

- Energy of atoms is basically n dependent, moderate dependents on L, S values and slightly dependents on J value (light atoms).
- Spherical symmetry $\Longrightarrow$ $\hat{J}^2$ and $\hat{J}_z$ commute with the Hamiltonian: J and M_J are good quantum numbers.
- Without ΔH_{so} the L, M_L, S, M_S are also good quantum numbers

Electronic structure of atoms

Aufbau/building-up principle, diagonal rule

- orbitals with a lower $n+\ell$ value are filled before those with higher $n+\ell$ values
- in the case of equal $n+\ell$ values, the orbital with a lower n value is filled first



1s

2s 2p

3s 3p 3d

4s 4p 4d 4f

5s 5p 5d 5f ...

6s 6p 6d ... ...

Direction of increasing $n+l$ value

Examples: He, Li, C, N, O

$\langle r_{3d}\rangle < \langle r_{4s}\rangle \Longrightarrow$: For the 3d electrons the e-e repulsion is so strong that in most of the cases the $4s$ orbitals are prefered: Sc, [Ar] $3d^1 4s^2$

There are exceptions too: Cu, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$ is

predicted instead of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Due to the e-e interaction the shell-, sub-shell configuration can not describe the atomic spectra (see the case of the He atom: $1s^1 2s^1$ configuration describes two states [a singlet and a triplet state] with different energies.)

Electronic structure of atoms

Atomic term symbols, vector and scalar,z-projection, additions

- total orbital angular quantum number

  $\hat{\mathbf{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$, $\hat{\underline{\ell}}_i = (\hat{\ell}_{xi}, \hat{\ell}_{yi}, \hat{\ell}_{zi})$

  $\hat{\mathbf{L}} = \sum \hat{\underline{\ell}}_i$ and $M_L = \sum m_{\ell_i}$, $M_L = 0, \pm 1, \pm 2, \ldots, \pm L$

L=	0	1	2	3	4
	S	P	D	F	G

- total spin angular momentum quantum number

  $\hat{\mathbf{S}} = \sum \hat{\mathbf{s}}_i$ or $M_S = \sum m_{s_i}$, $M_S = 0, \pm 1, \pm 2, \ldots, \pm S$

- total angular quantum number

  $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, $M_J = 0, \pm 1, \pm 2, \ldots, \pm J$

Electronic structure of atoms

Atomic term symbols, Clebsch-Gordan series

- total orbital angular quantum number

  $L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, ..., |\ell_1 - \ell_2|$

- total spin angular momentum quantum number

  $S = s_1 + s_2, s_1 + s_2 - 1, ..., |s_1 - s_2|$

- $max\{M_L\} = L$ and $max\{M_S\} = S$; $(2L+1)(2S+1) = \sum_J 2J+1$

- $\hat{J}^2$, $\hat{J}_z$ eigenfunctions $\Psi^J_{m_J}$ can be mixed from the $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, $\hat{S}_z$ eigenfunctions ${}^{2S+1}\Psi^L_{m_s m_L}$,

  $$\Psi^J_{m_J = m_L + m_S} = \sum_{m_L}^{m_S = m_J - m_L} C^{J,m_J}_{LS,m_L} \cdot {}^{2S+1}\Psi^L_{m_s m_L} \quad (C^{J,m_J}_{LS,m_L}\text{: CG coeffs})$$

- total angular quantum number

  $J = L + S, L + S - 1, ..., |L - S|$

Electronic structure of atoms

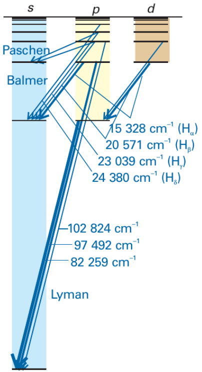
Atomic term symbols

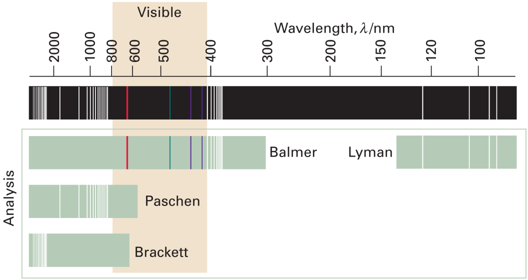
- atomic term symbol: $^{2S+1}L_J$
- term: ^{2S+1}L
- microstate: a unique configuration of quantum numbers
- n = num of spin orbitals; k = num. of electrons
- number of microstates: $\binom{n}{k}$
- multiplicity: $2S+1$

S=	0	1/2	1	3/2
2S+1=	1	2	3	4
	singlet	doublet	triplet	quartet

Electronic structure of atoms

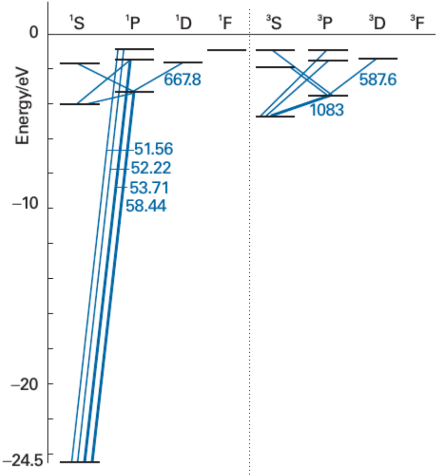
H electronic transitions, $^2S_{1/2}$, $^2P_{1/2}$, $^2P_{3/2}$, $^2D_{5/2}$, $^2D_{3/2}$, etc.





Electronic structure of atoms

Atomic term symbols, helium atom



Electronic structure of atoms

Atomic term symbols, $^{2S+1}L_J$

- $1s^2$: $^1S_0$
- $2p^6$: $^1S_0$
- $3d^{10}$: $^1S_0$
- $1s^1$: $^2S_{1/2}$
- $1s^22s^22p^1$, i.e. [Ne]$2p^1$: $^2P_{3/2}$, $^2P_{1/2}$

- atoms with closed subshells are in the $^1S_0$ state
- atoms with one e^- in an open subshell nℓ are in the ^2L state
- In general, the open subshells define the atomic term

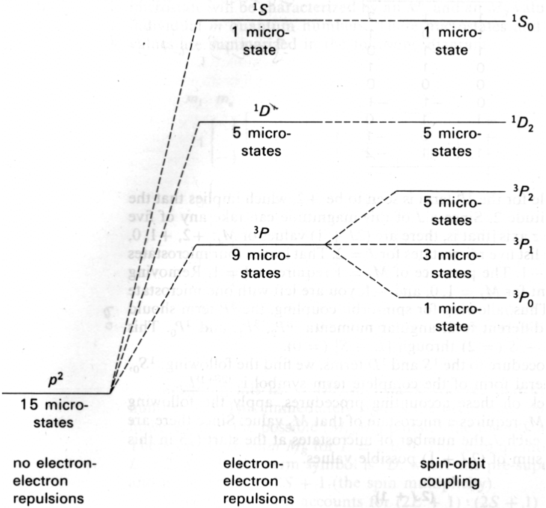
Electronic structure of atoms

Atomic term symbols, non-relativistic case, LS / Russel-Saunders coupling

- In the non-relativistic case ${}^{2S+1}L$ defines the energy.
- The relativistic effects (e.g., spin-orbit coupling) are small perturbations. The spin-orbit coupling for the individual electrons is small. An average can be calculated using the total $\hat{L}$ and $\hat{S}$ operators: $\Delta\hat{H}_{so} = A(L,S)\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$.
- The energy leveles are splitted according to the various values of J: $\Delta E_{so} = \frac{1}{2}A(L,S)(J(J+1) - L(L+1) - S(S+1))$
- As in a given term the L and S are constant (and $\Delta J = 1$) the observable splitting is $E(J) - E(J-1) = A(L,S)J$.
- $\Longrightarrow$ Fine or multiplett structure of the spectra

Electronic structure of atoms

Atomic term symbols, $^{2S+1}L_J$, spin-orbit coupling



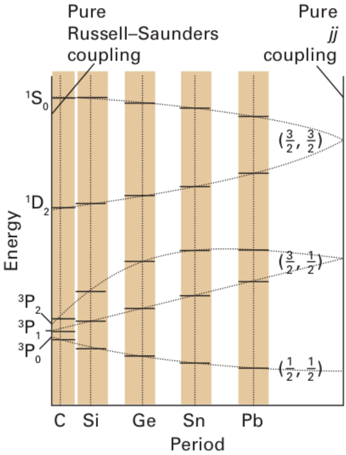
Electronic structure of atoms

Relativistic case, jj-coupling

- In the relativistic case (Z»1) the spin-orbit effect dominates over the e^--e^- repulsion, thus $\sum_{i<j} \frac{1}{r_{ij}}$ can be considered as a perturbation.
- $\hat{H}_{so} = \sum_i \alpha_i \hat{\ell}_i \hat{s}_i = \sum_i \frac{\alpha_i}{2}(\hat{j}_i^2 - \ell_i^2 - s_i^2)$.
- Spin and orbital momenta of the electrons coupled into $\hat{j}_i$ eigenfunctions. The anti-symmetrized products of these functions are the eigenfunctions of the zero-order Hamiltonian ($\hat{H}$ without the e^--e^- repulsion).
- $\Delta E_{so} = \sum_i \frac{\alpha_i}{2}(j_i(j_i+1) - \ell_i(\ell_i+1) - s_i(s_i+1))$.
- The good quantum numbers are J, j_1, j_2, *etc.*

Electronic structure of atoms

LS- and jj-coupling



Coupling of ℓ=1 and s=1/2 results in either a j=1/2 or a j=3/2 state.

Possible J values:

j_1	j_2	J
$1/2$	$1/2$	$0, 1$
$1/2$	$3/2$	$1, 2$
$3/2$	$3/2$	$0, 1, 2, 3$

Electronic structure of atoms

Hund's rules

an atom in its ground state adopts a configuration with the greatest number of unpaired electrons

Electronic structure of atoms

Hund's rules

Rules to determine the lowest state for a given electron configuration

- the term of highest S (maximum multiplicity, $2S + 1$) will lie lowest in energy
- if more than one term exist with maximum multiplicity then the term having the highest L will lie lowest in energy
- for terms having a spin-orbit splitting, if the outermost subshell is half-full or less than half-full the states will be ordered with the lowest J values lying lowest; if the outermost subshell is more than half-filled, the level with the highest value of J, is lowest in energy

Electronic structure of atoms

Selection rules for electronic transitions

transition dipole moment:

$$\hat{\mu} = -e \sum_{electrons} \hat{\mathbf{r}}$$

$$\mu_{fi} = \int \psi_f \hat{\mu} \psi_i d\tau$$

one electron

- $\Delta s = 0$
- $\Delta \ell = \pm 1$; $\Delta m_\ell = 0, \pm 1$

multi electron

- $\Delta S = 0$
- $\Delta L = 0, \pm 1$
- $\Delta J = \pm 1, 0, \; J = 0 \not\leftrightarrow J = 0$

Atomic term symbols

$^{2S+1}L_J$

- any atomic state can be specified
- any spectroscopic transition can be described

Atomic spectroscopy

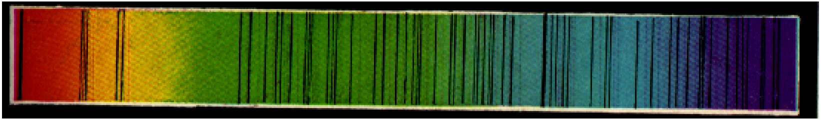
Purpose: analysis of the elementary composition.

Sample preparation: heating to high temperature.

Atomic absorption spectroscopy and atomic emission spectroscopy

Concentration of atoms can be measured (Beer–Lambert law[see later]/intensities)

Atomic spectroscopy



Composition of stars

Relative speed and temperature of stars and galaxies.

Born–Oppenheimer approximation

argument: elephant herd and the flies

- electrons
    - light particles
    - fast
- nuclei
    - heavy particles
    - slow

Born–Oppenheimer approximation

Hamiltonians, $\hat{\mathrm{H}}\Psi = E\Psi$

$$\hat{\mathrm{H}} = -\frac{1}{2}\nabla_e^2 - \frac{1}{r}, \text{ fixed nucleus, one electron atom}$$

$$\hat{\mathrm{H}} = -\frac{1}{2}\nabla_e^2 - \frac{1}{2M_p}\nabla_p^2 - \frac{1}{R_{ep}}, \text{ one electron atom}$$

$$\hat{\mathrm{H}} = -\sum_i^N \frac{1}{2}\nabla_i^2 - \frac{1}{2M_A}\nabla_A^2 - \sum_i^N \frac{Z_A}{R_{iA}} + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}}, \text{ multielectron atom}$$

polyatomic molecule, general case:

$$\hat{\mathrm{H}} = -\sum_i^N \frac{1}{2}\nabla_i^2 - \sum_A^M \frac{1}{2M_A}\nabla_A^2 - \sum_i^N \sum_A^M \frac{Z_A}{R_{iA}} + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_A^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$$

$$"E_{\mathrm{kin}}(\mathrm{electrons}) + E_{\mathrm{kin}}(\mathrm{nuclei}) + E_{\mathrm{pot}}(\mathrm{el., nuc.}) + E_{\mathrm{pot}}(\mathrm{el, el}) + E_{\mathrm{pot}}(\mathrm{nuc, nuc})"$$

Born–Oppenheimer approximation

Hamiltonians, $\hat{\mathrm{H}} = \hat{\mathrm{H}}_e + \hat{\mathrm{H}}_N$

$$\hat{\mathrm{H}} = -\sum_{i}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A}^{M} \frac{1}{2M_A}\nabla_A^2 - \sum_{i}^{N}\sum_{A}^{M} \frac{Z_A}{R_{iA}} + \sum_{i}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$

$$\hat{\mathrm{H}}_e = -\sum_{i}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i}^{N}\sum_{A}^{M} \frac{Z_A}{R_{iA}} + \sum_{i}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}}$$

The electronic Hamiltonian $\hat{H}_e$ can be approximated by an average, $\langle \Psi_e \left| \hat{\mathrm{H}}_e \right| \Psi_e \rangle = E_e(\{R_A\})$, where Ψ_e is the eigenfunction of the electronic Hamiltonian.

$$\begin{aligned}\hat{\mathrm{H}}_N &= -\sum_{A}^{M} \frac{1}{2M_A}\nabla_A^2 + \left\langle \Psi_e \left| \hat{\mathrm{H}}_e \right| \Psi_e \right\rangle + \sum_{A}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \\ &= -\sum_{A}^{M} \frac{1}{2M_A}\nabla_A^2 + E_{\mathrm{TOT}}\end{aligned}$$

Born–Oppenheimer approximation

Hamiltonians, $\hat{\mathrm{H}} = \hat{\mathrm{H}}_e + \hat{\mathrm{H}}_N$

$$E_{\mathrm{TOT}} = E_e(\{R_A\}) + \sum_A^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$$

$$\hat{\mathrm{H}}_N \Psi_N = E \Psi_N$$

E_{TOT} is the potential energy surface governing the motion of the nuclei.

E is the Born–Oppenheimer approximation to the total energy including the translational, rotational, vibrational, and electronic energy.

When solving for the electronic WF, $\hat{\mathrm{H}}_e \Psi_e(\{r_i\},\{R_A\}) = E\Psi_e(\{r_i\},\{R_A\})$:

kinetic energy of the nuclei is zero, $-\sum_A^M \frac{1}{2M_A}\nabla_A^2 = 0$, and

nuclei-nuclei potential energy is constant, $\sum_A^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} = const$

The variational principle

assumptions

- ground state: Ψ_0, $E_0 = \int \Psi_0^* \hat{\boldsymbol{H}} \Psi_0 d\tau$
- set of orthonormal eigenfunctions is available, $\hat{\boldsymbol{H}}\psi_i = \varepsilon_i \psi_i$ and $\int \psi_i^* \psi_j = \delta_{ij}$
- $\varepsilon_i \geq E_0$
- the trial wavefunction is constructed as $\Psi = \sum_i c_i \psi_i$

variational principle

the energy obtained with the trial wavefunction, Ψ, is always an upper bound to the ground state energy, E_0, i.e., $E = \frac{\int \Psi^* \hat{\boldsymbol{H}} \Psi d\tau}{\int \Psi^* \Psi d\tau} \geq E_0$

The variational principle

proof

$$E = \frac{\int \Psi^* \hat{\boldsymbol{H}} \Psi d\tau}{\int \Psi^* \Psi d\tau} = \frac{\displaystyle\int \sum_i c_i^* \psi_i^* \hat{\boldsymbol{H}} \sum_j c_j \psi_j d\tau}{\displaystyle\int \sum_i c_i^* \psi_i^* \sum_j c_j \psi_j d\tau}$$

$$= \frac{\displaystyle\sum_{ij} c_i^* c_j \int \psi_i^* \hat{\boldsymbol{H}} \psi_j d\tau}{\displaystyle\sum_{ij} c_i^* c_j \int \psi_i^* \psi_j d\tau} = \frac{\displaystyle\sum_{ij} c_i^* c_j \int \psi_i^* \varepsilon_j \psi_j d\tau}{\displaystyle\sum_{ij} c_i^* c_j \int \psi_i^* \psi_j d\tau}$$

$$= \frac{\sum_i c_i^2 \varepsilon_i}{\sum_i c_i^2} \geq \frac{\sum_i c_i^2 E_0}{\sum_i c_i^2} = E_0$$

The variational principle

The variational method

Supposing to have an anzats for the wavefunction with some parameters $c_1, c_2, \dots$, $\Psi = \Psi(c_1, c_2, c_3, \dots)$, then the energy can be approximated by the 'expectation value':

$$E(c_1, c_2, \dots) = \frac{\left\langle \Psi(c_1,c_2,\dots) | \hat{H} | \Psi(c_1,c_2,\dots) \right\rangle}{\langle \Psi(c_1,c_2,\dots) | \Psi(c_1,c_2,\dots) \rangle} =$$

$$\frac{\int \Psi^*(c_1,c_2,\dots) \hat{H} \Psi(c_1,c_2,\dots) d\tau}{\int \Psi^*(c_1,c_2,\dots) \Psi(c_1,c_2,\dots) d\tau}$$

One can think that the parameter set minimizing the energy $E(c_1, c_2, \dots)$ is the optimal choice. $\Longrightarrow$

$$\frac{\partial E(c_1,c_2,\dots)}{\partial c_i} = 0, \quad \forall i$$

The variational principle

The variational method, linear parametrization

For the sake of simplicity it is assumed that functions $\phi_i, i = 1, \dots$ are orthogonal to each other.

The optimal wavefunction can be approximated in a linear form, $\Psi = \sum_i c_i \psi_i$.

$$E = \frac{\int \Psi^* \hat{\boldsymbol{H}} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$
$$= \frac{\sum_i \sum_j c_i^* c_j \int \psi_i^* \hat{\boldsymbol{H}} \psi_j d\tau}{\sum_i \sum_j c_i^* c_j \int \psi_i^* \psi_j d\tau} = \frac{\sum_i \sum_j c_i^* c_j \langle \psi_i | \hat{\boldsymbol{H}} | \psi_j \rangle}{\sum_i c_i^2}$$

Using the condition of the minima, $\frac{\partial E}{\partial c_k} = 0$, an eigenvalue equation can be derived:

$$\sum_l \langle \psi_k | \hat{\boldsymbol{H}} | \psi_l \rangle c_l = E c_k$$

In vector notation : $\mathbf{H}\mathbf{c} = E\mathbf{c}$

The variational principle

The variational method, optimal determinant wavefunction

- In the theoretical calculations the one-electron molecular orbitals, ϕ_k are chosen as the linear combination of atomic orbitals (LCAO), χ_μ: $\phi_k = \sum_\mu c_{k\mu}\chi_\mu$.
- In the simplest approximation the wavefunction is a Slater determinant (anti-symmetrized product) composed from a set of LCAO's: $\Psi_{det}(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_N}) = \frac{1}{\sqrt{N!}}\hat{A}(\phi_1(\mathbf{r_1})\phi_2(\mathbf{r_2})\ldots\phi_\mathbf{N}(\mathbf{r_N}))$
- The optimal $c_{k\mu}$ molecular orbital coefficients are obtained from the variational principle. $\Longrightarrow$
- Hartree-Fock equations: $\hat{F}\phi_i = \varepsilon_i\phi_i$, where $\hat{F}$ is a one-electron operator, $\hat{F} = \hat{h} + \hat{V}_{\text{eff}}(\phi_1, \phi_2, \ldots \phi_N)$ and ε_i is (some kind of) energy of the molecular orbital. Mean field approximation: the e-e interaction is described by a single averaged effective potential, $\hat{V}_{\text{eff}}$, which depends on the molecular orbitals $\phi_1, \phi_2, \ldots \phi_N$.
- Pseudo-eigenvalue problem ($\hat{F}$ depends on the molecular orbitals ϕ_i), $\Longrightarrow$ iterative solution.

The variational principle

The variational method, Configuration interaction

- The determinant wavefunction is not exact.
- Better approximation: linear combination of determinants.
- Hartree-Fock calculation $\Longrightarrow$ occupied and virtual orbitals $\Longrightarrow$ ground state, Ψ^0_{det} , and excited determinants, $\Psi^1_{det}, \Psi^2_{det}, \ldots$.
- Configuration interaction wavefunction: $\Psi_{CI} = \sum_{i=0} c_i \Psi^i_{det}$
- c_i coefficients can be calcuated from the variational principle.
- Corrections with respect to the mean field approximation, electron correlation.

The effect of temperature, Boltzmann distribution

Mathematical background, conditional extremum

Condition of the extrama at $\mathbf{x_0}$ of $f(\mathbf{x}) = f(x_1, x_2, \ldots, x_n)$:

$\frac{\partial f}{\partial x_1}\Big|_{\mathbf{x}=\mathbf{x_0}} = 0,\ \frac{\partial f}{\partial x_2}\Big|_{\mathbf{x}=\mathbf{x_0}} = 0,\ \ldots,\ \frac{\partial f}{\partial x_n}\Big|_{\mathbf{x}=\mathbf{x_0}} = 0$

Where are the extrama of $f(\mathbf{x})$ if $x_1, x_2, \ldots$ are not independent,

but connected by the $g_1(\mathbf{x}) = 0$, $g_2(\mathbf{x}) = 0$,…,$g_m(\mathbf{x}) = 0$

conditions?

Example: $f(x, y) = x + y$ and $g(x, y) = x^2 + y^2 - 1 = 0$

The effect of temperature, Boltzmann distribution

Mathematical background, conditional extremum

Lagrange multiplication method: a new function is introduced:

$$\Lambda(\mathbf{x}, \lambda_1, \lambda_2, \ldots, \lambda_m) = f(\mathbf{x}) - \lambda_1 g_1(\mathbf{x}) - \lambda_2 g_2(\mathbf{x}) \cdots - \lambda_m g_m(\mathbf{x})$$

The necessary condition of the conditional extremum at $\mathbf{x_0}$:

$$\left.\frac{\partial\Lambda}{\partial x_1}\right|_{\mathbf{x}=\mathbf{x_0},\lambda=\lambda_\mathbf{0}} = 0,\ \left.\frac{\partial\Lambda}{\partial x_2}\right|_{\mathbf{x}=\mathbf{x_0},\lambda=\lambda_\mathbf{0}} = 0,\ \ldots,\ \left.\frac{\partial\Lambda}{\partial x_n}\right|_{\mathbf{x}=\mathbf{x_0},\lambda=\lambda_\mathbf{0}} = 0$$

and

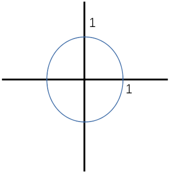
$$\left.\frac{\partial\Lambda}{\partial \lambda_1}\right|_{\mathbf{x}=\mathbf{x_0},\lambda=\lambda_\mathbf{0}} = 0,\ \left.\frac{\partial\Lambda}{\partial \lambda_2}\right|_{\mathbf{x}=\mathbf{x_0},\lambda=\lambda_\mathbf{0}} = 0,\ \ldots,\ \left.\frac{\partial\Lambda}{\partial \lambda_m}\right|_{\mathbf{x}=\mathbf{x_0},\lambda=\lambda_\mathbf{0}} = 0$$

Equations in the above line are identical with the constains:

$$g_i(\mathbf{x}) = 0 \text{ for } \forall i \Longrightarrow f(\mathbf{x_0}) = \Lambda(\mathbf{x_0}, \lambda_\mathbf{0})\ .$$

The effect of temperature, Boltzmann distribution

Mathematical background, conditional extremum



In our example: $\Lambda(x, y, \lambda) = x + y - \lambda(x^2 + y^2 - 1)$

$\frac{\partial \Lambda}{\partial x} = 1 + 2\lambda x = 0$, $\frac{\partial \Lambda}{\partial y} = 1 + 2\lambda y = 0 \Rightarrow x = -\frac{1}{2\lambda}$, $y = -\frac{1}{2\lambda}$

Substituting these into the condition:

$1 = x^2 + y^2 = 2\frac{1}{4\lambda^2} \Rightarrow x = y = \pm\frac{1}{\sqrt{2}}$

The effect of temperature, Boltzmann distribution

Mathematical background, Stirling's formula

Let's suppose that N is a large integer.

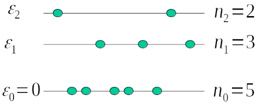
$$\ln(N!) = \sum_{i=1}^{N} \ln(i) \approx \int_{1}^{N} \ln(x)dx = [x\ln(x) - x]_1^N$$

$$\ln(N!) \approx N \ln N - N$$

The effect of temperature, Boltzmann distribution

Energy levels and populations

We will suppose that our system contains N particles distributed on energy levels $\varepsilon_0 = 0, \varepsilon_1, \varepsilon_2, \ldots$ with populations $n_0, n_1, n_2, n_3, \ldots$.



Internal energy:

$$U = U_0 + \sum_{i=0} n_i \varepsilon_i$$

The effect of temperature, Boltzmann distribution

Thermodynamic probability

The number of individual distributions belonging to the given $n_0, n_1, n_2, n_3, \ldots$ popluations are called the thermodynamic probability,

$$W = \frac{N!}{n_0!n_1!n_2!n_3!\ldots}.$$

Number of combinations with repetition.

Hypothesis: If N and n_i numbers are large (thermodynamic limit), the observed macroscopic state is defined by the W with the maximal value.

The effect of temperature, Boltzmann distribution

Extremum of the thermodynamic probability

As the $\ln(x)$ function is a monotonically increasing function, the extremum of W and $\ln(W)$ defines the same set of populations.

We have two constrains to take into account: $\sum_i n_i = N = const.$ and $\sum_i \varepsilon_i n_i = E = const.$ (isolated system)

Using the Lagrange multiplication method:

$$\Lambda(n_0, n_1, n_2, \ldots, \alpha, \beta) =$$
$$\ln(W(n_0, n_1, n_2, \ldots)) - \beta \left(\sum_{i=0} \varepsilon_i n_i - E \right) + \alpha \left(\sum_{i=0} n_i - N \right)$$

The effect of temperature, Boltzmann distribution

Extremum of the thermodynamic probability

Necessary condition for the maximum: $\frac{\partial \Lambda}{\partial n_i} = 0$ for each n_i.

$$\frac{\partial \ln(W)}{\partial n_i} - \beta\varepsilon_i + \alpha = 0$$

$$\ln(W) = \ln(N!) - \textstyle\sum_{i=0} ln(n_i!) \approx$$

$$N\ln(N) - N - \textstyle\sum_i (n_i \ln(n_i) - n_i) = N\ln(N) - \sum_i n_i \ln(n_i)$$

$\frac{\partial \ln(W)}{\partial n_i} \approx -\ln(n_i)$, where $n_i >> 1$

$$n_i = e^{\alpha - \beta\varepsilon_i}$$

$$\sum_i n_i = e^{\alpha} \sum_i e^{-\beta\varepsilon_i} = N \Longrightarrow e^{\alpha} = \frac{N}{\sum_i e^{-\beta\varepsilon_i}} = \frac{N}{q}$$

q is the partition function: $q = \sum_i e^{-\beta\varepsilon_i}$

The effect of temperature, Boltzmann distribution

Thermodynamic average

Boltzmann distribution:

$$n_i = \frac{Ne^{-\beta\varepsilon_i}}{q}$$

$$E = \sum_i \varepsilon_i n_i = N\frac{\sum_i \varepsilon_i e^{-\beta\varepsilon_i}}{q}$$

To find the β parameter these results should be applied to the ideal gas (see Atkins, ...) : $E = \frac{N}{\beta}$, $p = \frac{N}{V\beta} \Longrightarrow \beta = \frac{1}{kT}$

where p is the pressure. Compering this results with the equation of states for the ideal gas, we can see that $\beta = \frac{1}{kT}$.

The effect of temperature, Boltzmann distribution

Partition function

- $T \to 0K, \beta \to \infty$, $(\varepsilon_0 = 0) \Longrightarrow q = \sum_i e^{-\beta\varepsilon_i} = 1$,

  $n_0 = N\frac{e^{-\varepsilon_0\beta}}{1} = N$

  $n_i = N\frac{e^{-\varepsilon_i\beta}}{1} = 0$, where $i \neq 0$

- $T \to \infty K, \beta \to 0$, supposing that the system has only two states, $q = \sum_i e^{-\beta\varepsilon_i} = 2$,

  $\varepsilon_0 = 0$ and $\varepsilon_1 > 0 \Longrightarrow n_0 = n_1 = N/2$.

- In general, the value of the partition function gives the number of states available for the system.

The effect of temperature, Boltzmann distribution

Partition function, separation of the degrees of freedom

- The energy of a molecule can be approximetly divided into more or less independent contributions: translation, rotation, vibration, electronic excitation, *etc.*,

  $\varepsilon_K = \varepsilon_i^{tr} + \varepsilon_j^{rot} + \varepsilon_k^{vib} + \varepsilon_l^{el}.$
- Partition function:

  $$q = \sum_K e^{-\beta\varepsilon_K} = \sum_{i,j,k,l} e^{-\beta\left(\varepsilon_i+\varepsilon_j+\varepsilon_k+\varepsilon_l\right)} = q^{tr} q^{rot} q^{vib} q^{el}$$
- Typical values for the partition functions (room temeperature, 1 mol gas): $q^{el} = 1$, $q^{vib} = 1.001$, $q^{rot} = 10$, $q^{tr} = 10^6$

Molecular symmetry

molecular symmetry operation: the initial and final states are indistinguishable

- physical properties are invariant with respect to symmetry operations
- for every operation there exists a corresponding symmetry element

Molecular symmetry

molecular symmetry operation: the initial and final states are indistinguishable

symmetry operations	symmetry elements
reflection	plane
rotation	axis
inversion	center

one symmetry element can generate more than one operation

for example: clockwise, anticlockwise rotation

Molecular symmetry

group

set of elements (e.g., $a, b, c, \ldots$) together with a binary operation (multiplication)

four conditions: (i) one of the elements is the identity($aI = a$), (ii) associativity of multipication($a\,(bc) = (ab)\,c$), (iii) each elemenet has an inverse (for any a there is a b for which $ab = I$), (iv) closure(if a and b are elements of the set than ab is also in the set)

examples:

- the set of integers with addition (identity element?)
- the set $\{1, i, -1, -i\}$ with ordinary multiplication
- the set of matrices $\left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \right\}$ with matrix multiplication

Molecular symmetry

group

set of elements together with a binary operation

the set $\{1, i, -1, -i\}$ with ordinary multiplication

- identity element, E, is the number 1
- associativity: $a(bc) = (ab)c$
- inverse and closure → group table

	1	i	-1	-i
1	1	i	-1	-i
i	i	-1	-i	1
-1	-1	-i	1	i
-i	-i	1	i	-1

↔

	1	i	-1	-i
1	1	i	-1	-i
-i	-i	1	i	-1
-1	-1	-i	1	i
i	i	-1	-i	1

↔

	E	A	B	C
E	E	A	B	C
C	C	E	A	B
B	B	C	E	A
A	A	B	C	E

Molecular symmetry

group

set of elements together with a binary operation

the set of matrices $\left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \right\}$ with matrix multiplication

- identity element, $E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
- associativity: $A(BC) = (AB)C$
- inverse and closure → Cayley/group table, A= $\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$, B= $\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$, C= $\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$

	E	A	B	C
E	E	A	B	C
C	C	E	A	B
B	B	C	E	A
A	A	B	C	E

$$CA = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Molecular symmetry

group

set of elements together with a binary operation

the sets $\{1, i, -1, -i\}$ and $\left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \right\}$ are different representations of the same group (C_{2v}, see later ...)

	E	A	B	C
E	E	A	B	C
C	C	E	A	B
B	B	C	E	A
A	A	B	C	E

Molecular symmetry

group

set of elements together with a binary operation

point group

the center of mass is invariant for the operations, i.e., the symmetry elements have a common point

elements of the point group are the symmetry operations (not the symmerty elements)

binary operation is the successive application of two symmetry operations;

$PQ \rightarrow$ first Q then P

Molecular symmetry

symmetry operations

1. identity
2. rotation
3. reflection
4. inversion
5. improper rotation

symmetry tutorial website

Molecular symmetry

rotation

C_n denotes the *n*-fold axis of symmetry

the rotational angle, α, is $360^\circ/n$ or $n = 360^\circ/\alpha$

more than one rotational axis ⇒ greatest C_n is called the principal axis

Molecular symmetry

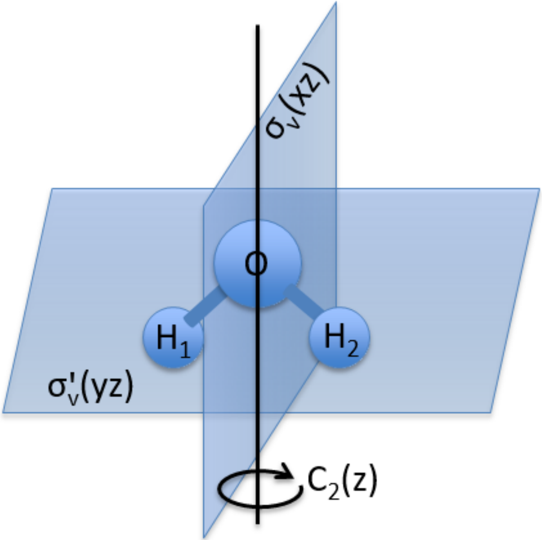
reflection

σ denotes the mirror plane

- vertical, σ_v, parallel to the principal axis (vertical planes bisects as many atoms as possible)
- horizontal, σ_h, perpendicular to the principal axis
- dihedral, σ_d, vertical and bisects two C_2 axes (dihedral planes are such planes, which bisects as many bonds as possible)

Molecular symmetry

H_2O, σ_v



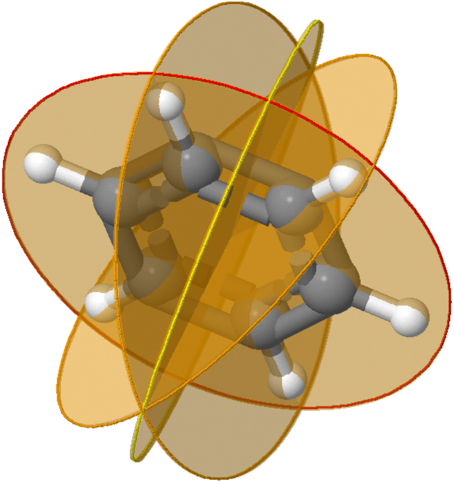
Molecular symmetry

benzene, σ_v, σ_h, and σ_d

σ_h: red

σ_v: brown

σ_d: yellow



Molecular symmetry

inversion, improper rotation

i denotes the center of symmetry

S_n denotes the n-fold improper axis of symmetry

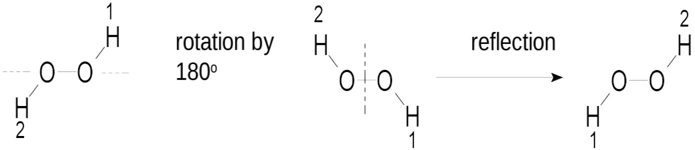
S_n - two successive transformation:

- rotation by $360^\circ/n$
- reflection through a perpendicular plane

note that $S_2 = i$ and $S_1 = \sigma$

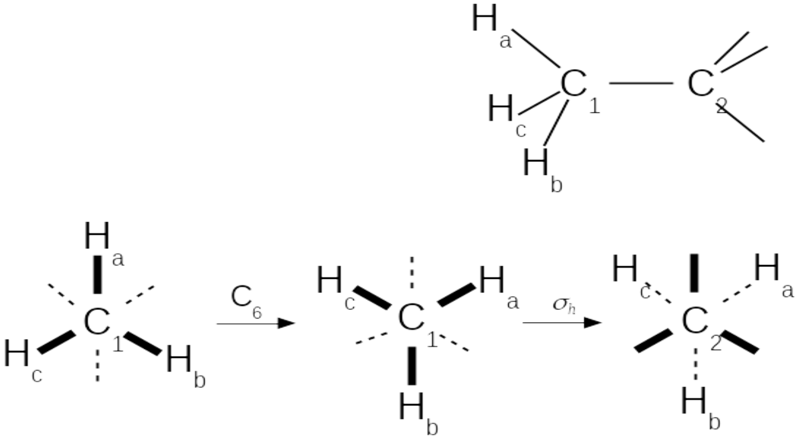
Molecular symmetry

hydrogen peroxide, $S_2 = i$



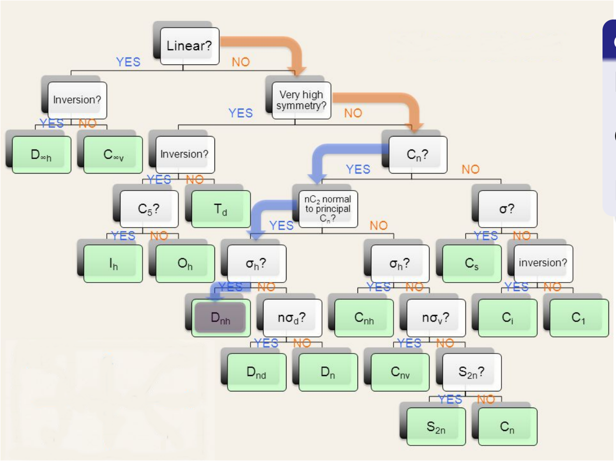
Molecular symmetry

Staggered ethane, S_6



Molecular symmetry

flowchart of point groups



examples

H_2O

C_6H_6

NH_3

Molecular symmetry

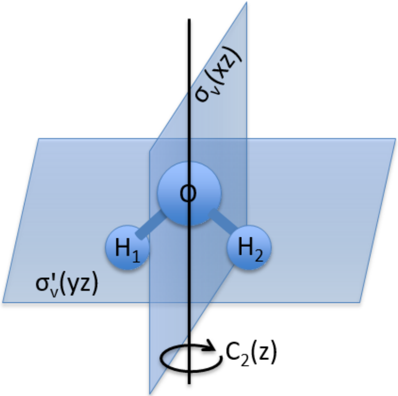
applications

chiral molecules: S_n is absent (non-superimposable on its mirror image)

polar molecules: C_n, C_{nv}, and C_s (dipole moment)

Molecular symmetry

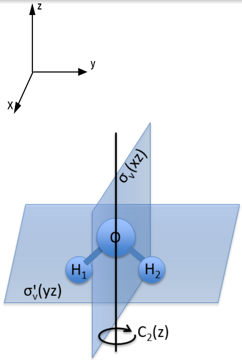
the C_{2v} group multiplication table



	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

Molecular symmetry

matrix representation of the C_{2v} group



$$\boldsymbol{C_2}\begin{pmatrix} p_x^O \\ p_x^{H_1} \\ p_x^{H_2} \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} p_x^O \\ p_x^{H_1} \\ p_x^{H_2} \end{pmatrix} = \begin{pmatrix} -p_x^O \\ -p_x^{H_2} \\ -p_x^{H_1} \end{pmatrix}$$

$$\boldsymbol{\sigma_v}\begin{pmatrix} p_x^O \\ p_x^{H_1} \\ p_x^{H_2} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} p_x^O \\ p_x^{H_1} \\ p_x^{H_2} \end{pmatrix} = \begin{pmatrix} p_x^O \\ p_x^{H_2} \\ p_x^{H_1} \end{pmatrix}$$

$$\boldsymbol{\sigma_v'}\begin{pmatrix} p_x^O \\ p_x^{H_1} \\ p_x^{H_2} \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} p_x^O \\ p_x^{H_1} \\ p_x^{H_2} \end{pmatrix} = \begin{pmatrix} -p_x^O \\ -p_x^{H_1} \\ -p_x^{H_2} \end{pmatrix}$$

The p_x^O, $p_x^{H_1}$, and $p_x^{H_2}$ orbitals define a representation

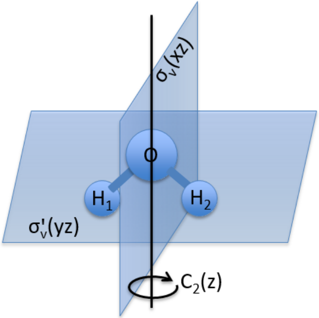
of the C_{2v} group.

$$\boldsymbol{E}\begin{pmatrix} p_x^O \\ p_x^{H_1} \\ p_x^{H_2} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_x^O \\ p_x^{H_1} \\ p_x^{H_2} \end{pmatrix} = \begin{pmatrix} p_x^O \\ p_x^{H_1} \\ p_x^{H_2} \end{pmatrix}$$

Molecular symmetry

matrix representation of the C_{2v} group

	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E



$$\boldsymbol{C_2} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$\boldsymbol{\sigma_v} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\boldsymbol{\sigma_v'} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\sigma_v \sigma_v' = C_2 \leftrightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Molecular symmetry

matrix representation of the C_{2v} group

$$\boldsymbol{E} = \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right) \qquad \boldsymbol{C_2} = \left(\begin{array}{c|cc} -1 & 0 & 0 \\ \hline 0 & 0 & -1 \\ 0 & -1 & 0 \end{array}\right)$$

$$\boldsymbol{\sigma_v} = \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 0 & 1 \\ 0 & 1 & 0 \end{array}\right) \qquad \boldsymbol{\sigma_v'} = \left(\begin{array}{c|cc} -1 & 0 & 0 \\ \hline 0 & -1 & 0 \\ 0 & 0 & -1 \end{array}\right)$$

$$\mathbf{BD} = \left(\begin{array}{c|cc} \bullet & & \\ \hline & \bullet & \bullet \\ & \bullet & \bullet \end{array}\right)$$

block diagonal matrix

p_x^O does not mix with $p_x^{H_1}$ or $p_x^{H_2}$

Molecular symmetry

reducible representations

$$
\begin{array}{lcllll}
\Gamma^{(3)} & = & \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right) & \left(\begin{array}{c|cc} -1 & 0 & 0 \\ \hline 0 & 0 & -1 \\ 0 & -1 & 0 \end{array}\right) & \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 0 & 1 \\ 0 & 1 & 0 \end{array}\right) & \left(\begin{array}{c|cc} -1 & 0 & 0 \\ \hline 0 & -1 & 0 \\ 0 & 0 & -1 \end{array}\right) \\
\Gamma^{(1)} & = & \quad 1 & \quad -1 & \quad 1 & \quad -1 \\
\Gamma^{(2)} & = & \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} & \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}
\end{array}
$$

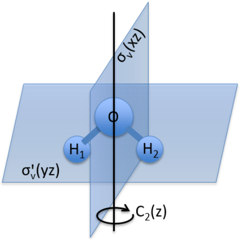
$\Gamma^{(3)} = \Gamma^{(1)} \oplus \Gamma^{(2)}$

- $\Gamma^{(3)}$ - a 3-dimensional reducible representation
- $\Gamma^{(1)}$ - a 1-dimensional irreducible representation
- $\Gamma^{(2)}$ - a 2-dimensional (reducible) representation

Molecular symmetry

how to reduce $\Gamma^{(2)}$ further

$p_x^{H_1}$ and $p_x^{H_2}$ are degenerate orbitals let's try their linear combinations



$$p_+ = p_x^{H_1} + p_x^{H_2}$$

$$p_- = p_x^{H_1} - p_x^{H_2}$$

$$\boldsymbol{E}\begin{pmatrix} p_+ \\ p_- \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} p_+ \\ p_- \end{pmatrix} = \begin{pmatrix} p_+ \\ p_- \end{pmatrix} \qquad \boldsymbol{C_2}\begin{pmatrix} p_+ \\ p_- \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} p_+ \\ p_- \end{pmatrix} = \begin{pmatrix} -p_+ \\ p_- \end{pmatrix}$$

$$\boldsymbol{\sigma_v}\begin{pmatrix} p_+ \\ p_- \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} p_+ \\ p_- \end{pmatrix} = \begin{pmatrix} p_+ \\ -p_- \end{pmatrix} \qquad \boldsymbol{\sigma_v'}\begin{pmatrix} p_+ \\ p_- \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} p_+ \\ p_- \end{pmatrix} = \begin{pmatrix} -p_+ \\ -p_- \end{pmatrix}$$

Molecular symmetry

reducible representations

$$\begin{array}{lccccc}
\Gamma^{(3)} & = & \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right) & \left(\begin{array}{c|cc} -1 & 0 & 0 \\ \hline 0 & 0 & -1 \\ 0 & -1 & 0 \end{array}\right) & \left(\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 0 & 1 \\ 0 & 1 & 0 \end{array}\right) & \left(\begin{array}{c|cc} -1 & 0 & 0 \\ \hline 0 & -1 & 0 \\ 0 & 0 & -1 \end{array}\right) \\
\Gamma^{(1)} & = & 1 & -1 & 1 & -1 \\
\Gamma^{(2)} & = & \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} & \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}
\end{array}$$

$$\begin{array}{lccccc}
\Gamma^{(2)} & = & \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} & \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \\
\Gamma^{(1)} & = & 1 & -1 & 1 & -1 \\
\Gamma'^{(1)} & = & 1 & 1 & -1 & -1
\end{array}$$

$\Gamma^{(3)} = 2\Gamma^{(1)} \oplus \Gamma'^{(1)}$

Molecular symmetry

irreducible and reducible representations

$$\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n-1} & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n-1} & a_{2n} \\ & \ddots & & & \\ \vdots & & a_{ii} & & \vdots \\ & & & \ddots & \\ a_{n-11} & a_{n-12} & \cdots & a_{n-1n-1} & a_{n-1n} \\ a_{n1} & a_{n2} & \cdots & a_{nn-1} & a_{nn} \end{pmatrix}$$

- character:

  trace of the matrix,

  $\mathrm{tr}\mathbf{a} = \sum_i a_{ii}$
- characters do not depend on the form of representation: the matrices defined by $p_x^{H_1}$ and $p_x^{H_2}$ have the same characters than the ones defined by p_+ and p_-.

Molecular symmetry

character tables, irreducible representations, symmetry operations

Character tables: collection of the possible transformation properties of wave functions under symmetry operations

$\boldsymbol{C_{2v}}$	E	C_2	σ_v	σ_v'	lin., rot.	quad.
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
$\Gamma^{(3)}$	3	-1	1	-3		

A_1 is the so-called totally symmetric representation.

$$\boldsymbol{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\boldsymbol{C_2} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}$$

$$\boldsymbol{\sigma_v} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\boldsymbol{\sigma_v'} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Molecular symmetry

Class

- Symmetry operations fall into the same *class* if they are of the same type (for example, rotations) and can be transformed into one another by a symmetry operation of the group: a and b are in the same class if there is a group element c for which $cac^{-1} = b$.
- Number of irreducible representations = number of classes
- The value of character is uniform in a class.

Molecular symmetry

irreducible and reducible representations, reduction formula

$$n_i = \frac{1}{h} \sum_{classes} g_c \chi_{irr} \chi_{red}$$

- n_i number of times the irreducible representation occurs
- h order of the group
- g_c number of operations in the class
- χ_{irr} character of the irreducible representation
- χ_{red} character of the reducible representation

Molecular symmetry

the C_{2v} group character table

$\boldsymbol{C_{2v}}$	E	C_2	σ_v	σ_v'	lin., rot.	quad.
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
$\Gamma^{(3)}$	3	-1	1	-3		

$$\Rightarrow \quad \Gamma^{(3)} = A_2 \oplus 2B_1$$

$$N_{A_1} = \frac{1}{4}\{1\cdot 1\cdot 3 + 1\cdot 1\cdot(-1) + 1\cdot 1\cdot 1 + 1\cdot 1\cdot(-3)\} = 0$$

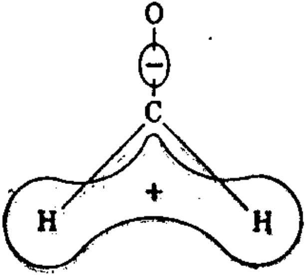
$$N_{A_2} = \frac{1}{4}\{1\cdot 1\cdot 3 + 1\cdot 1\cdot(-1) + 1\cdot(-1)\cdot 1 + 1\cdot(-1)\cdot(-3)\} = 1$$

$$N_{B_1} = \frac{1}{4}\{1\cdot 1\cdot 3 + 1\cdot(-1)\cdot(-1) + 1\cdot 1\cdot 1 + 1\cdot(-1)\cdot(-3)\} = 2$$

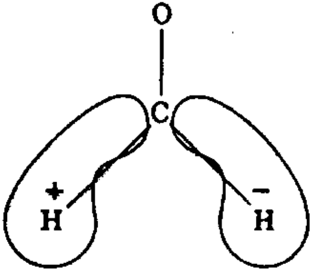
$$N_{B_2} = \frac{1}{4}\{1\cdot 1\cdot 3 + 1\cdot(-1)\cdot(-1) + 1\cdot(-1)\cdot 1 + 1\cdot 1\cdot(-3)\} = 0$$

Molecular symmetry

Two molecular orbitals of formaldehyde



(b)



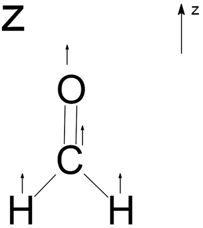
(c)

	E	C_2	σ_{xz}	σ_{yz}	irrep.
(b)	+1	+1	+1	+1	A_1
(c)	+1	-1	+1	-1	B_1

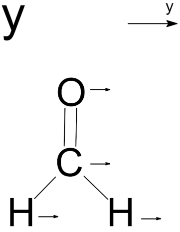
Molecular symmetry

Assignment of translations and rotations

Tz



Ty



	E	C_2	σ_{xz}	σ_{yz}	irrep.
T_z	+1	+1	+1	+1	A_1
T_y	+1	-1	-1	+1	B_2
T_x	+1	-1	+1	-1	B_1

Rotations can be assigned similarly:

	E	C_2	σ_{xz}	σ_{yz}	irrep.
R_x	+1	-1	-1	+1	B_2
R_y	+1	-1	+1	-1	B_1
R_z	+1	+1	-1	-1	A_2

Molecular symmetry

character tables

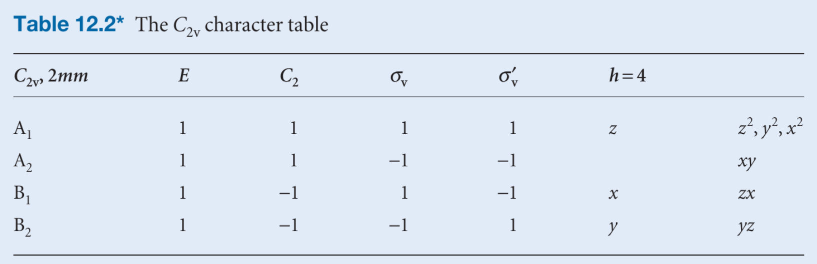


Table 12.2* The C_{2v} character table

C_{2v}, $2mm$	E	C_2	σ_v	σ'_v	$h=4$	
A_1	1	1	1	1	z	z^2, y^2, x^2
A_2	1	1	−1	−1		xy
B_1	1	−1	1	−1	x	zx
B_2	1	−1	−1	1	y	yz

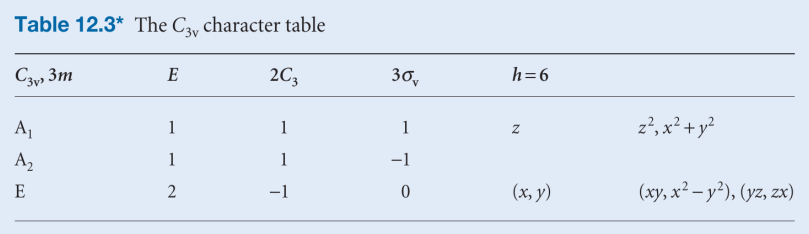
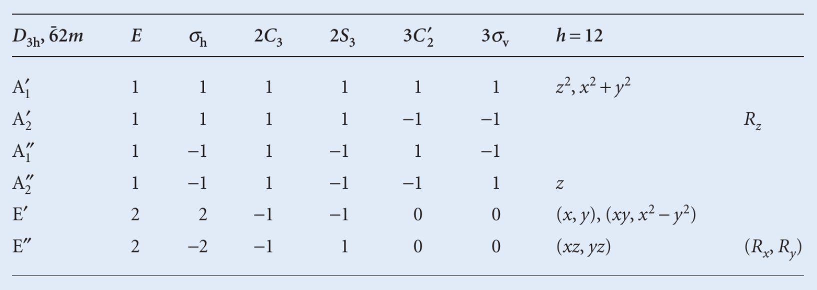


Table 12.3* The C_{3v} character table

C_{3v}, $3m$	E	$2C_3$	$3\sigma_v$	$h=6$	
A_1	1	1	1	z	z^2, x^2+y^2
A_2	1	1	−1		
E	2	−1	0	(x, y)	$(xy, x^2-y^2), (yz, zx)$

Molecular symmetry

irreducible and reducible representations



$D_{3h}, \bar{6}2m$	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$	$h=12$	
A_1'	1	1	1	1	1	1	z^2, x^2+y^2	
A_2'	1	1	1	1	−1	−1		R_z
A_1''	1	−1	1	−1	1	−1		
A_2''	1	−1	1	−1	−1	1	z	
E'	2	2	−1	−1	0	0	$(x, y), (xy, x^2-y^2)$	
E''	2	−2	−1	1	0	0	(xz, yz)	(R_x, R_y)

E.g., eclipsed ethane.

Let's suppose we have two functions describing some properties of a molecule, f_1 and f_2 (e.g., two molecular orbitals). The value of integral $I = \int f_1 f_2 d\tau$ can be non-zero only if integrand $f_1 f_2$ must have symmetry species A_1. "If the integrand changed sign under a symmetry operation, the integral would be the sum of equal and opposite contributions, and hence would be zero. (Atkins book)"

E.g., $f_1 = \psi_{(b)}$ and $f_2 = \psi_{(c)}$ (see page 274).

	E	C_2	σ_{xz}	σ_{yz}	irrep.
$\psi_{(b)}$	+1	+1	+1	+1	A_1
$\psi_{(c)}$	+1	-1	+1	-1	B_1
$\psi_{(b)}\psi_{(c)}$	+1	-1	+1	-1	B_1

As the $\psi_{(b)}\psi_{(c)}$ transforms as B_1 than the $I = \int \psi_{(b)}\psi_{(c)} d\tau = 0$.

Molecular symmetry

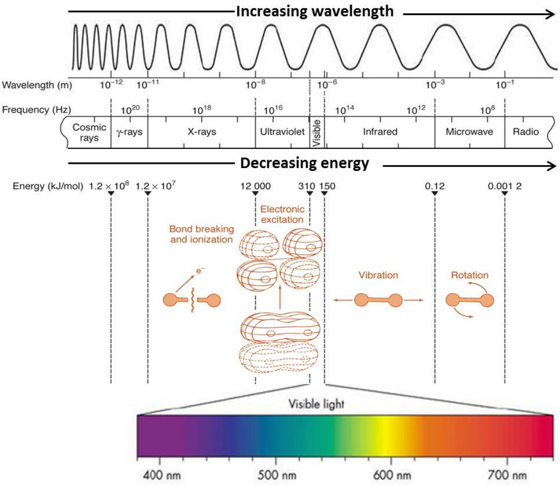
Vanishing integrals, dipol moment

$$\mu = \int \rho(\mathbf{r})\mathbf{r}d\mathbf{r}^3$$

Here $\rho(\mathbf{r})$ is the charge density of the molecule. It is a totally symmetric quantity (transforms as A_1). To have a non-vanishing integral, $\mathbf{r}(x, y, z)$ must contain a component which also transforms as A_1. (See the character tables!)

Optical spectroscopy

general remarks



Optical spectroscopy: from microwave to ultraviolet

Optical spectroscopy

general remarks

- Theoretical background: molecular Schrödinger equation
- Separate treatment of the electonic and nuclei motions: Born-Oppenheimer approximation
- Molecular degrees of freedom: electronic(UV-visible sp.), vibrational(IR sp.), rotational(microwave sp.), and translational

Optical spectroscopy

general remarks

the origin of spectral lines is the interaction of electromagnetic wave and matter

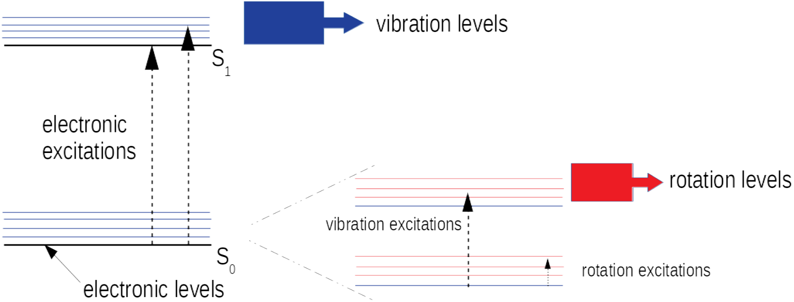
photon

- absorption ($h\nu$ absorbed by the molecule: low → high)
- emission ($h\nu$ emitted by the (molecule: high → low)
- scattering elastic (Rayleigh), inelastic (Stokes, anti-Stokes)

Optical spectroscopy

general remarks

- atomic spectroscopy - electronic transitions
- rotation
- vibration (accompanied by rotational lines)
- electronic (accompanied by rotational and vibrational lines)



Optical spectroscopy

Units for the absorbed light

- UV-visible spectra:

  the wavelength of the absorbed light (λ, in nm [typical range: 200 nm - 1000 nm])

- Infrared spectra:

  the wavenumber of the absorbed light

  (ν^*, in cm^{-1} [in the order of 100 - 1000 cm^{-1}])

- Microwave spectra:

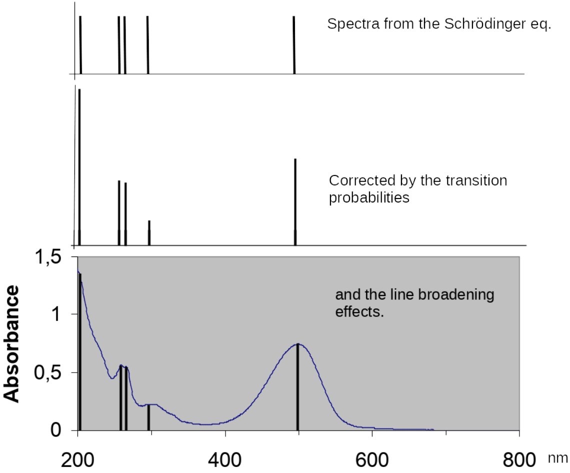
  frequency of the absorbed light

  ($\nu = \frac{c}{\lambda}$, in MHz or GHz)

Optical spectroscopy

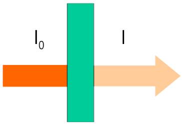
general remarks

The observed spectra do not consist of discrete lines rather are continuous functions, $I(\lambda)$, where I is the intensity as a function of wavelength.



Optical spectroscopy

Quantities characterizing the intensity



$dI = -\kappa c I dx$, where κ is proportional to the molar absorption(see later) and c is the molar concentartion.

$$\frac{dI}{I} = -\kappa c dx$$

$$\int_{I_0}^{I} \frac{dI}{I} = -\kappa c \int_0^L dx$$

$$\ln(\frac{I}{I_0}) = -\kappa c L, \text{ where } \kappa = \epsilon \ln 10$$

line intensities

- transmittance: $T = I/I_0$ transmitted/incident intensity
- Beer-Lambert law: $I = I_0 10^{-\epsilon c L}$ (ϵ - molar absorption coefficient)
- absorbance: $A = log_{10}(I_0/I)$ $(A = -log_{10} T)$
- Beer-Lambert law with absorbance: $A = \epsilon c L$

The absorbance is proportional to the concentration!

Optical spectroscopy

Quantities characterizing the spectral bands

- The properties of the maximum are given as:

  λ_{max}, ν_{max}, or ν^*_{max} and the corresponding A_{max}, or ϵ_{max}.

  ϵ_{max} is independent of the concentration!

- The intensity of a spectral band is defined by the area under the band: $\int_{\nu_1}^{\nu_2} \epsilon(\nu) d\nu$

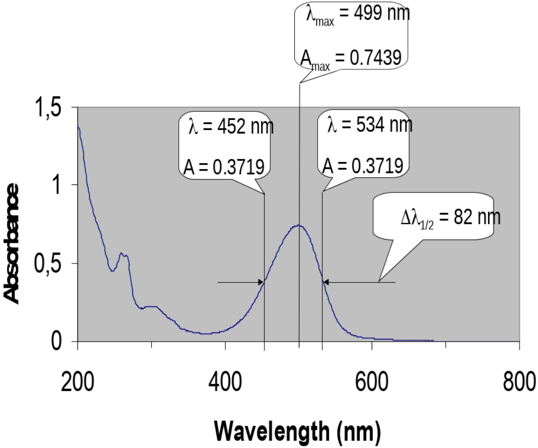
- The width of a band is characterized by its full width at half maximum (FWHM):

  $\Delta\lambda_{max}$, $\Delta\nu_{max}$, or $\Delta\nu^*_{max}$ is the distance between the spectral points corresponding to $\frac{A_{max}}{2}$

Optical spectroscopy

UV-visible spectrum of the "Nile Blue A" dye

solvent: acetonitrile, high absorbtion $\Longrightarrow$ dilute solution ($c = 10^{-5}$ mol/l)



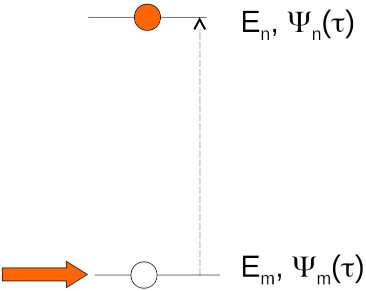
Optical spectroscopy

Interpretation of optical spectra

Schrödinger equation: $\hat{H}\Psi(\tau) = E\Psi(\tau)$

Solutions: $\Psi_0(\tau), \Psi_1(\tau), \Psi_2(\tau), \ldots$ wave functions and the corresponding $E_0, E_1, E_2, \ldots$

The positions of the maxima correspond to the differences of eigenvalues derived from the Schrödinger equation.



ν_{max} is determined by the difference of the energies of the initial (*m*) and final (*n*) states:

$$E_n - E_m = h\nu_{mn}$$

The band intensity reflects the probability of absorption of a photon.

The collision of a photon and a molecule in state m

Bimolecular reaction: $M_m + h\nu \rightarrow M_n$

Optical spectroscopy

Bimolecular reaction, rate equation

$$-\frac{dN_m}{dt} = A_{mn} N_m \rho_\nu$$

- N_m : concentration of molecules in state m
- ρ_ν : concentration of photons
- A_{mn} : rate constant for the absorption

A_{mn} interrelates the observed band intensities to wave functions Ψ

obtained from the Schrödinger equation

Relation to the intensity: $\displaystyle\int_{\nu_1}^{\nu_2} \epsilon(\nu) d\nu = \frac{8\pi N_A h^2 c^4 \nu_{mn}^4}{\ln 10} A_{mn}$

- c : speed of light

Optical spectroscopy

transition moment

Relation to the wave functions:[2]

$A_{mn} \propto |R_{mn}|^2$,

where $|R_{mn}|^2$ is the square of the transition moment.

$\mathbf{R}_{mn} = \int \Psi_m^*(\tau)\hat{\mu}\Psi_n(\tau)d\tau$, where the elementes of vector $\hat{\mu}$ has componenets $\mu_x = \sum_i e_i x_i$, $\mu_y = \sum_i e_i y_i$, and $\mu_z = \sum_i e_i z_i$.

---

[2] $A_{mn} = \frac{2(2\pi)^{\mathbf{3}}c^{\mathbf{4}}\nu^{\mathbf{4}}}{(4\pi\epsilon_{\mathbf{0}})3h}|R_{mn}|^2$

Optical spectroscopy

Linewidth

In our model the following assumptions have been made:

- the molecule is isolated from the other ones,
- the coordinate system is fixed to the molecule, that is, the motion of the molecule with respect to the environment is not considered,
- the lifetimes of the states are infinite (“stationary states”).

Optical spectroscopy

Linewidth

The broadening of spectral lines can be traced back to the following reasons:

1. Interaction of the molecules. The energy levels of molecules are perturbed by other molecules located closely, thus the energy levels broaden. This effect is not quantized. The linewidth is determined by this effect in solids, liquids, and high-pressure gases.

Optical spectroscopy

Linewidth

2. Doppler effect: the molecules are traveling with various velocities and in various directions. The absorption frequency is modified by their velocity relative to the detector

$$\nu' = \nu \left(1 \pm \tfrac{v}{c}\right)$$

The shape of the band reflects the (non-quantized) velocity distribution of the molecules.

Equipartition theorem:

$\langle E_{kin} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \implies v \propto \sqrt{k_B T} \implies \delta\nu \propto \frac{\nu}{c}\sqrt{k_B T} \implies$ low temperature (FWHM decreases)

3. Natural line broadening (Fourier-limit)

The finite lifetime of the molecular states limits the accuracy of the observed energy levels.

Broadening of the initial state: $\tau_m \Delta E_m \geq h$

Broadening of the final state: $\tau_n \Delta E_n \geq h$

Similar to the Heisenberg uncertainty principle.

low pressure $\Longrightarrow$ deactivation decreases $\Longrightarrow$ τ increases

It determines the minimal achievable linewidth!

Rotational spectroscopy

Model: rigid rotor

It consists of point masses (the nuclei) and it is

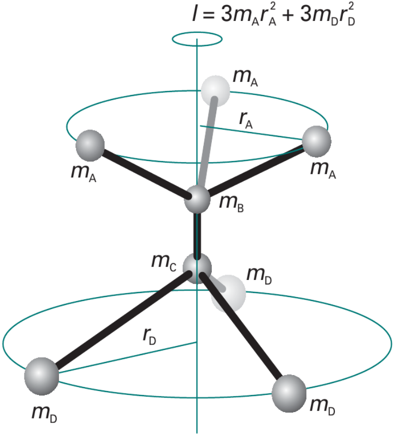
- a rotor (it rotates about its center of mass)
- rigid (it is not deformed by centrifugal forces, that is, bond distances and angles are constant)

Rotational spectroscopy

Moment of inertia

moment of inertia: $I = \sum_i m_i r_i^2$

r_i is the distance to the rotation axis. (Not to the center of mass!)



Rotational spectroscopy

Principal axes of inertia

a, b, c - Cartesian coordinate system fixed to the molecule

axis a: the moment of inertia has its minimum value about it

axis c: the moment of inertia has its maximum value about it

axis b: the third perpendicular axis

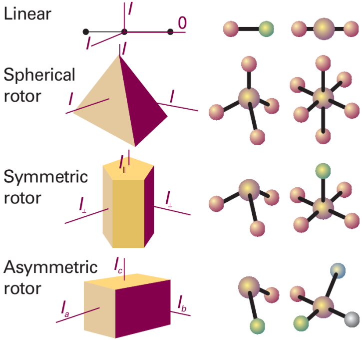
$$I_a \leq I_b \leq I_c$$

Rotational spectroscopy

Classification of rotors

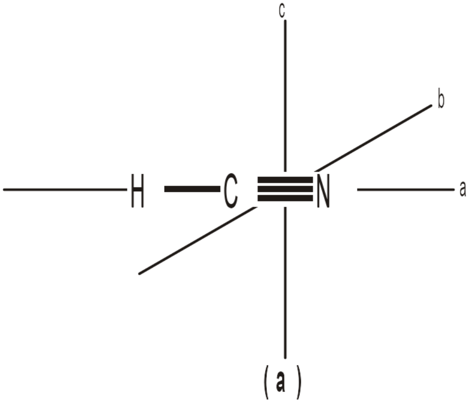
principal axes of inertia: $I_a < I_b < I_c$

1. linear $I_a = 0,\ I_b = I_c = I$
2. spherical top $I_a = I_b = I_c = I$
3. symmetric top
    - prolate $I_a = I_{\|},\ I_b = I_c = I_{\perp}$
    - oblate $I_a = I_b = I_{\perp},\ I_c = I_{\|}$
4. asymmetric top $I_a \neq I_b \neq I_c$



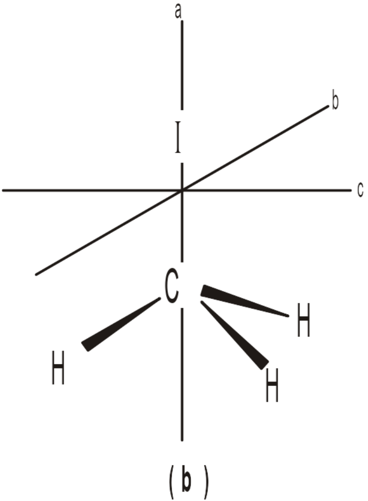
Rotational spectroscopy

Linear rotor: HCN



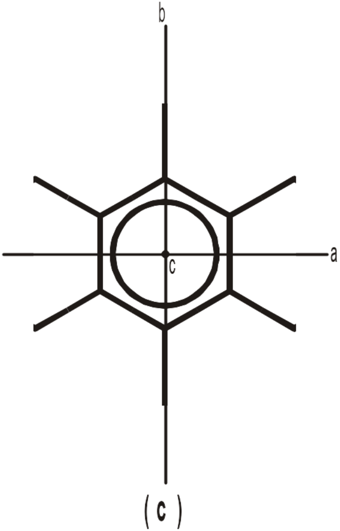
Rotational spectroscopy

Prolate symmetric rotor: methyl iodide



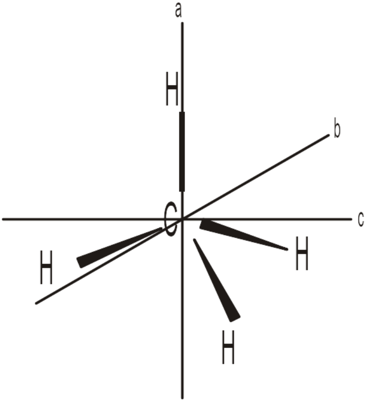
Rotational spectroscopy

Oblate symmetric rotor: benzene



Rotational spectroscopy

Spherical rotor: methane



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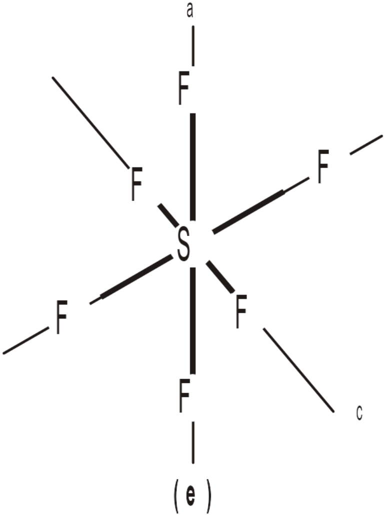
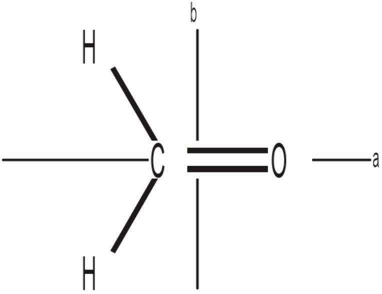
Rotational spectroscopy

Spherical rotor: sulfur hexafluoride



Rotational spectroscopy

Asymmetric rotor: formaldehyde



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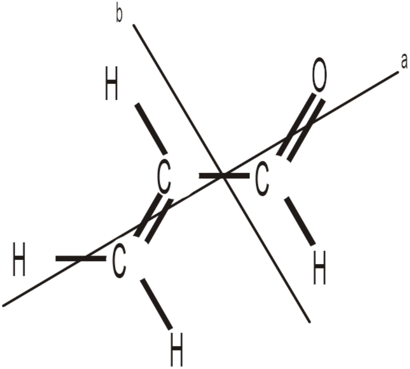
Rotational spectroscopy

Asymmetric rotor: acrolein



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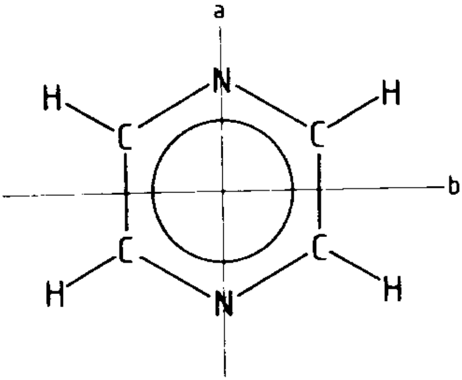
Rotational spectroscopy

Asymmetric rotor: pyrazine



(h)

Rotational spectroscopy

rotational spectroscopy, energy levels

recall the particle on the sphere problem:

$$\text{classical } \rightarrow E = \frac{1}{2}mv^2 = \frac{1}{2}\frac{(mrv)^2}{mr^2} = \frac{\ell^2}{2I}$$

$$\text{quantum } \rightarrow E_\ell = \ell(\ell+1)\frac{\hbar^2}{2I},\ \ell = 0, 1, 2, \ldots,\ m_\ell \in [-\ell, \ell]$$

$$E_i = \frac{1}{2}I_i\omega_i^2 = \frac{J_i^2}{2I_i},\ i \in (a, b, c)$$

$$E = \sum_i \frac{J_i^2}{2I_i},\ i \in (a, b, c)$$

Rotational spectroscopy

rotational spectroscopy, energy levels

spherical tops: $I_a = I_b = I_c = I$

$$\text{classical } \rightarrow E = \frac{J_a^2 + J_b^2 + J_c^2}{2I} = \frac{J^2}{2I}$$

$$\text{quantum } \rightarrow E_J = J(J+1)\frac{\hbar^2}{2I},\ J = 0, 1, 2, \ldots$$

rotational constant: $B = \frac{1}{hc} \times \frac{\hbar^2}{2I}$

$$F(J) = \frac{E_J}{hc} = BJ(J+1),\ J = 0, 1, 2, \ldots$$

$$\tilde{\nu} = F(J+1) - F(J) = 2B(J+1)$$

Rotational spectroscopy

rotational spectroscopy, energy levels

symmetric tops: $I_a = I_\parallel$, $I_b = I_c = I_\perp$, $I_\parallel$ is called the principal axis

$$\text{classical} \;\; \to E = \frac{J_a^2}{2I_\parallel} + \frac{J_b^2 + J_c^2}{2I_\perp}$$

$$J^2 = J_a^2 + J_b^2 + J_c^2$$

$$E = \frac{J_a^2}{2I_\parallel} + \frac{J^2 - J_a^2}{2I_\perp} = \frac{J^2}{2I_\perp} + \left\{ \frac{1}{2I_\parallel} - \frac{1}{2I_\perp} \right\} J_a^2 \text{ (prolate)}$$

$$\text{quantum} \;\; \to E_{J,K} = J(J+1)\frac{\hbar^2}{2I_\perp} + \left\{ \frac{\hbar^2}{2I_\parallel} - \frac{\hbar^2}{2I_\perp} \right\} K^2$$

$$J = 0, 1, 2, \ldots \;\; K = 0, \pm 1, \pm 2, \ldots, \pm J$$

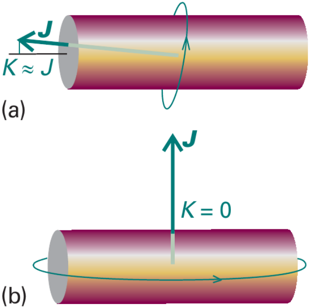
$$F(J,K) = BJ(J+1) + (A-B)K^2 \text{ with } B = \frac{\hbar}{4\pi c I_\perp} \text{ and } A = \frac{\hbar}{4\pi c I_\parallel}$$

Rotational spectroscopy

rotational spectroscopy, energy levels

$$F(J,K) = BJ(J+1) + (A-B)K^2$$

$$B = \frac{\hbar}{4\pi c I_\perp} \text{ and } A = \frac{\hbar}{4\pi c I_\parallel}$$



Rotational spectroscopy

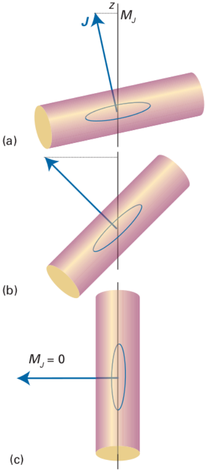
rotation in the laboratory-fixed frame

In general, the total angular momentum (J) can be oriented in $2J + 1$ directions,

$M_J = -J, -J + 1, \ldots, J - 1, J.$

M_J: magnetic quantum number.

The wave function depends on quantum numbers: J,K, and M_J



Rotational spectroscopy

rotational spectroscopy, energy levels

symmetric tops:

$$F(J,K) = BJ(J+1) + (A-B)K^2$$

$$J = 0, 1, 2, \dots \quad K = 0, \pm 1, \pm 2, \dots, \pm J$$

linear rotors: $K = 0$ (classical: $E = \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} = \frac{J^2}{2I}$, where $I = I_b = I_c$)

$$F(J) = BJ(J+1),\ J = 0, 1, 2, \dots$$

$$B = \frac{\hbar}{4\pi c I}$$

spherical tops: $A = B$

$$F(J) = BJ(J+1),\ J = 0, 1, 2, \dots$$

$$B = \frac{\hbar}{4\pi c I}$$

Rotational spectroscopy

rotational spectroscopy, energy levels

degeneracy of the levels

- symmetric tops: $2(2J+1)$, for $K \neq 0$, otherwise $2J+1$

  $(M_J = -J, -J+1, \ldots, J-1, J)$

  $F(J,K) = BJ(J+1) + (A-B)K^2$

- linear rotor: $2J+1$

  $(M_J = -J, -J+1, \ldots, J-1, J)$

  $F(J) = BJ(J+1)$, $K = 0$

- spherical tops: $(2J+1)(2J+1)$

  $(M_J = -J, -J+1, \ldots, J$, $K = -J, -J+1, \ldots, J)$

  $F(J) = BJ(J+1)$, $A = B$

Rotational spectroscopy

Linear rotor, selection rules

- The molecule must have a permanent dipole moment [3] (C_n, C_{nv}, C_s), $\mu_{perm} \neq 0$. E.g., there is no observable rotation spectra of the N_2, O_2, Cl_2 moleculs, but CO, HCl, HCN moleculs have rotational spectra.
- $\Delta J = \pm 1$

  $\Delta E(J \rightarrow J+1) = h\nu = \frac{\hbar^2}{2I}\left((J+1)(J+2) - J(J+1)\right) = \frac{\hbar^2}{I}(J+1) = 2B(J+1)$

---

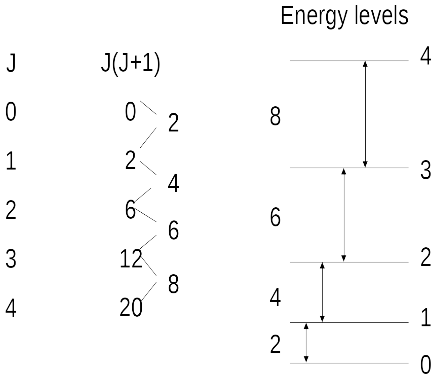
[3] When the transition moment is evaluated for all possible relative orientations of the molecule wrt the photon: $|\mu_{J,J+1}|^2 = |\frac{J+1}{2J+1}|^2 \mu_{perm}$

Rotational spectroscopy

Linear rotor, spectra

Smoothly increasing distances between the energy levels.

The spectrum is composed of equidistant lines.

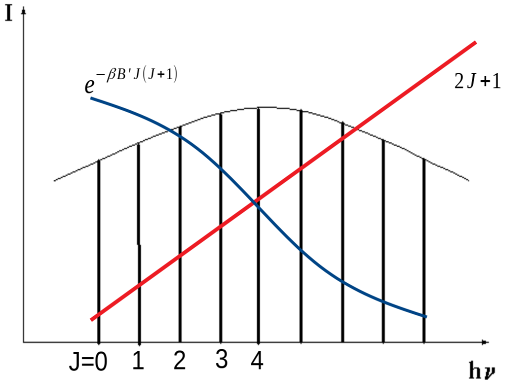


Rotational spectroscopy

Linear rotor, spectra

Absorption frequencies: equidistant lines.

Intensity: first increases, then decreases.



Rotational spectroscopy

Linear rotor, spectra

- Two opposing effects.
- Boltzman's distribution: The most populated state is the ground state, the population of the states decreases with increasing J, thus peaks of various intensities are expected.
- M_J quantum number: The number of degenerate states increases with increasing J. (The statistical weight increases.)
- The sum of the two contributions results in the maximum of intensities (Temperature-dependent!)

Rotational spectroscopy

rotational spectroscopy, population

intensities depend on the population of the lower state

Boltzmann: $\frac{N_J}{N} = \frac{e^{-\epsilon_J/kT}}{q}$

$$\frac{N_J}{N} = g_J \frac{e^{-hcBJ(J+1)/kT}}{q}$$ (the level of degeneracy can be also considered:g_J)

$$\frac{N_J}{N} = (2J+1)\frac{e^{-hcBJ(J+1)/kT}}{q}$$

$$\frac{dN_J/N}{dJ} = 0 \text{ at the maximum}$$

$$\frac{d}{dJ}\{(2J+1)e^{-hcBJ(J+1)/kT}\} = 0$$

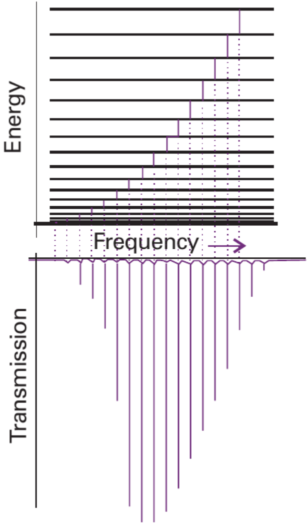
$$2e^{-hcBJ(J+1)/kT} + (2J+1)\frac{-hcB}{kT}(2J+1)e^{-hcBJ(J+1)/kT} = 0$$

$$(2J+1)^2 = \frac{2kT}{hcB}$$

$$J_{max} \approx \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

Rotational spectroscopy

rotational spectroscopy, population



Rotational spectroscopy

rotational spectroscopy, CO molecule

$$F(J) = BJ(J+1),\ J = 0, 1, 2, \ldots$$

$$\tilde{\nu}(J+1 \leftarrow J) = F(J+1) - F(J) = 2B(J+1), \text{ and } B = \frac{\hbar}{4\pi c I}$$

Isotope effects: ^{13}C, ^{18}O

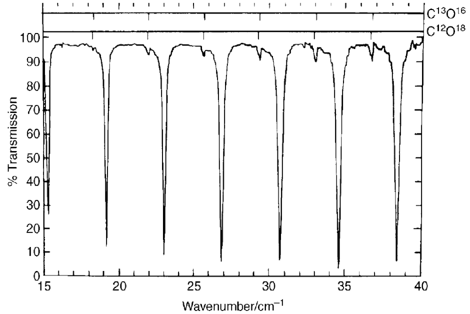


Figure 5.3 Far-infrared spectrum of CO showing transitions with $J'' = 3$ to 9. (Reproduced, with permission, from Fleming, J. W. and Chamberlain, J., *Infrared Phys.*, **14**, 277, 1974. Copyright 1974 Pergamon Press)

Rotational spectroscopy

rotational spectroscopy, population

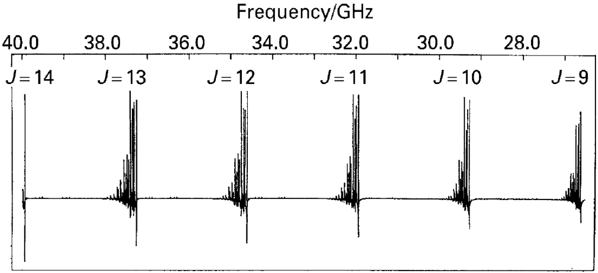


Figure 5.4 Part of the microwave spectrum of cyanodiacetylene. (The many 'satellite' transitions in each group are due to the molecule being in not only the zero-point vibrational state but also a multitude of excited vibrational states.) (Reproduced, with permission, from Alexander, A. J., Kroto, H. W. and Walton, D. R. M., *J. Mol. Spectrosc.*, **62**, 175, 1967)

Rotational spectroscopy

Spherical rotor, selection rules

- The molecule must have a permanent dipole moment, $\mu_{perm} \neq 0$.
- $\Longrightarrow$ For each spherical rotor $\mu_{perm} = 0$, hence there is no rotational spectrum.

Rotational spectroscopy

Symmetric rotor, selection rules

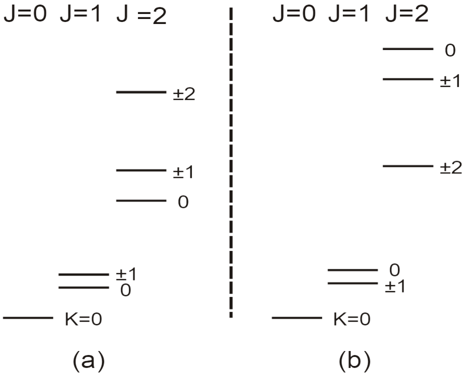
- The molecule must have a permanent dipole moment, $\mu_{perm} \neq 0$.
- $\Delta J = \pm 1$
- $\Delta K = 0$

Because of the last rule, equidistant lines are expected:

$F(J+1) - F(J) = 2B(J+1)$

In practice a slight splitting wrt K is observed. (K=0 $\rightarrow$ 0, K=1 $\rightarrow$ 1, K=2 $\rightarrow$ 2) (centrifugal distortion)

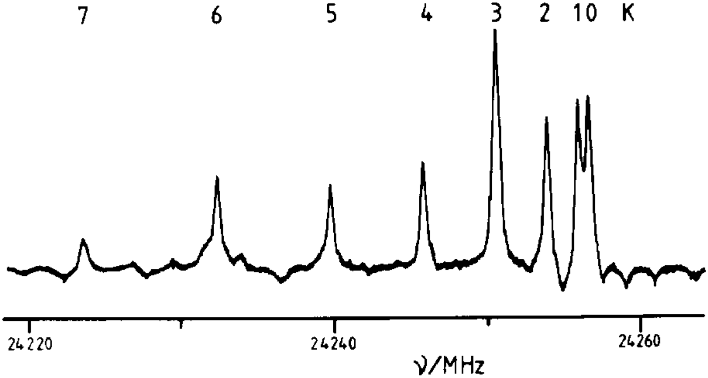
Rotational energy levels of prolate (a) and oblate (b) symmetric rotors



Rotational spectroscopy

Symmetric rotor, selection rules, effect of centrifugal distortion

Splitting wrt K (K=0 → 0, K=1 → 1, K=2 → 2)



Splitting of the J=7 → J=8 transition wrt K in the rotational spectrum of SiH_3NCS

Rotational spectroscopy

Asymmetric rotor

Transition between the prolate and oblate symmetric rotors.

Asymmetry parameter:

$$\kappa = \frac{2I_aI_c - I_b(I_c + I_a)}{I_b(I_c - I_a)}$$

Prolate symmetric

$I_a < I_b = I_c$

$$\kappa = \frac{2I_aI_b - I_b(I_b + I_a)}{I_b(I_b - I_a)} = -1$$

Oblate symmetric

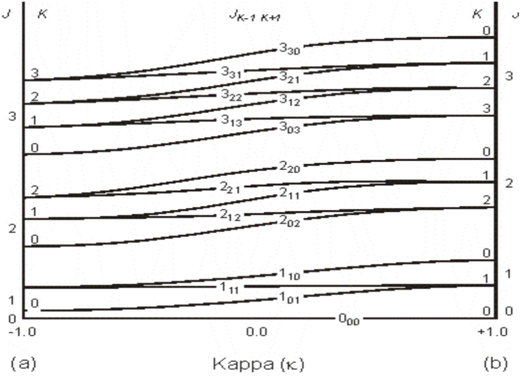
$I_a = I_b < I_c$

$$\kappa = \frac{2I_aI_c - I_a(I_c + I_a)}{I_a(I_c - I_a)} = 1$$

Rotational spectroscopy

Energy levels of the asymmetric rotor

(a) prolate symmetric rotor, (b) oblate symmetric rotor, κ asymmetry parameter



Selection rule:

a, $\mu_{perm} \neq 0$

b, $\Delta J = 0, \pm 1$

Rotational transitions are located in the microwave(1mm-1cm) and far infrared(0.03-1mm) regions.

On the abscissa, instead of λ:

- frequency (ν) in MHz or GHz in the microwave region
- wavenumbers (ν^*) in cm^{-1} in the far IR region

Molecular geometry

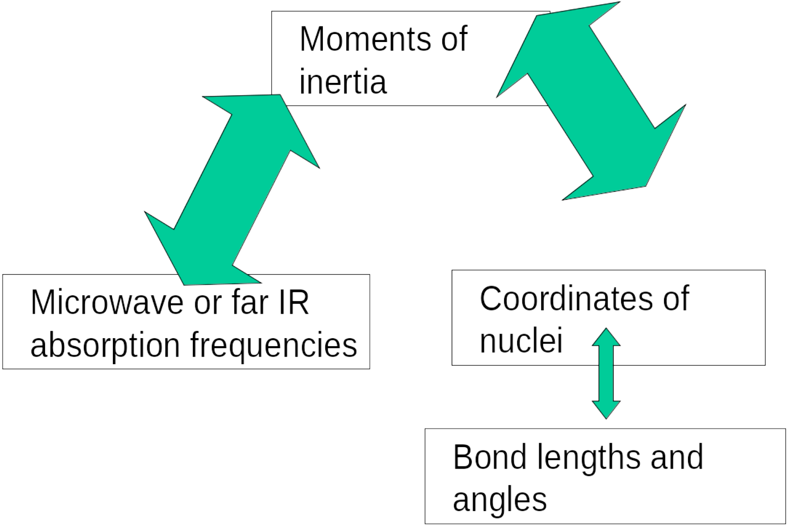
- coordinates of nuclei (In rotational spectroscopy the coordinates are given wrt the principal axes of inertia a, b, and c.)

or:

- bond lengths and bond angles calculated from the coordinates of the nuclei

Rotational spectroscopy

Determination of molecular geometries from rotational spectra



Moments of inertia

Microwave or far IR absorption frequencies

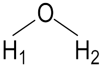
Coordinates of nuclei

Bond lengths and angles

Rotational spectroscopy

Determination of molecular geometries from rotational spectra

How many independent bond lengths and angles does a H_2O molecule have?



$d(H_1—O)$

$\theta(H_1—O—H_2)$

The other parameters can be calculated from these ones if the molecule is regarded as an isosceles triangle.

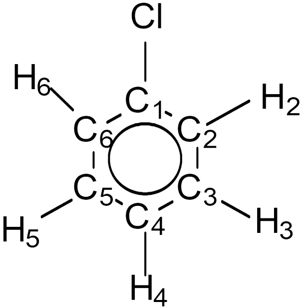
Pl. $d(H_2—O) = d(H_1—O)$

$d(H_1—H_2) = 2\ d(H_1—O) \cos[\theta(H_1—O—H_2)/2]$

Rotational spectroscopy

Determination of molecular geometries from rotational spectra

How many independent bond lengths and angles does a C_6H_5Cl molecule have?



d(C_1-Cl),

d(C_1-C_2), d(C_2-C_3), d(C_3-C_4),

d(C_2-H_2), d(C_3-H_3), d (C_3-H_3),

$\theta C_1C_2C_3)$, $\theta(C_2C_3C_4)$, $\theta(C_3C_4C_5)$, $\theta(ClC_1C_2)$,

$\theta(H_2C_2C_3)$, $\theta(H_3C_3C_4)$, $\theta(H_4C_4C_5)$

How many equations do we have for the calculation?

Three!!!

$$\mathrm{I}_a = \mathrm{f}_a(\mathrm{d}_1, \mathrm{d}_2, \ldots, \theta_1, \theta_2, \ldots)$$
$$\mathrm{I}_b = \mathrm{f}_b(\mathrm{d}_1, \mathrm{d}_2, \ldots, \theta_1, \theta_2, \ldots)$$
$$\mathrm{I}_c = \mathrm{f}_c(\mathrm{d}_1, \mathrm{d}_2, \ldots, \theta_1, \theta_2, \ldots)$$

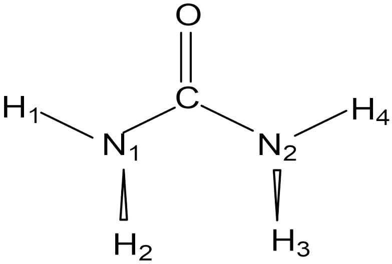
Solution: synthesis of isotopically substituted compounds and measurement of their microwave spectra.

It can be assumed that upon substitution,

- the changes in bond lengths and angles are negligible
- the changes in moments of inertia are significant.

Thus we can derive enough equations for the determination of the structure.

Example: determination of the molecular structure of carbamide



P. D. Godfrey, R. D. Brown, A. N. Hunter, J. Mol. Struct. **413-414**, 405 (1997)

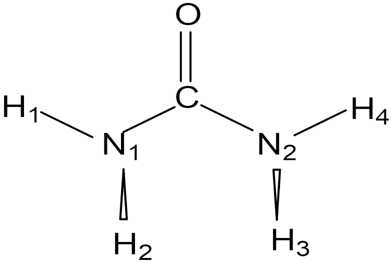
Isotopomers

H_2N—CO-NH_2

H_2N—CO-NHD

$H_2{}^{15}N$—CO—${}^{15}NH_2$

H_2N—$C^{18}O$—NH_2

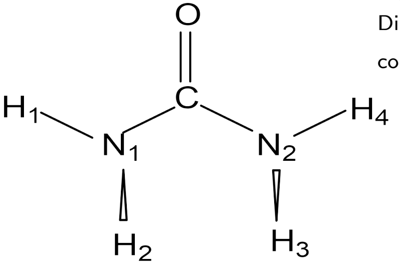


Results

Bond lengths (Å)	
C–O	1.2211
C–N_1	1.3779
N_1–H_1	0.9978
N_1–H_2	1.0212

Bond angles (^{o})	
C–O–N_1	122.64
N_1–C–N_2	114.71
C–N_1–H_1	119.21
C–N_1–H_2	112.78
C–N_1–H_2	118.61

Dihedral angles (characteristics of conformers)



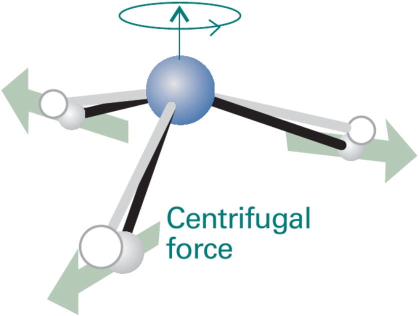
Rotational spectroscopy

Centrifugal distortion

rigid rotor so far (rotation has nothing to do with other internal coordinates)

centrifugal distortion (e.g., linear rotors)

- $F(J) = BJ(J+1) - D_J J^2(J+1)^2$
- D - centrifugal distortion constant $(\frac{4B^3}{\hat{\nu}^2})$, $\hat{\nu}$: vibrational wavenumber



Rotational spectroscopy

Stark effect

- The electric field interacts with the permanent electric dipol moment.
- Energy shift for a symmetric rotor: $\Delta E = -\frac{\mu \mathcal{E} K M_J}{J(J+1)}$, where $\mathcal{E}$ is the electric field and μ is the permanent dipol moment of the molecule.
- For a linear rotor the energy shift is quadratic : $\Delta E = \alpha(J, M_J)\mu^2\mathcal{E}^2$.

Rotational spectroscopy

Centrifugal distortion, spectra of T_d molecules

- T_d molecules are spherical rotors (SiH_4), $\mu_{perm} = 0$.
- centrifugal distortion $\Longrightarrow$ small permanent electric dipol moment $\Longrightarrow$ weak rot. spectra. Transition wavenumbers: $\tilde{\nu} = 2B(J+1)$

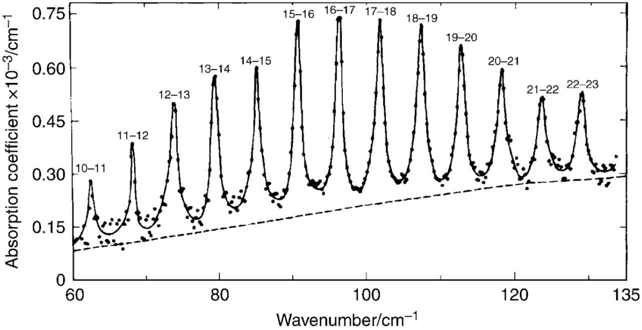


Figure 5.10 Part of the far-infrared spectrum of silane. (Reproduced, with permission, from Rosenberg, A. and Ozier, I., *Can. J. Phys.*, **52**, 575, 1974)

- No dipole moment is produced for O_h (e.g., SF_6) $\Longrightarrow$ no rotatialal spectra

Vibrational spectroscopy (diatomic molecules)

Energy levels

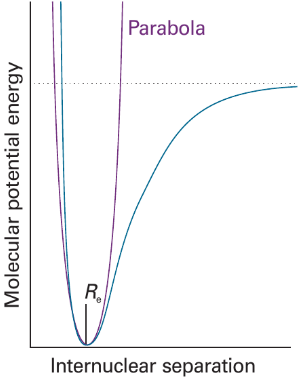
the harmonic oscillator problem:

$$V(x) = V(0) + \left\{\frac{dV}{dx}\right\}x + \frac{1}{2}\left\{\frac{d^2V}{dx2}\right\}x^2 + \dots$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2\Psi}{dx^2} + \frac{1}{2}kx^2\Psi = E\Psi$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \text{ effective/reduced mass}$$

$$E_v = (v + \frac{1}{2})\hbar\omega,\ v = 0, 1, 2, \dots;\ \omega = \sqrt{\frac{k}{\mu}}$$



Vibrational spectroscopy (diatomic molecules)

Energy levels

energies in wavenumbers (vibrational terms)

$$E_v = (v + \frac{1}{2})\hbar\omega,\ v = 0, 1, 2, \ldots \text{ divide by } hc$$

$$G(v) = (v + \frac{1}{2})\tilde{\nu},\ v = 0, 1, 2, \ldots;\ \tilde{\nu} = \frac{\omega}{2\pi c}$$

selection rule

- the electric dipole moment must change during vibration
- $\Delta v = \pm 1$

- infrared active/inactive vibrations
- $\Delta G_{(v+\frac{1}{2})} = G(v+1) - G(v) = \tilde{\nu}$ for all adjacent transitions
- The absorption frequency is independent of the state from which the transition takes place. It equals the eigenfrequency of the oscillator.

Vibrational spectroscopy (diatomic molecules)

Energy levels

Boltzmann population of the first vibrational excited state

$$1 \leftarrow 0 \text{ fundamental transition}$$

$$hc\Delta G_{\frac{1}{2}} = hc\tilde{\nu} = \Delta E \text{ in wavenumbers}$$

$$\frac{N_1}{N_0} = e^{-\Delta E/kT} = e^{-hc\tilde{\nu}/kT}$$

$$\tilde{\nu} \gg 600cm^{-1} \Rightarrow \frac{N_1}{N_0 + N_1} \times 100\% \ll 5\%$$

at room temperature (300K $\approx$ 209 cm^{-1}) practically only the ground state is occupied

Vibrational spectroscopy (diatomic molecules)

Anharmonicity

Shortcomings of the quadratic approximation: the vibration of diatomics is not fully harmonic.

$$V(r) = hcD_e\left\{1 - e^{-a(r-r_e)}\right\}^2$$

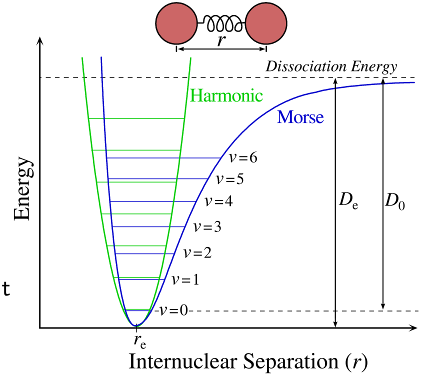
$$x_e = \frac{\tilde{\nu}}{4D_e},\ a = \sqrt{\frac{k}{2hcD_e}}$$

where x_e is the anharmonicity constant

$$G(v) = (v + \frac{1}{2})\tilde{\nu} - (v + \frac{1}{2})^2 x_e\tilde{\nu}$$

$$\Delta G_{(v+\frac{1}{2})} = G(v+1) - G(v)$$

$$= \tilde{\nu} - 2(v+1)x_e\tilde{\nu}$$



Vibrational spectroscopy (diatomic molecules)

Anharmonicity

$$\text{harmonic: } G(v) = (v + \frac{1}{2})\tilde{\nu},\ v = 0, 1, 2, \ldots$$

$$\Delta G_{(v+\frac{1}{2})} = G(v+1) - G(v) = \tilde{\nu}$$

$$\text{anharmonic: } G(v) = (v + \frac{1}{2})\tilde{\nu} - (v + \frac{1}{2})^2 x_e\tilde{\nu} + (v + \frac{1}{2})^3 y_e\tilde{\nu},\ v = 0, 1, 2, \ldots$$

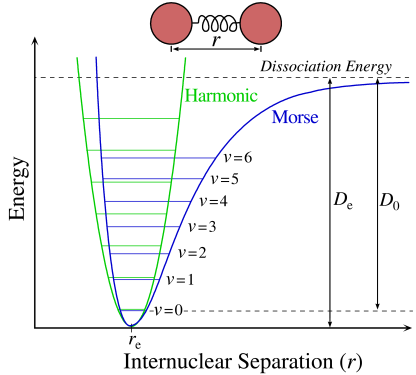
$$\Delta G_{(v+\frac{1}{2})} = G(v+1) - G(v) = \tilde{\nu} - 2(v+1)x_e\tilde{\nu} + \ldots$$

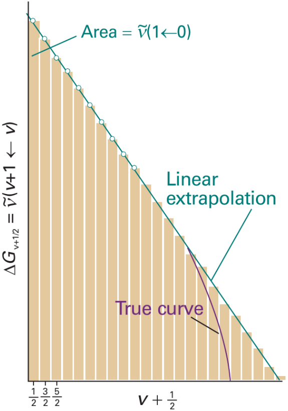
Selection rule is derived for the harmonic oscillator: additional weak absorption lines corresponding to the 'forbidden' transitions $0 \to 2$, $0 \to 3$.

Vibrational spectroscopy (diatomic molecules)

Birge-Sponer extrapolation, approximation of the dissociation energy

$$D_0 = \Delta G_{\frac{1}{2}} + \Delta G_{\frac{3}{2}} + \Delta G_{\frac{5}{2}} + \cdots = \sum_v \Delta G_{(v+\frac{1}{2})}$$





Vibrational spectroscopy (diatomic molecules)

Vibration-rotation (rovibrational) spectroscopy

The rotation and vibration cannot be entirely separated.

Both the vibrational and the rotational energy can change when absorbing a photon.

Rotational transitions accompany vibrational ones → band spectra

(close-spaced lines, 1-10 cm^{-1}, around the vibrational lines, 1000-4000 cm^{-1})

rotation-vibration terms

- rigid rotor - harmonic oscillator approximation
- $S(v, J) = G(v) + F(J) = (v + \frac{1}{2})\tilde{\nu} + BJ(J+1)$
- $\Delta v = \pm 1$, $\Delta J = \pm 1$, $\mu_{perm} \neq 0$ (selection rules)
- $\Delta J = 0$ is also allowed for NO molecule which have an angular momentum about its axis (an unpaired electron)

Vibrational spectroscopy (diatomic molecules)

Rovibration spectroscopy, branches

$$S(v,J) = (v+\tfrac{1}{2})\tilde{\nu} + BJ(J+1)$$

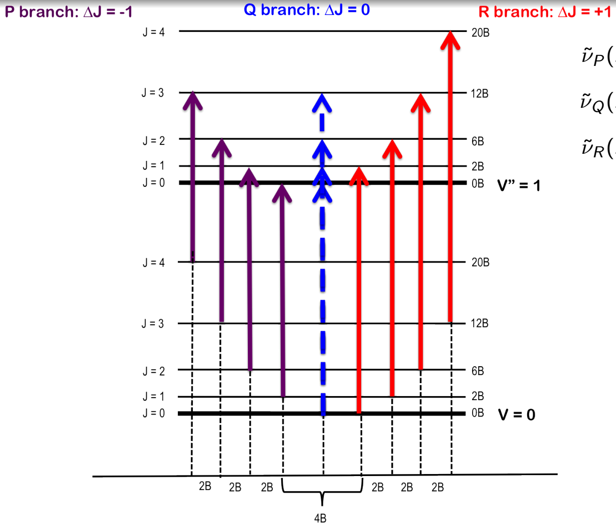
in practice $\Delta v = +1$ (excited states are not populated)

three combinations with J

- P branch: $\Delta J = -1$, $\tilde{\nu}_P(J) = S(v+1, J-1) - S(v,J) = \tilde{\nu} - 2BJ$
- Q branch: $\Delta J = \ 0$, $\tilde{\nu}_Q(J) = S(v+1, J) - S(v,J) = \tilde{\nu}$
- R branch: $\Delta J = +1$, $\tilde{\nu}_R(J) = S(v+1, J+1) - S(v,J) = \tilde{\nu} + 2B(J+1)$

Vibrational spectroscopy (diatomic molecules)

Rovibration spectroscopy, branches



$$\tilde{\nu}_P(J) = \tilde{\nu} - 2BJ$$

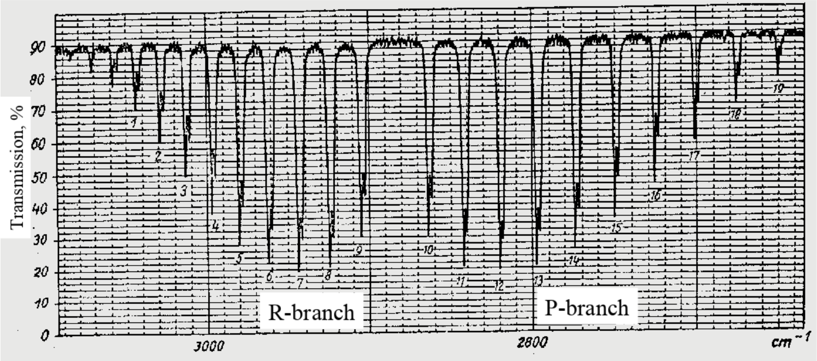
$$\tilde{\nu}_Q(J) = \tilde{\nu}$$

$$\tilde{\nu}_R(J) = \tilde{\nu} + 2B(J+1)$$

Vibrational spectroscopy (diatomic molecules)

Vibration-rotation spectrum of the HCl gas

Isotope effect: ^{35}Cl (75,77%), ^{37}Cl (24,23%)



P-branch: $\Delta J = -1$, Q-branch: $\Delta J = 0$, R-branch: $\Delta J = +1$

Vibrational spectroscopy

Rovibrational spectroscopy, combination differences

$$S(v,J) = (v+\tfrac{1}{2})\tilde{\nu} + BJ(J+1)$$

Method to determine the rotational constants:

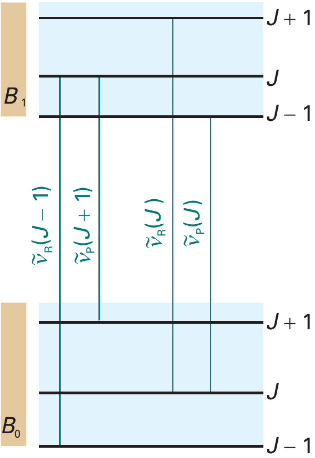
$$\tilde{\nu}_P(J) = \tilde{\nu} - (B_1+B_0)J + (B_1-B_0)J^2$$

$$\tilde{\nu}_Q(J) = \tilde{\nu} + (B_1-B_0)J(J+1)$$

$$\tilde{\nu}_R(J) = \tilde{\nu} + (B_1+B_0)(J+1) + (B_1-B_0)(J+1)^2$$

$$\tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1) = 4B_0(J+1/2)$$

$$\tilde{\nu}_R(J) - \tilde{\nu}_P(J) = 4B_1(J+1/2)$$



Vibrations of polyatomic molecules

Model: harmonic oscillator

- 3 or more point masses
- all points are connected to the others by springs
- it oscillates harmonically

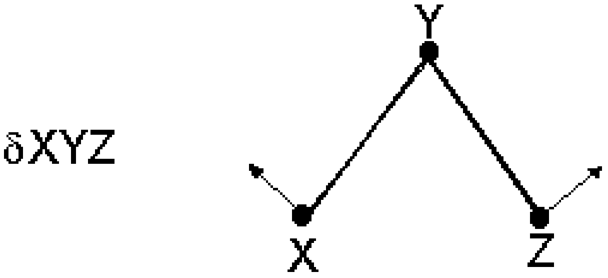
Internal coordinates

- The vibrational problem can be solved in Cartesian coordinates.
- For molecules it is more advantageous to use internal coordinates.
- Number of internal coordinates: 3N-6.

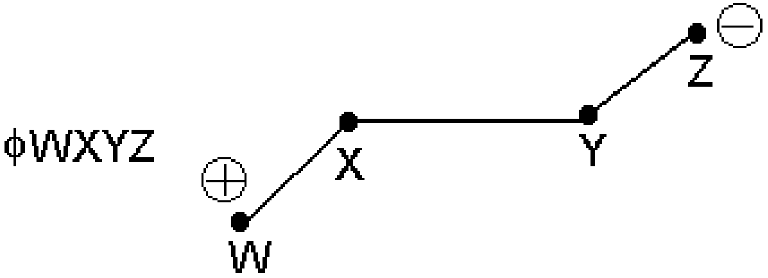
Internal coordinates

bond-stretching

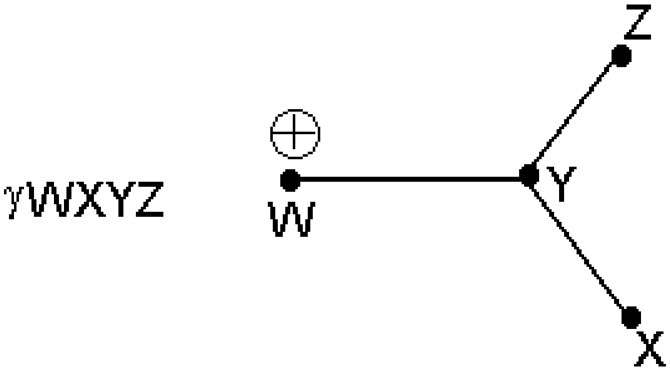
angle-bending



torsion



out-of-plane



Normal modes (coordinates)

The motion of an oscillator consisting of several point masses is complicated.

It can be resolved into 3N-6 normal modes. (N is the number of point masses)

A normal mode is a vibration in which all the mass points

- have the same frequency
- move in phase

Description of the oscillator of several degrees of freedom

Normal coordinate analysis

<u>Input data</u>

- masses of the points
- coordinates of the points (at equilibrium)
- force constants

<u>Results</u>

- frequencies of normal modes
- the normal modes (the contributions of internal coordinates)

Normal coordinates

$$\hat{H}_{nuc}=\sum_{i=1}^{3N}\frac{1}{2M_i}\frac{\partial^2}{\partial q_i^2}+V(\{q_i\},i=1,\dots,3N)$$

q_i is the displacement wrt the equilibrium geometry

$$\hat{H}_{nuc}=\sum_{i=1}^{3N}\frac{1}{2}\frac{\partial^2}{\partial q'^2_i}+V(\{q'_i\},i=1,\dots,3N)$$

mass-weighted coordinates: $q'_i=\sqrt{2M_i}\,q_i$

Taylor series →

$$\hat{H}_{nuc}=\sum_{i=1}^{3N}\frac{1}{2}\frac{\partial^2}{\partial q'^2_i}+V(\boldsymbol{q}'=0)+\sum_{i=1}^{3N}\left(\frac{\partial V}{\partial q'_i}\right)_{\boldsymbol{q}=0}q'_i+\frac{1}{2}\sum_{i,j=1}^{3N}\left(\frac{\partial^2 V}{\partial q'_i q'_j}\right)_{\boldsymbol{q}=0}q'_i q'_j+\dots$$

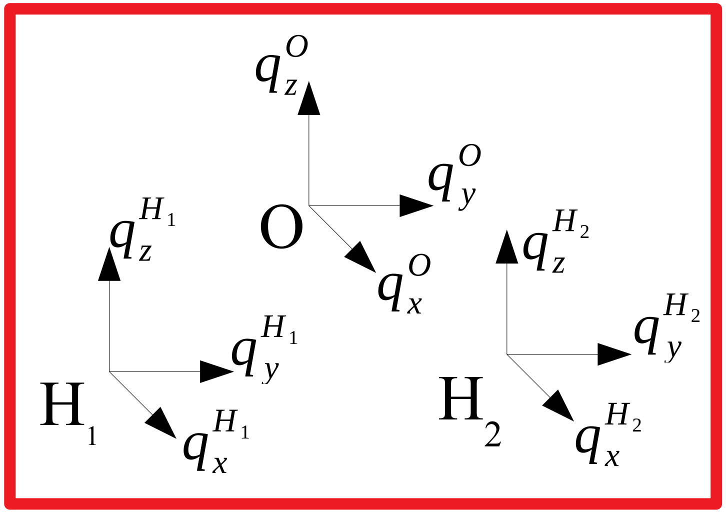
One can set the zero of the energy scale to have $V(\{q'_i=0\}_{i=1,\dots,3N})=0$

At the equilibrium geometry $\left(\frac{\partial V}{\partial q'_i}\right)_{\boldsymbol{q}=0}=0$

→

$$\hat{H}_{nuc}=\sum_{i=1}^{3N}\frac{1}{2}\frac{\partial^2}{\partial q'^2_i}+\frac{1}{2}\sum_{i,j=1}^{3N}F_{ij}q'_i q'_j+\dots$$

$F_{ij}=\frac{\partial^2 V}{\partial q_i \partial q_j}$ is a symmetric matrix with real eigenvalues:



$$\boldsymbol{F}\boldsymbol{u}^{(k)}=\lambda_k\boldsymbol{u}^{(k)}$$

With indices: $\sum_j F_{ij} u_j^{(k)} = \lambda_k u_i^{(k)}$

$$\sum_{i,j=1}^{3N} u_i^{(k)} F_{ij} u_j^{(k)} = \lambda_k \sum_{i=1}^{3N} u_i^{(k)} u_i^{(k)} = \lambda_k \qquad \sum_{i,j=1}^{3N} u_i^{(l)} F_{ij} u_j^{(k)} = \lambda_k \sum_{i=1}^{3N} u_i^{(l)} u_i^{(k)} = 0$$

$$q'_i = \sum_k u_i^{(k)} Q_k \quad \Longleftrightarrow \quad Q_i = \sum_j u_j^{(i)} q'_j$$

Normal coordinates

$$\frac{1}{2} \sum_{i,j=1}^{3N} F_{ij} q'_i q'_j = \frac{1}{2} \sum_{k,l=1}^{3N} \left(\sum_{i,j=1}^{3N} u_i^{(k)} F_{ij} u_j^{(l)} \right) Q_k Q_l = \frac{1}{2} \sum_{k=1}^{3N} \lambda_k Q_k^2$$

Among the eigenvalues there are six with zero value,
three rotational and three transitional degrees of freedom:

$$\hat{H}_{nuc} = \sum_{i=1}^{3N-6} \frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_{i=1}^{3N-6} \lambda_i Q_i^2 = \sum_{i=1}^{3N-6} \hat{H}_i^{harm.oscill.}$$

Symmetry → Degeneracy: $\frac{1}{2} \sum_{i=1}^{3N-6} \lambda_i Q_i^2 = \frac{1}{2} \sum_{\Gamma_\rho} \lambda_\rho \sum_{i \in \Gamma_\rho} Q_i^2$

Force constants

$$F_{ij}=\frac{\partial^2 V}{\partial Q_i \partial Q_j}=\lambda_i \delta_{ij}$$

Derivatives of the potential energy wrt the internal coordinates

Generalization of the spring constant introduced for simple harmonic oscillators

$$V=\frac{1}{2}kq^2 \xrightarrow{\textit{1. differentiation}} \frac{\partial V}{\partial q}=kq \xrightarrow{\textit{2. differentiation}} \frac{\partial^2 V}{\partial q \partial q}=k$$

There is a separate Schrödinger equation for each normal mode.

For normal mode i:

$$\frac{1}{2}\left[-\frac{\partial^2}{\partial Q_i^2}+\lambda_i Q_i^2\right]\Psi_v(Q_i)=E_{vi}\Psi_v(Q_i)$$

It is similar to that of diatomic molecules.

Q_i – normal coordinate i, the motion of the atoms in normal mode i

λ_i is related to the frequency of normal mode i:

$$\lambda_i=4\pi^2 v_i^2$$

It can be solved!

The total vibrational energy and wave function of the molecule

Eigenvalue:

$$E_{\nu i}^{(n_i)} = h\nu_i\left(n_i + \frac{1}{2}\right)$$

$$E_v = \sum_{i=1}^{3N-6} E_{\nu i}^{(n_i)}$$

Eigenfunction:

$$\Psi_v = \prod_{i=1}^{3N-6} \Psi_{\nu i}^{(n_i)}(Q_i)$$

$\prod$: product symbol, it implies the multiplication of all the factors

Interpretation of Ψ_v

$\Psi^*_v \Psi_v$ is the probability density of finding the nuclei in a given volume of space in the given vibrational state.

The Ψ_v functions can also be classified according to the molecular symmetry.

Selection rules

a) $\Delta n_i = \pm 1,$

$\Delta n_{j \neq i} = 0$

Only one normal mode can be excited by a photon

b) The dipole moment of the molecule must change during the vibration (but no permanent dipole moment is required, e.g.,CCl_4, benzene)

c) Analyzing the $\int \Psi_v^* \hat{\underline{\mu}} \Psi'_v d\tau$

transition moment it can be proven that the irrep of the normal mode must be identical to that for any component of the translation, T_x, T_y, or T_z.

$$\Psi_v^{(n_0 n_1 n_2 \ldots)} = \prod_{i=1}^{3N-6} \Psi_{n_i}(Q_i) = \prod_{i=1}^{3N-6} e^{-\frac{1}{2}\alpha_i Q_i^2} H_{n_i}\left(\sqrt{\alpha_i} Q_i\right), \qquad \alpha_i = \sqrt{\lambda_i}$$

$$H_0(x) = 1, H_1(x) = 2x, H_2 = 4x^2 - 2, H_3(x) = 8x^3 - 12x, \ldots$$

$$\Psi_v^{(000\ldots)} = \prod_{i=1}^{3N-6} e^{-\frac{1}{2}\alpha_i Q_i^2} = e^{-\frac{1}{2}\sum_{i=1}^{3N-6} \alpha_i Q_i^2} = e^{-\frac{1}{2}\sum_{\rho} \alpha_\rho \sum_{i \in \Gamma_\rho} Q_i^2}$$

$\sum_{\rho} \alpha_\rho \sum_{i \in \Gamma_\rho} Q_i^2$ commutes with the symmetry operations ➡

$\sum_{\rho} \alpha_\rho \sum_{i \in \Gamma_\rho} Q_i^2$ is a totally symmetric quantity (A_1) ➡

$\Psi_v^{(000\ldots)}$ is a totally symmetric state

To have a transition from the ground state

$\underline{R}_{mn} = \int \Psi_m^* \underline{\mu} \Psi_n \, d\tau \neq 0$, $\Psi_n = \Psi_v^{(000\ldots)}$, $\underline{\mu} = (\mu_x, \mu_y, \mu_z)$ ➡

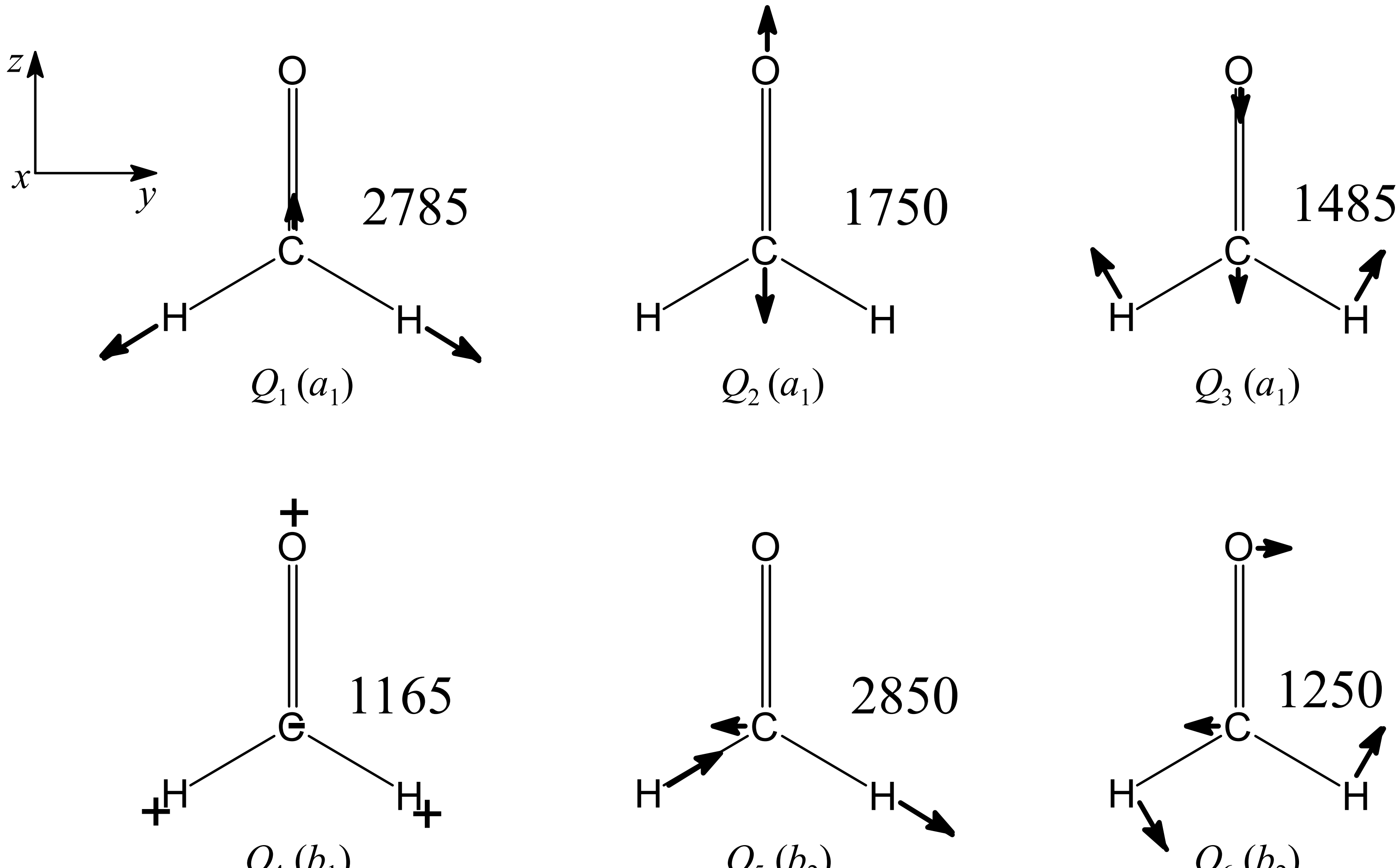
$\Psi_m^* \mu$ product should contain A_1 ➡

Ψ_m should transform as T_x, T_y, or T_z

Character table of the C_{2v} point group

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	+1	+1	+1	+1	$T_z,\alpha_{xx},\alpha_{yy},\alpha_{zz}$
A_2	+1	+1	-1	-1	R_x,α_{xy}
B_1	+1	-1	+1	-1	T_x,R_y,α_{xz}
B_2	+1	-1	-1	+1	T_y,R_z,α_{yz}

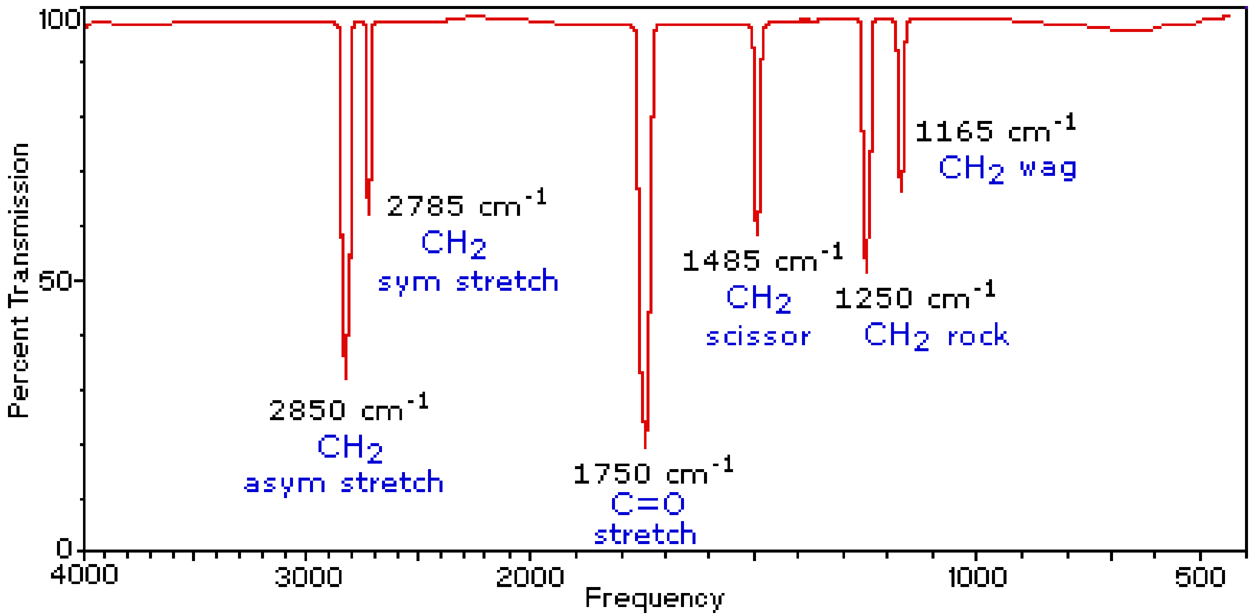
Example: normal modes of formaldehyde[cm^{-1}]



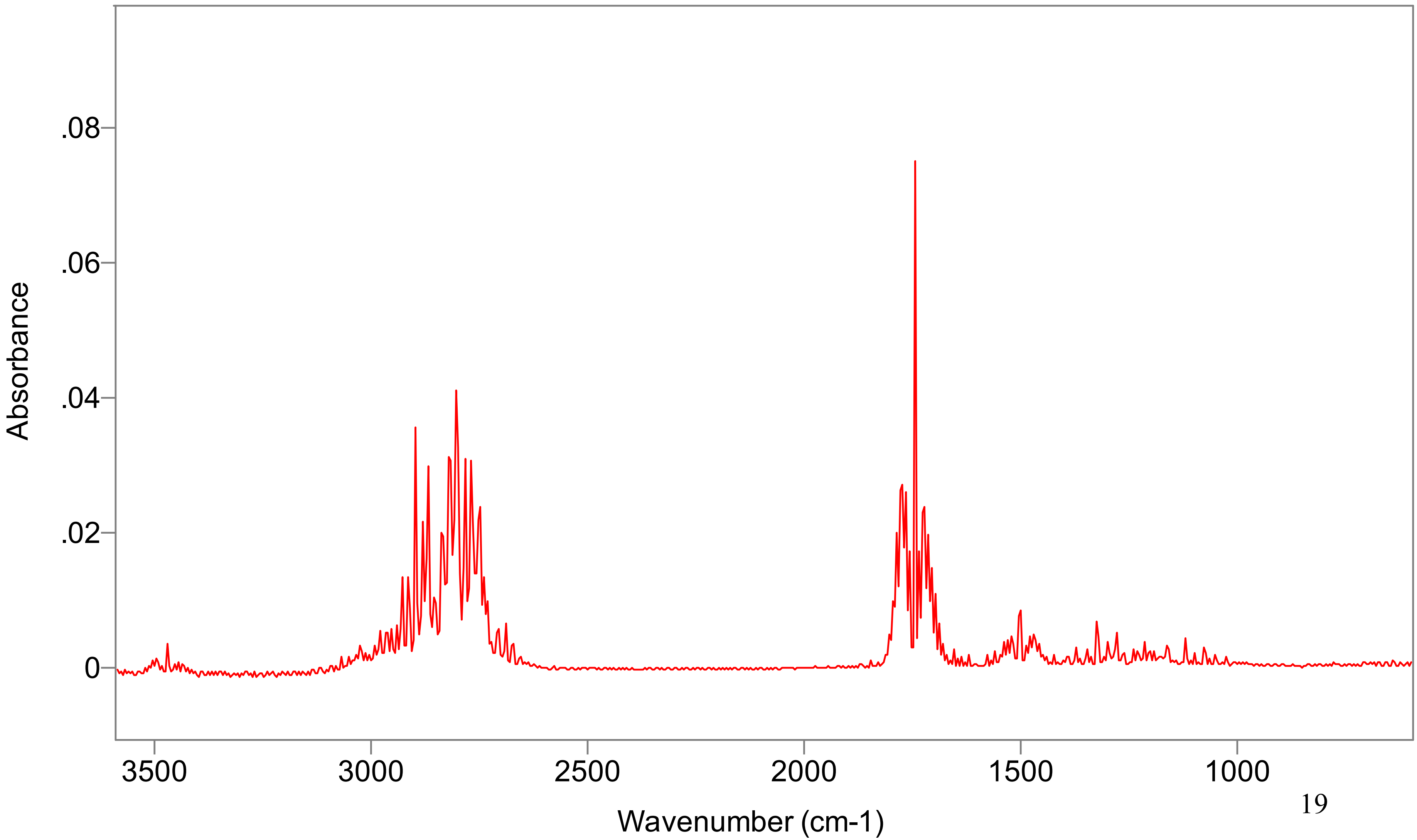
Vibrational frequencies

ν_1	symmetric CH stretching
ν_2	CO stretching
ν_3	CH_2 bending (scissoring)
ν_4	out-of-plane bending (wagging)
ν_5	antisymmetric CH stretching
ν_6	CH_2 rocking

Formaldehyde gas IR spectra



Formaldehyde gas IR spectra



Infrared spectra

Vibrational transitions:

They are located in the IR region

λ=2-100 μm

Features of the spectra:

Abscissa: wavenumbers (ν^* [cm^{-1}]) instead of λ

Value: 4000-400 cm^{-1}

Ordinate: intensity

absorbance

$$A = \log \frac{I_o}{I}$$

transmittance

$$T = \frac{I}{I_o} \cdot 100 (\%)$$

Sample: gas, liquid, solution, solid.

Sample preparation

Gas:

- cuvette of 10-100 cm length with KBr windows

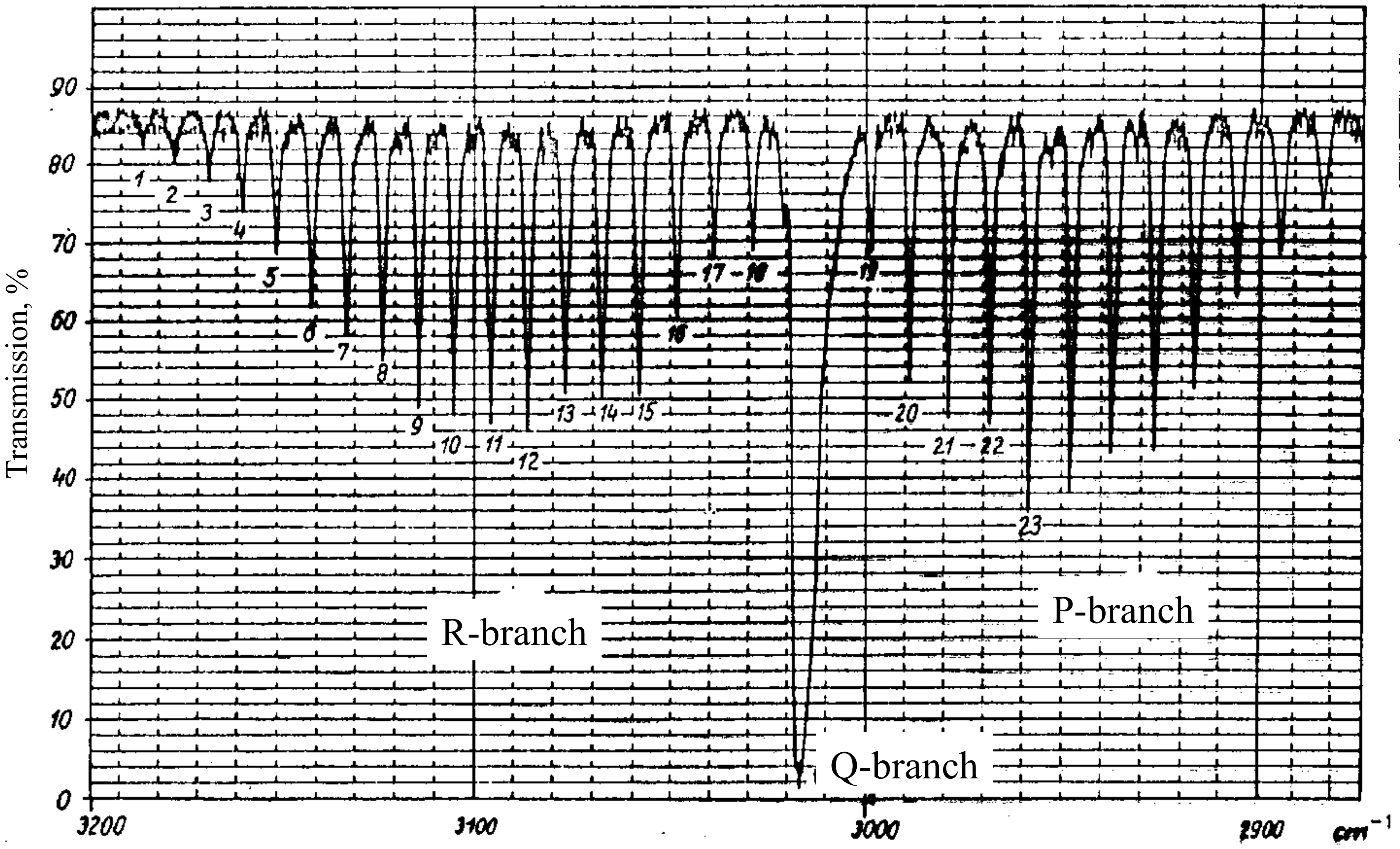
Solution:

- solvents: CCl_4, CS_2, or CH_3CN, chloroform
- cuvette of a couple of μm path length with KBr windows

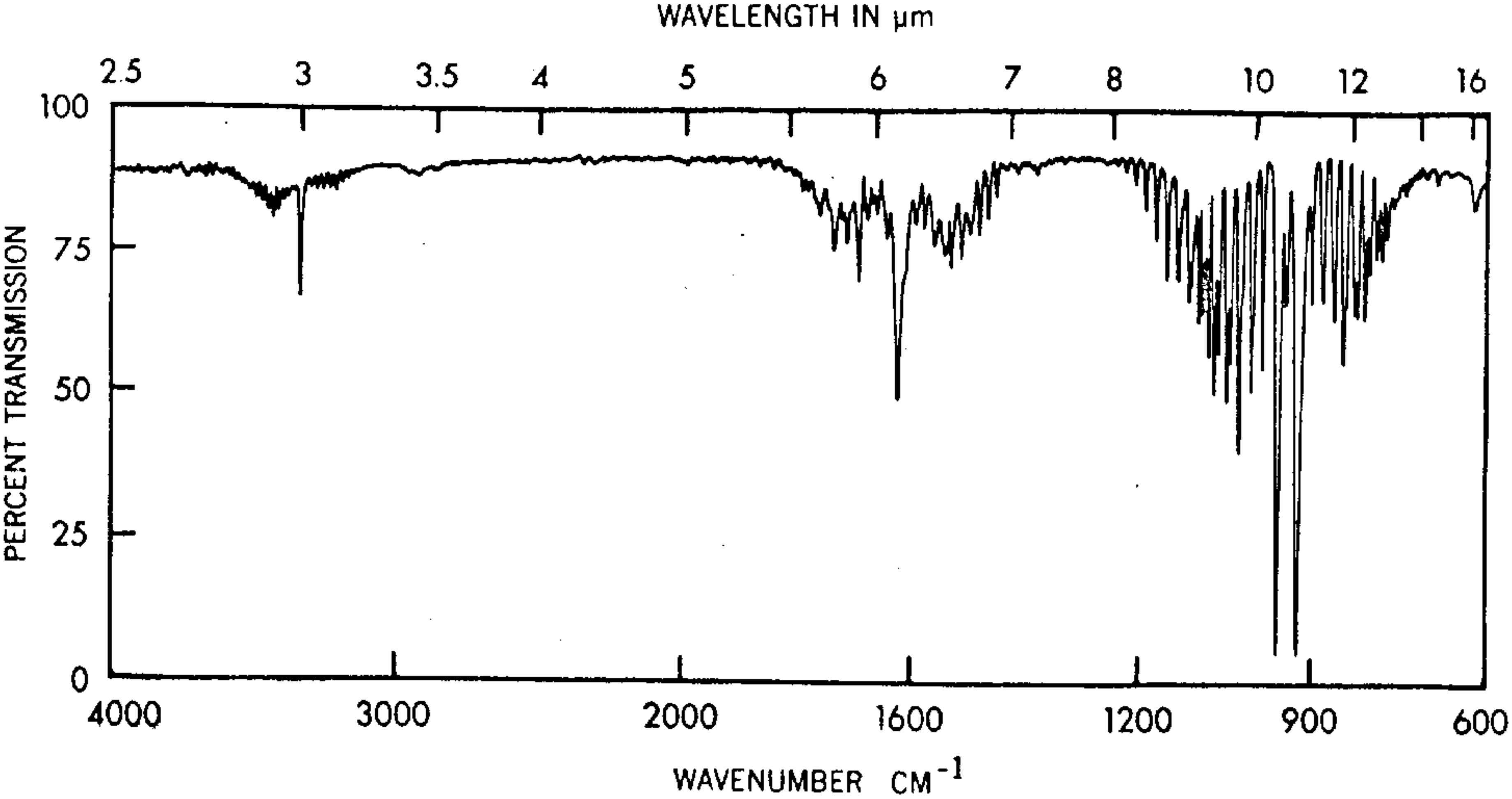
Solid

- KBr pellet (grind with KBr, compression)
- film (the solution is placed on a KBr pellet, the solvent is evaporated)
- paraffin suspension

The infrared spectrum of methane (part)

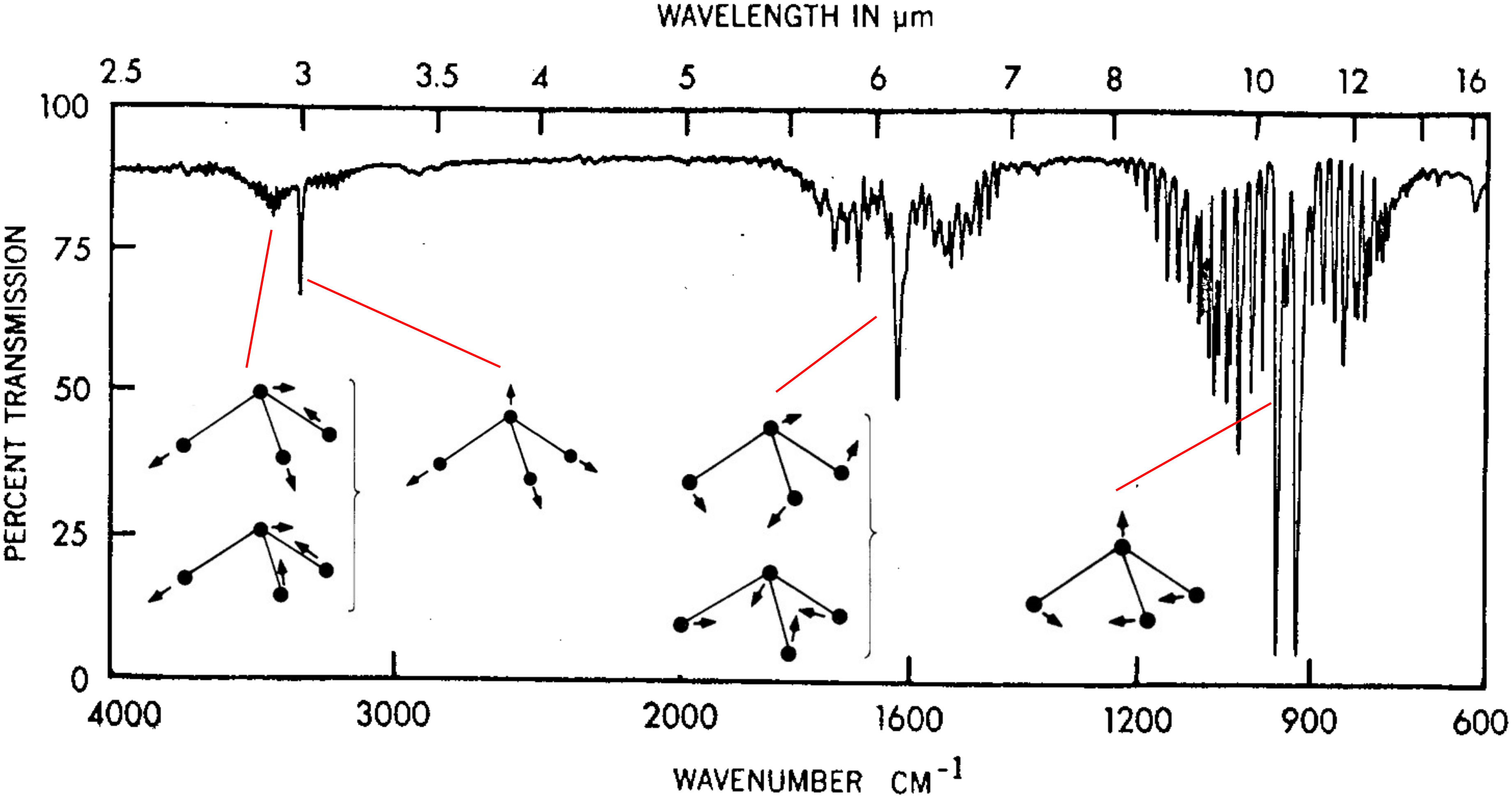


The infrared spectrum of ammonia

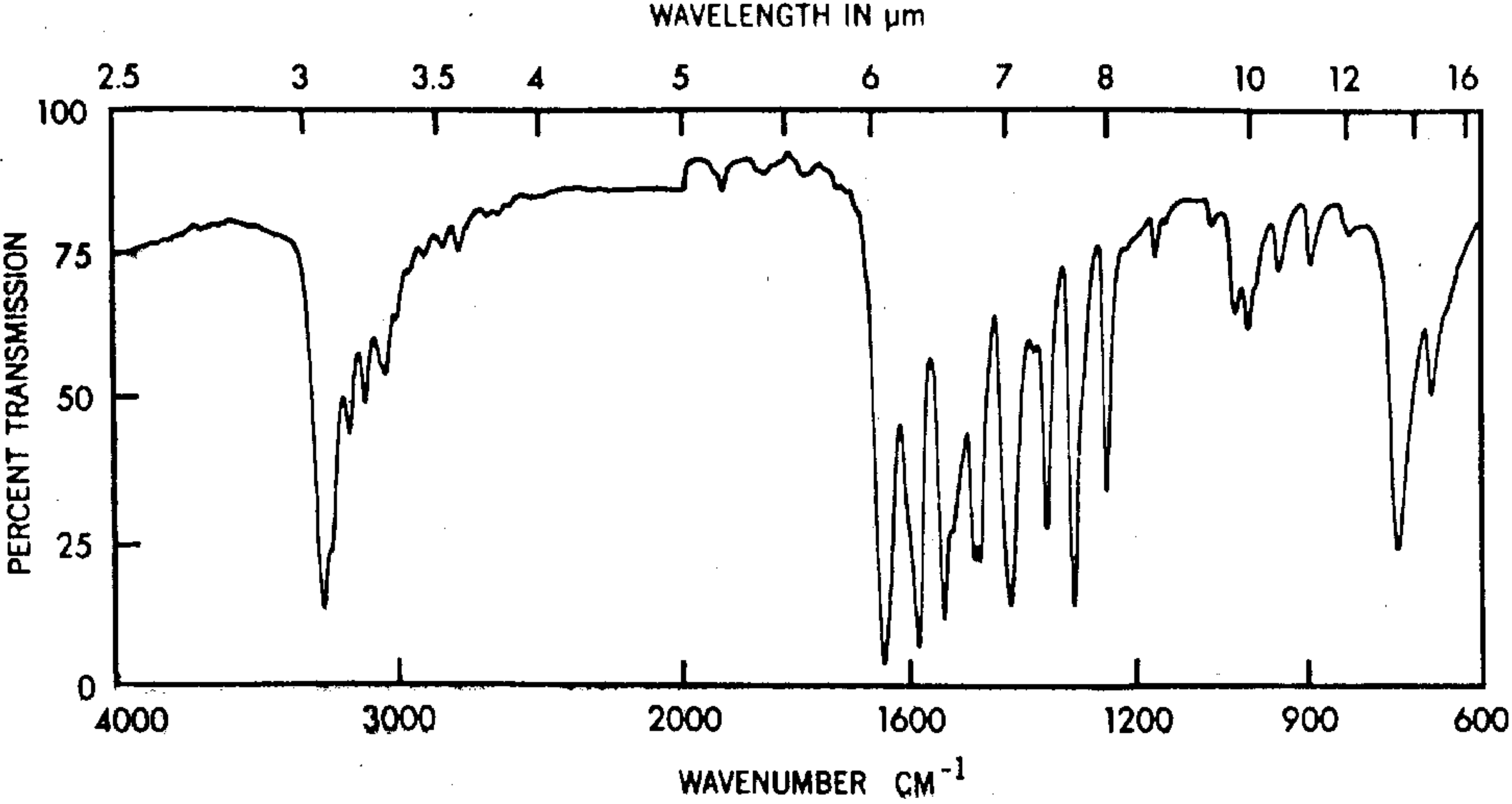


Symmetric rotor: energy of transitions depends on J and K: relatively complex spectra

The infrared spectrum of ammonia



The infrared spectrum of acetanilide crystal in KBr pellet



For liquid and solid samples there is no rotational fine structure.

crystals: splitting due to the lattice vibrations

Analytical application

Identification of functional groups

‘‘characteristic vibrations’’: a normal mode is dominated by one of the motions of a functional group, hence similar absorption frequencies are expected for different molecules including the same functional group

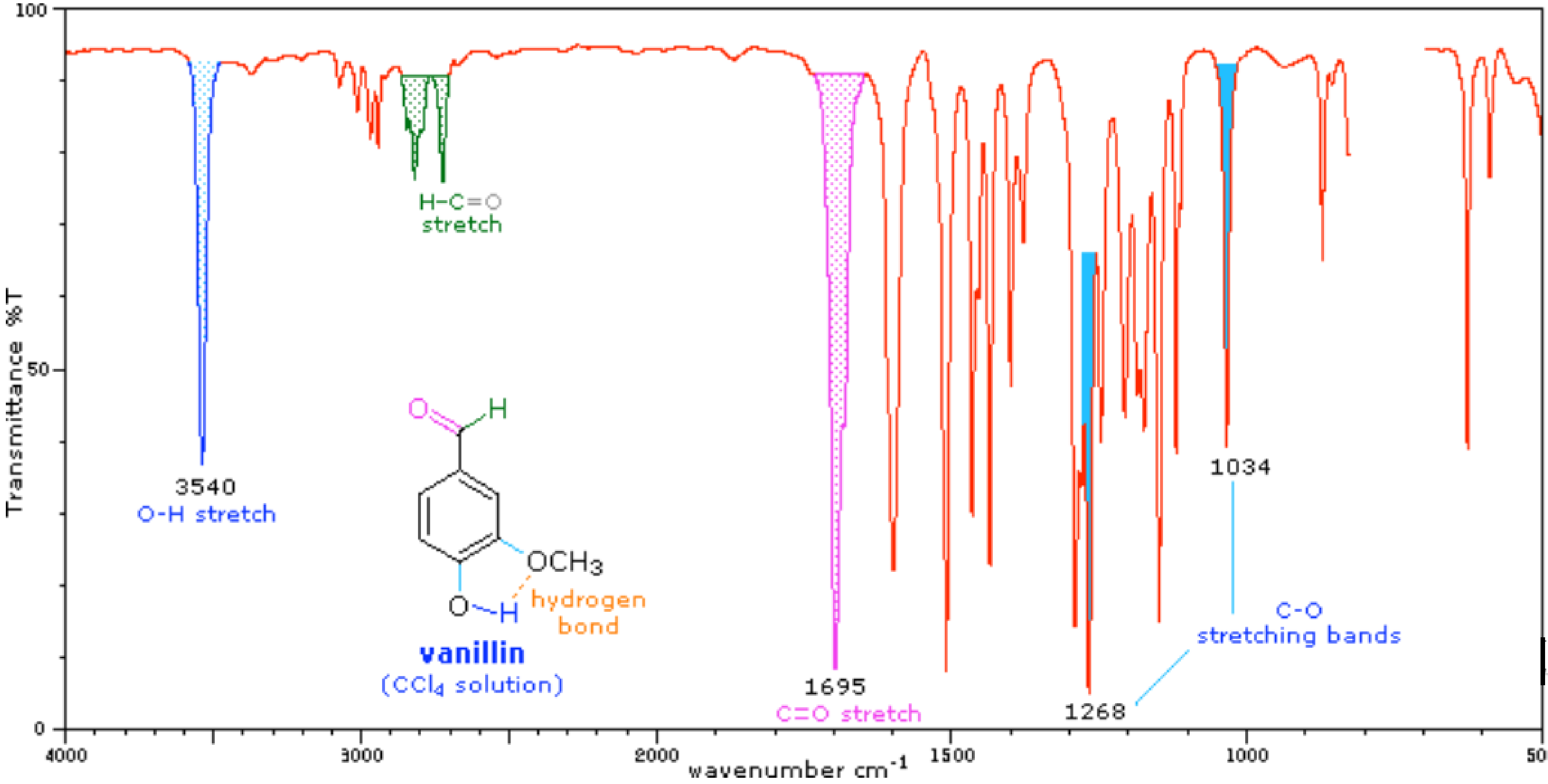
E.g.:

νCH_3 2860-2900 cm^{-1} and 2950-3000 cm^{-1}

νCH_2 2840-2880 cm^{-1} and 2920-2950 cm^{-1}

$\nu C{=}O$ 1660-1720 cm^{-1}

Vanillin IR spectra (CCl_4 solution) characteristic frequencies



Fourier-transform infrared spectroscopy

Fourier transform (mathematical summary)

Abbreviation for Fourier transform: FT.

It maps a function to another function, the independent variables of the two functions are the reciprocal of each other.

For instance: time-frequency

$$F\left\{x\left(t\right)\right\}=X\left(v\right)$$

Discrete Fourier transform

In the -a,a interval any f(t) function can be reperesented as a linear combination of sin and cos functions: $f(t)=\sum_{i=0} c_i \phi_i(t)$, where

$$\phi_0(t)=\frac{1}{\sqrt{2a}}$$

$$\phi_n(t)=\frac{1}{\sqrt{a}}\sin\left(\frac{n\pi t}{2a}\right), \qquad n=2,4,6,\ldots$$

$$\phi_n(t)=\frac{1}{\sqrt{a}}\cos\left(\frac{n\pi t}{2a}\right), \qquad n=1,3,5,7,\ldots$$

These functions form an orthogonal basis set: $\int_{-a}^{a} \phi_i(t)\,\phi_j(t)\,dt=\delta_{ij}$

The coefficients can be easily obtained: $c_j=\int_{-a}^{a} \phi_j(t) f(t)\,dt$

If $a \to \infty$ the possible values of $\omega_n=\frac{n\pi}{2a}$ become continuous

and we obtain the continuous Fourier transform

Fourier transform

Transformation from the time domain to the frequency domain

$$X(v)=\int_{t=-\infty}^{+\infty} x(t)\exp(i2\pi \mathrm{v}t)dt$$

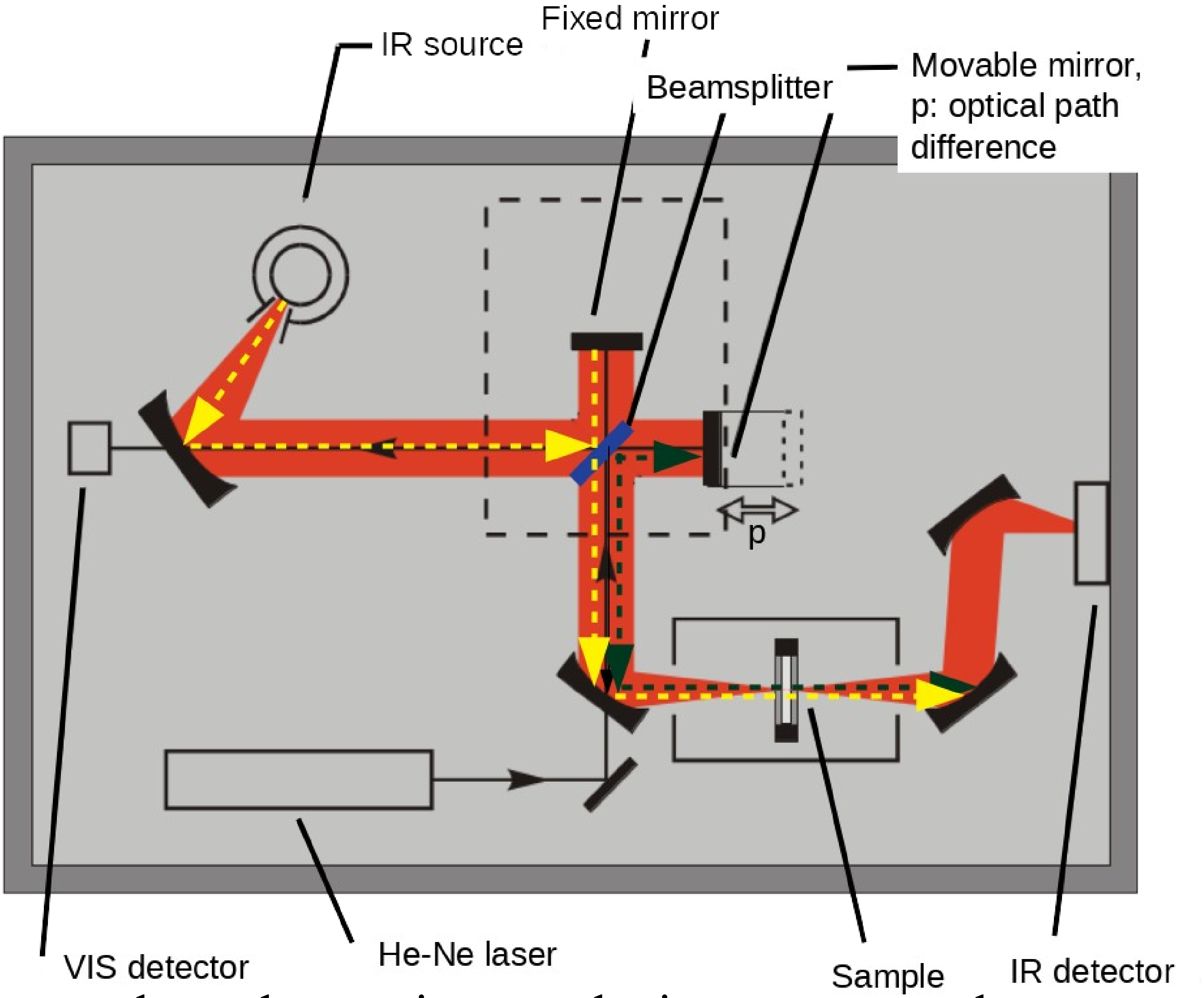
Inverse transformation:

$$x(t)=\frac{1}{2\pi}\int_{t=-\infty}^{+\infty} X(v)\exp(-i2\pi \mathrm{v}t)dt$$

Using Euler's formula:

$$X(v)=\int_{t=-\infty}^{+\infty} x(t)\cos(2\pi \mathrm{v}t)dt+i\int_{t=-\infty}^{+\infty} x(t)\sin(2\pi \mathrm{v}t)dt$$

Fourier transform spectrometers



Source: heated ceramic-coated wire or tungsten lamp
Detector: thermocouple or piroelectric crystal

Sum of the original and the shifted beam:

$$E(x,t)=A\left(e^{i\omega t-ikx}+e^{i\omega t-ik(x+p)}\right)=A e^{i\omega t-ikx}\left(1+e^{-ikp}\right)$$

The intensity is proportional to the square of E(x,t):

$$I\propto|E|^2=A^2 e^{i\omega t-ikx}e^{-i\omega t+ikx}\left(1+e^{-ikp}\right)\left(1+e^{ikp}\right)=2A^2\left(1+\cos(kp)\right)=2A^2\left(1+\cos(2\pi\tilde{\nu}p)\right)$$

<u>Constructive($\tilde{\nu}p=0,1,2,\ldots$)</u> or <u>destructive(</u>$\tilde{\nu}p=\frac{1}{2},\frac{3}{2},\ldots$) interference (monochrome radiation, $\tilde{\nu}$: wavenumber, p: path difference)

$$I(p,\tilde{\nu})=I(\tilde{\nu})\left(1+\cos(2\pi\tilde{\nu}p)\right)$$

As the radiation has a contiguous spectra:

$$I(p)=\int_0^\infty I(p,\tilde{\nu})\,d\tilde{\nu}=\int_0^\infty I(\tilde{\nu})\left(1+\cos(2\pi\tilde{\nu}p)\right)d\tilde{\nu}$$

$$I(p)-\frac{I(p=0)}{2}=\int_0^\infty I(\tilde{\nu})\cos(2\pi\tilde{\nu}p)\,d\tilde{\nu}$$

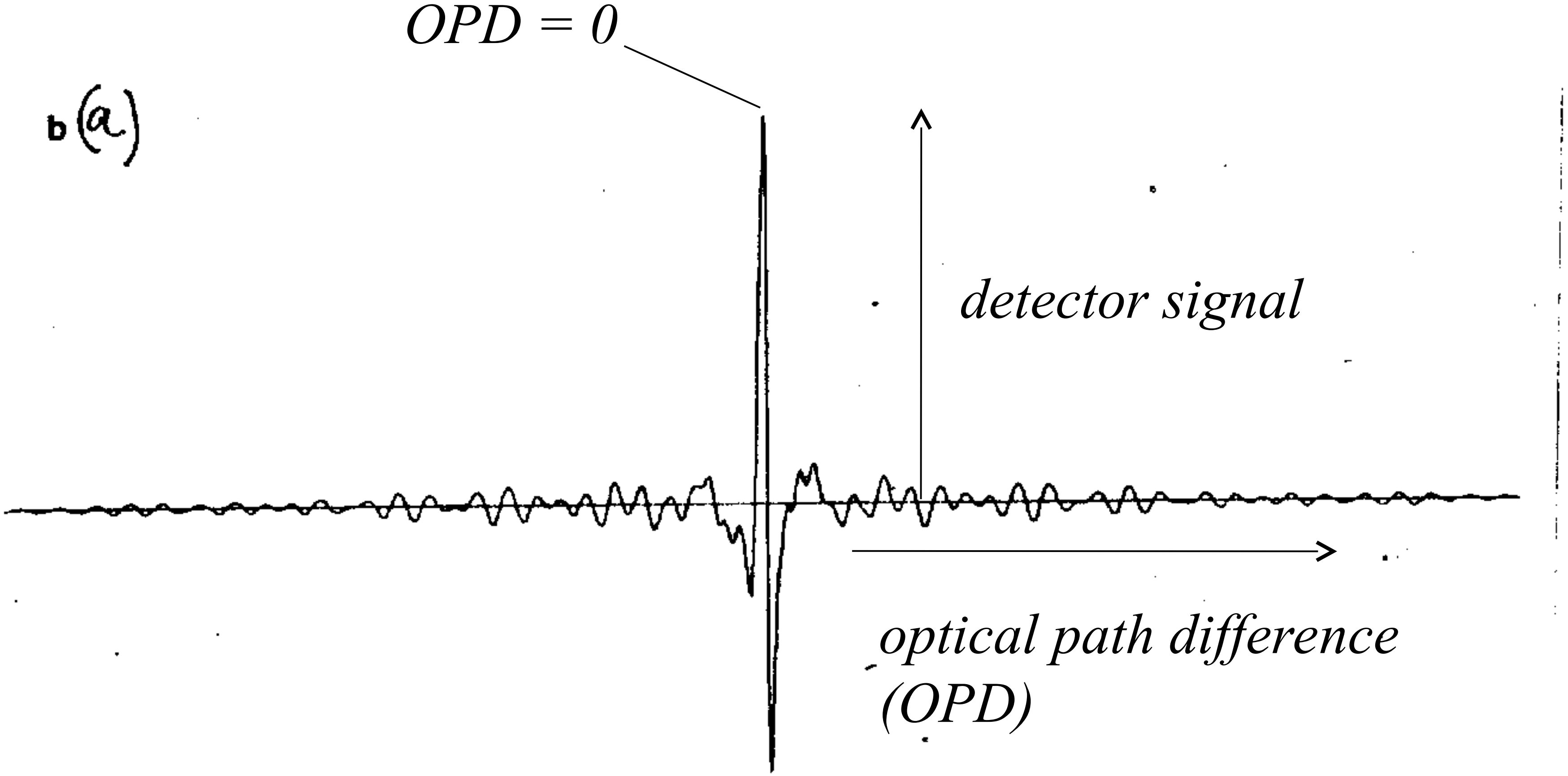
Directly measured: interferogram, I(p)

Inverse FT

Spectrum: I($\tilde{\nu}$)

- All the radiation frequency is monitored simultaneously!
- Good sign-to-noise ratio
- → Fast measurement: FT spectroscopy can be applied to investigate processes in time
- FT spectrometers can be combined with gas and liquid chomatographs or microscopes

Interferogram for acetone vapor

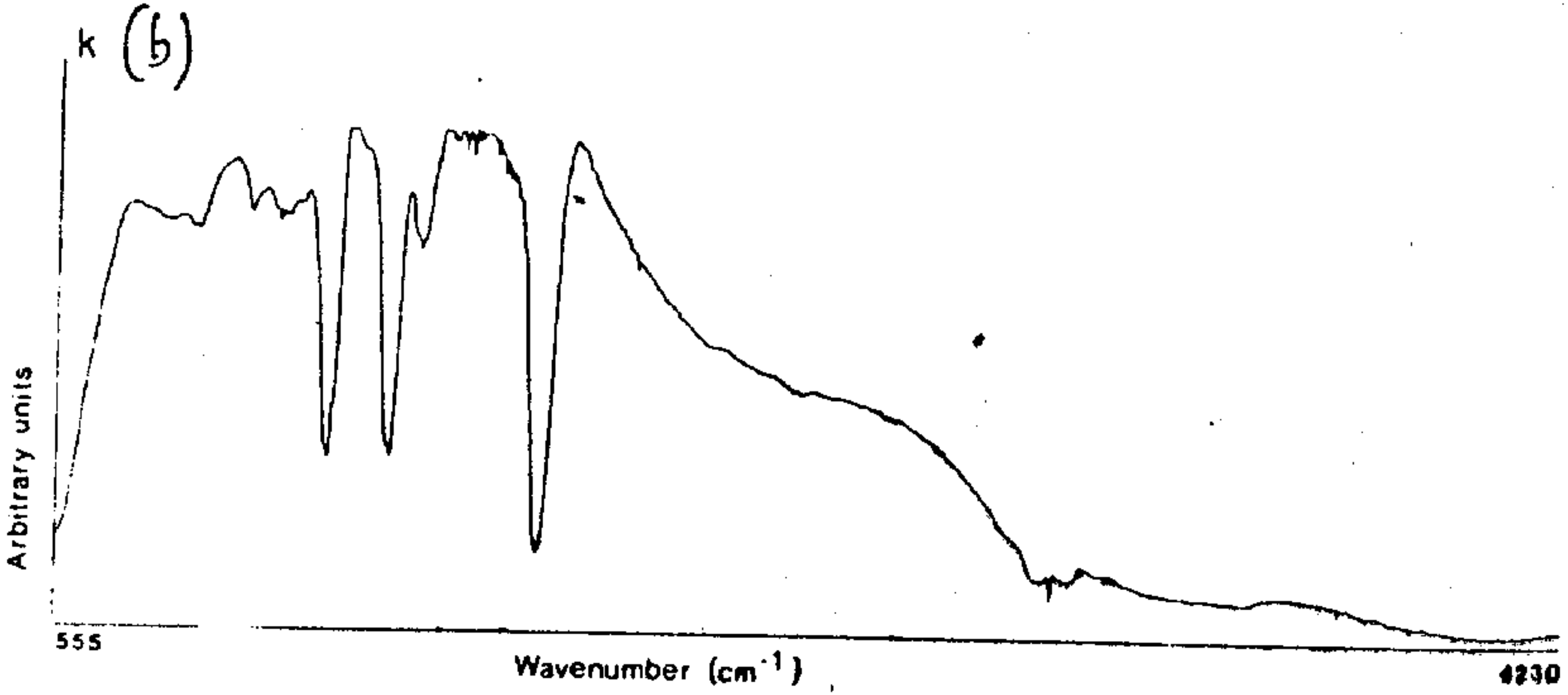


OPD = 0

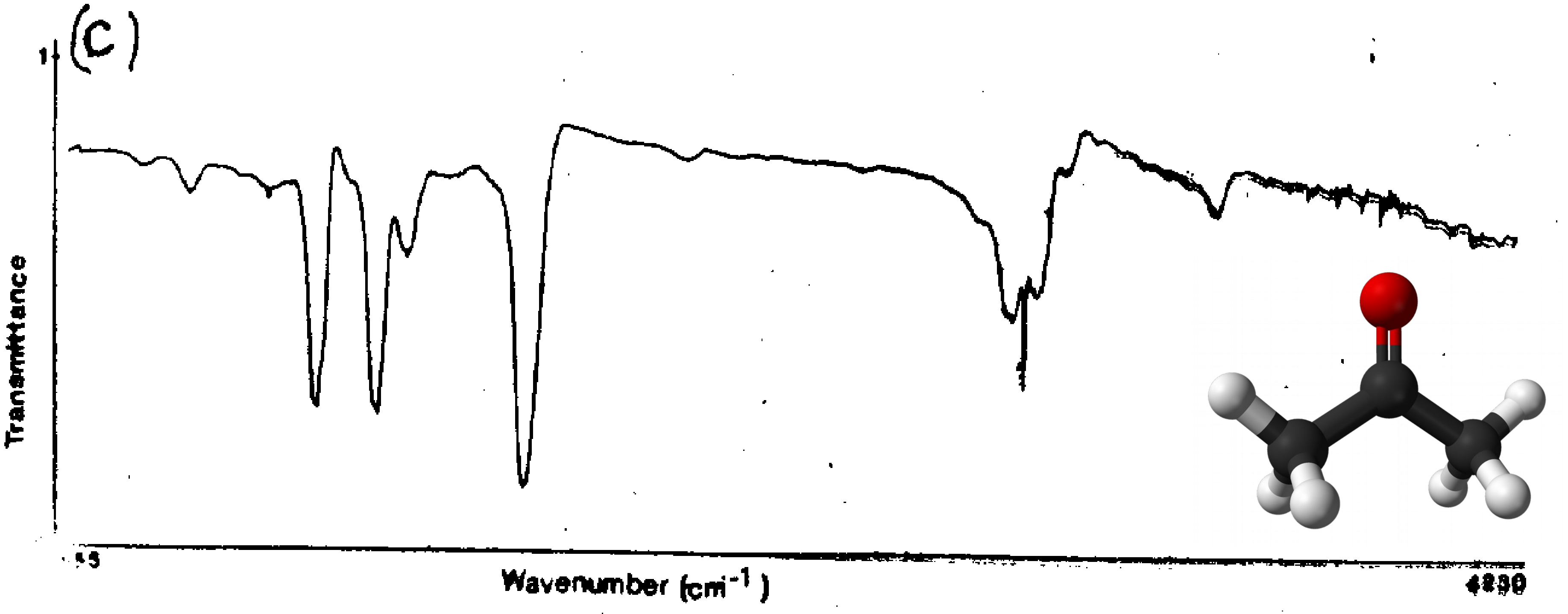
detector signal

optical path difference (OPD)

The spectrum obtained by Fourier transform



The spectrum of acetone vapor after division by the background intensity



- For larger molecules the individual rotational lines of the P, Q, and R branches can not be seen, only the contour.

ELECTRONIC STRUCTURE OF MOLECULES

The model (Born-Oppenheimer approximation):

The nuclei are clamped, the electrons move in their field.

Schrödinger equation:

$$\left(\hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + V_{nn}\right)\Psi_e = \left(E_e + V_{nn}\right)\Psi_e$$

$\hat{T}_e$: kinetic energy of the electrons

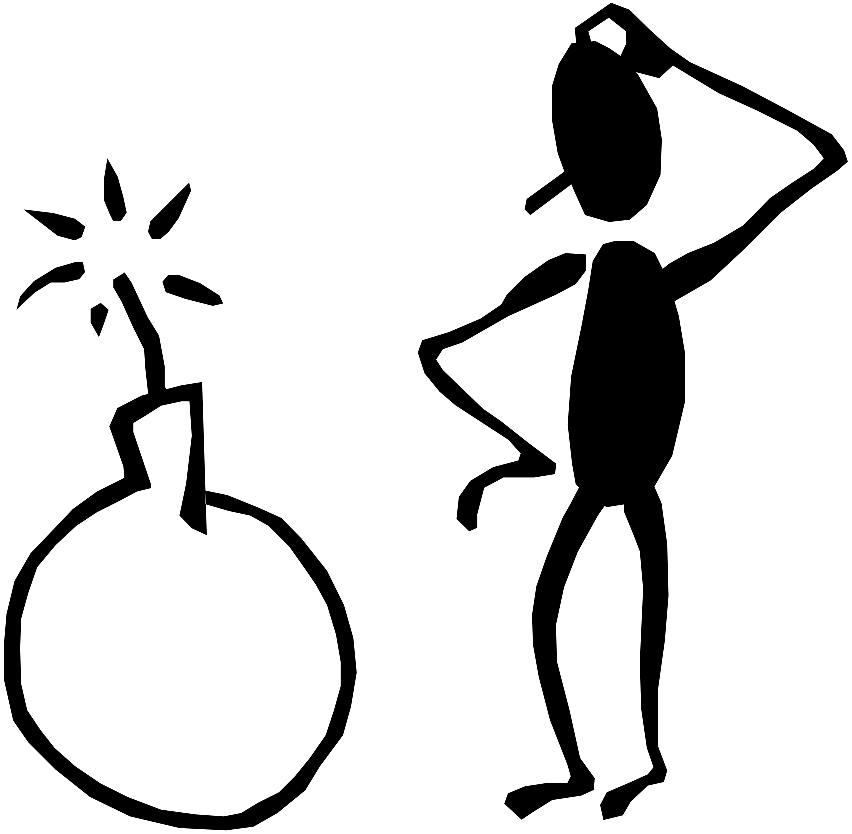
$\hat{V}_{ne}$: attraction of the electrons and the nuclei

$\hat{V}_{ee}$: electron-electron repulsion

V_{nn} : nuclear attraction—a constant because of the clamped nuclei approximation.

E_e : electronic energy

This differential equation cannot be solved analytically, only approximate (numerical) solutions are possible.



E.g, methods based on the variational principle (Hartree-Fock)

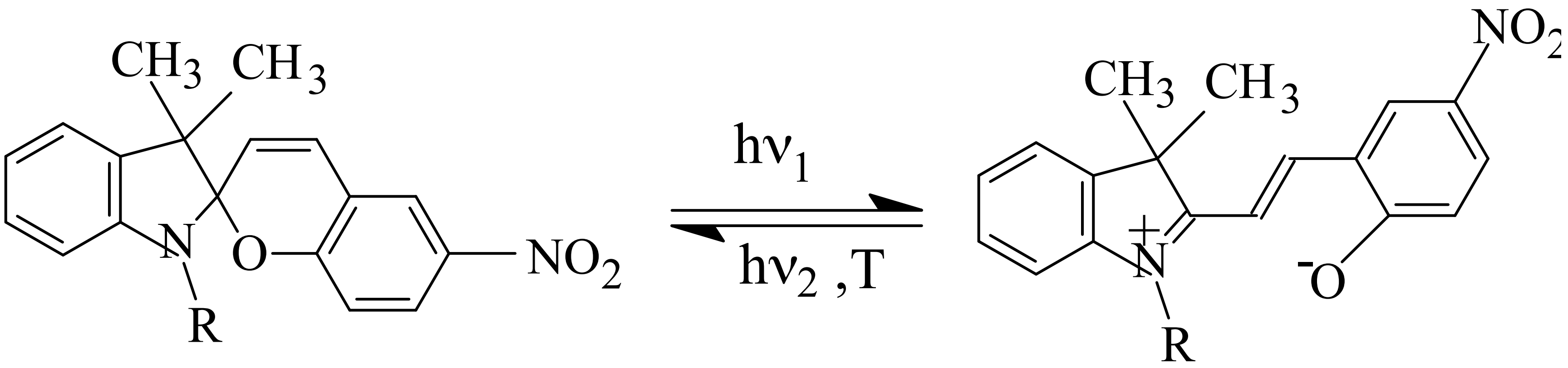
Electronic states

Quantum chemistry:

- equilibrium geometry of molecules
- vibrational frequencies and normal modes
- charge distribution
- chemical reactions
- excited states

Example for photochemical reactions:

a photochrome pigment



spiropyrane

colorless

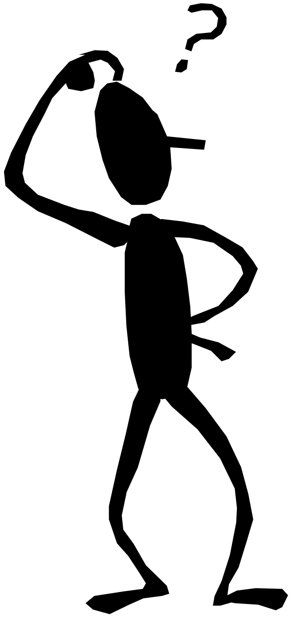
ring opening under UV irradiation

merocyanine

red

ring closure under visible (green) irradiation

How shall we choose the electronic wave functions?



The molecular orbital model

LCAO-MO method

MO: molecular orbital

LCAO : linear combination of atomic orbitals

The approximate wave function is written as a Slater-determinant

A row: an electron

A column: an MO

$$\Psi = \begin{vmatrix} \phi_{1\alpha}(1) & \phi_{1\beta}(1) & \dots & \phi_{N\beta}(1) \\ \phi_{1\alpha}(2) & \phi_{1\beta}(2) & \dots & \phi_{N\beta}(2) \\ \vdots & & \ddots & \\ \phi_{1\alpha}(N) & \phi_{1\beta}(N) & \dots & \phi_{N\beta}(N) \end{vmatrix}$$

There are no quantum numbers, but spin

Linear combination

The molecular orbitals are constructed by linear combination of atomic orbitals.

$$\phi = N \sum_i c_i \chi_i$$

N: normalization factor

χ_i : atomic orbital

c_i : combination coefficient

Construction of molecular orbitals: those atomic orbitals are combined

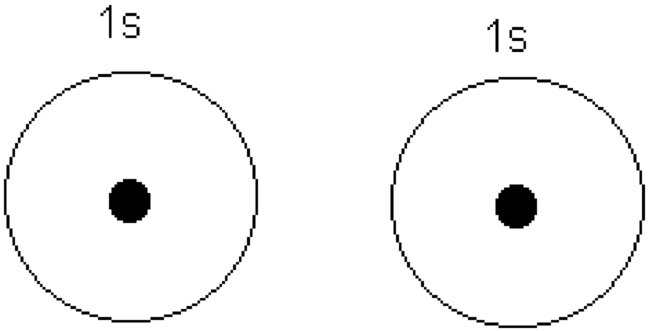
a) which lie closely in energy
b) which have significant overlap (or which are core orbitals)
c) whose linear combination transforms according to some irrep under the symmetry operations of the point group of the molecule

Example: N_2 molecule

Simplest combinations:

- one atomic orbital from both atoms
- $c_1 = c_2 = +1$, or $c_1 = +1$, $c_2 = -1$

Example: N_2 molecule (1)

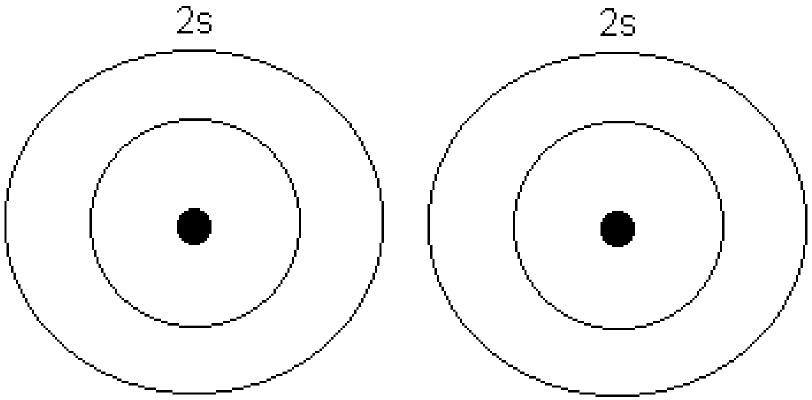


a) satisfied

b) satisfied

c) satisfied

Example: N_2 molecule (2)

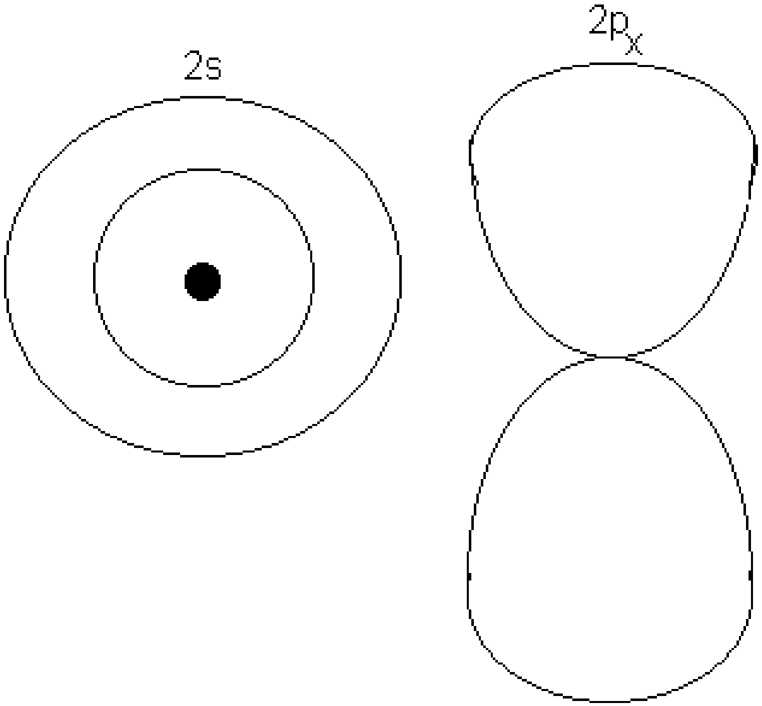


a) satisfied

b) satisfied

c) satisfied

Example: N_2 molecule (3)

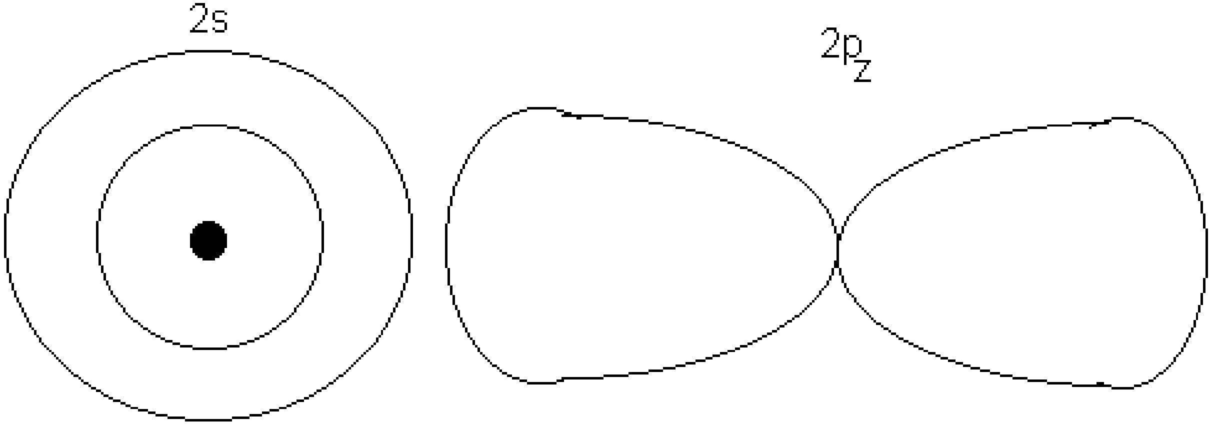


a) satisfied

b) not satisfied

c) not satisfied

Example: N_2 molecule (4)



a) satisfied

b) satisfied

c) not satisfied

Electronic structure of diatomic molecules

Diatomic molecules

Homonuclear
(H_2, N_2, Cl_2)

Heteronuclear
(NO, CO, HCl)

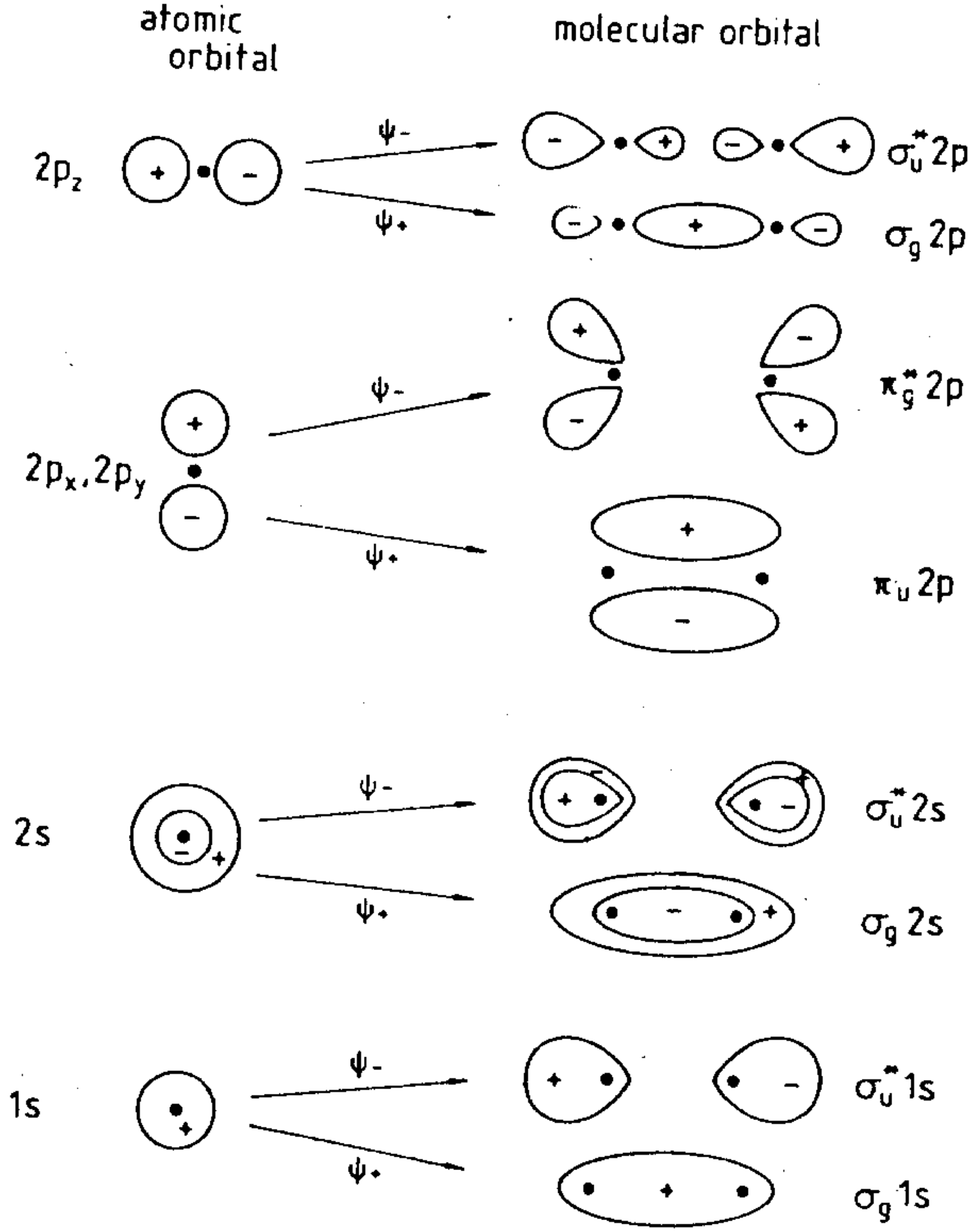
E.g.: a homonuclear diatomic molecule, N_2

Simplest molecular orbitals: the linear combinations of the identical atomic orbitals of the two atoms.

$$\phi^{+}(1s)=\frac{1}{\sqrt{2}}[\chi_1(1s)+\chi_2(1s)]$$

$$\phi^{-}(1s)=\frac{1}{\sqrt{2}}[\chi_1(1s)-\chi_2(1s)]$$

Construction of molecular orbitals from atomic orbitals



ϕ^{+} : ‘‘bonding’’ orbital (lower-energy combination)

ϕ^{-} : ‘‘antibonding’’ orbital (higher-energy combination)

<u>Notation:</u>

* index : antibonding orbital

no index : bonding orbital

σ -orbital : cylindrical symmetry around the bond

π -orbital : nodal plane going through the bond

‘‘g’’ index : symmetric wrt the inversion (gerade = even)

‘‘u’’ index : antisymmetric wrt the inversion (ungerade = odd)

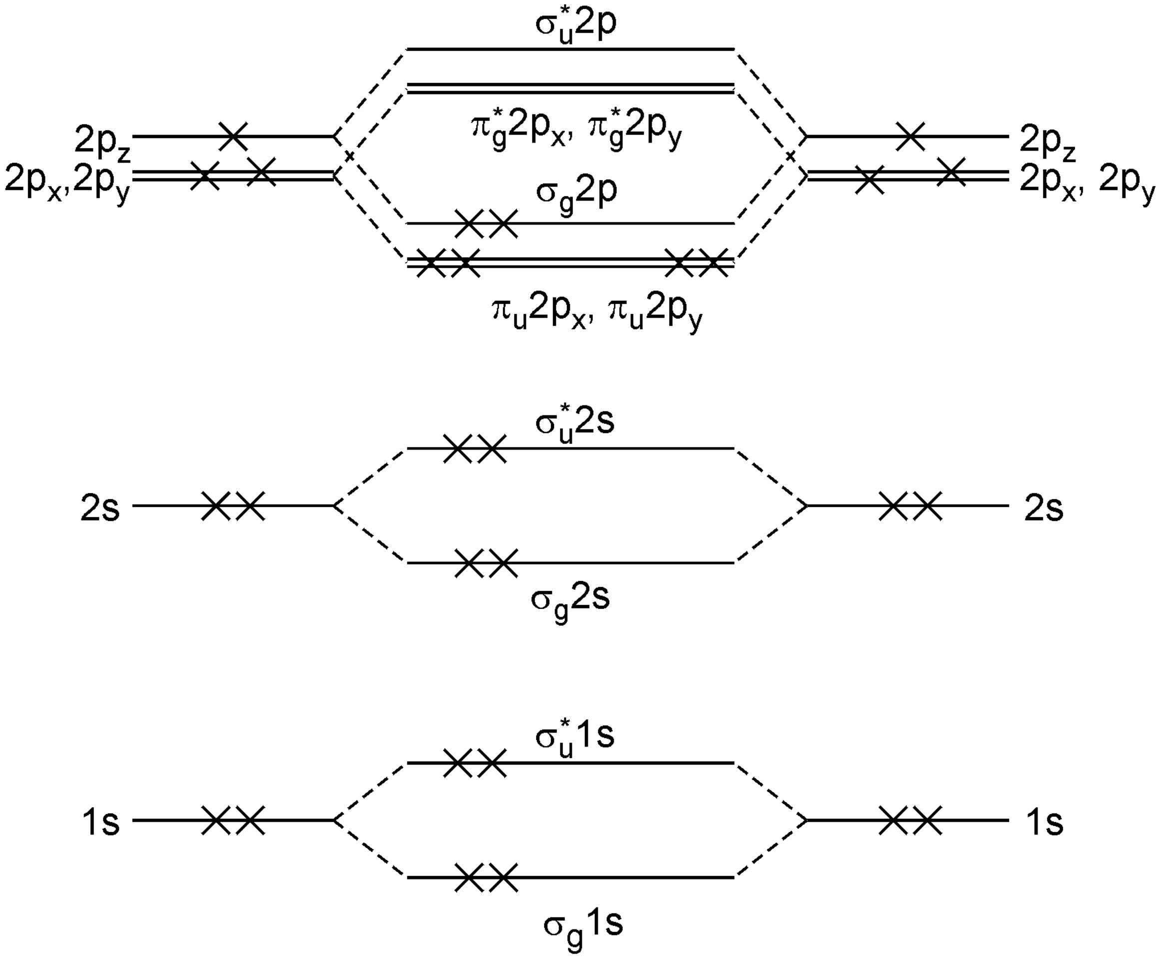
n-orbital : non-bonding molecular orbital

Note:

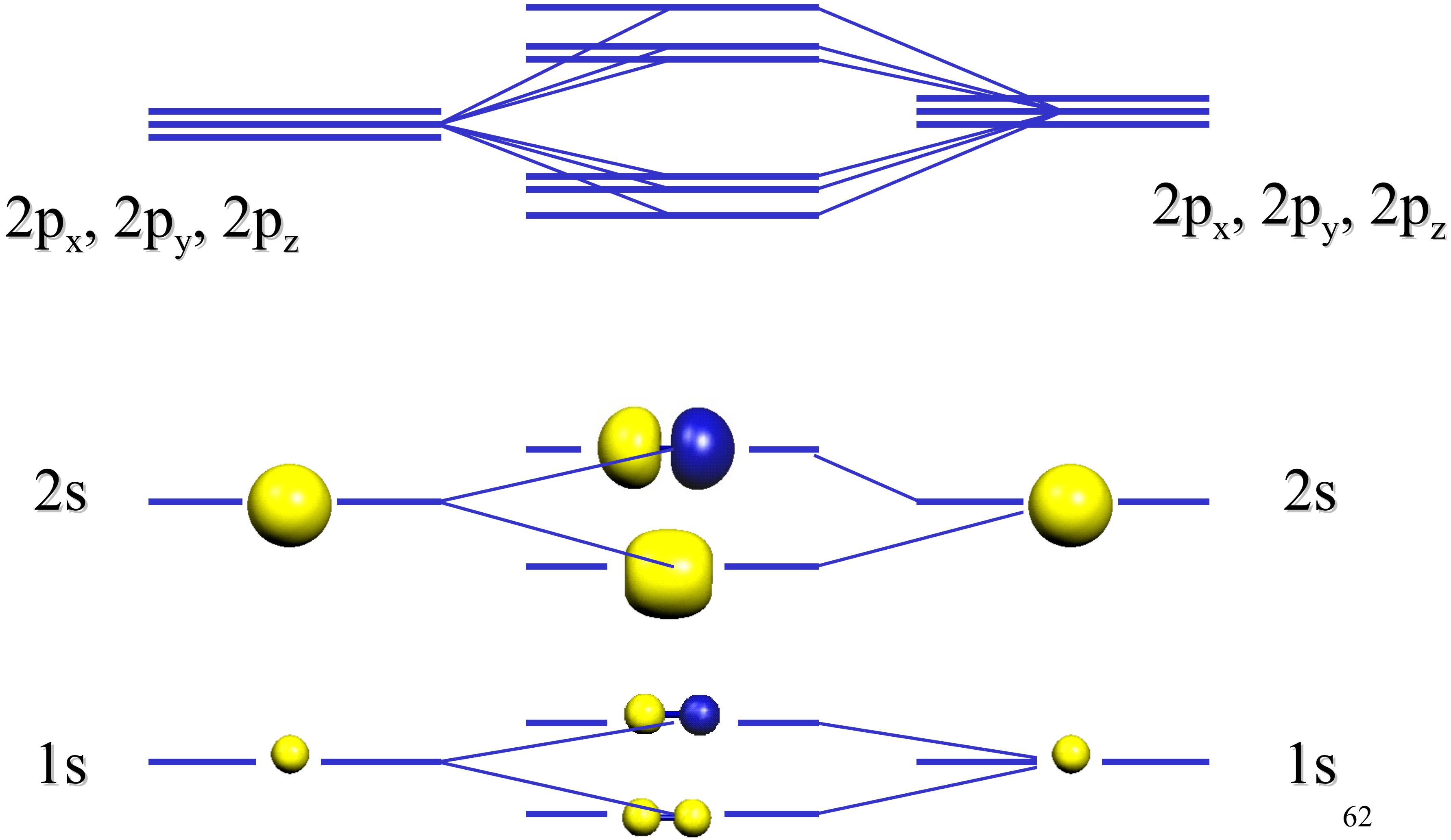
cylindrical symmetry → Molecular orbitals are L_z eigenfunctions with $m_l\hbar, \quad m_l = 0, 1, 2, 3, \ldots \quad (\sigma, \pi, \delta, \ldots)$ eigenvalues.

More than two atomic orbitals can also be combined.

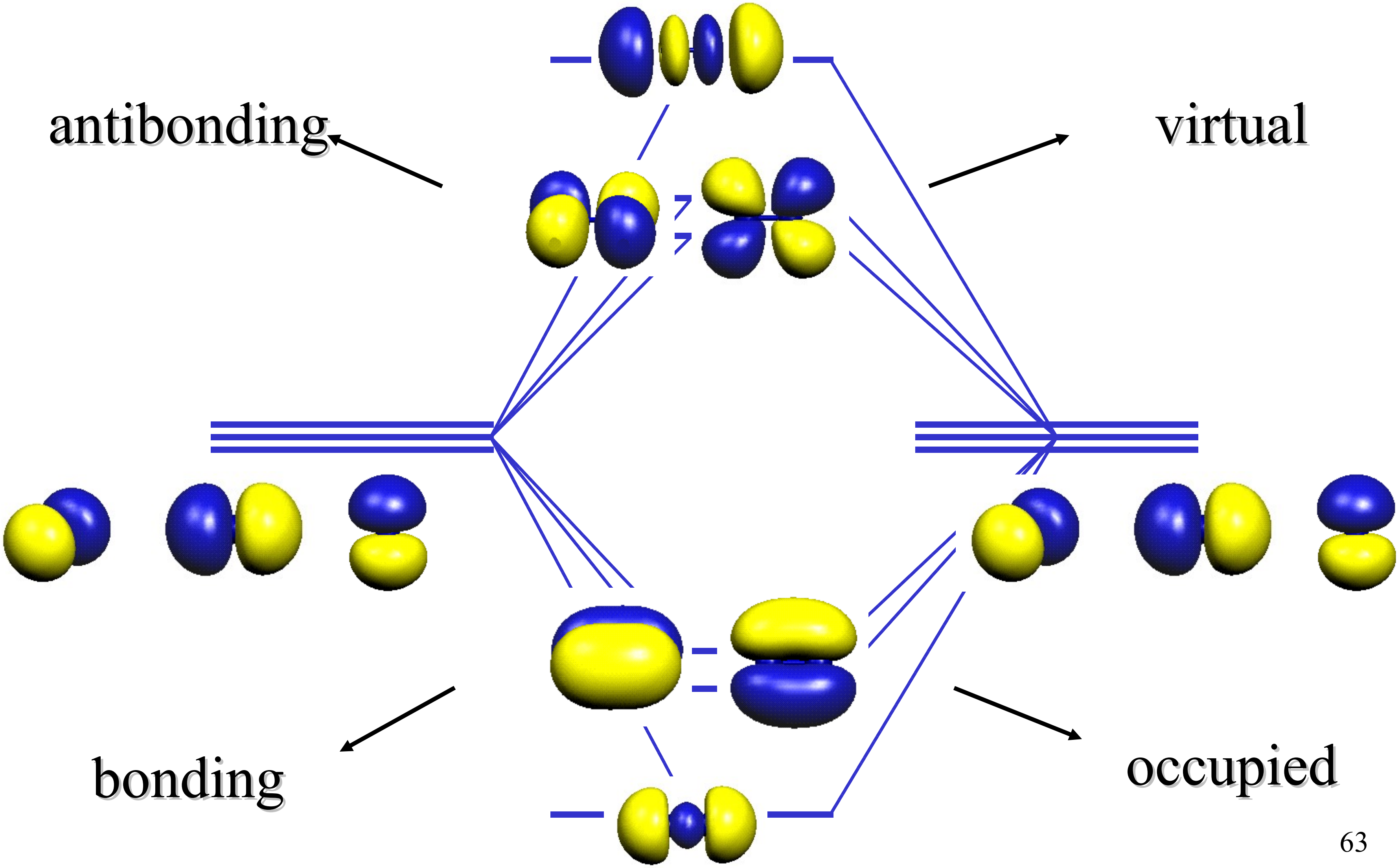
Molecular orbital energy diagram for N_2



Molecular orbital diagram for N_2



MO diagram for N_2 : *p* combinations



antibonding

virtual

bonding

occupied

Electronic configuration

Ground state:

$$\left(\sigma_g 1s\right)^2\left(\sigma_u^* 1s\right)^2\left(\sigma_g 2s\right)^2\left(\sigma_u^* 2s\right)^2\left(\pi_u 2p\right)^4\left(\sigma_g 2p\right)^2$$

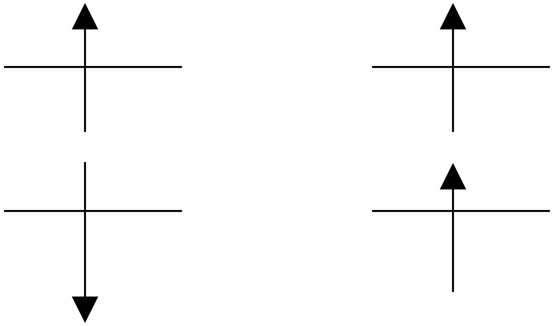
Excited state, e.g.:

$$\left(\sigma_g 1s\right)^2\left(\sigma_u^* 1s\right)^2\left(\sigma_g 2s\right)^2\left(\sigma_u^* 2s\right)^2\left(\pi_u 2p\right)^4\left(\sigma_g 2p\right)^1\left(\sigma_u^* 2p\right)^1$$

Singlet and triplet states

Excited state:

$$\left(\sigma_g 1s\right)^2\left(\sigma_u^* 1s\right)^2\left(\sigma_g 2s\right)^2\left(\sigma_u^* 2s\right)^2\left(\pi_u 2p\right)^4\left(\sigma_g 2p\right)^1\left(\sigma_u^* 2p\right)^1$$



S = 0 S = 1

Singlet state Triplet state

Molecular orbitals of polyatomic molecules

MOs of polyatomic molecules: in principle they are constructed by combining the AOs of all the atoms.

Core MOs

Valence MOs

Core MOs:

The overlap between the core orbitals of different atoms is very small. Therefore:

- the core orbitals are localized on an atom (or on a symmetric group of atoms)

- their shape and energy are hardly different from those of the isolated atom

Valence MOs: the AOs mix

Features:

- Energy
- Shape – localized or delocalized character
  - – point-group symmetry

Energy of valence MOs:

HOMO: highest occupied MO
LUMO: lowest unoccupied MO

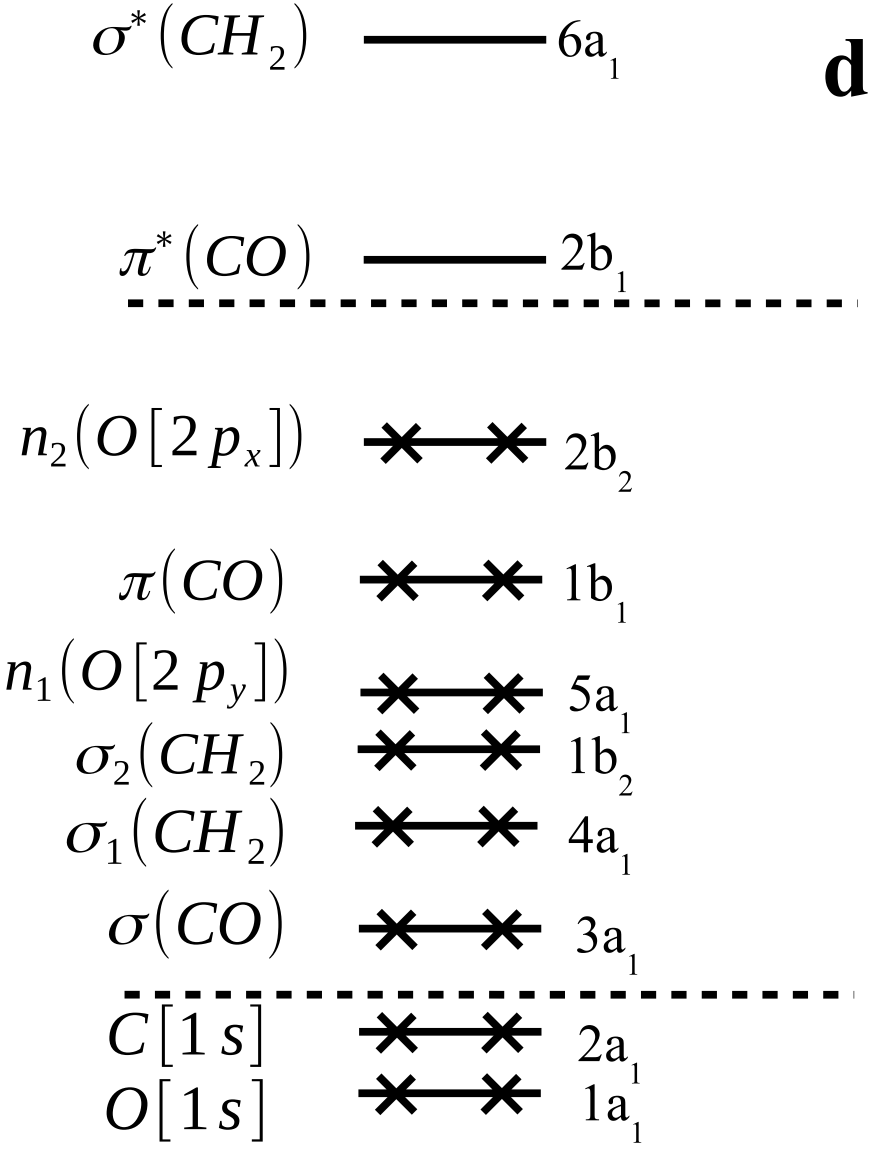
Localized and delocalized MOs

- Localized on an atom:
  - non-bonding electron pair
- Localized on two atoms
  - σ-bond: cylindrical symmetry around the bond
  - π-bond: nodal plane through the bond

local symmetry

- Localized on a functional group, combination of the valence AOs of many atoms

Molecular orbital energy diagram of formaldehyde


$\sigma^*(CH_2)$ 6a$_1$

$\pi^*(CO)$ 2b$_1$

$n_2(O[2p_x])$ 2b$_2$

$\pi(CO)$ 1b$_1$

$n_1(O[2p_y])$ 5a$_1$

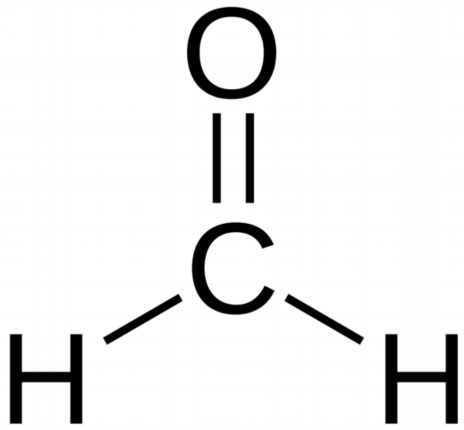
$\sigma_2(CH_2)$ 1b$_2$

$\sigma_1(CH_2)$ 4a$_1$

$\sigma(CO)$ 3a$_1$

$C[1s]$ 2a$_1$

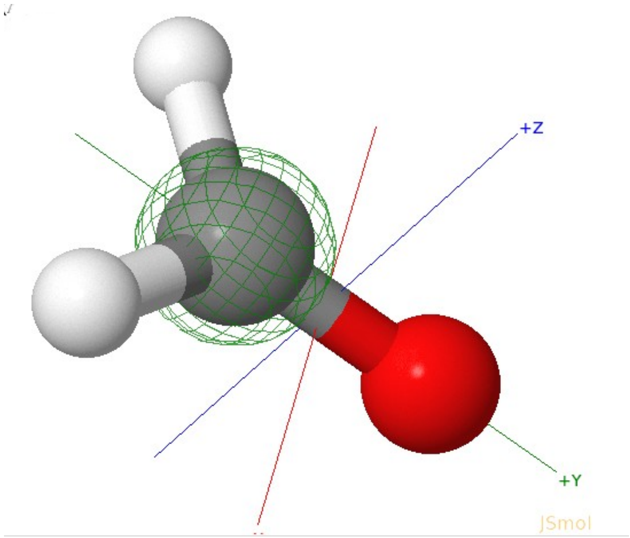
$O[1s]$ 1a$_1$



- Molecular orbitals from a Hartree-Fock calculation.
- “minimal” basis set (STO-3G)
- Orbitals are not normalized

Core orbitals

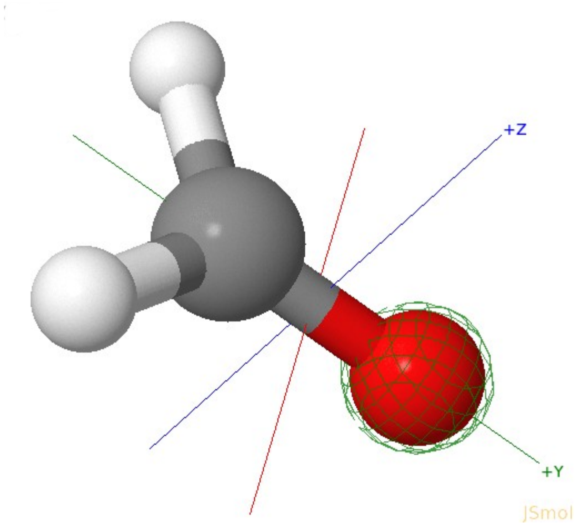
$2a_1$



$-11.125\ E_h$

$\Psi_{2a_1} \propto \Psi_{C[1s]}$

$1a_1$



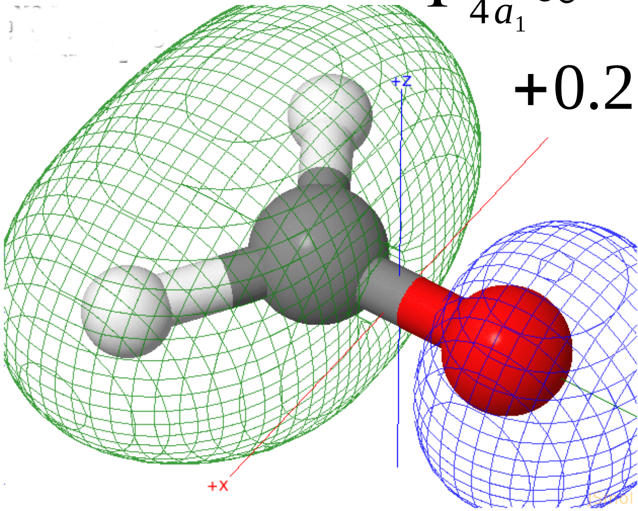
$-20.312\ E_h$

$\Psi_{1a_1} \propto \Psi_{O[1s]}$

Sigma bonding CO and symmetric bonding CH_2 orbitals

$\sim \sigma_1(CH_2)$

4a$_1$

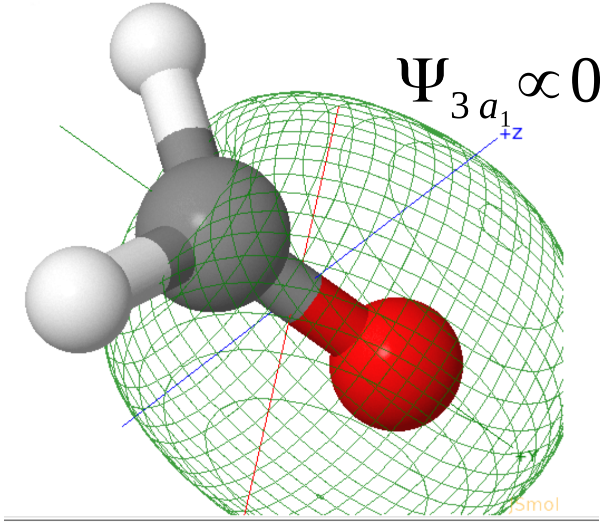


$$\Psi_{4a_1} \propto -0.43\,\Psi_{O[2s]} + 0.57\,\Psi_{C[2s]}$$
$$+0.26\,\Psi_{H_{(1)}[1s]} + 0.26\,\Psi_{H_{(2)}[1s]}$$

-0.808 E_h

3a$_1$

$\sim \sigma(CO)$



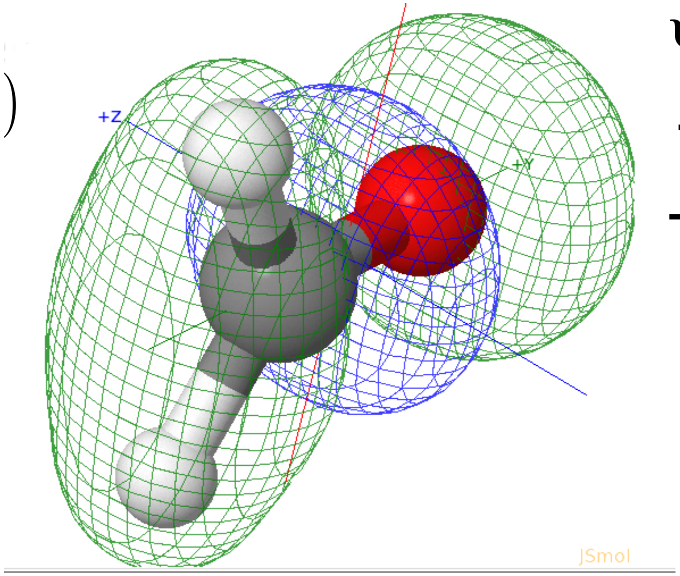
$$\Psi_{3a_1} \propto 0.77\,\Psi_{O[2s]} + 0.28\,\Psi_{C[2s]}$$

-1.337 E_h

Antisymmetric CH_2 sigma and symmetric non-bonding orbital of O

$\sim n_1(O[2p_y])$

$5a_1$

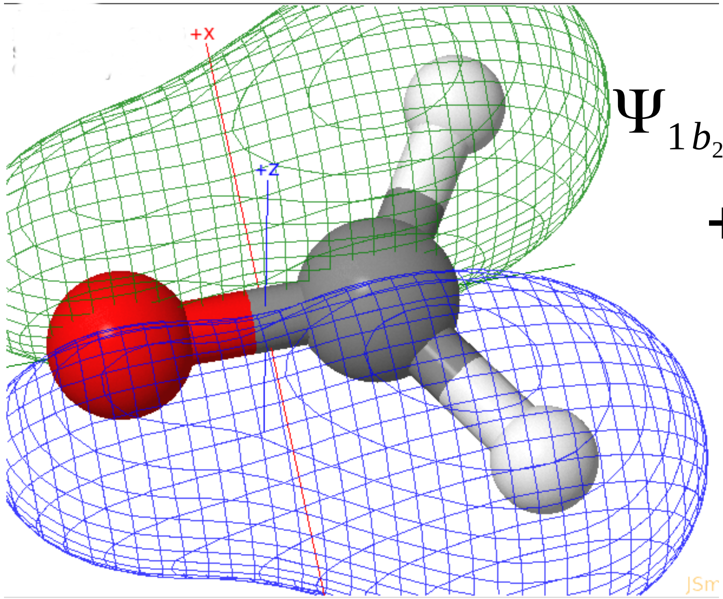


$$\Psi_{5a_1} \propto 0.5\,\Psi_{O[2s]} + 0.68\,\Psi_{O[2p_y]} - 0.45\,\Psi_{C[2p_y]} + 0.16\,\Psi_{H_{(1)}[1s]} + 0.16\,\Psi_{H_{(2)}[1s]}$$

-0.546 E_h

$\sim \sigma_2(CH_2)$

$1b_2$



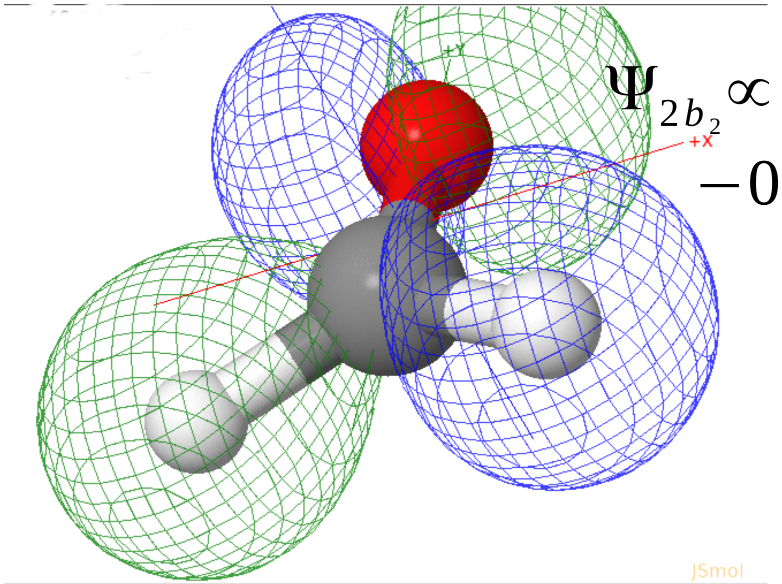
$$\Psi_{1b_2} \propto 0.44\,\Psi_{O[2p_x]} + 0.53\,\Psi_{C[2p_x]} + 0.30\,\Psi_{H_{(1)}[1s]} - 0.30\,\Psi_{H_{(2)}[1s]}$$

-0.633 E_h

Pi and non-bonding orbitals

$\sim n_2(O[2p_x])$

$2b_2$



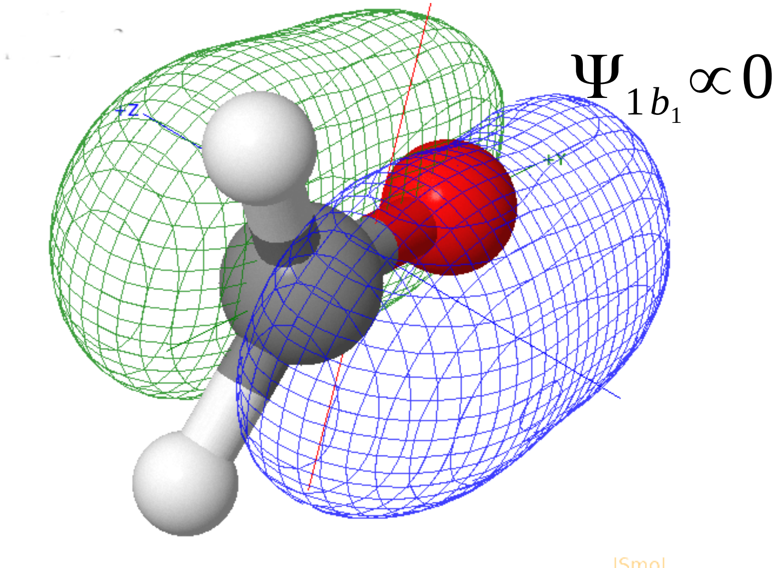
$$\Psi_{2b_2} \propto 0.87\,\Psi_{O[2p_x]} - 0.18\,\Psi_{C[2p_x]} - 0.36\,\Psi_{H_{(1)}[1s]} + 0.36\,\Psi_{H_{(2)}[1s]}$$

-0.354 E_h

(HOMO)

$\sim \pi(CO)$

$1b_1$



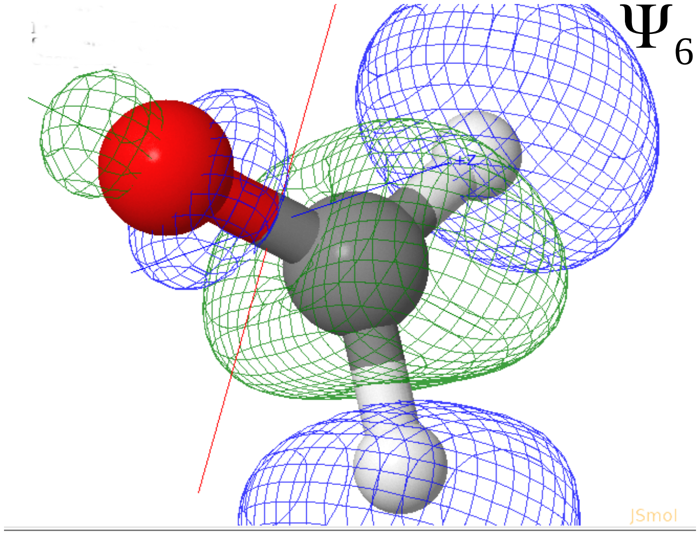
$$\Psi_{1b_1} \propto 0.68\,\Psi_{O[2p_z]} + 0.61\,\Psi_{C[2p_z]}$$

-0.443 E_h

Pi CO and sigma CH$_2$ antibonding orbitals

$\sim \sigma^*(CH_2)$

6a$_1$

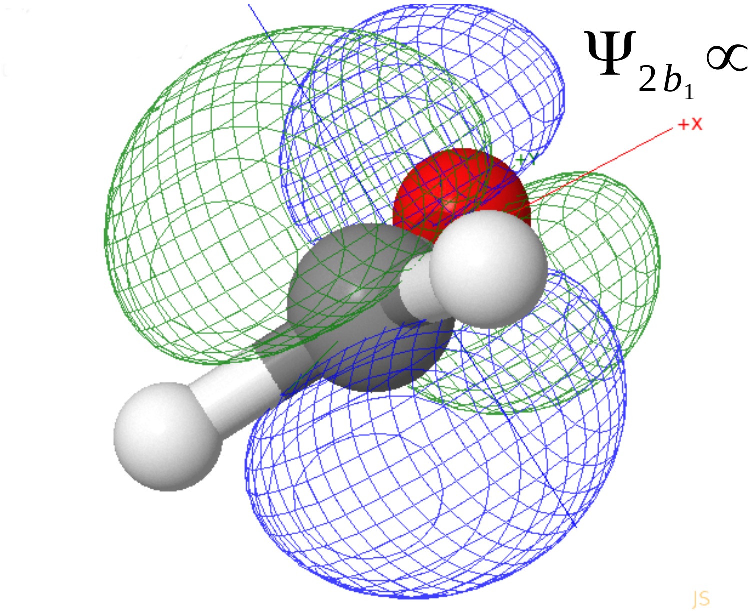


$$\Psi_{6a_1} \propto 1.30\,\Psi_{C[2s]} - 0.44\,\Psi_{C[2p_y]} - 0.89\,\Psi_{H_{(1)}[1s]} - 0.89\,\Psi_{H_{(2)}[1s]}$$

0.629 E$_h$

$\sim \pi^*(CO)$

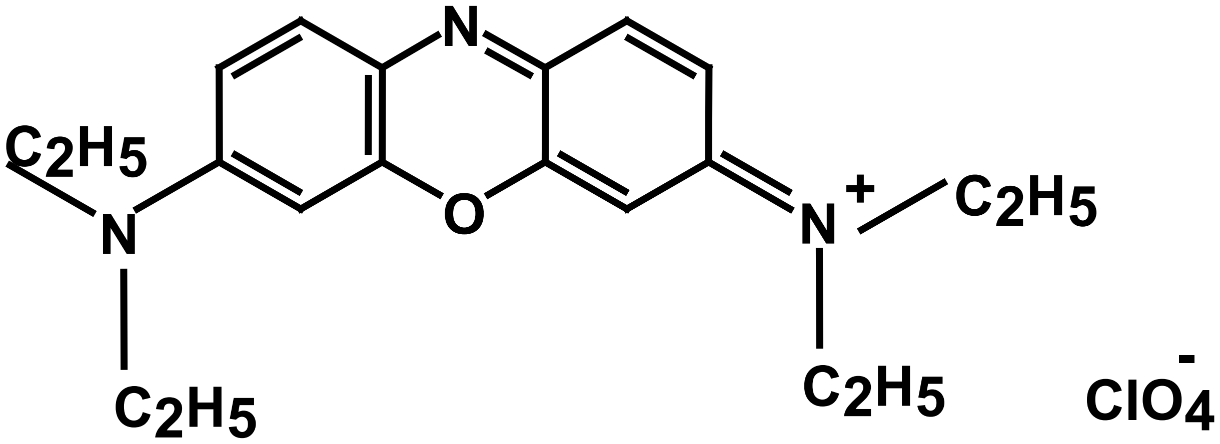
2b$_1$

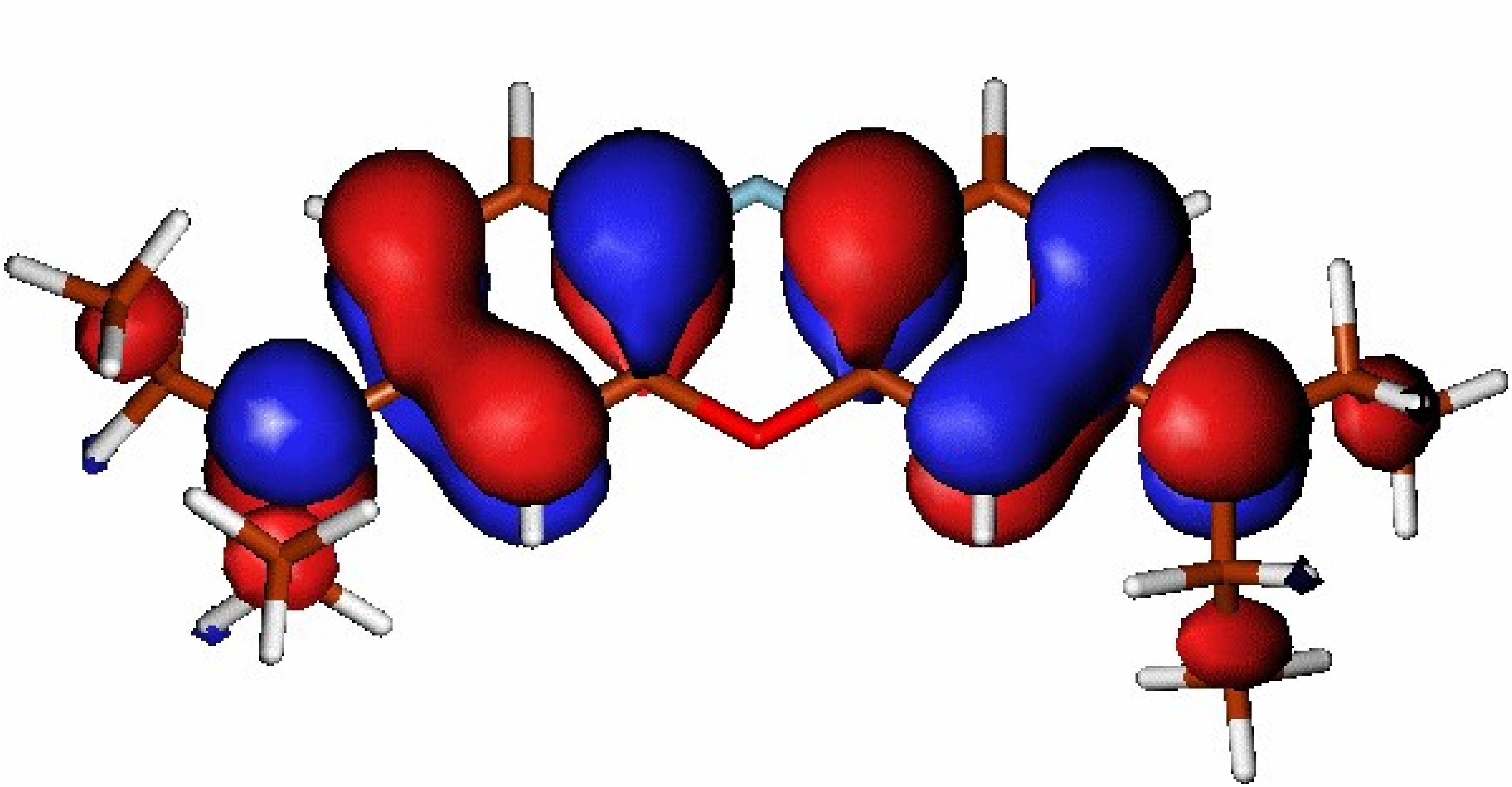


$$\Psi_{2b_1} \propto 0.77\,\Psi_{O[2p_z]} - 0.82\,\Psi_{C[2p_z]}$$

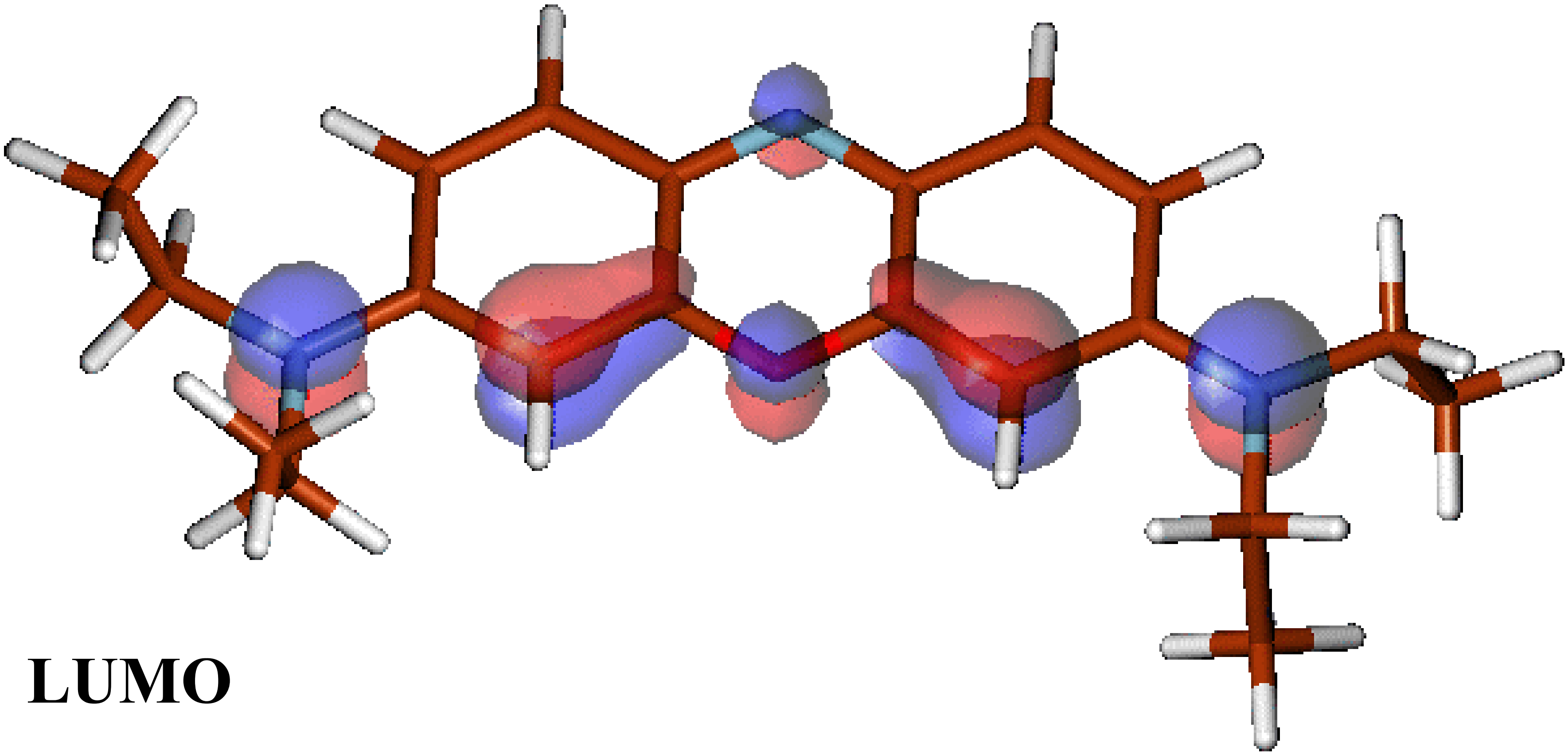
0.282 E$_h$

Oxazine 1





HOMO



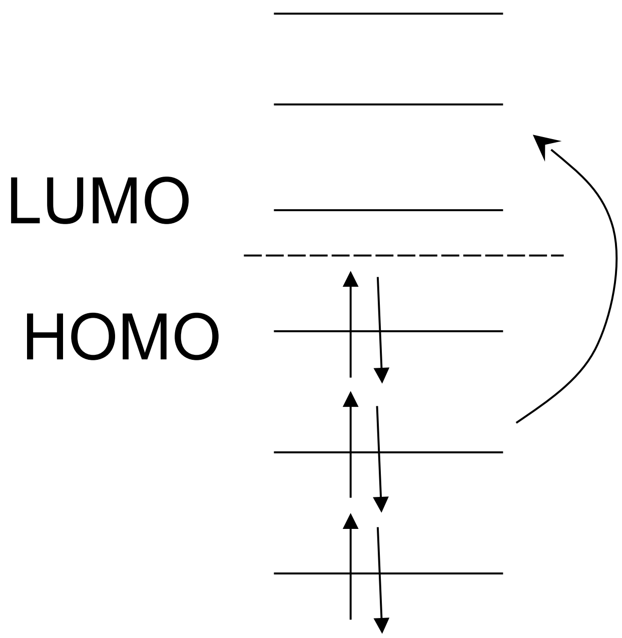
LUMO

Molecular orbitals	Chemical bond
All the atoms contribute	It connects two atoms
electronic excitation	bond length
ionization	valence vibration

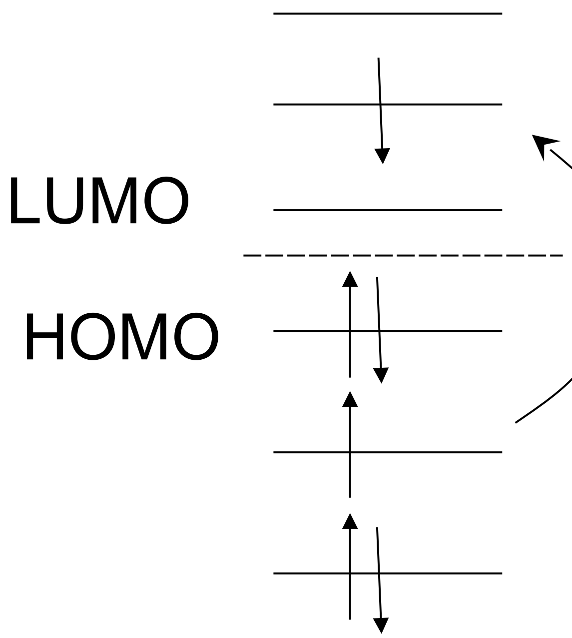
Two different concepts!!!

Electronic excitations in polyatomic molecules

Electronic excitation in MO theory:



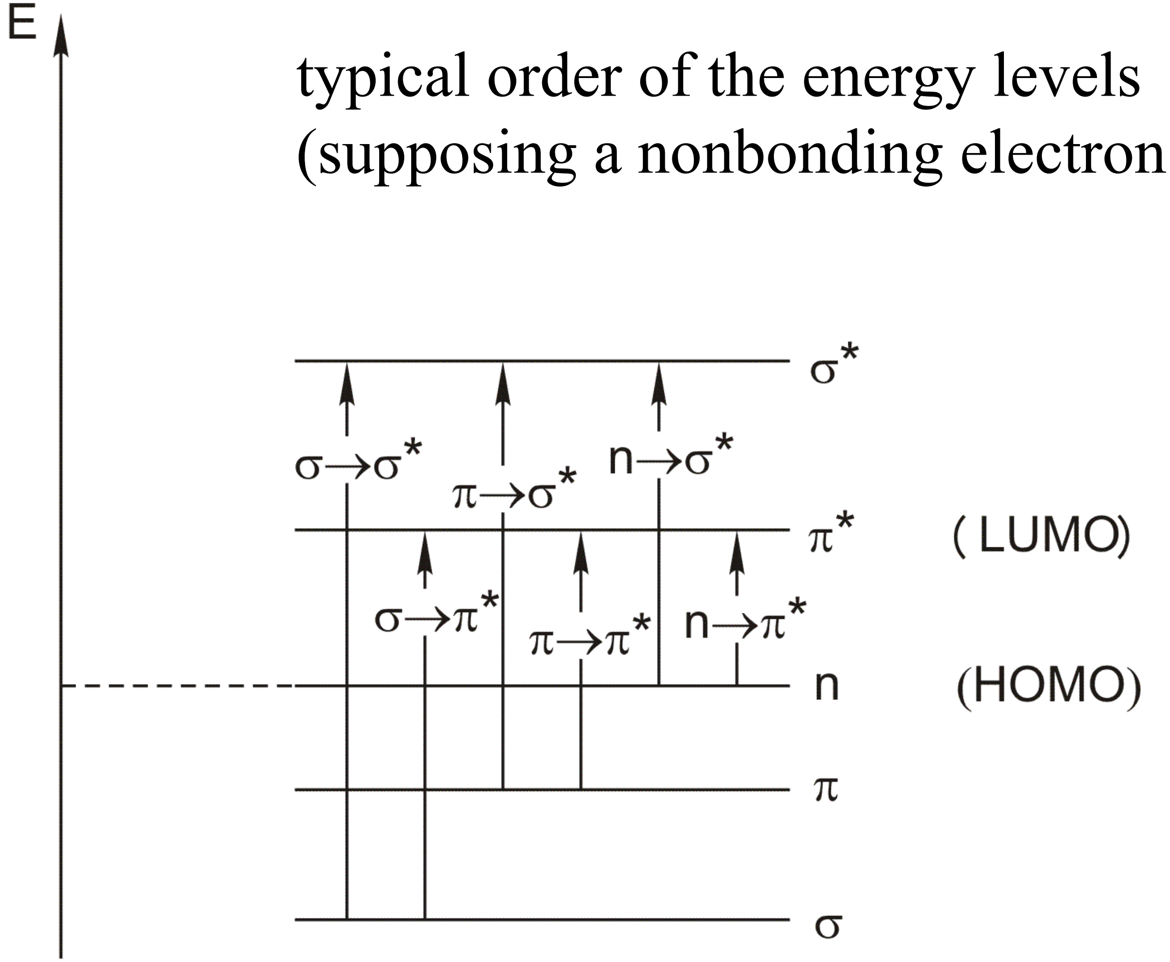
Electronic excitation in MO theory:



Energy and intensity of electronic excitations: Main aspects

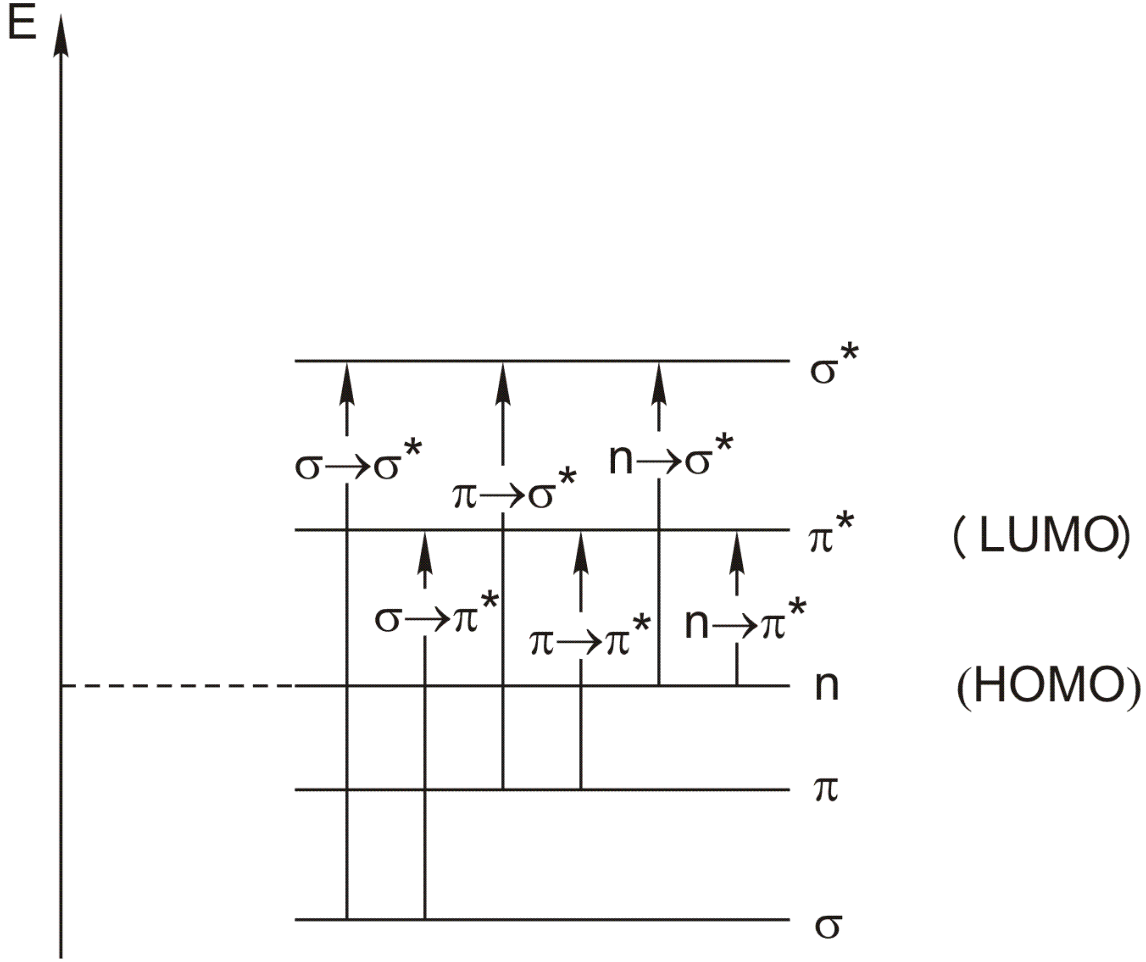
- Local symmetry of orbitals
- Symmetry of the electronic states
- Spin

Classification of electronic transitions according to the local symmetry (e.g., formaldehyde)


typical order of the energy levels
(supposing a nonbonding electron pair)

Order of excitation energies:

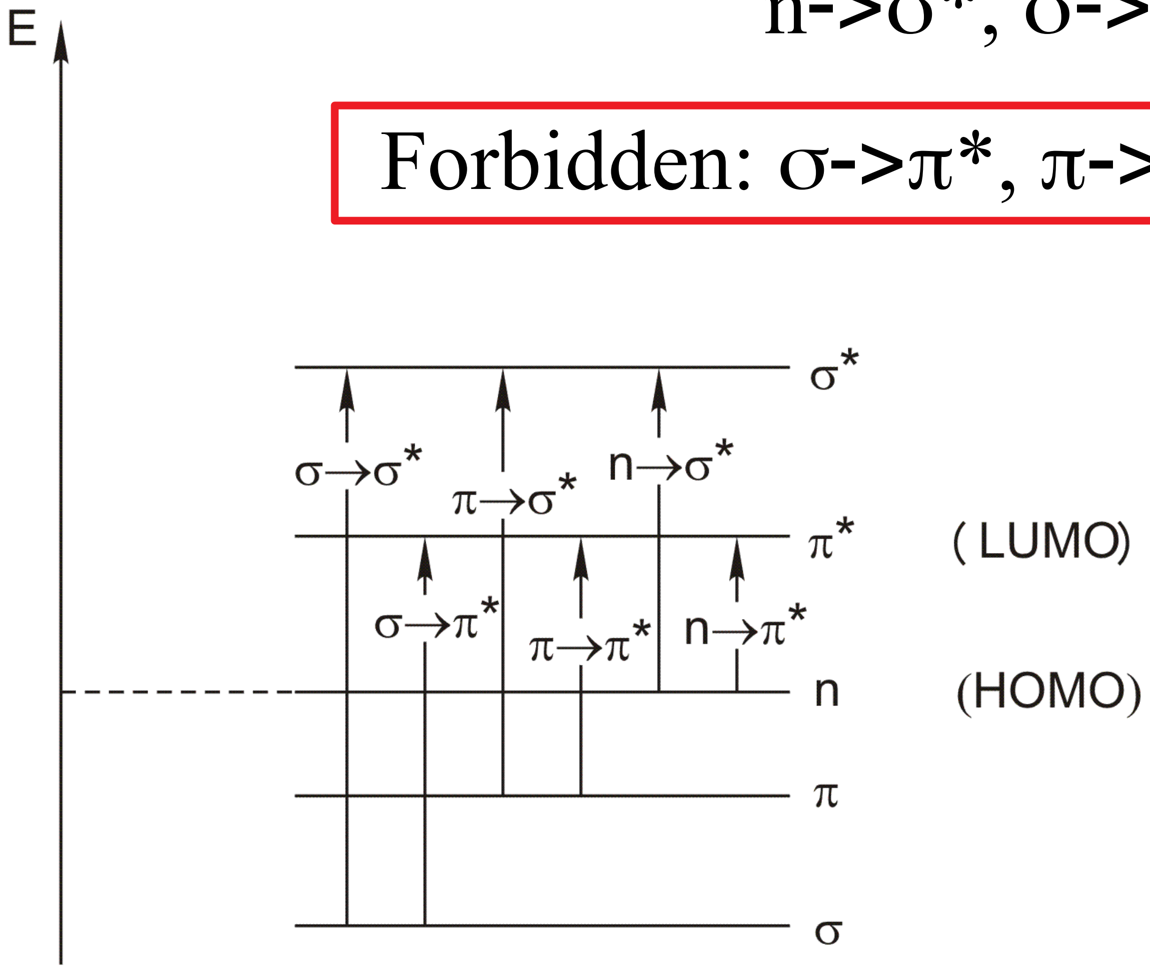
$n \rightarrow \pi^* < \pi \rightarrow \pi^* \sim n \rightarrow \sigma^* < \sigma \rightarrow \pi^* \sim \pi \rightarrow \sigma^* < \sigma \rightarrow \sigma^*$



Selection rule:

Allowed: n->π*, π->π*, n->σ*, σ->σ*

Forbidden: σ->π*, π->σ



Symmetry (irreducible representation) of electronic states

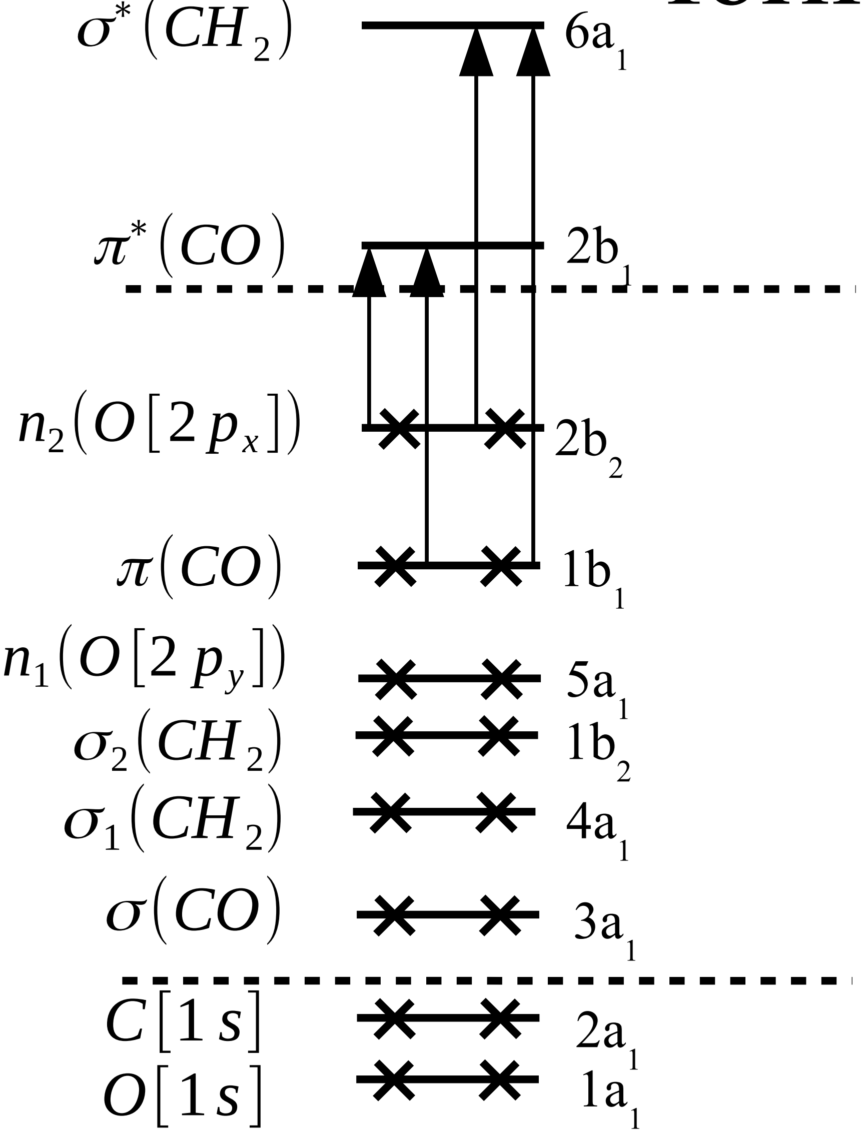
Example: formaldehyde

Point group: C_{2v}

Character table of the C_{2v} point group

C_{2v}	E	$C_2^1(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	+1	+1	+1	+1	T_z,α_{xx},c
A_2	+1	+1	-1	-1	R_x,c
B_1	+1	-1	+1	-1	T_x,R_y
B_2	+1	-1	-1	+1	T_y,R_z

MO energy diagram of formaldehyde



Valence shell

virtual orbitals

Valence shell

occupied orbitals

Inner shell

core orbitals

Electronic configurations of formaldehyde

Electron configuration of the ground state:

$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2$

n-π* transition

Lowest-energy excited configuration:

$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^1\,(2b_1)^1$

Determination of the symmetry (irrep) of electronic states

Irrep of electronic states: the direct product of the irreps of the singly occupied MOs

Direct product: multiplication of characters for each symmetry operation.

Ground-state configuration :

A_1 state

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2$$

<u>Closed-shell configurations</u> always belong to the A_1 irrep.

A_2 state

Lowest-energy excited configuration:

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^1(2b_1)^1$$

	E	$C_2^1(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
B_1	+1	-1	+1	-1
B_2	+1	-1	-1	+1
$B_1 \times B_2 = A_2$	+1	+1	-1	-1

<u>Selection rule:</u> a transition is allowed if the final state belongs to the same irrep as any of the translations, T_x, T_y, or T_z

C_{2v}	E	$C_2^1(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	+1	+1	+1	+1	$T_z, \alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
A_2	+1	+1	-1	-1	R_x, α_{xy}
B_1	+1	-1	+1	-1	T_x, R_y, α_{xz}
B_2	+1	-1	-1	+1	T_y, R_z, α_{yz}

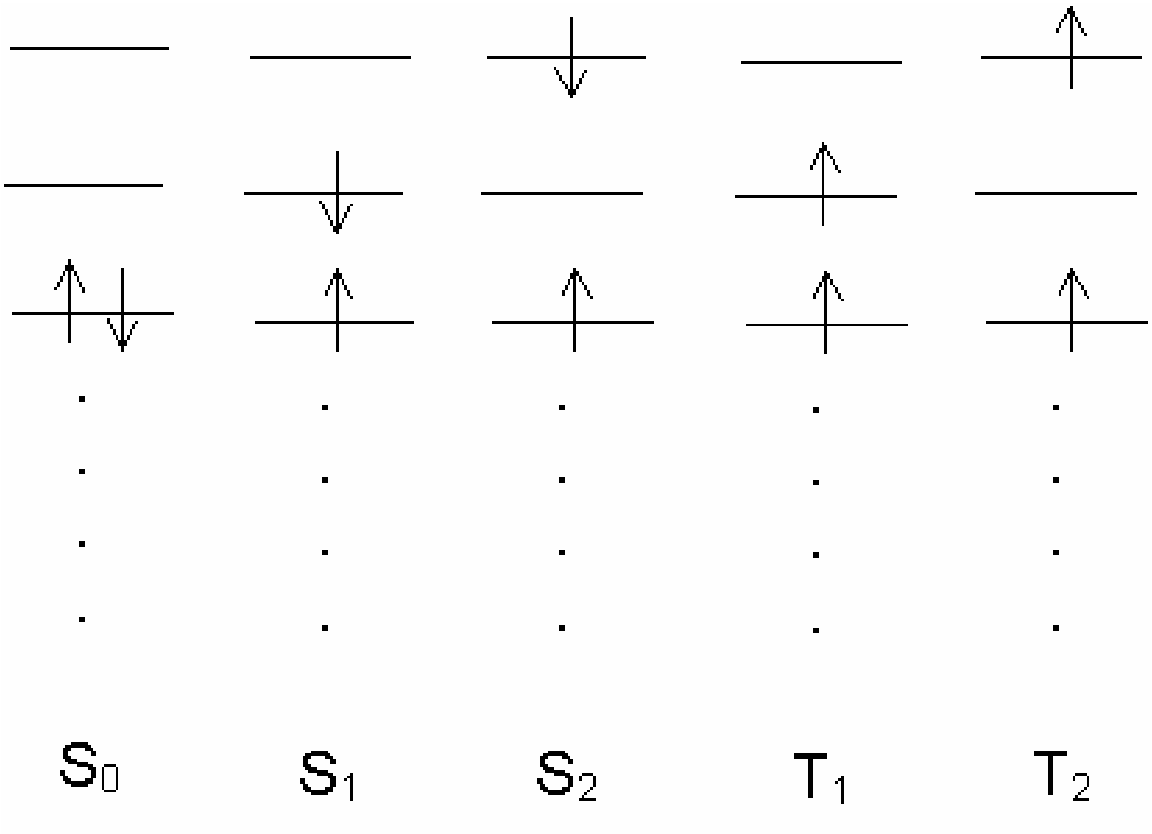
Spin:
Singlet and triplet states

$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^1\,(2b_1)^1$

A_2 state

$^1A_2$ $^3A_2$

Singlet state Triplet state



S_0: ground state

S_1, S_2: singlet excited states

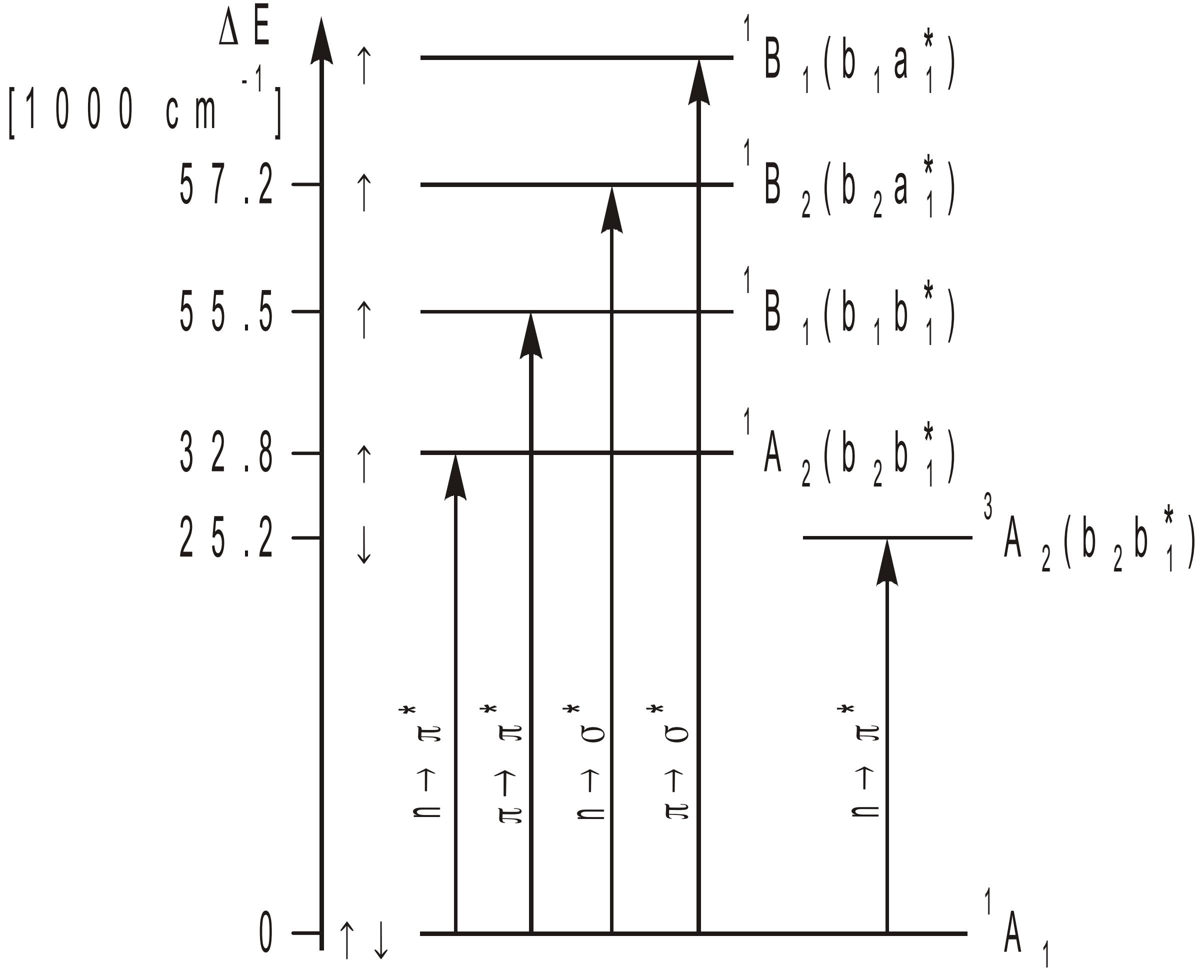
T_1, T_2: triplet excited states

Selection rule

$\Delta S = 0$

Singlet-singlet	Allowed
Triplet-triplet	Allowed
Singlet-triplet	Forbidden
Triplet-singlet	Forbidden

Transitions in the electronic excitation spectrum of formaldehyde



Ultraviolet-visible spectroscopy

Excitation of core electrons: X-ray radiation

Excitation of valence electrons: UV and visible light.

λ = 100-1000 nm

Far (vacuum: O_2 and N_2 absorb here) UV region: 100-200 nm

Near UV: 200-400 nm

Visible region: 400-800 nm

Near IR region: from 800 nm.

The spectrum:

Abscissa: λ [nm]

Ordinate: intensity

absorbance

$$A = \log \frac{I_o}{I}$$

transmission

$$T = \frac{I}{I_o} \cdot 100 (\%)$$

More frequently solvent samples are studied. (Solvent: n-hexane(sigma-sigma* is the lowest tr.) , water or ethanol (sigma-sigma*, n-sigma*), etc.)

Studied compounds

Organic compounds

a) molecules containing functional groups with both π-bonds and nonbonding electron pairs (CO, CN, NO_2-groups; n-π* transitions)

b) molecules with weakly-bonded nonbonding electron pairs (Cl, Br, I, Se-containing compounds; n-σ* transitions, above 200 nm)

c) molecules containing conjugated π-electron system (π-π* transitions, above 200 nm)

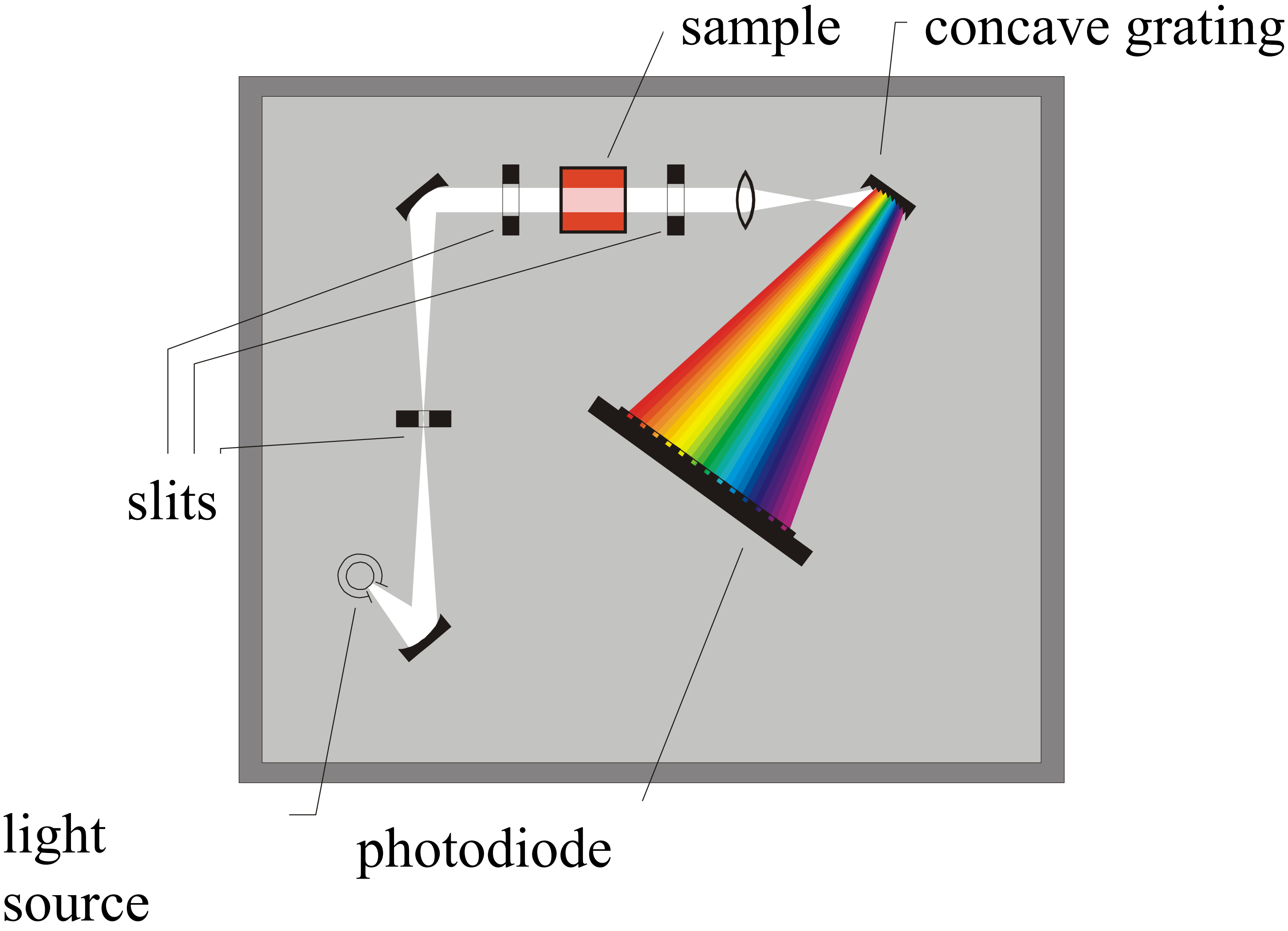
Inorganic compounds

Transition metal complexes

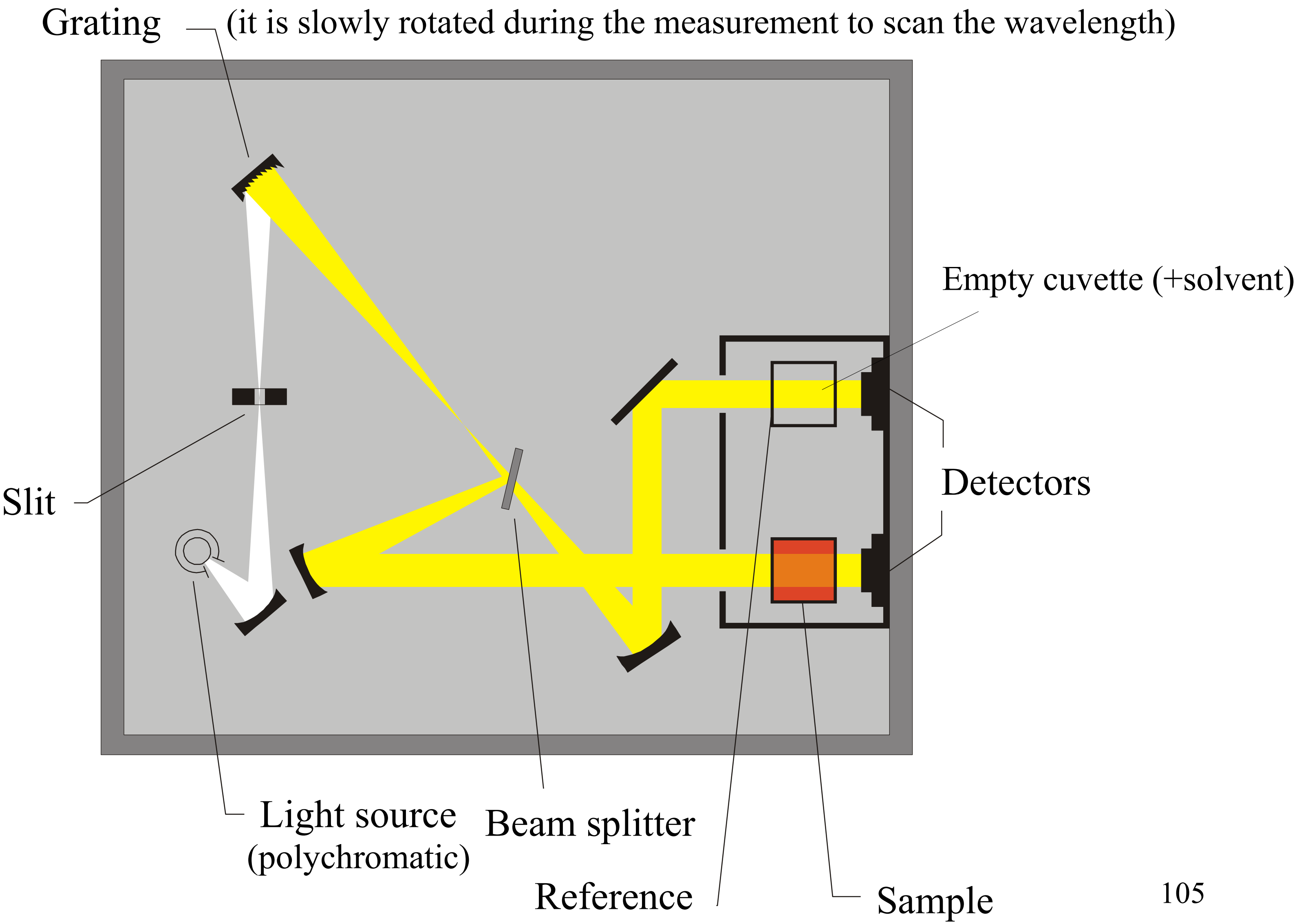
The degenerate d or f orbitals of the metal atom split due to the ligands. The energy difference between split orbitals is small. These transitions are located in the UV-visible spectral region.

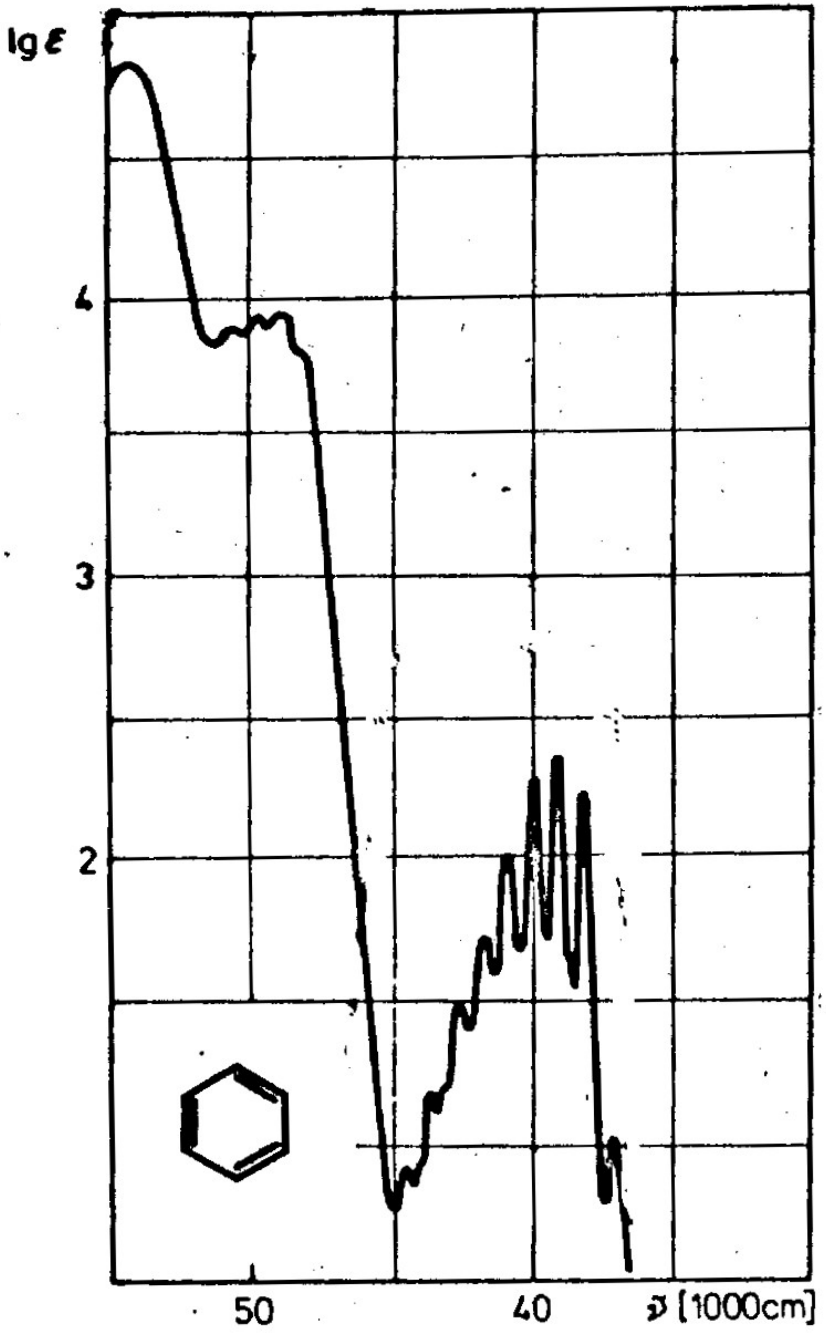
Theoretical fundamentals: ligand-field theory.

Single-beam UV-visible absorption spectrophotometer



Double-beam UV/VIS absorption spectrophotometer





Electronic spectrum of benzene (in ethanol)

Above the dissociation limit: absorption is a continuum. Below the dissociation limit: electronic spectrum contains the vibrational states.

Electronic spectrum of benzene (gas phase)

N_a^b: excitation from state a to state b of normal mode N

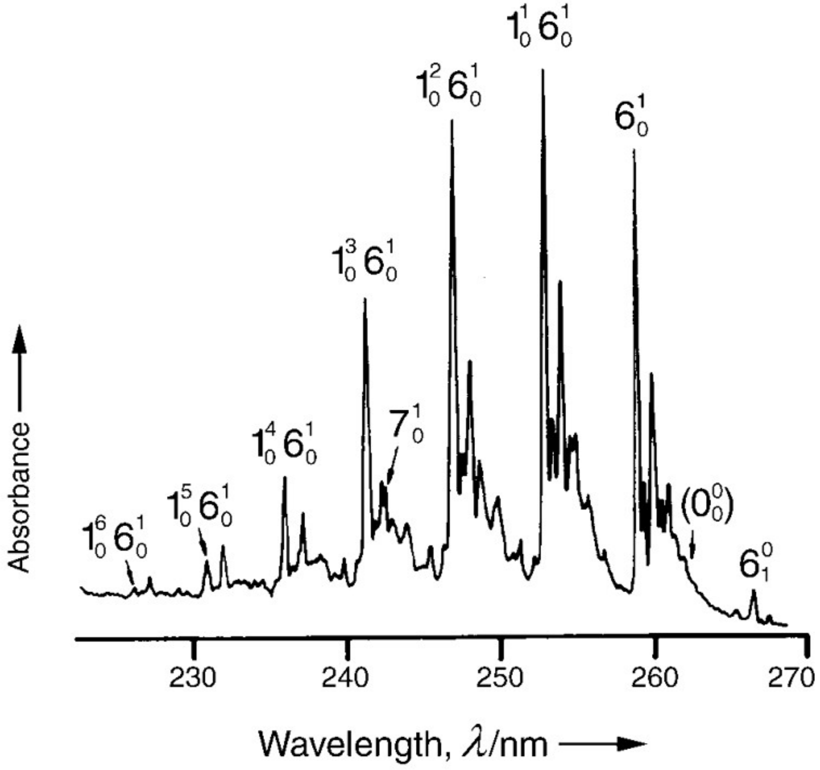
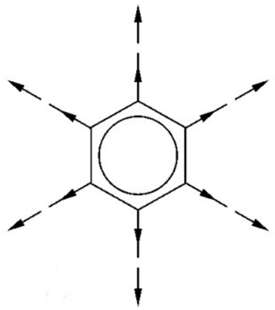
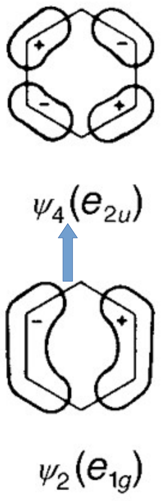


Figure 7.42 Low-resolution $\tilde{A}^1B_{2u} - \tilde{X}^1A_{1g}$ absorption spectrum of benzene

Normal mode 6:



e^- excitation:



Theory of fluorescence and phosphorescence

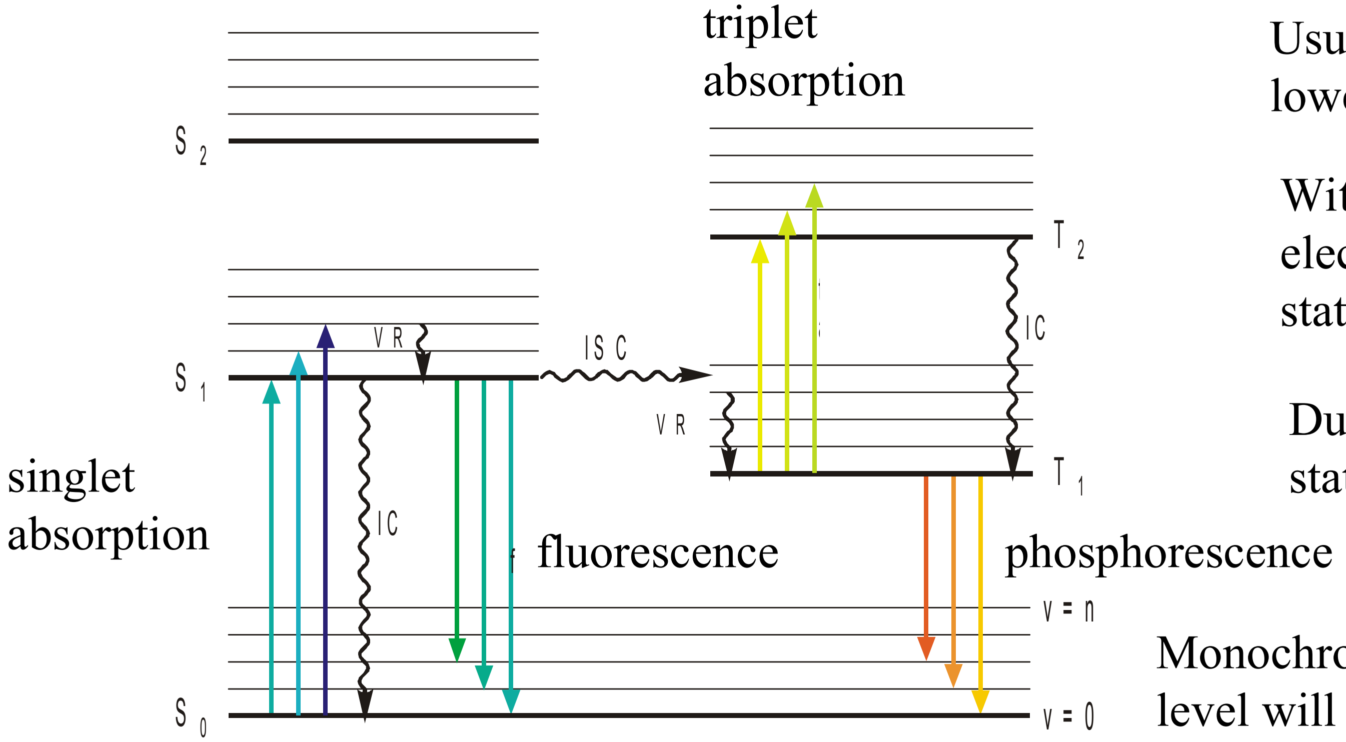
Absorption: all compounds

Emission: few materials, mainly large, aromatic compounds

Demonstration of emission: Jablonski diagram

(a schematic electronic energy diagram for molecules with vibrational fine structure, so-called ‘‘vibronic’’ states)

Jablonski-diagram (fate of excited states)



VR: vibrational relaxation
ISC: intersystem crossing
IC: internal conversion
S, T: singlet and triplet states

⟿ non-radiative transition

→ radiative transition

Usually the triplet states have lower energy (see: He atom)

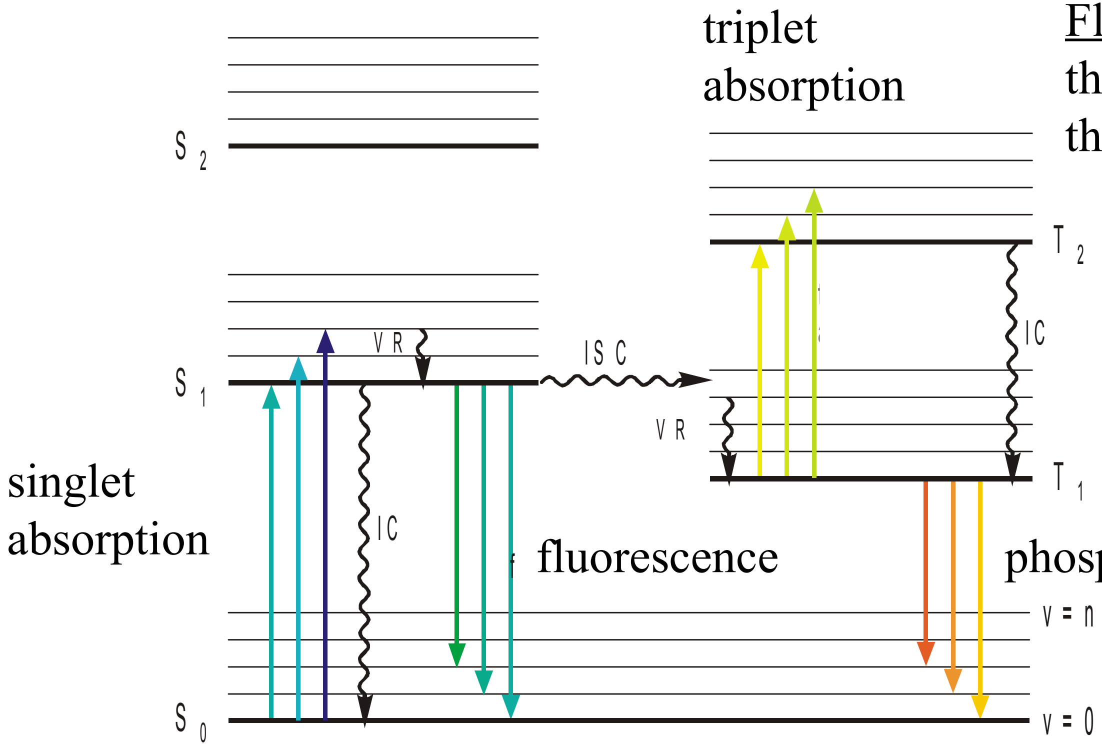
Without radiations the electrons are in the ground state S_0 (see: Boltzmann dist.).

Due to the radiation the state S_1 will be populated.

Monochrome radiation: few vibr. level will be populated, polychrome rad: many occupied vibr.states

<u>vibrational relaxation</u>: no radiation, the extra energy transferred to the solvent (rapid process, 10^{-12}s).

Jablonski-diagram (fate of excited states)



<u>Fluorescence:</u> emission process where the initial and final electronic states have the same multiplicity. From the lowest S_1 to one of the vib. states of S_0.

Due to VR the emitted radiation has lower energy than the absorbed.

Typical for rigid molecules (fixed saturated rings).

<u>ISC:</u> intersystem crossing:non-ratiative siglet-triplet transition.

<u>Phosphorescence:</u> forbidden at first order → small probability, T_1 has long lifetime in the order of micro- or millisec.

<u>IC:</u> the liberated energy transforms into heat: rotational and vibrational states will be excited. No radiation. No spin multiplicity changed. Typical for flexible molecules.

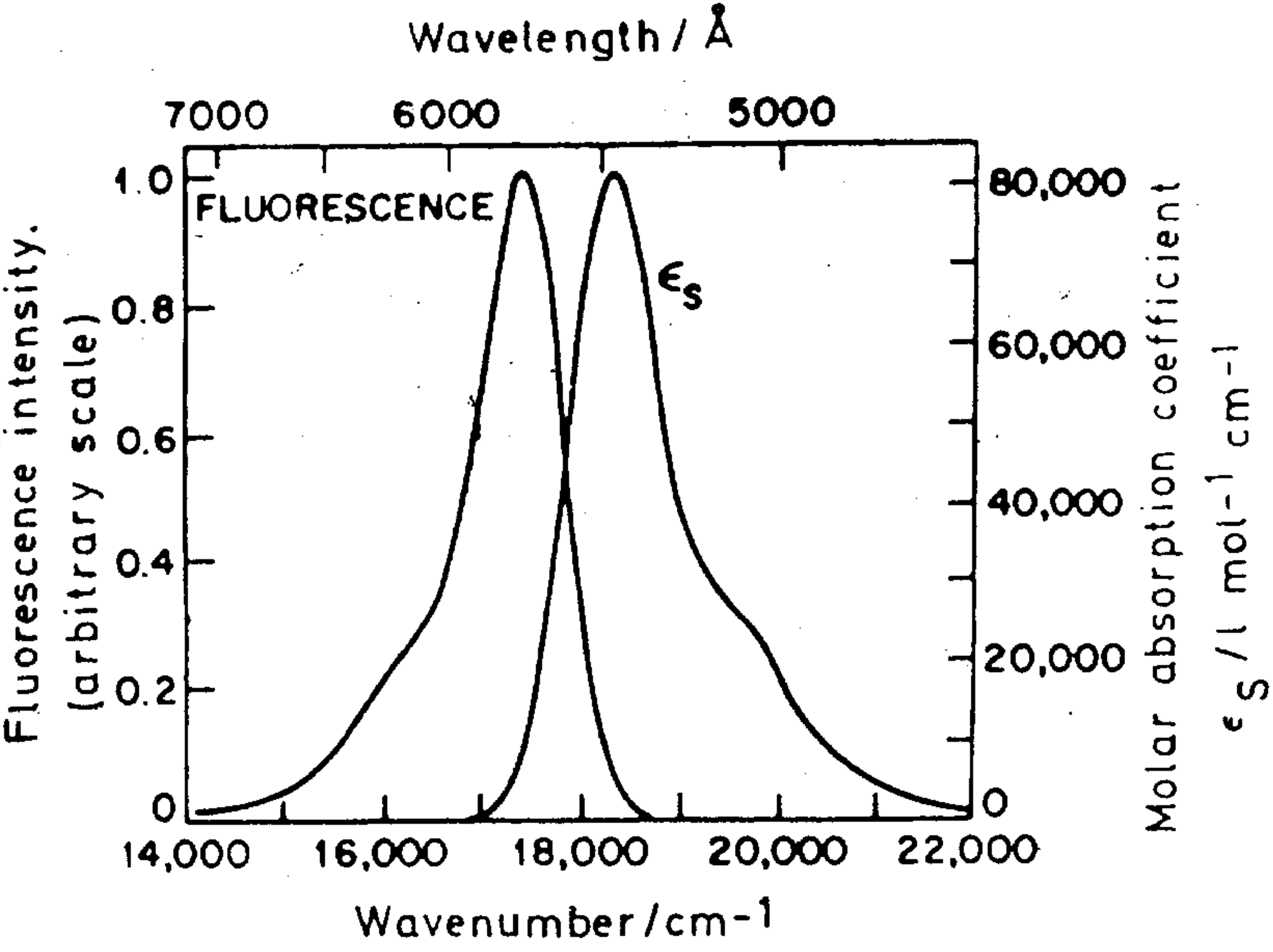
<u>Photoinduced absorption:</u> S_1 eliminates a second photon.

Phosphorescence

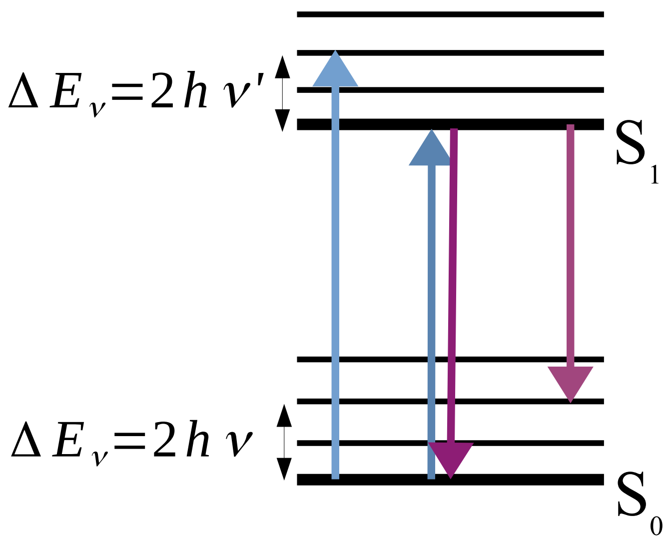
If the Hamiltonian does not contain the spin, the S is a good quantum number, and the singlet-triplet transition is not possible.

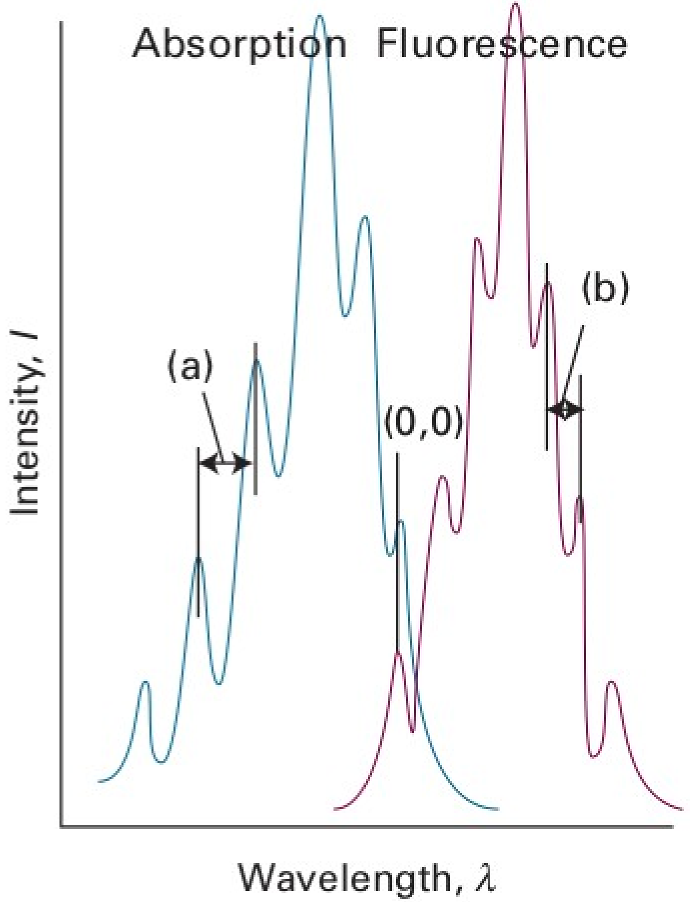
Due to the significant spin-orbit coupling, the spin of molecule containing moderately heavy atom (e.g., sulfur) is not a exact quantum number any more and the intersystem crossing is possible.

Absorption and emission spectra of the Rodamine-B dye



Absorption and fluorescence





$$\Delta E\left(S_{0,}\, n_\nu = 0 \rightarrow S_{1,}\, n_\nu = 2\right) = \Delta E_e + 2h\nu'$$

$$\Delta E\left(S_{0,}\, n_\nu = 0 \rightarrow S_{1,}\, n_\nu = 0\right) =$$
$$-\Delta E\left(S_{1,}\, n_\nu = 0 \rightarrow S_{0,}\, n_\nu = 0\right) = \Delta E_e$$

$$\Delta E\left(S_{1,}\, n_\nu = 0 \rightarrow S_{0,}\, n_\nu = 2\right) = -\left(\Delta E_e - 2h\nu\right)$$

Fluorescence-spectroscopy

The emission is measured after the absorption of light.

This is mainly fluorescence (sometimes phosphorescence)

The spectrum:

Abscissa: λ [nm]

Ordinate: intensity

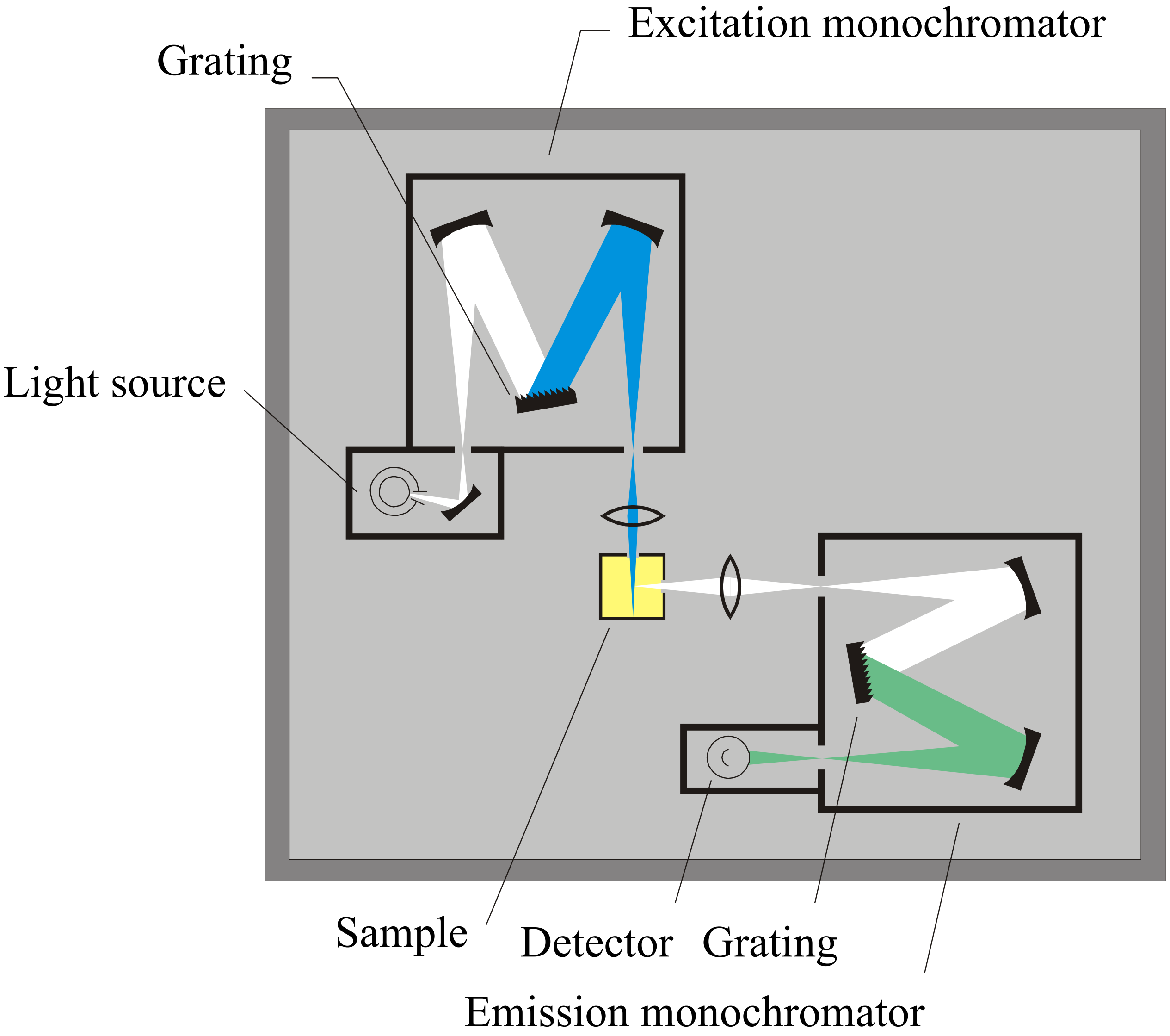
I_F (arbitrary units)

Φ_F fluorescence quantum yield

$$\Phi_F = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}}$$

Solvents: (see UV/VIS spectroscopy)

Spectrofluorimeter



The advantages of fluorescence spectroscopy

1. Much higher sensitivity in contrast to absorption experiments since the intensity is measured compared to I = 0 (“darkness”).

The ideal concentration of a strongly fluorescing compound is ~10^{-6} M.

2. Double selectivity due to the

- wavelength of the absorbed light
- wavelength of the emitted light

Important analytical method!

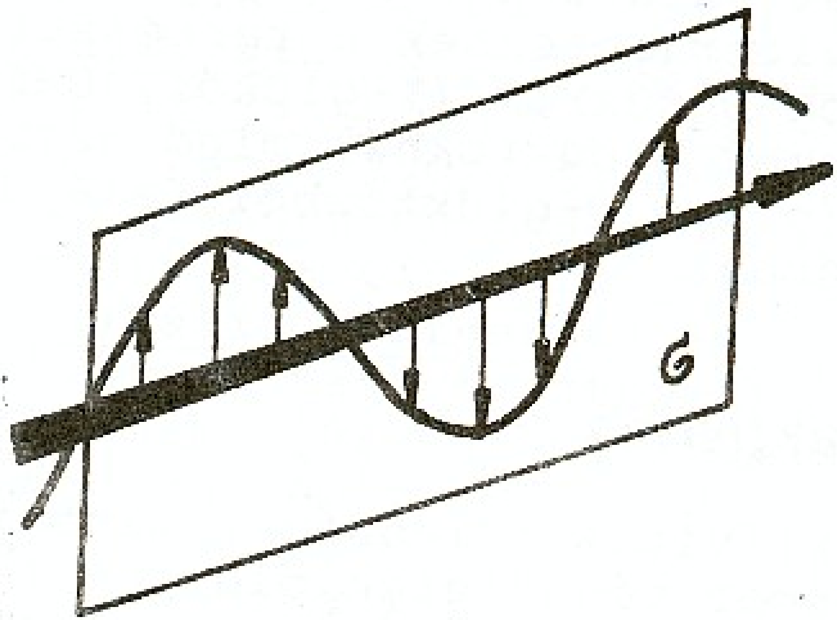
Optical rotation and circular dichroism

There are many chiral compound in the living matter:

amino acids, sugars, amines, steroids, alkaloids, terpenoids

These can be investigated by chiroptical methods:

optical rotation, optical rotatory dispersion (ORD), circular dichroism (CD)



Linearly polarized light

Optical rotation

The solution of chiral molecules rotates the plane of polarization:

$\alpha = [M] \cdot c \cdot \ell$

$[M]$ molar (optical) rotation

c concentration

ℓ path length of the cuvette

Molar optical rotation is wavelength-dependent

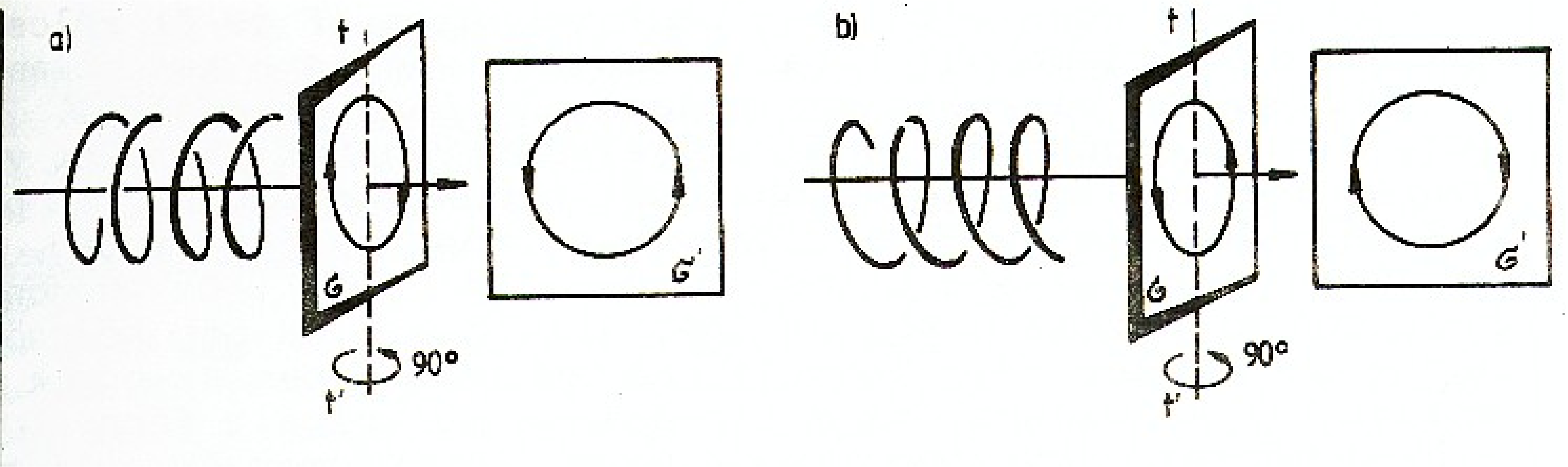
- Polarimeter: [M] is measured at a given wavelength, usually at the D-line of Na ($[M]_D$)

  application: optical purity, $100 * \frac{[M]}{[M]_{pure\ enantiomer}}$

- Spectropolarimeter: [M] - λ spectrum is measured (Optical rotatory dispersion, ORD)

  application: structure analysis

CD



(a) left (b) right

circularly-polarized light

Circular dichroism

The absorption coefficients of the left and right circularly-polarized light are different!

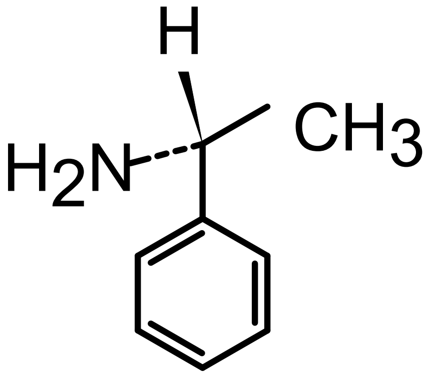
This effect is measured:

$$A_L = \varepsilon_L \cdot c \cdot \ell, \text{ and } A_R = \varepsilon_R \cdot c \cdot \ell$$

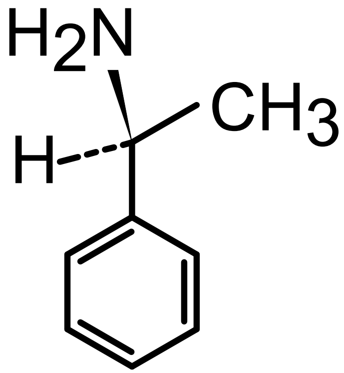
CD signal: $\Delta A = A_L - A_R = (\varepsilon_L - \varepsilon_R) \cdot c \cdot \ell$

CD spectrum: ΔA as a function of the wave length

Example: CD spectrum of (R)- and (S)-phenyl-ethyl-amine



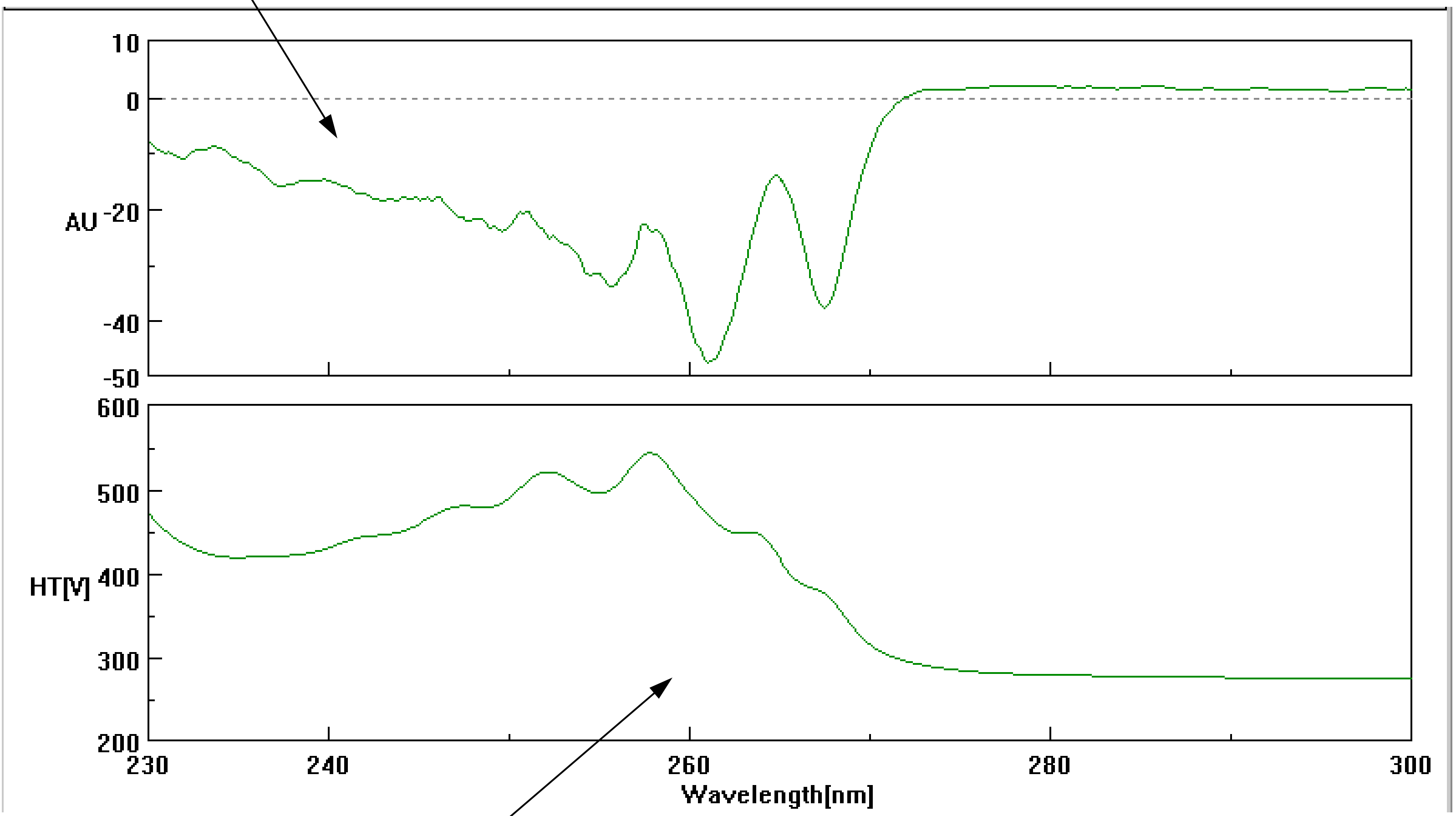
(R)-FEA



(S)-FEA

CD spectrum of (R)-phenyl-ethyl-amine

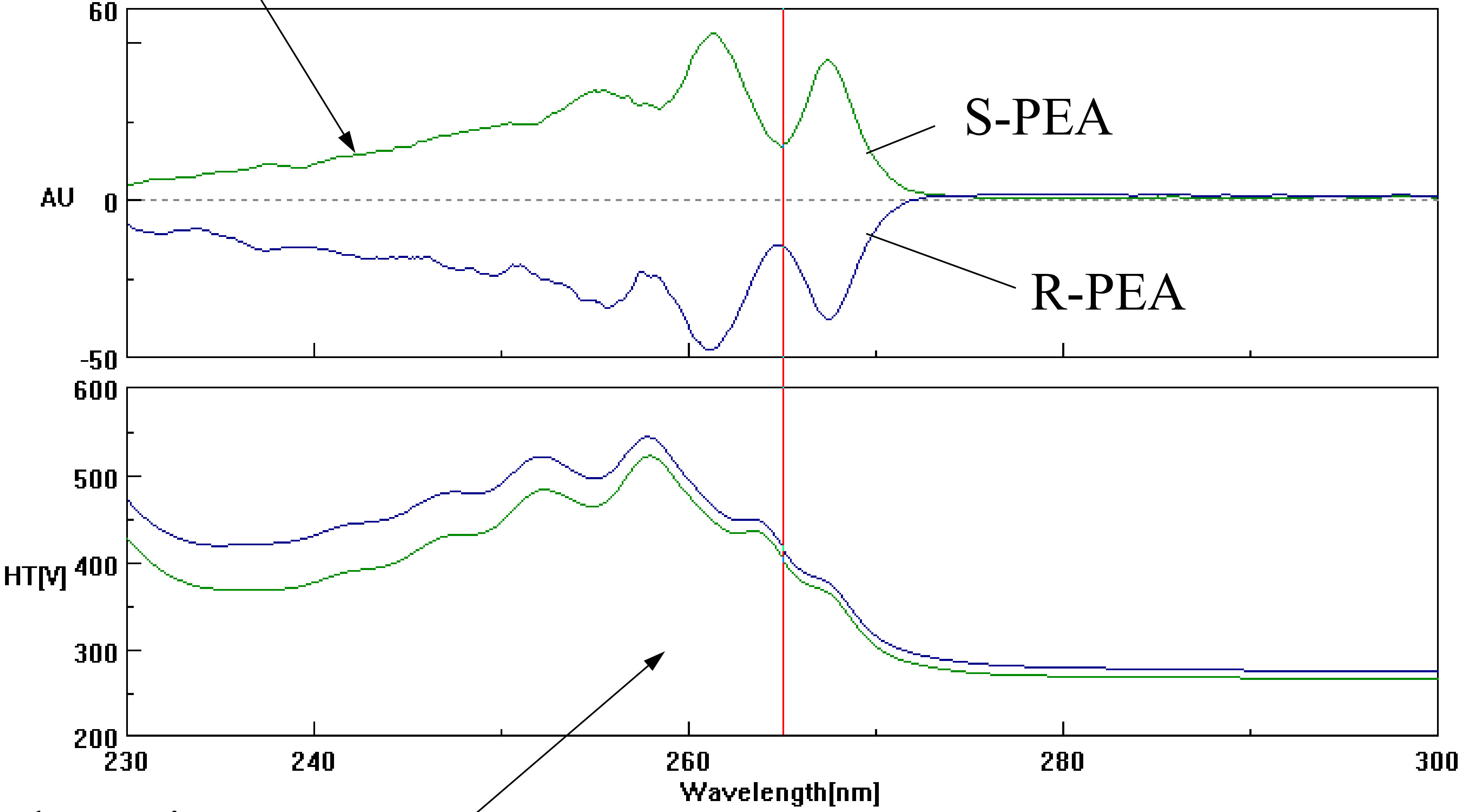
CD-spectrum



absorption spectrum

CD spectrum of (R)- and (S)-phenyl-ethyl-amine

CD-spectrum



S-PEA

R-PEA

absorption spectrum

Application of CD spectroscopy

1. Structure analysis: determination of the configuration

2. Analytical chemistry: measurement of the concentration of chiral compounds

3. Analysis of biological systems (HPLC + CD spectrometer)

PHOTOELECTRON SPECTROSCOPY

The fundamentals of photoelectron-spectroscopical methods. The Koopmans’ theorem

Photoelectron spectroscopy = PES

A spectroscopical method based on ionization!

- the sample is bombarded with monochromatic high-energy (far UV or X-ray) photons, which ionize the molecule

- the kinetic energies of the ejected electrons are measured, and the ionization energy is calculated therefrom

Molecular-orbital theory

- the electrons are in molecular orbitals

- the orbital energies (ε_i) can be calculated by quantum-chemical methods (eigenvalues of the Fock operator)

Koopmans' theorem: $I_i = - \varepsilon_i$

Ionization potential (energy): the energy required to strip a molecule of an electron

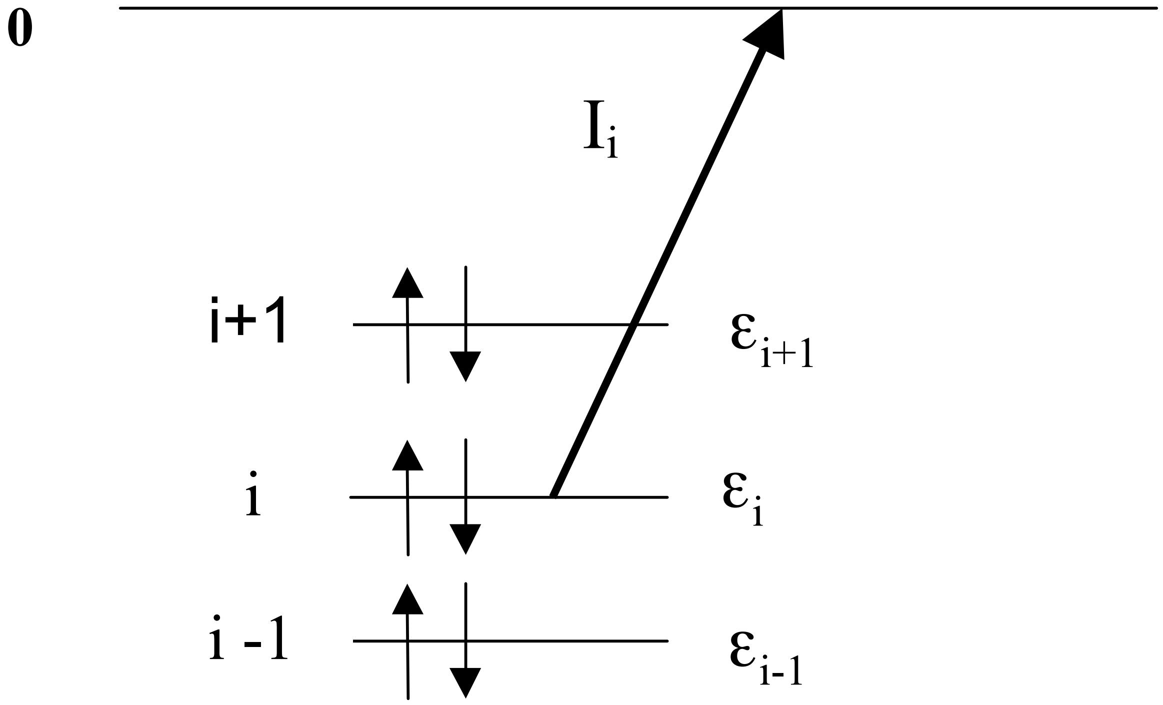
An experimentally observable quantity

A molecule has n ionization potentials with n being the number of electrons.

Notation: I_i

I_i is the energy required to strip the molecule of the *i*th electron after the first $i-1$ have already been removed

Ionization on the MO energy diagram



The Koopmans' theorem is a good approximation only for the first ionization potential, because the electrons reorganize after ionization, and the orbital energies of the ions are different.

Ionization: reaction equation

$M + \text{photon} \rightarrow M^+ + e^-$

Ionization: energy balance

photon energy

ionization potential

change in vibrational energy

change in rotational energy

kinetic energy of the electron

kinetic energy of the ion

$$\mathrm{h}\nu = I + \Delta\mathrm{E}_{\mathrm{vib}} + \Delta\mathrm{E}_{\mathrm{rot}} + \frac{1}{2} m_e v_e^2 + \frac{1}{2} m_{M^+} v_{M^+}^2$$

The basic principle of photoelectron spectroscopy

$$\overset{\text{known (monochromatic light)}}{h\nu} = \overbrace{I}^{\textbf{calculated}} + \overset{\text{negligible } I \gg \Delta E_{vib} \gg \Delta E_{rot}}{\Delta E_{vib} + \Delta E_{rot}} + \overset{\text{measured}}{\frac{1}{2} m_e v_e^2} + \overset{\text{negligible (momentum conservation)}}{\frac{1}{2} m_{M^+} v_{M^+}^2}$$

Photoelectron spectrum: distribution of the electronic kinetic energy

Ionizing radiations

<u>Far UV light</u>

It is capable of removing valence electrons

UPS = ultraviolet photoelectron spectroscopy

<u>X-ray</u>

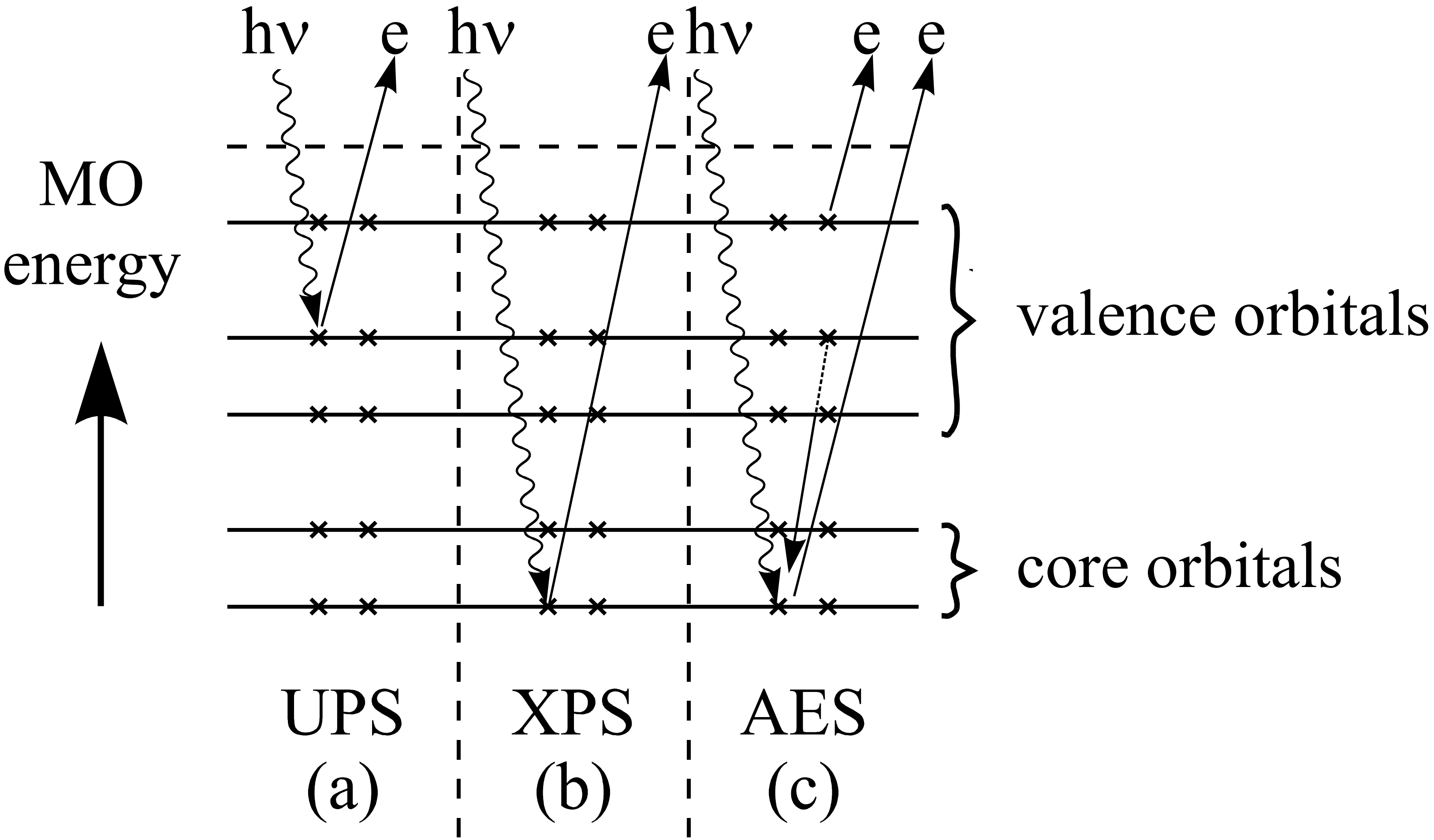
It is also capable of removing core electrons

XPS = X-ray photoelectron spectroscopy

AES = Auger electron spectroscopy

XF = X-ray fluorescence

Electron spectroscopies



Stabilization after removing a core electron

Another (valence or core) electron falls down from a higher-energy orbital, and the corresponding energy is released by

- ejecting a second electron—Auger-effect, experimental method: Auger electron spectroscopy (AES)

- emitting an X-ray photon—X-ray fluorescence (XF), the frequency of the emitted photon characterizes the element, XF is an analytical method, e.g., determination of alloy composition

Ultraviolet photoelectron spectroscopy (UPS)

The valence electrons of molecules are ejected by far UV photons.

Light source

He discharge lamp.

He plasma (a plasma is a collection of ground- and excited-state ions, atoms, and molecules as well as electrons)

Two lines are used:

He(I) radiation:

$2^1P_1 \rightarrow 1^1S_0$ transition of the He atom

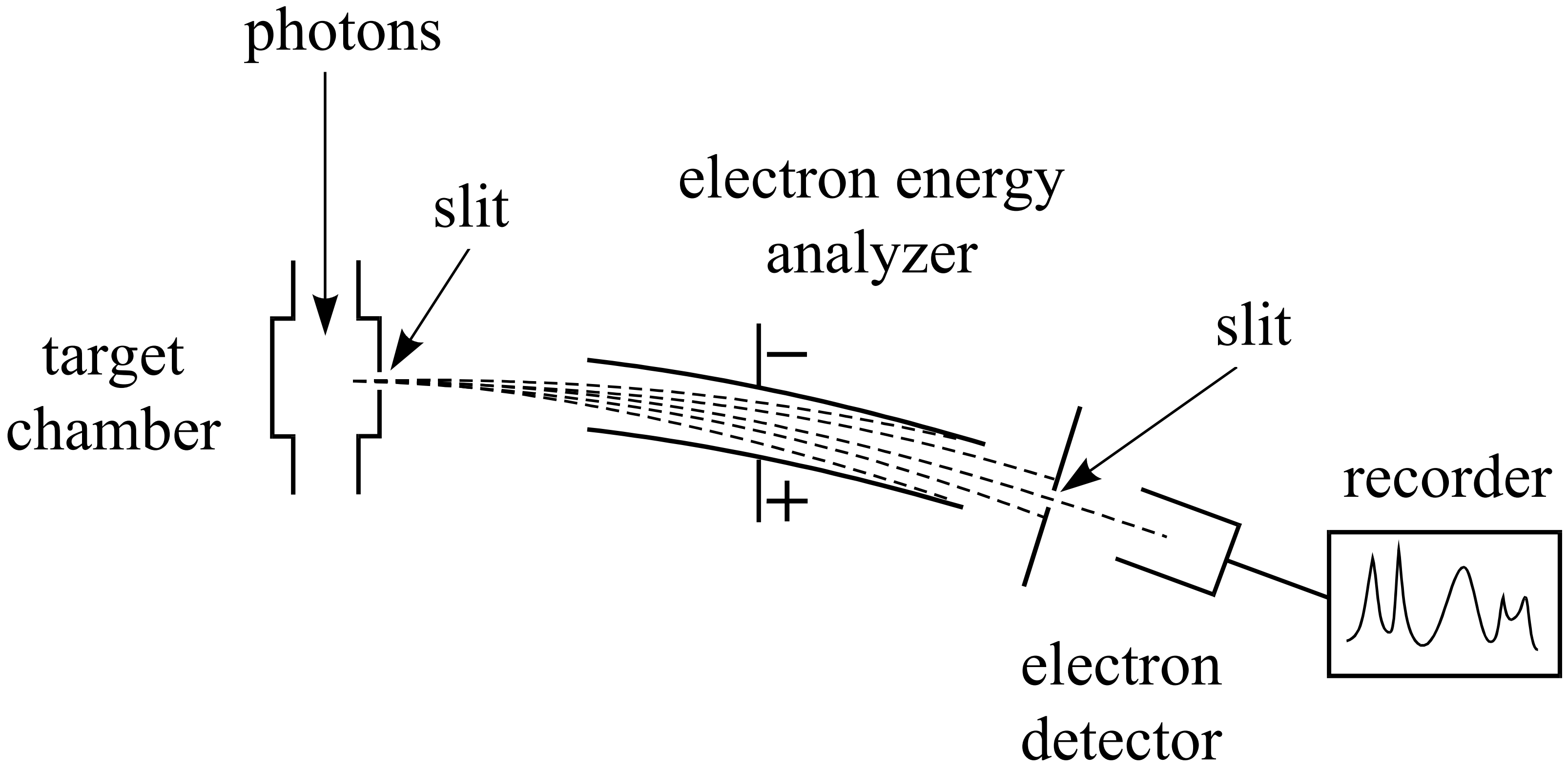
21.22 eV ($\lambda = 58.4$ nm)

He(II) radiation:

$n=2 \rightarrow n=1$ transition of the He^+ ion

40.81 eV ($\lambda = 30.4$ nm)

Components of a photoelectron spectrometer



photons

slit

target chamber

electron energy analyzer

slit

recorder

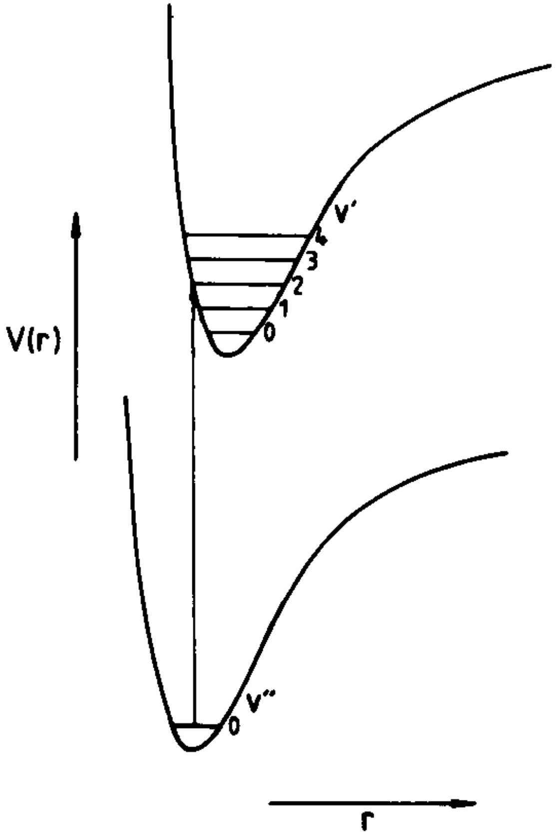
electron detector

The Franck-Condon principle

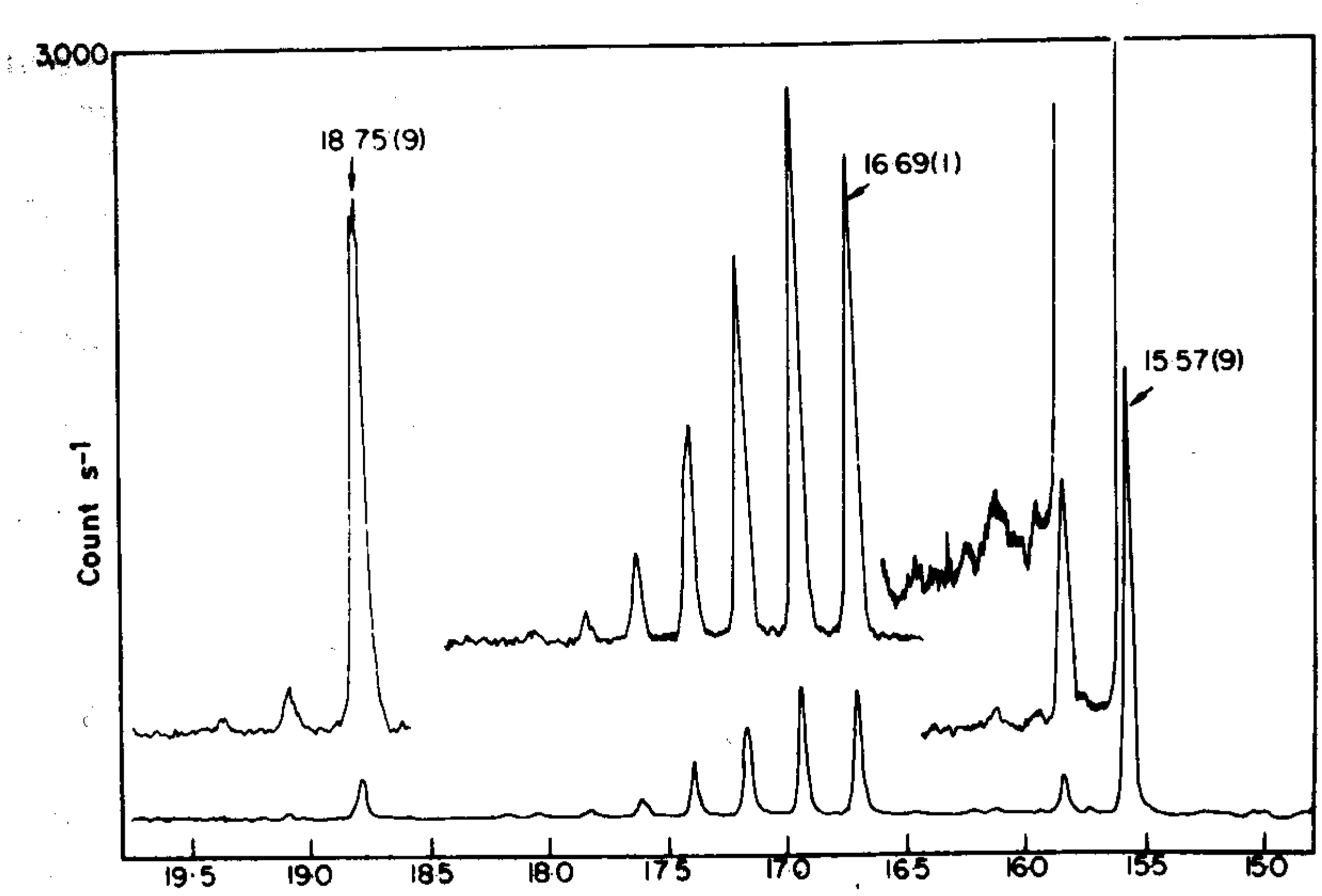
The electronic excitation and ionization are much faster than the motion of the nuclei. Thus the change in interatomic distances can be neglected during these processes.

<u>Adiabatic ionization potential</u>: the difference between the vibrational ground state of the ion and the molecule

<u>Vertical ionization potential</u>: energy of the ionization at a fixed internuclear distance. The resultant ion is often in excited vibrational state.

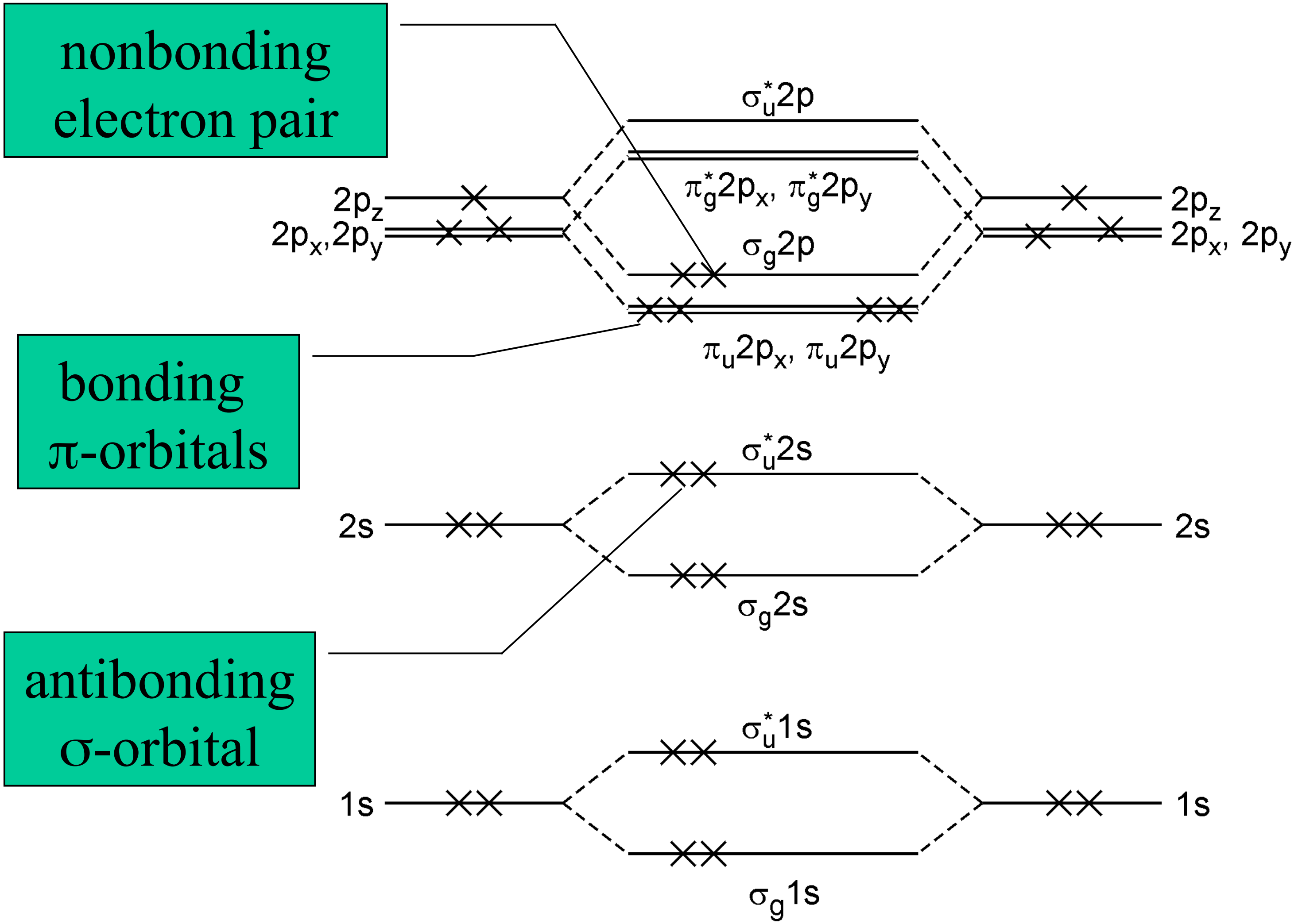


The UPS spectrum of N_2



Ionization energy/eV (1eV=8065.6 cm^{-1})

MO energy diagram of N_2



nonbonding electron pair

bonding π-orbitals

antibonding σ-orbital

Application of UPS

Testing quantum-chemical methods

measured

calculated

$$I_i = -\varepsilon_i$$

Low-pressure samples!

X-ray photoelectron spectroscopy (XPS)

Both the core and the valence electrons can be ejected by X-ray radiation.

Sources of X-ray radiation

A metal target (usually Mg or Al) which is bombarded with high-energy electrons resulting in ejecting electrons from the innermost (n=1, „K”) shell. The vacancy is filled by an electron falling back from the next highest energy shell (n=2, „L”), the energy is emitted as characteristic X-ray.

Mg K_α lines: 1253.4 keV and 1253.7 keV

Al K_α lines: 1486.3 keV and 1486.7 keV

One component of the doublet is chosen by a quartz crystal (it works as a diffraction grating).

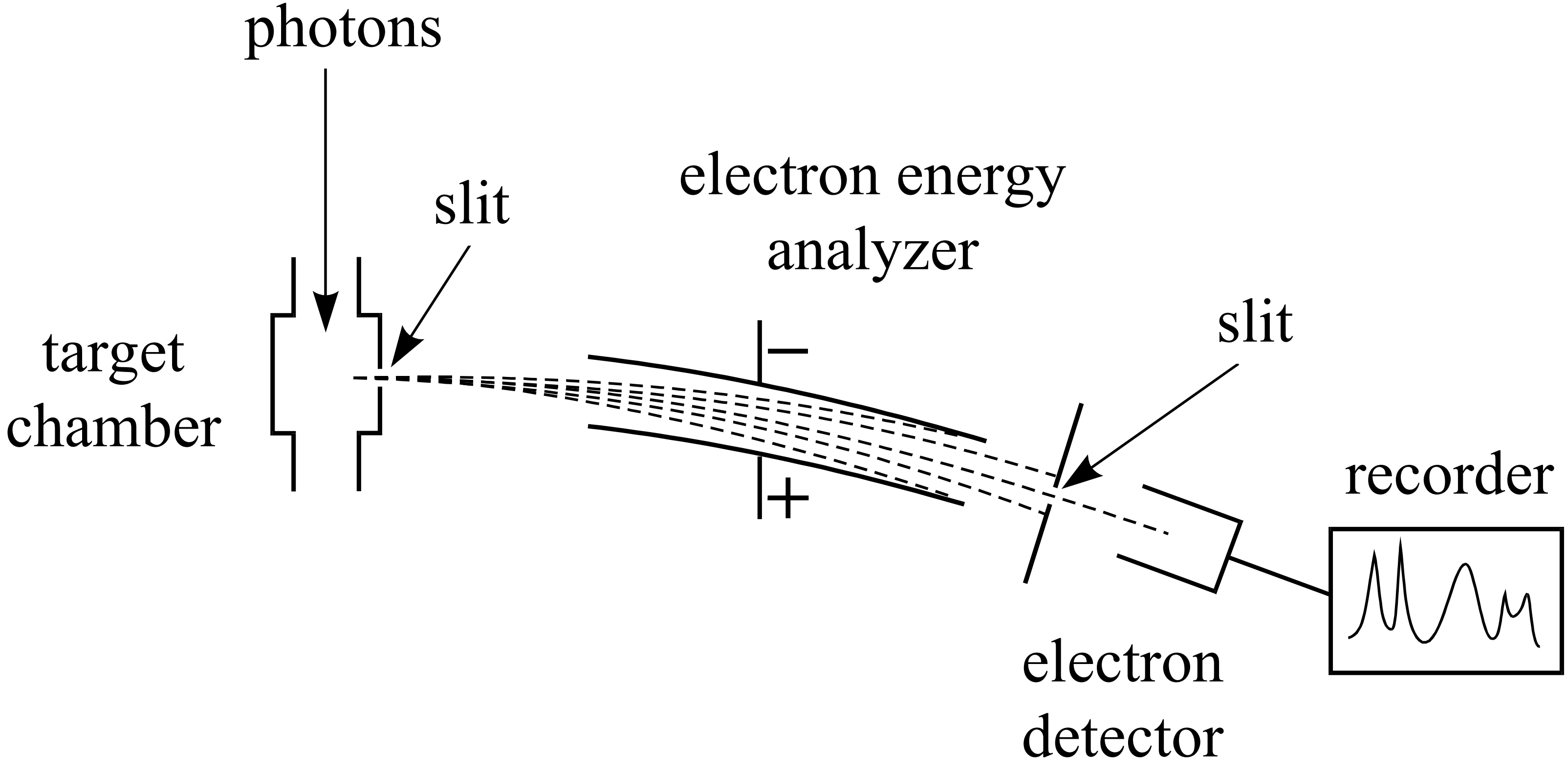
Resolution: ~ 0.2 keV (1600 cm^{-1}), the vibrational fine structure cannot be observed.

Applications of XPS

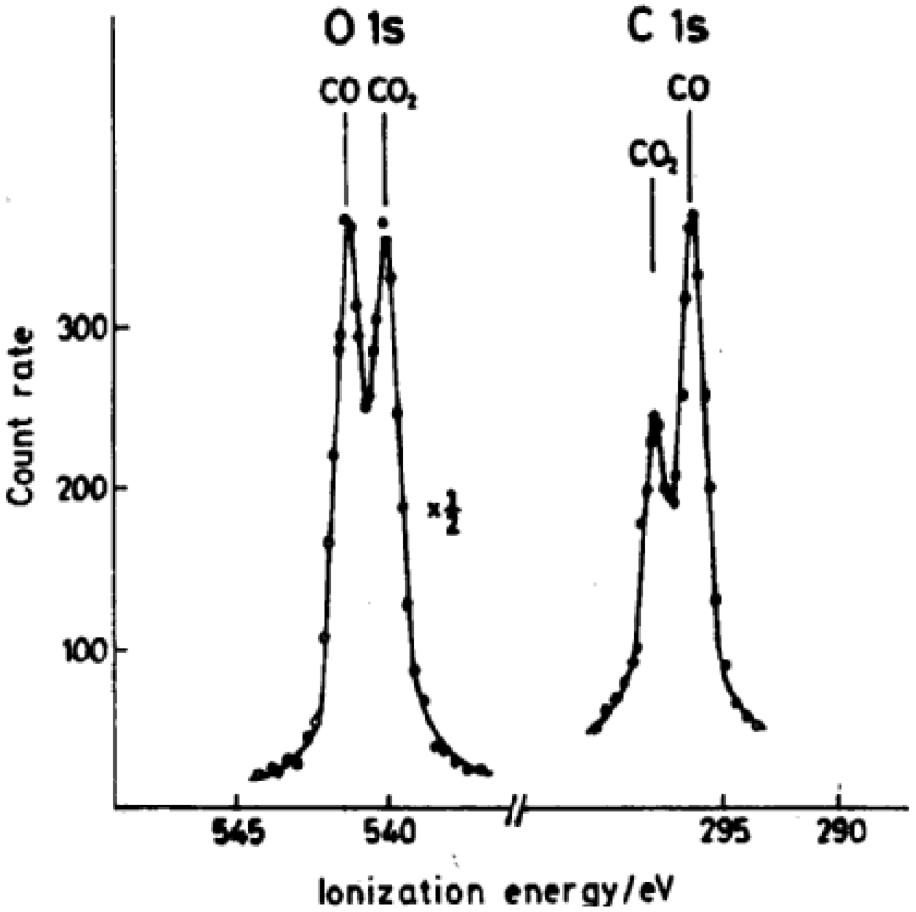
- the cross section of the ionization due to X-rays is by 2-3 orders of magnitude smaller than that by far UV photons.
- thus it is mainly used for the analysis of solid samples.
- the ionization potential of core electrons is characteristic of the atoms, hence it can be applied to the determination of the atomic composition of the samaples.
- chemical shift: provides info about the surrounding elements
- the penetrability of X-rays is good, however, that of the electrons is small, therefore the composition of the surface of the sample is measured.

Surface analysis!

Components of an XP spectrometer (the same as a UP spectrometer)

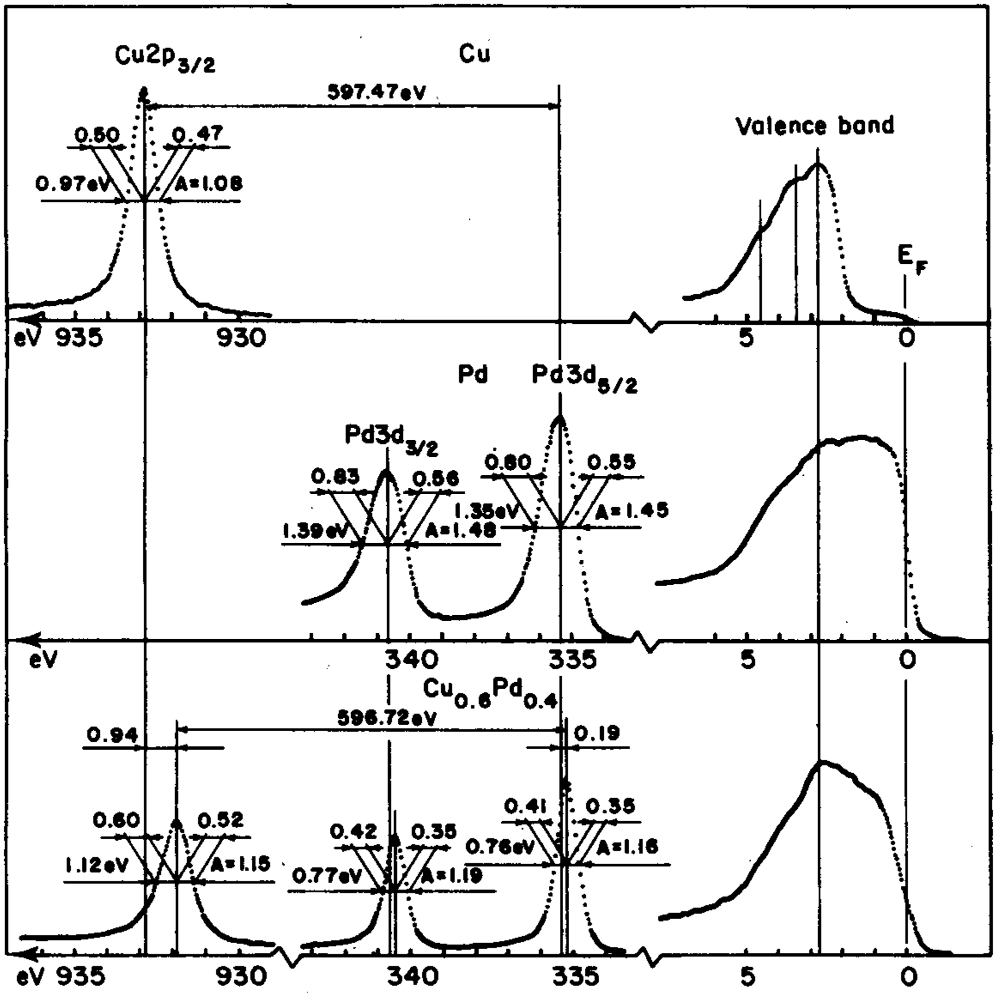


XPS spectra of a 2:1 mixture of CO and CO_2 gases

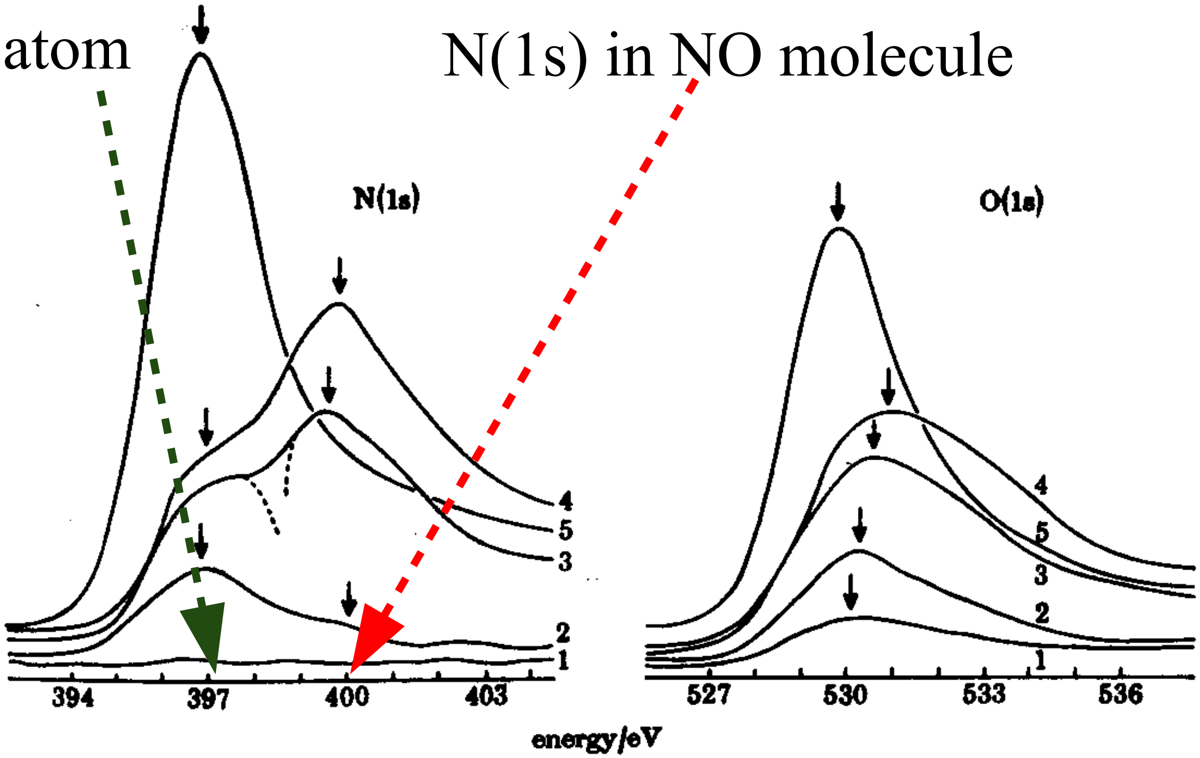


Chemical shift

XPS spectrum of Cu, Pd, and a 60% Cu and 40% Pd alloy



Ionization energy/eV


N(1s) in N atom

N(1s) in NO molecule

XPS spectra of nitric oxide (NO) absorbed on an iron surface

1) Iron surface without NO at 85 K
2) Exposed to NO at 85 K and 2.65×10^{-5} Pa for 80 s
3) As for 2 but exposed for 200 s
4) As for 2 but exposed for 480 s
5) After warming to 280 K

LASERS AND LASER SPECTROSCOPY

Laser: a source of strong, coherent, and near-monochromatic light (electromagnetic radiation)

L A S E R

Light Amplification by Stimulated Emission of Radiation

First laser: ruby laser

Theodore Maiman (1960)

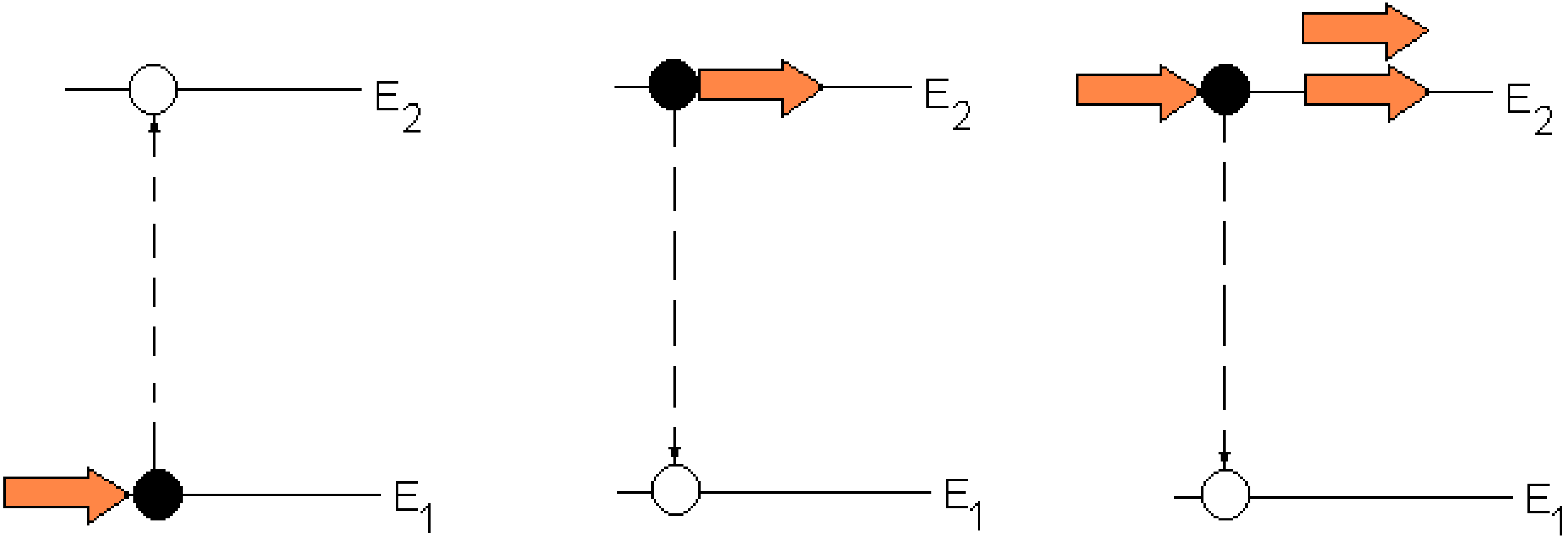
Application of lasers

- optics
- medical technology
- military technology
- informatics
- material processing
- applications in chemistry:
  - spectroscopy
  - photochemistry

Operation of lasers

- Stimulated emission
- Population inversion
- Optical resonator

Radiative transitions



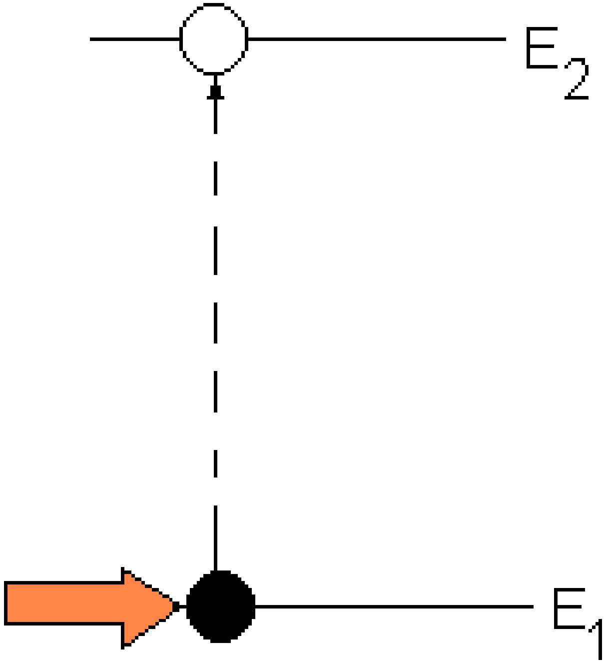
absorption spontaneous emission stimulated emission

Absorption

$$M_1 + h\nu \rightarrow M_2$$

Rate equation:

$$-dN_1/dt = A_{12} N_1 \rho_\nu$$



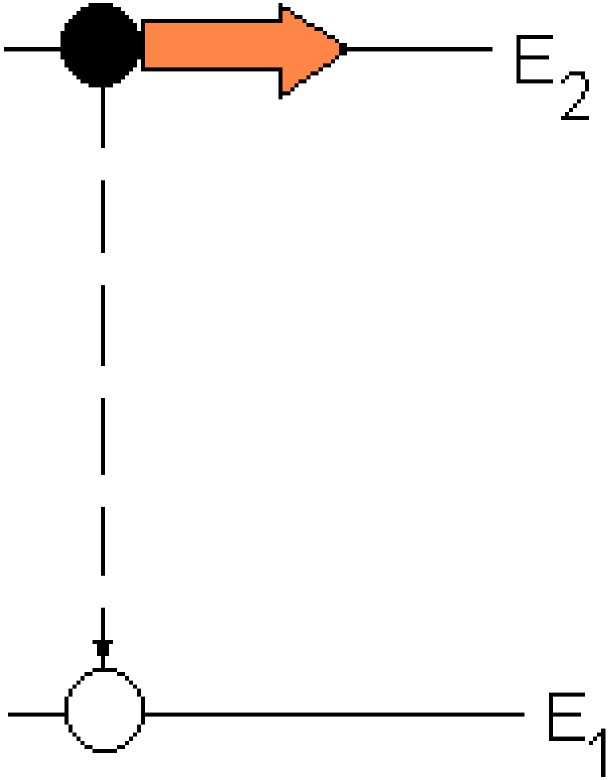
absorption

N_1 : concentration of molecules in the initial state

ρ_ν : concentration of photons

A_{12} : rate constant of the absorption

Spontaneous emission



$$M_2 \rightarrow M_1 + hv$$

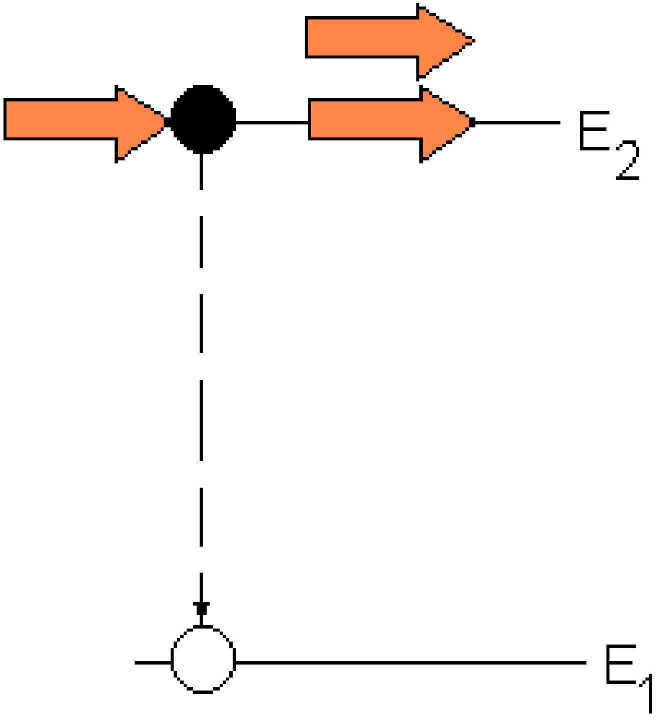
Rate equation:

$$-dN_2/dt = dN_1/dt = B_{21}N_2$$

B_{21} : rate constant of the spontaneous emission

spontaneous emission

Stimulated emission



stimulated emission

$$M_2 + h\nu \rightarrow M_1 + 2h\nu$$

The frequency, direction, and polarization of the emitted photon is identical to those of the stimulating photon.

Rate equation:

$$-dN_2/dt = dN_1/dt = A_{21} N_2 \rho_\nu$$

A_{21} : rate constant of the stimulated emission

Einstein coefficients

At equilibrium the rate constants can not be independent: Net effect of absorption+spontaneous emission+induced emission to the population of state 2 is zero.

$$A_{12} N_1 \rho_v - B_{21} N_2 - A_{21} N_2 \rho_v = 0$$

Connections among the three rate constants:

$$B_{21} = \frac{8\pi h v^3}{c^3} A_{12}$$

$$A_{21} = A_{12}$$

In lasers (there is no equilibrium!) the light is amplified by stimulated emission, more photons are emitted by stimulated emission than absorbed.

Stimulated emission:

$$-dN_2/dt = dN_1/dt = A_{21} N_2 \rho_\nu$$

Absorption:

$$-dN_1/dt = A_{12} N_1 \rho_\nu$$

Since $A_{21}=A_{12}$, the condition for lasers:

$$N_2 > N_1$$

(The spontaneous emission is ignored.)

Inverse population

In thermal equilibrium: Boltzmann distribution

$$N_1/N_2=\exp((E_2-E_1)/kT)$$

If T increases, N_1 approaches N_2.

But $N_1<N_2$ always holds.

In lasers $N_2>N_1$.
This state is referred to as <u>inverse population</u>.

No thermal equilibrium!

The establishment of inverse population is possible using special systems of three or four energy levels.

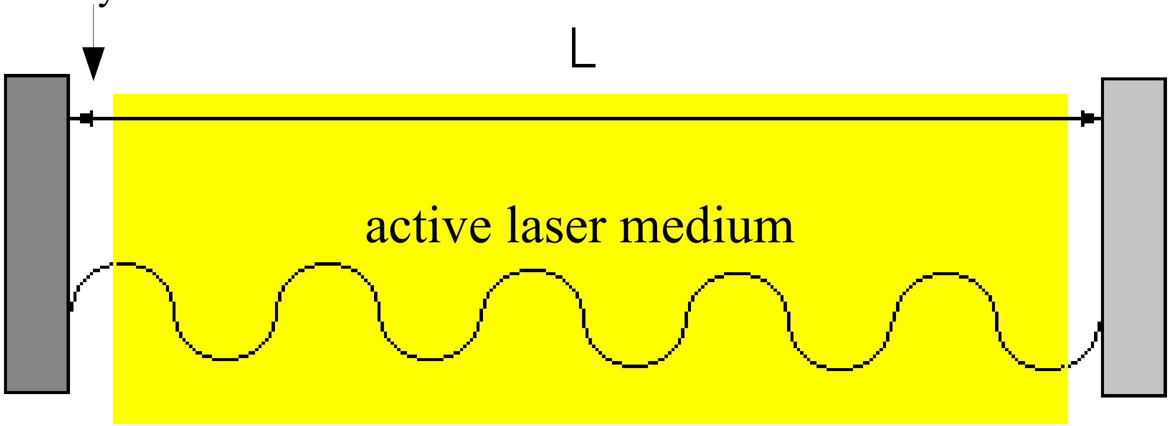
Pumping of lasers

Transmission of the energy to the laser is required for the stimulated emission.

The pumping can be carried out in several ways:

- optical (flash lamp, light of another laser)
- electrical (discharge in gas)
- chemical (chemical reaction)

Optical resonator



resonant optical cavity

L

active laser medium

end mirror
R=100%

exit mirror
R=80-99%
T=1-20%

The active medium is placed between two mirrors.

The light is reflected back and forth, consequently the path length of the photons, thus the likelihood of the stimulated emission increases.

Condition for constructive interference

Standing waves:

$$L = m\frac{\lambda}{2}$$

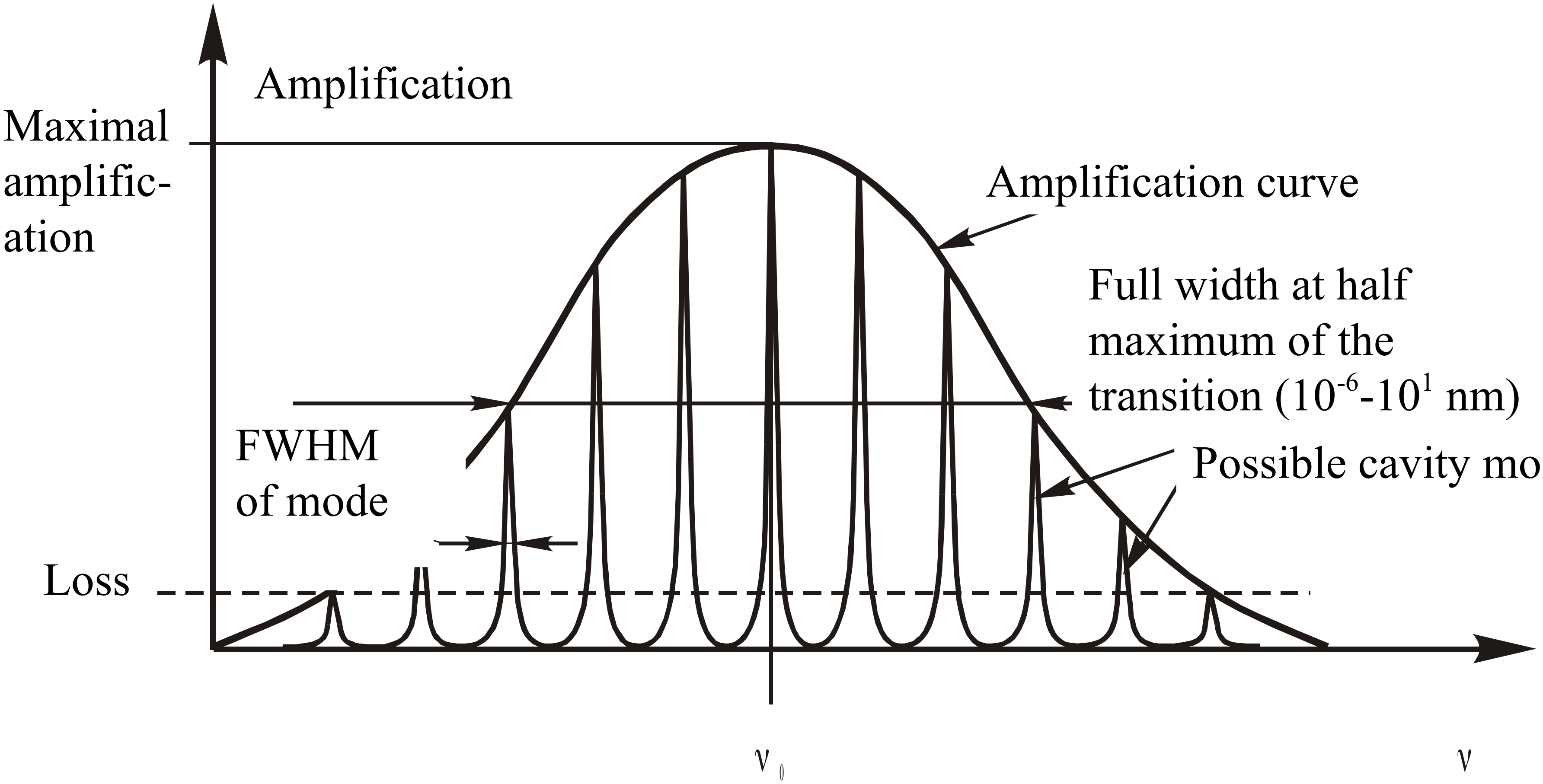
λ - wavelength, m - integer

Frequency:

$$\nu = \frac{c}{\lambda} = \frac{mc}{2L}$$

Spectrum of lasers

The gas lasers have some modes, the dye lasers have infinitely many



Types of lasers
(by the active medium)

- doped insulator lasers
- semiconductor lasers
- gas lasers
- dye lasers

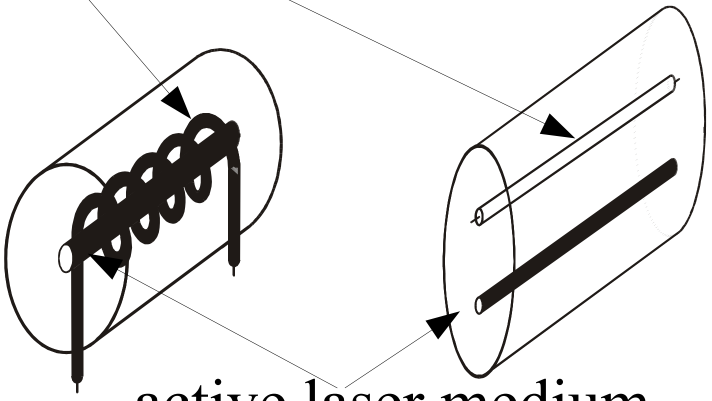
Doped insulator lasers

Active medium: ionic insulator doped with metal ions

The laser radiation is produced by the doping ions.

Pumping: optical (white-light emitting lamp or semiconductor laser)

- ruby laser (Al_20_3:Cr)
- Nd:YAG laser
- titanium sapphire laser

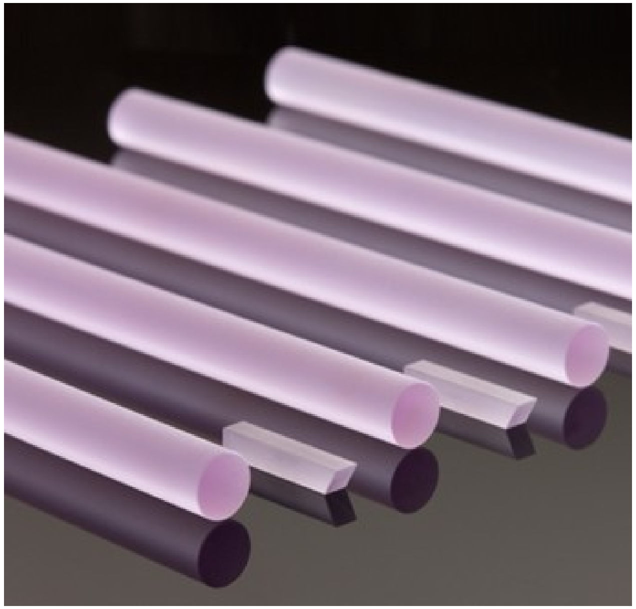


Neodymium-YAG laser

Crystalline host: $Y_3Al_5O_{12}$

yttrium aluminium garnet = **YAG**

Dopant ion: Nd^{3+} (~1% by weight)



Neodynium is the 60th element.

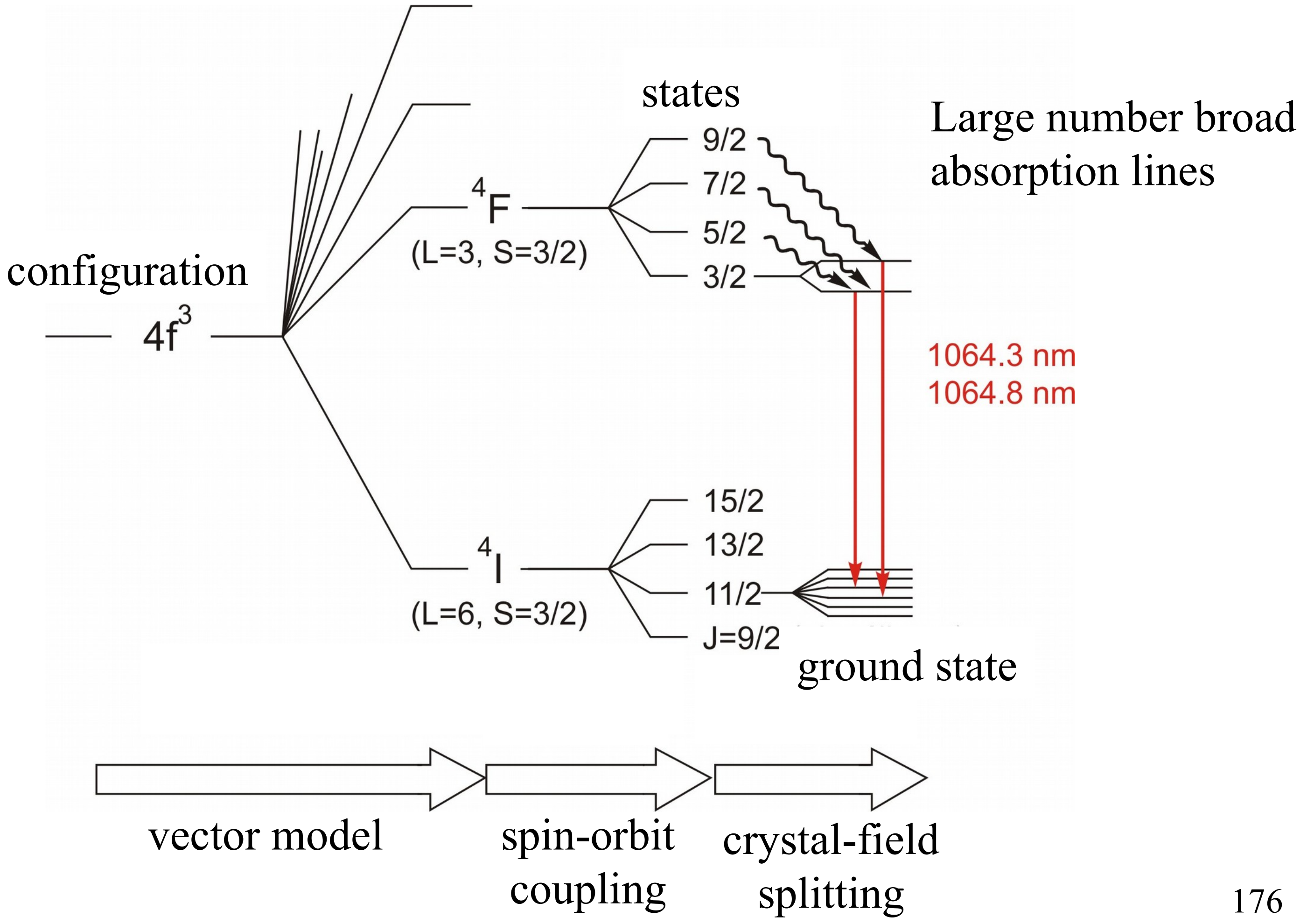
The electron configuration of the Nd atom:

$\mathrm{KLM}4s^24p^64d^{10}4f^45s^25p^66s^2$

The electron configuration of the Nd^{3+} ion:

$\mathrm{KLM}4s^24p^64d^{10}4f^35s^25p^6$

Energy levels of the Nd:YAG laser



states

Large number broad absorption lines

configuration

ground state

vector model

spin-orbit coupling

crystal-field splitting

Gas lasers

Active medium: pure gas (e.g., nitrogen laser)

gas mixture (e.g., carbon dioxide laser)

For a gas the absorption bands are narrow →

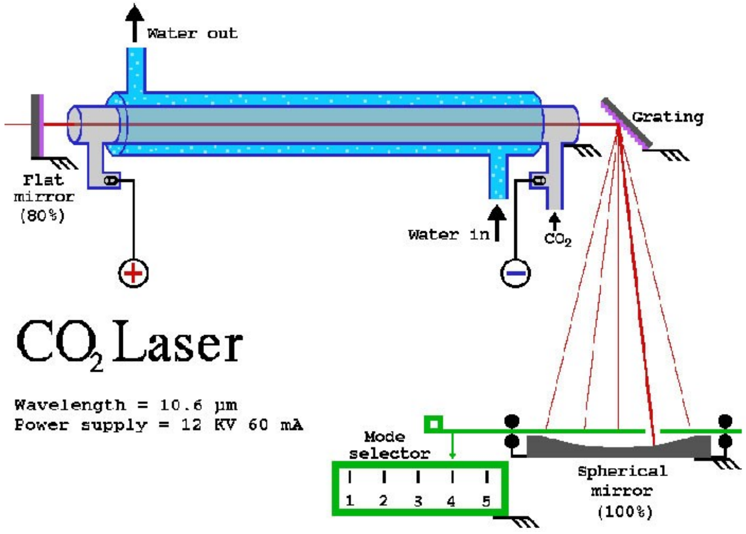
Pumping: electrical (gas discharge)

Helium-neon laser (electronic tr., visible light)

Argon laser (electronic tr., visible)

N_2 laser (electronic tr., UV light)

CO_2 laser (vibrational tr., IR light)



Argon laser

Active medium: argon gas of ~0.5 Torr pressure, in a discharge tube

In the discharge

$$\left.\begin{array}{l}\text{- excited molecules}\\ \text{- ground-state ions}\\ \text{- excited ions}\end{array}\right\}\text{arise (plasma)}$$

Operating characteristics of the discharge tube: current, voltage, pressure, temperature—the population of various energy levels of the Ar ions depends on these factors.

Population inversion can be achieved in particular excited states of Ar ions wrt to the lower states.

Ar is the 18th element.

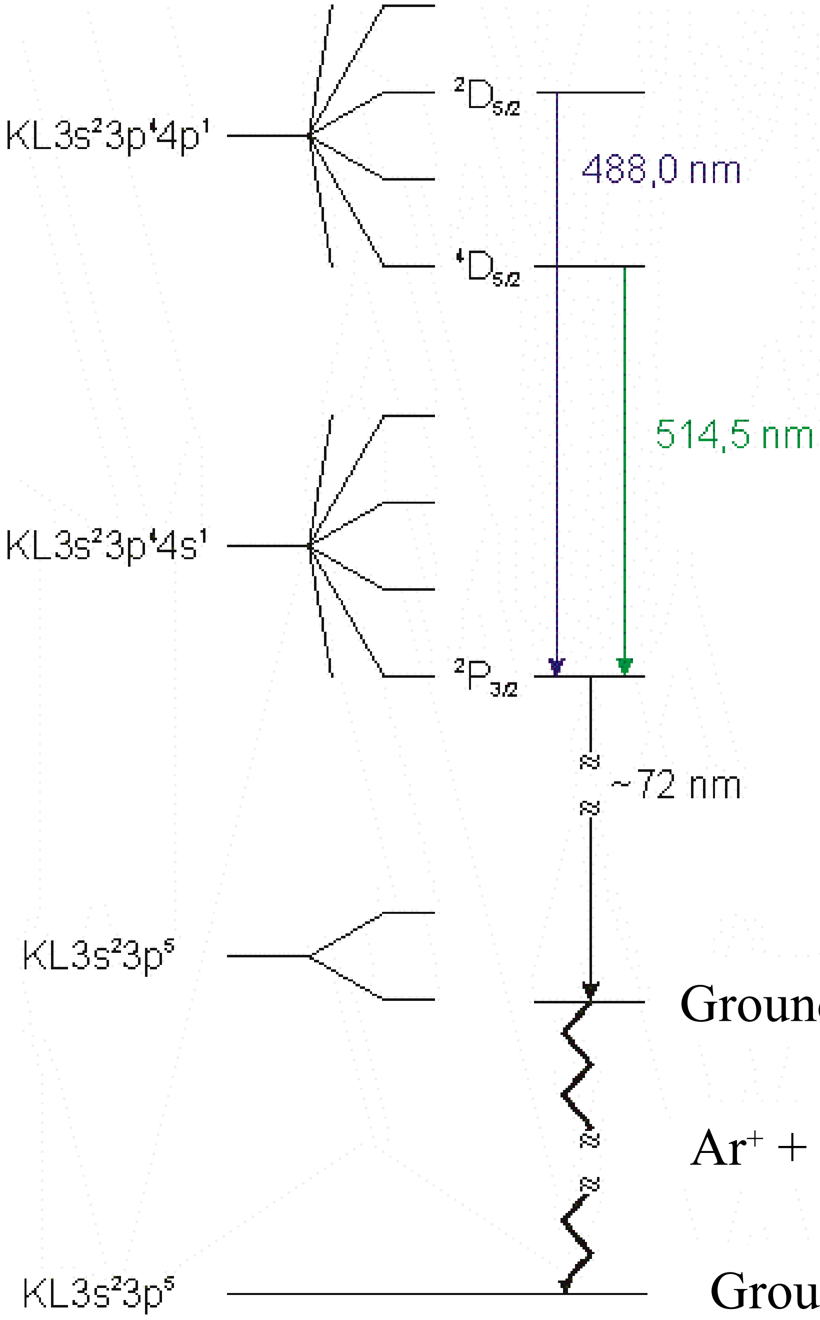
Electron configuration of the Ar atom:

$$1s^2 2s^2 2p^6 3s^2 3p^6$$

Ground-state electron configuration of the Ar^+ ion:

$$1s^2 2s^2 2p^6 3s^2 3p^5$$

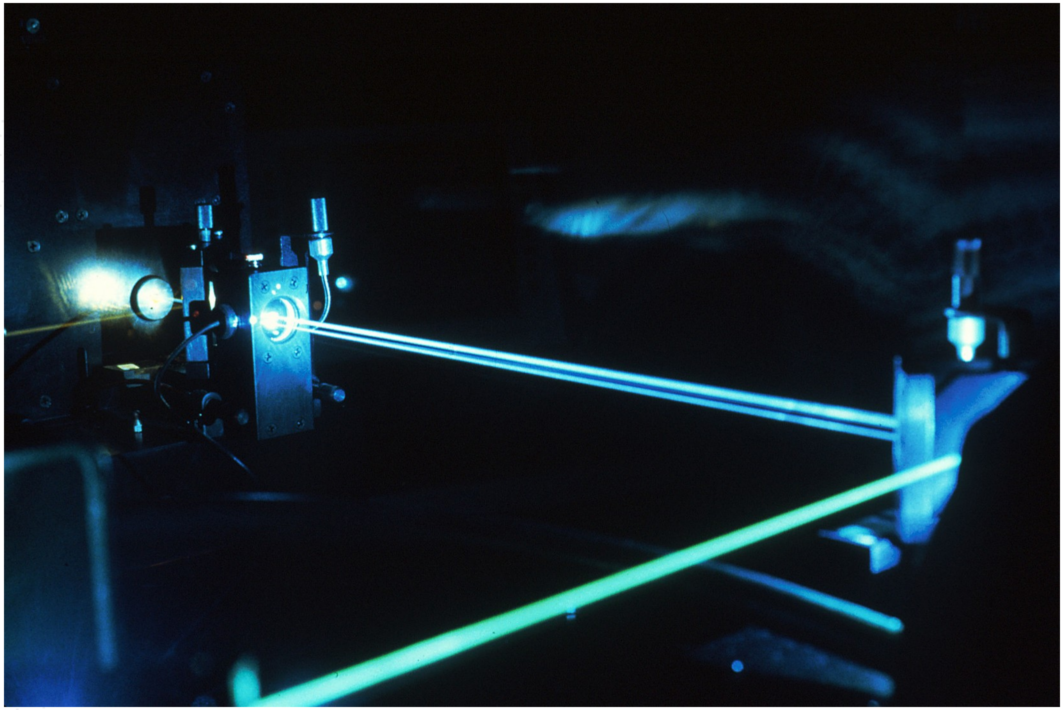
Energy levels of the argon atom



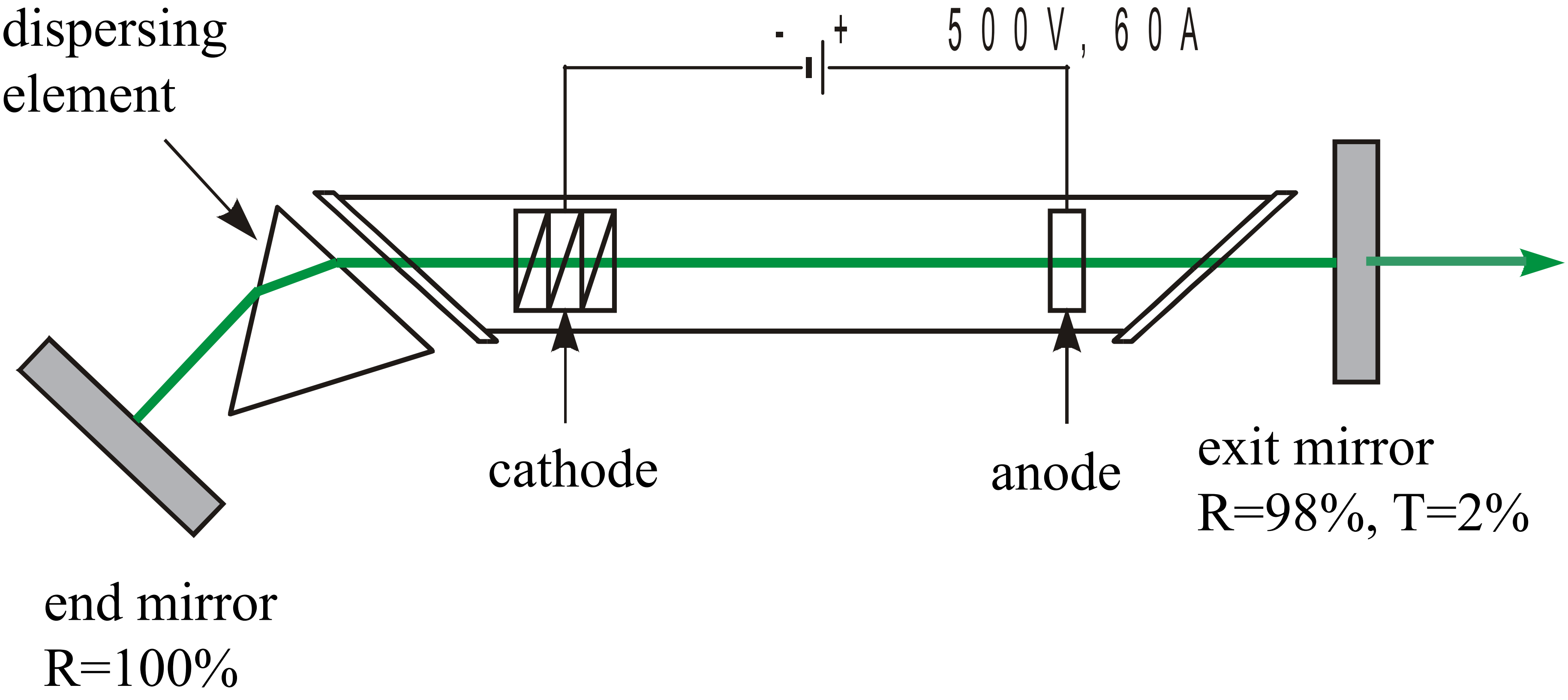
Ground state of the argon ion

$Ar^+ + e^-$ recombination

Ground state of the argon atom



The argon laser


dispersing element

- +

500V, 60A

cathode

anode

exit mirror
R=98%, T=2%

end mirror
R=100%

CO_2 laser

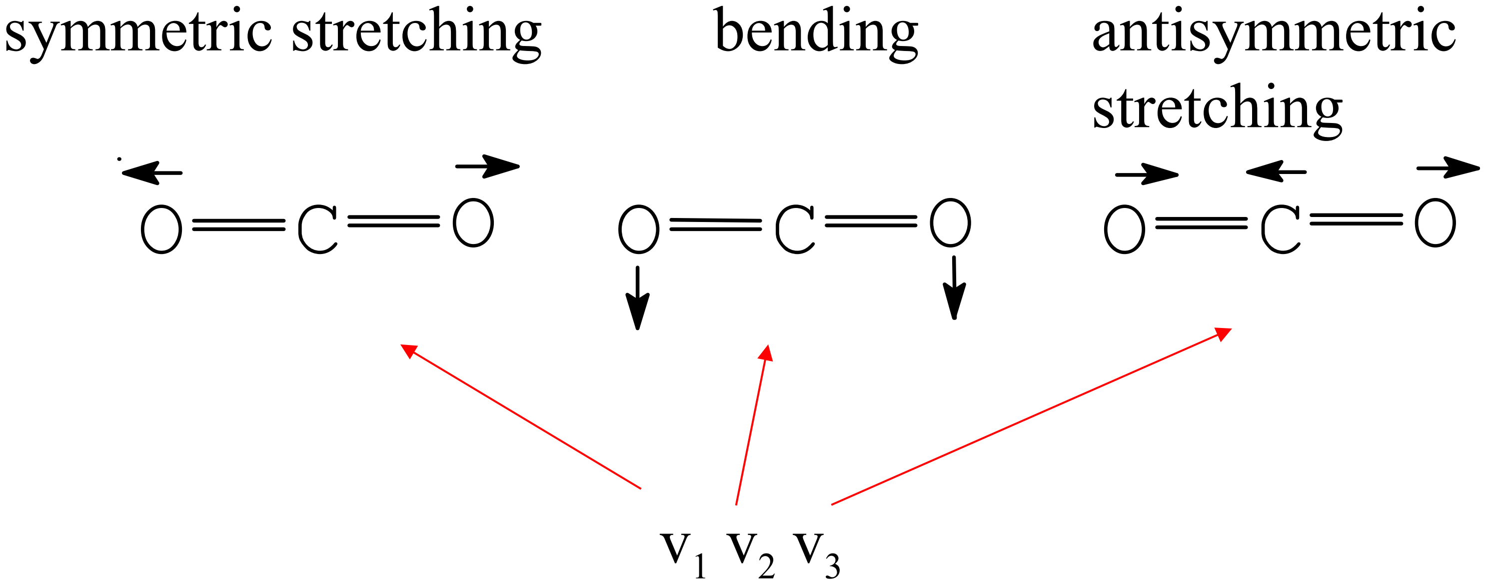
Active medium: ~ 1:1 mixture of CO_2 and N_2 gases

sealed: closed discharge tube of ~10 Torr pressure
open: gas flow through the cavity at ~ atmospheric pressure

The laser transition takes place between the excited vibrational states of the CO_2 molecule, therefore infrared light is emitted.

N_2 – buffer gas.

Normal modes of the CO_2 molecule



symmetric stretching

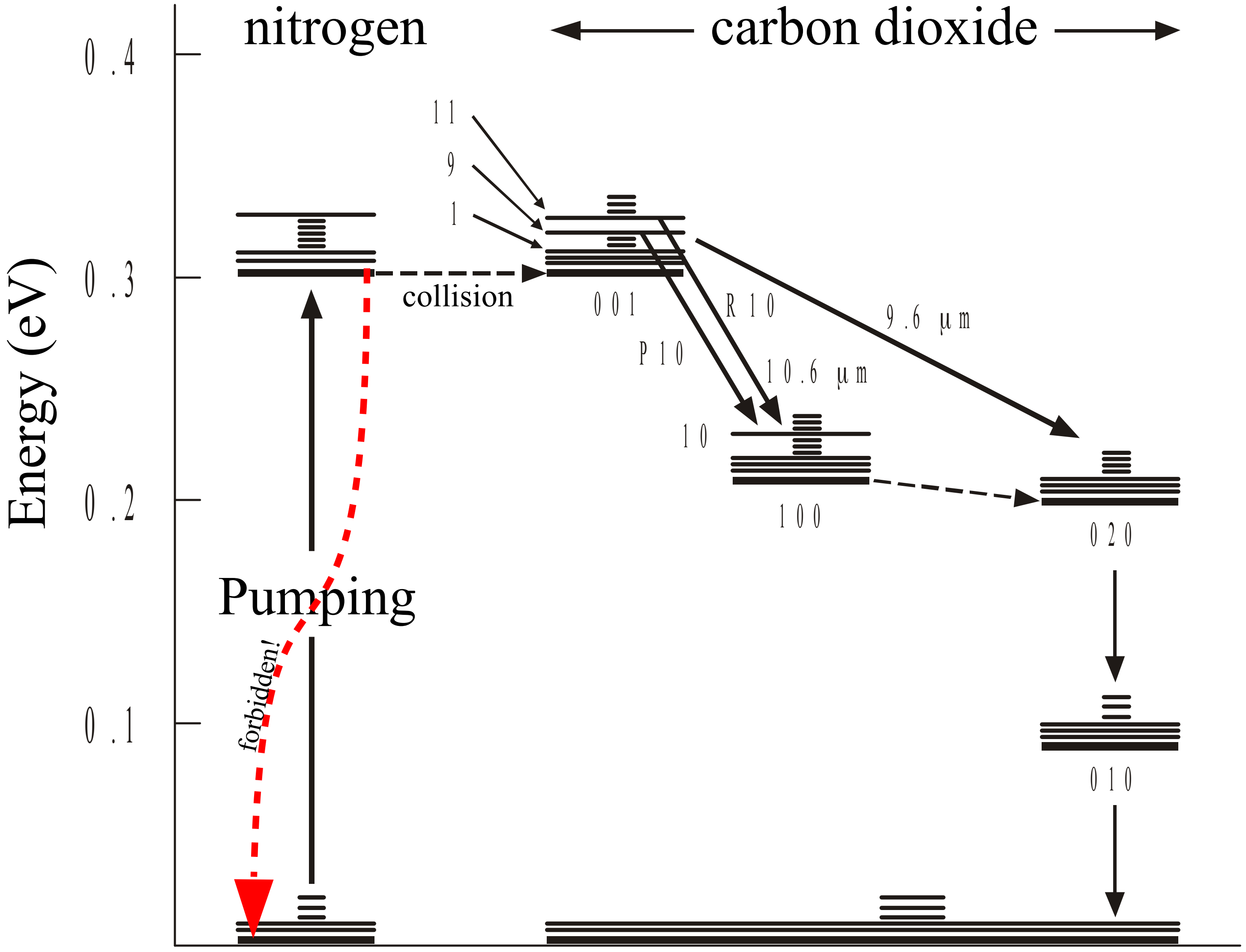
bending

antisymmetric stretching

v_1 v_2 v_3

Quantum numbers for the three normal modes.

Energy levels relevant to the CO_2 laser



Advantage:

the electric energy is efficiently converted to infrared light

Application:

- metal processing
- surgery
- spectroscopy: plasma generation

The dye lasers

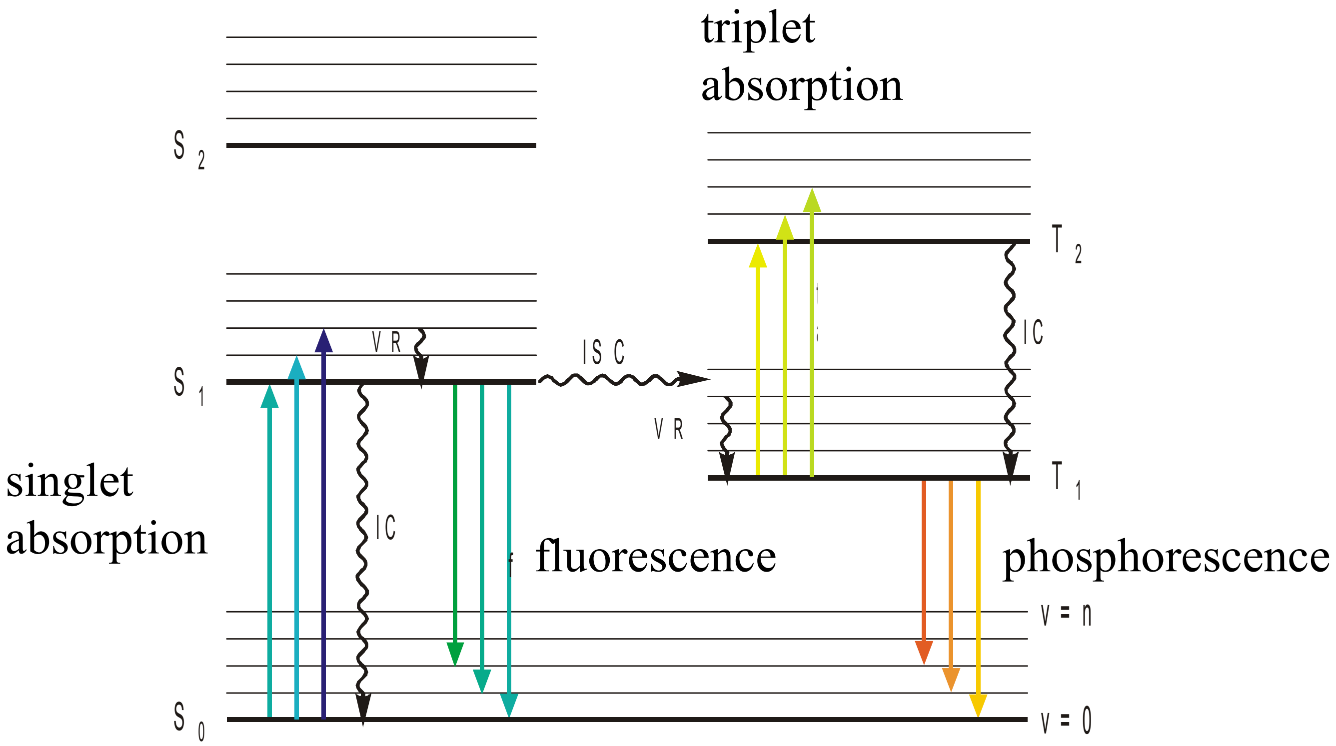
Active medium: solution of strongly fluorescing dyes.

Pumping: optical (white-light lamp or another laser).

Advantage: tunable

The laser transition takes place between the vibrational ground state of the S_1 electronic state and the excited vibrational state of S_0.

Jablonski-diagram

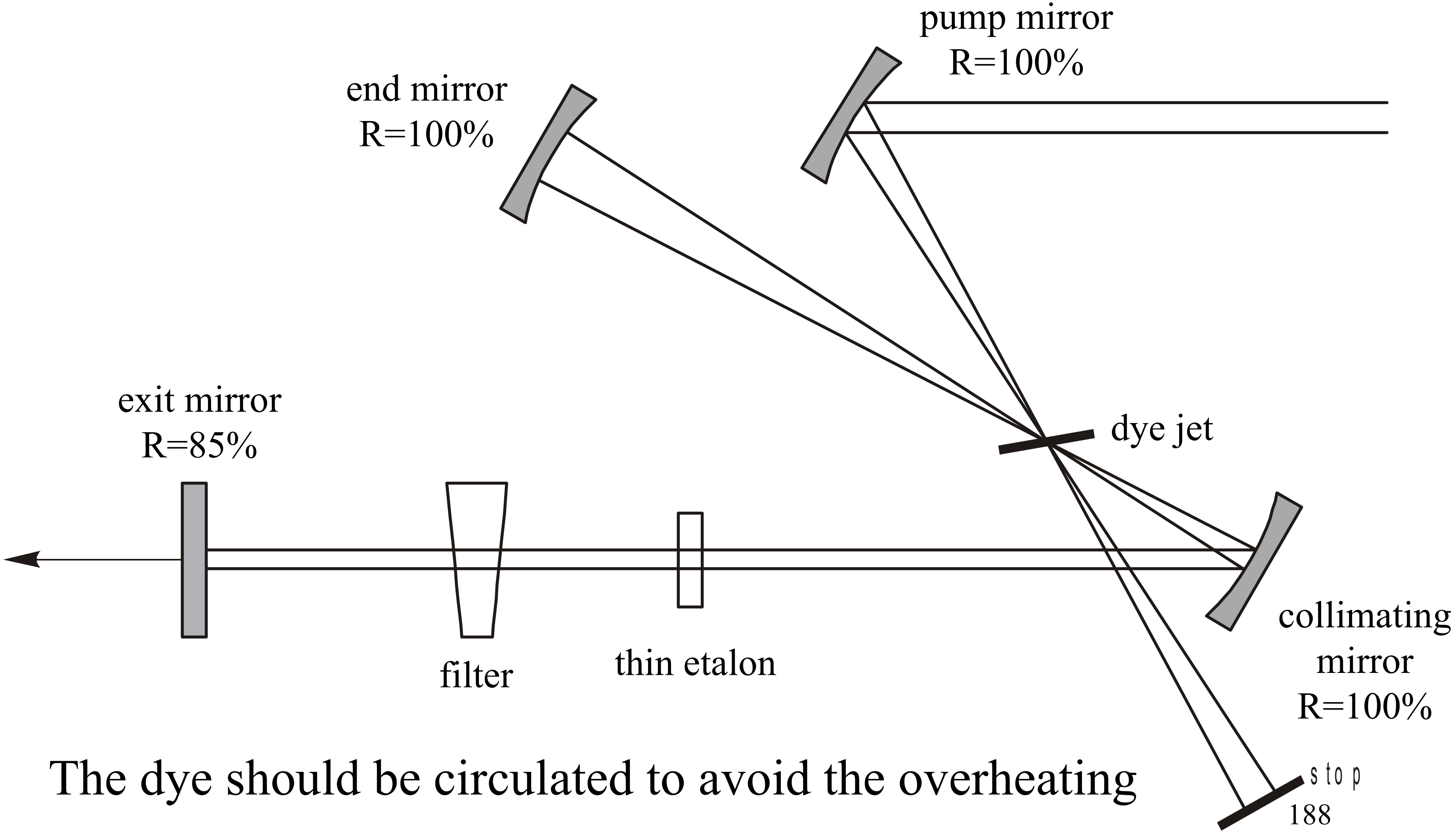


VR: vibrational relaxation
ISC: intersystem crossing
IC: internal conversion
S, T: singlet and triplet states

⟿ non-radiative transition

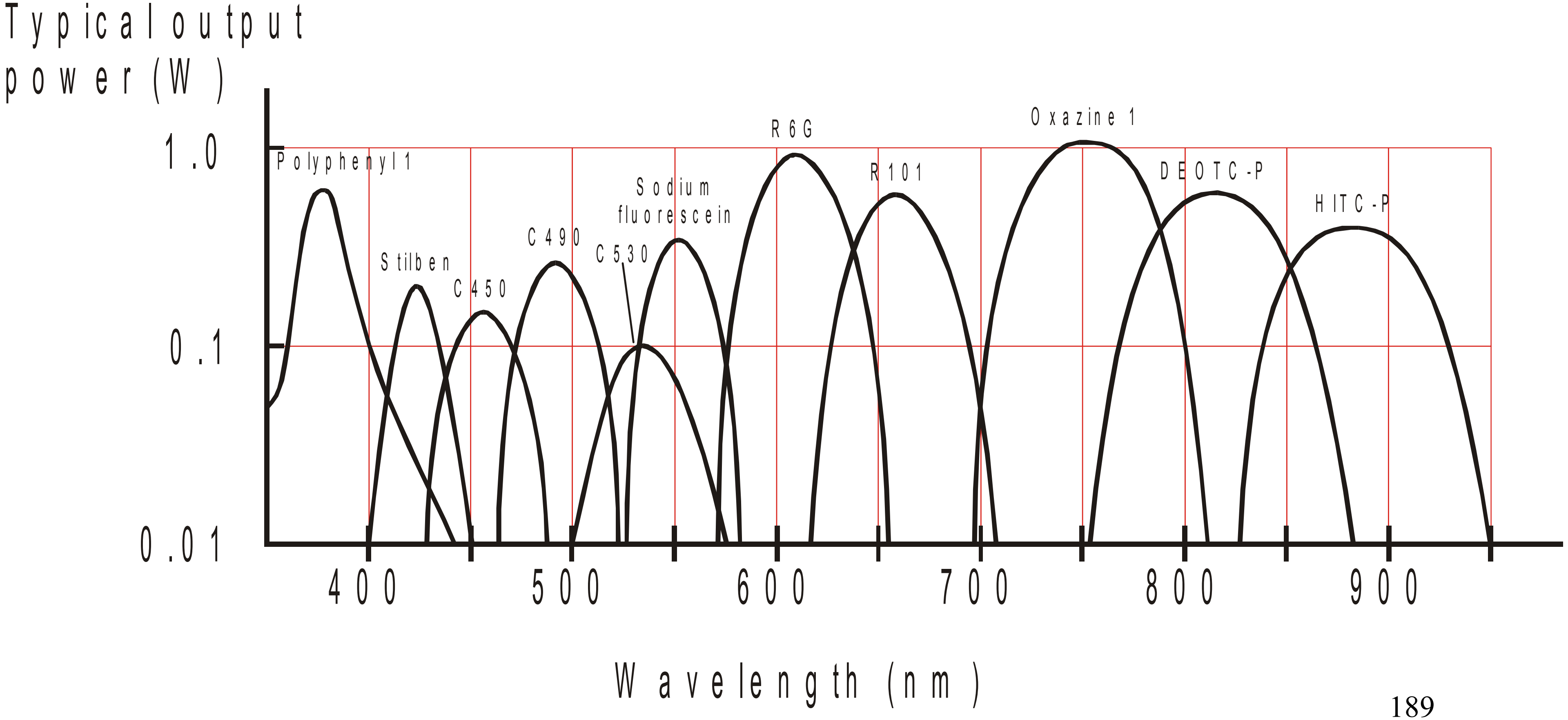
→ radiative transition

A dye laser

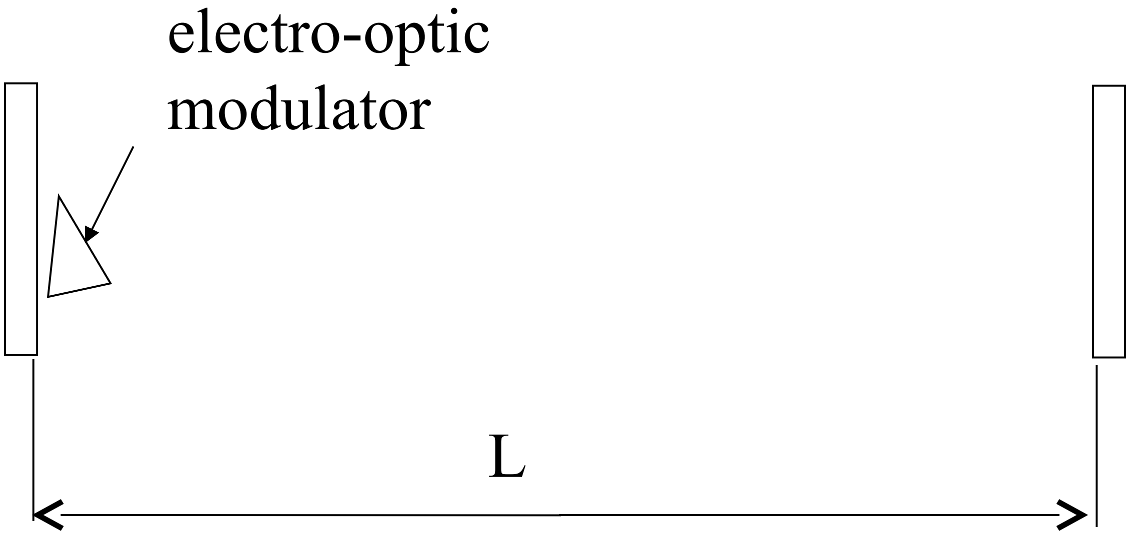


The dye should be circulated to avoid the overheating

Spectral ranges of emission bands for different laser dyes



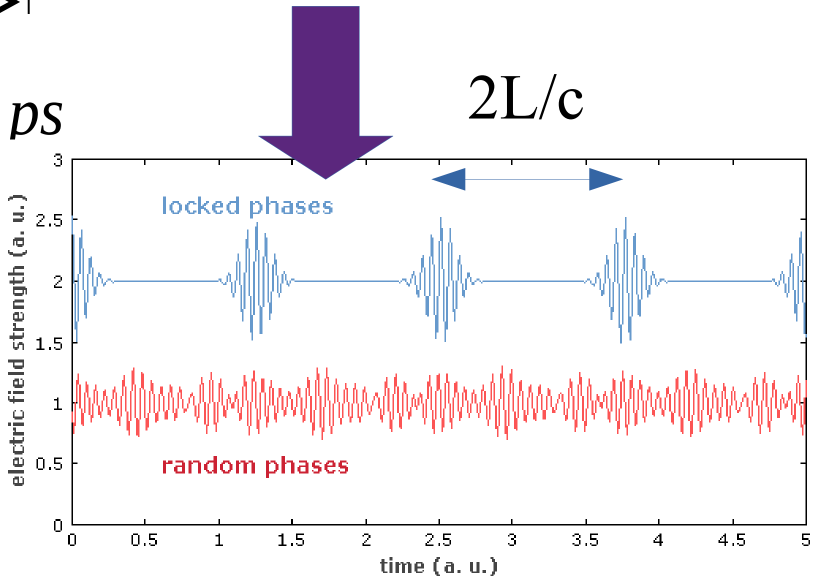
Mode-locking



E.g., $t=\frac{2L}{c}=\frac{2\cdot 1.5\,m}{3\cdot 10^{8}\frac{m}{s}}=10^{-8}\,s=10000\,ps$

electro-optic modulator: refraction coefficient is changed when voltage applied, after each t period it lets a short pulse to reflect from the mirror.

Laser radiates at a number of different frequencies: these modes have random phases relative to each other. It is possible to lock their phases together (see Atkins).



Synchronous pumping

A mode-locked, non-tunable laser is employed to pump another laser of the same optical cavity length.

Advantage: - tunable

- much shorter pulses

E.g.: the pulsewidth of the mode-locked argon laser is 300 ps, which is reduced to 10 ps when pumping a dye laser.

Properties of the laser beam

They are superior in many aspects to those of the light produced by conventional light sources.

Power density

High power density within a small region.

Typical diameter of a laser beam is 1 mm^2.

The power of laser beams varies from the mW to the kW region.

High degree of collimation

The diameter of a laser beam does not change significantly even at 100 m from the source (very nearly parallel front and back mirrors)

Spectral linewidth

Very thin linewidth, especially for gas lasers, e.g., that for the 514.5 nm light of the argon laser is 10^{-4} nm.

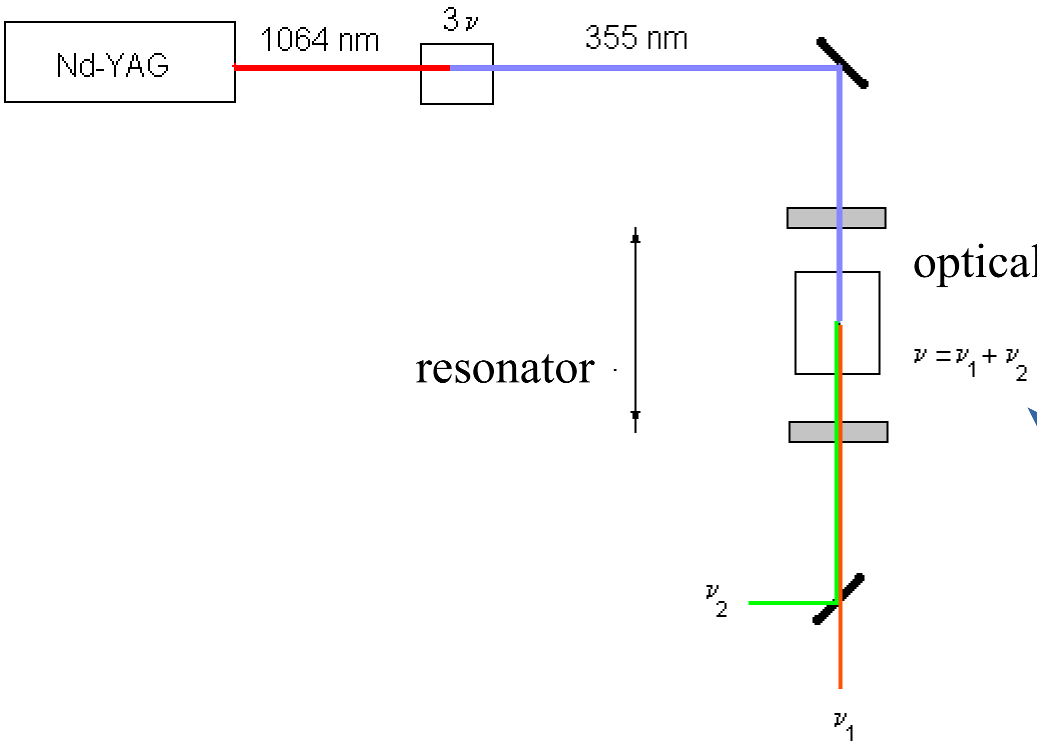
Short pulses

The pulse lasers generate pulses in the μs (ruby laser, Nd:YAG laser) or ns (N_2 laser) range.

Picosecond and femtosecond pulses are generated by mode-locked lasers.

Tuning the frequency of lasers

- dye laser
- non-linear materials (non-linearity is typically observed only at very high light intensities)
  - harmonic generation (2ν, 3ν, 4ν)
  - frequency conversion ($\nu = \nu_1 + \nu_2$)



resonator

optical parametric oscillator

Tunable by
changing the
orientation or
the temperature.

Raman scattering

Interactions of the photons and molecules

- absorption
- emission
- stimulated emission
- elastic scattering
- inelastic scattering
- ionization
- etc.

Rayleigh scattering

Elastic scattering of light by molecules.

Elastic scattering involves no (or very small) loss or gain of energy by the radiation.

Application: determination of particle size in colloids.

Blue sky and red sunset: $I \propto \frac{I_o}{\lambda^4}$

Raman scattering

Inelastic scattering of photons by molecules.

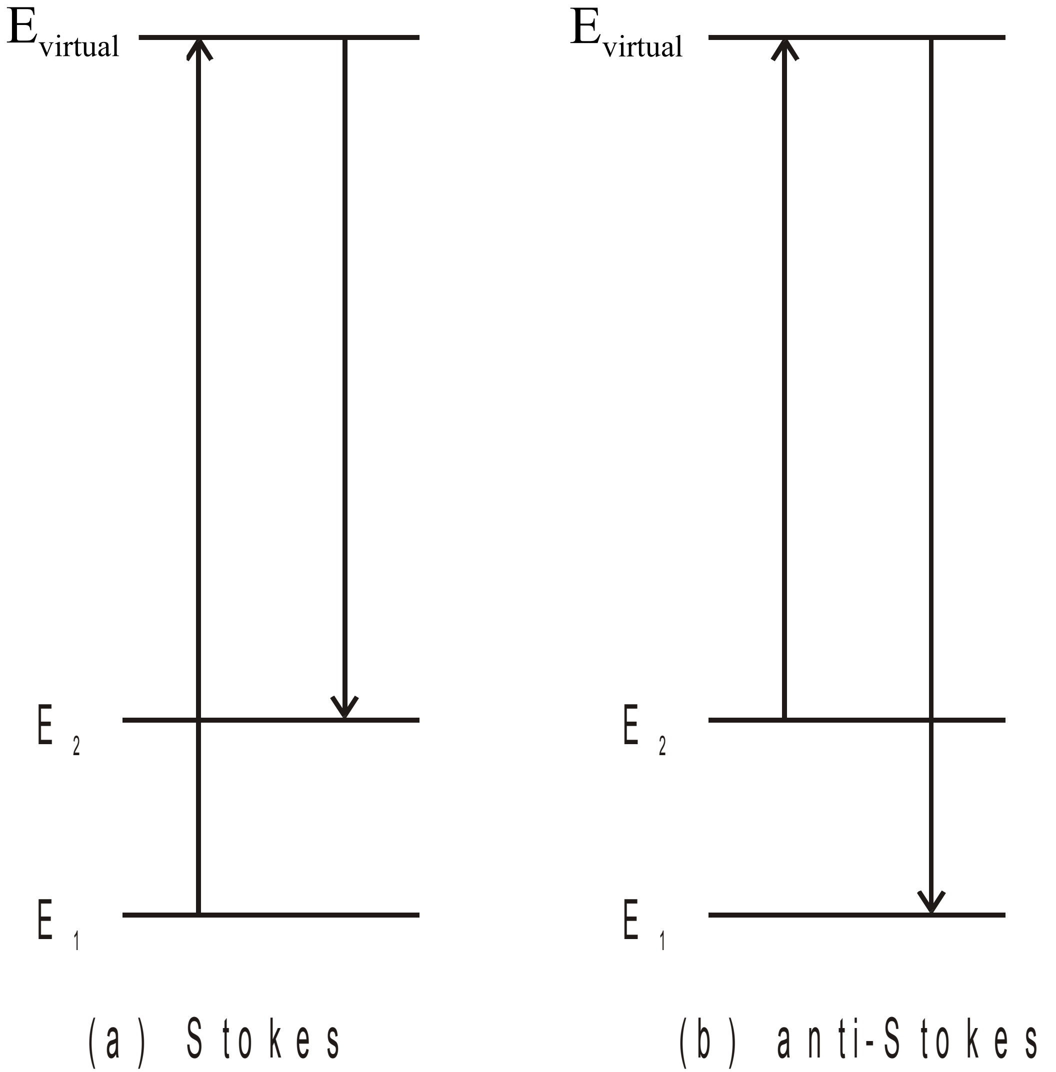
The energy of both the photon and the molecule is changed:

- the molecule absorbs energy: Stokes scattering
- the molecule loses energy: anti-Stokes scattering

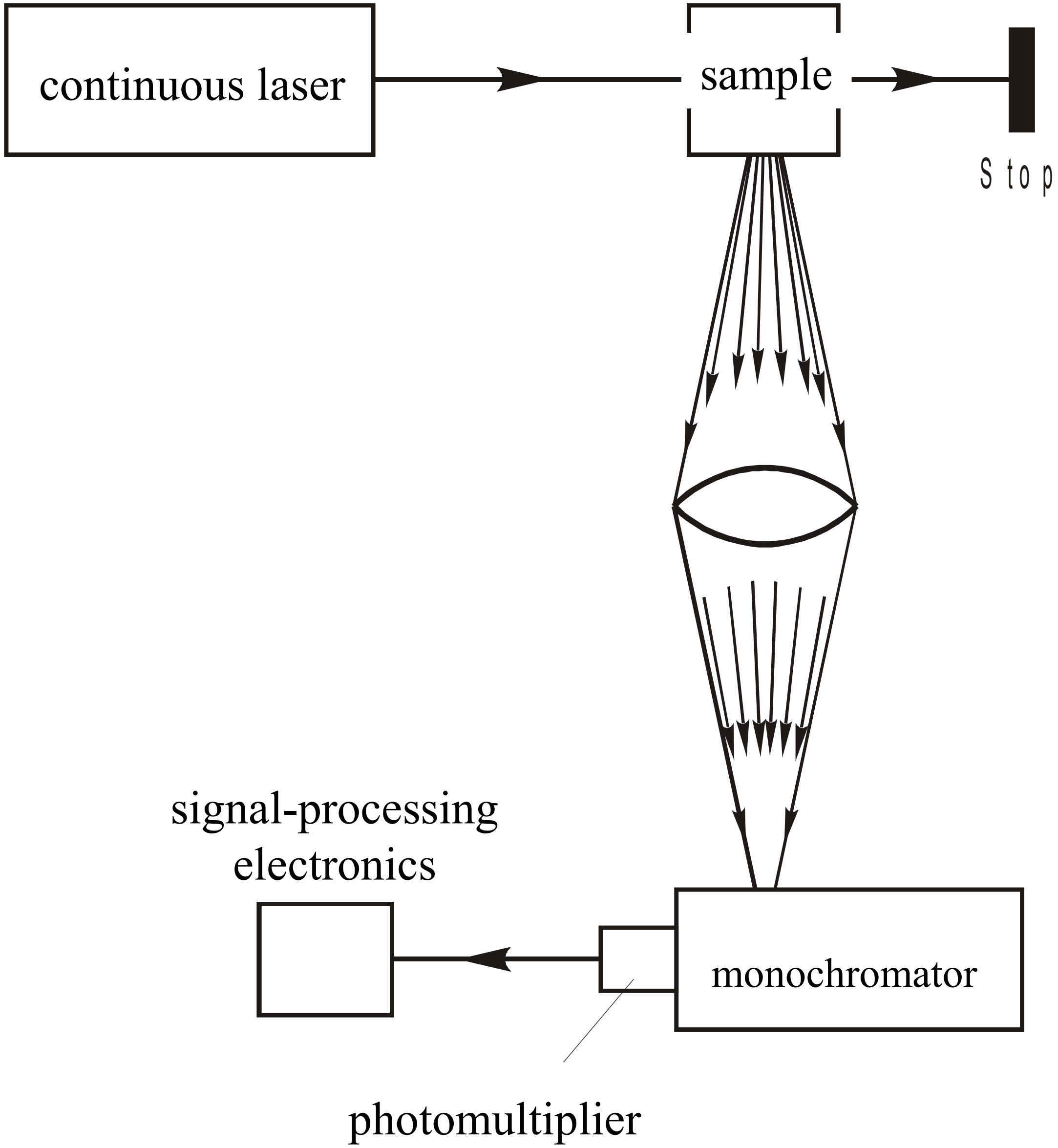
Rotational, vibrational, and electronic levels may all be involved in Raman scattering.

Sir CHANDRASEKHARA VENKATA RAMAN (1888-1970)

The Raman scattering process



The Raman spectrometer



Selection rules

They differ from those for the absorption and emission spectra:

$$\underline{\mu}_{perm} = q \cdot \underline{d}$$

In the case of the Raman scattering the induced dipole moment is considered (not the permanent!).

$$\underline{\mu}_{ind} = \underline{\underline{\alpha}} \cdot \underline{\underline{E}}$$

$\underline{\underline{\alpha}}$: polarizability tensor

$\underline{\underline{E}}$: electric field

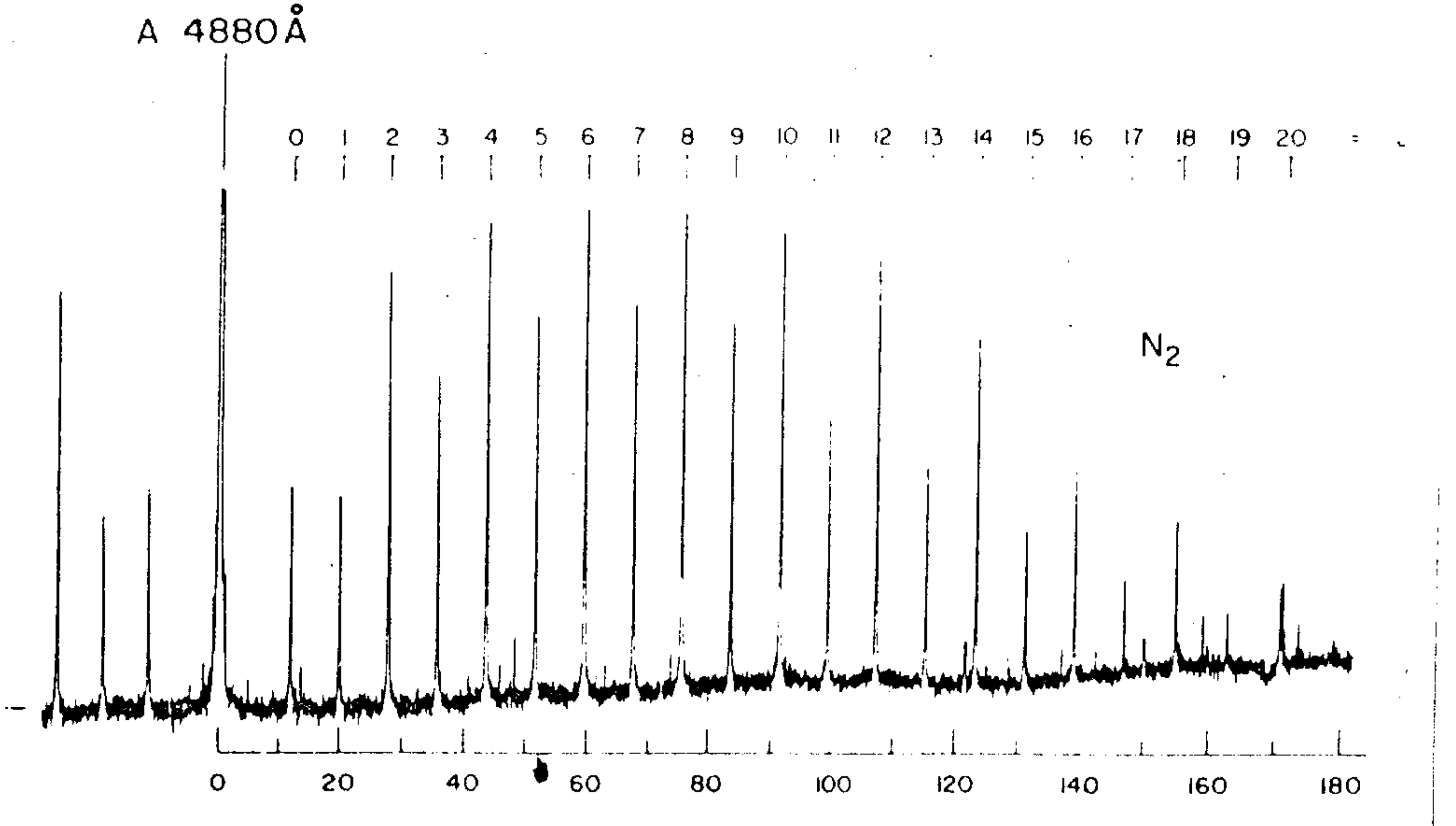
Polarizability tensor

$$\underline{\underline{\alpha}} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

$\underline{\underline{\alpha}}$ symmetric tensor, that is, $\alpha_{xy} = \alpha_{yx}$, $\alpha_{xz} = \alpha_{zx}$, and $\alpha_{yz} = \alpha_{zy}$

Rotational Raman spectra of N_2

In contrast to conventional rotational spectroscopy, molecules without permanent dipole moment also have allowed rotational transitions.



Vibrational Raman spectra

Selection rules:

a) $\Delta v_i = \pm 1,$

$\Delta v_{j \neq i} = 0$

only one normal vibration can be excited

b) Analyzing the $\int_{-\infty}^{+\infty} \Psi^*_{v'} \hat{\mu}_{ind} \Psi_v \, d\tau$

transition moment it can be proven that the irrep of the normal mode must be identical to that of any component of the polarizability tensor α.

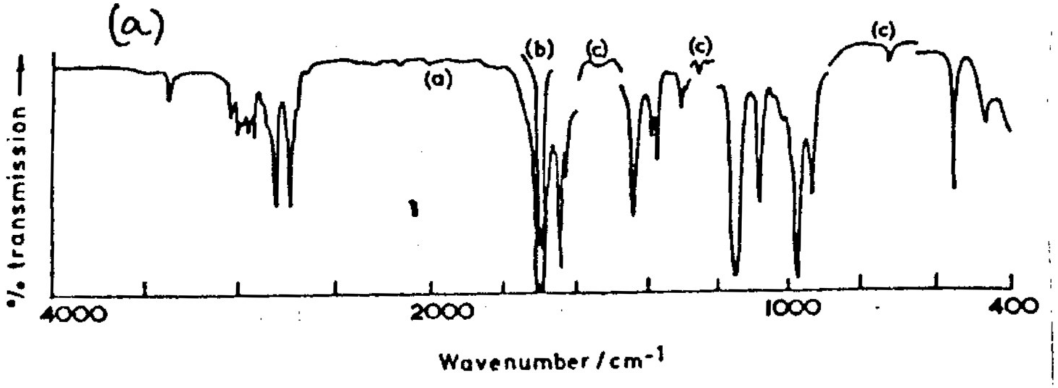
Character table of the C_{2v} point group

C_{2v}	E	$C_2^1(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	
A_1	+1	+1	+1	+1	$T_z, \alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
A_2	+1	+1	-1	-1	R_x, α_{xy}
B_1	+1	-1	+1	-1	T_x, R_y, α_{xz}
B_2	+1	-1	-1	+1	T_y, R_z, α_{yz}

The infrared and Raman spectra are complementary

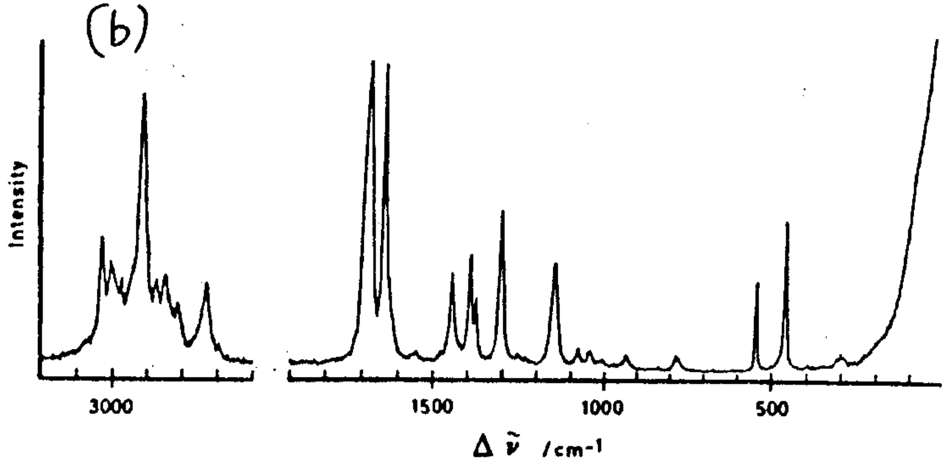
The IR-forbidden vibrations may be active in the Raman spectrum and vice versa.

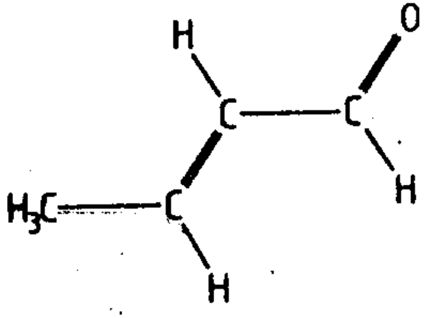
The vibrational spectrum of crotonaldehyde



IR spectrum

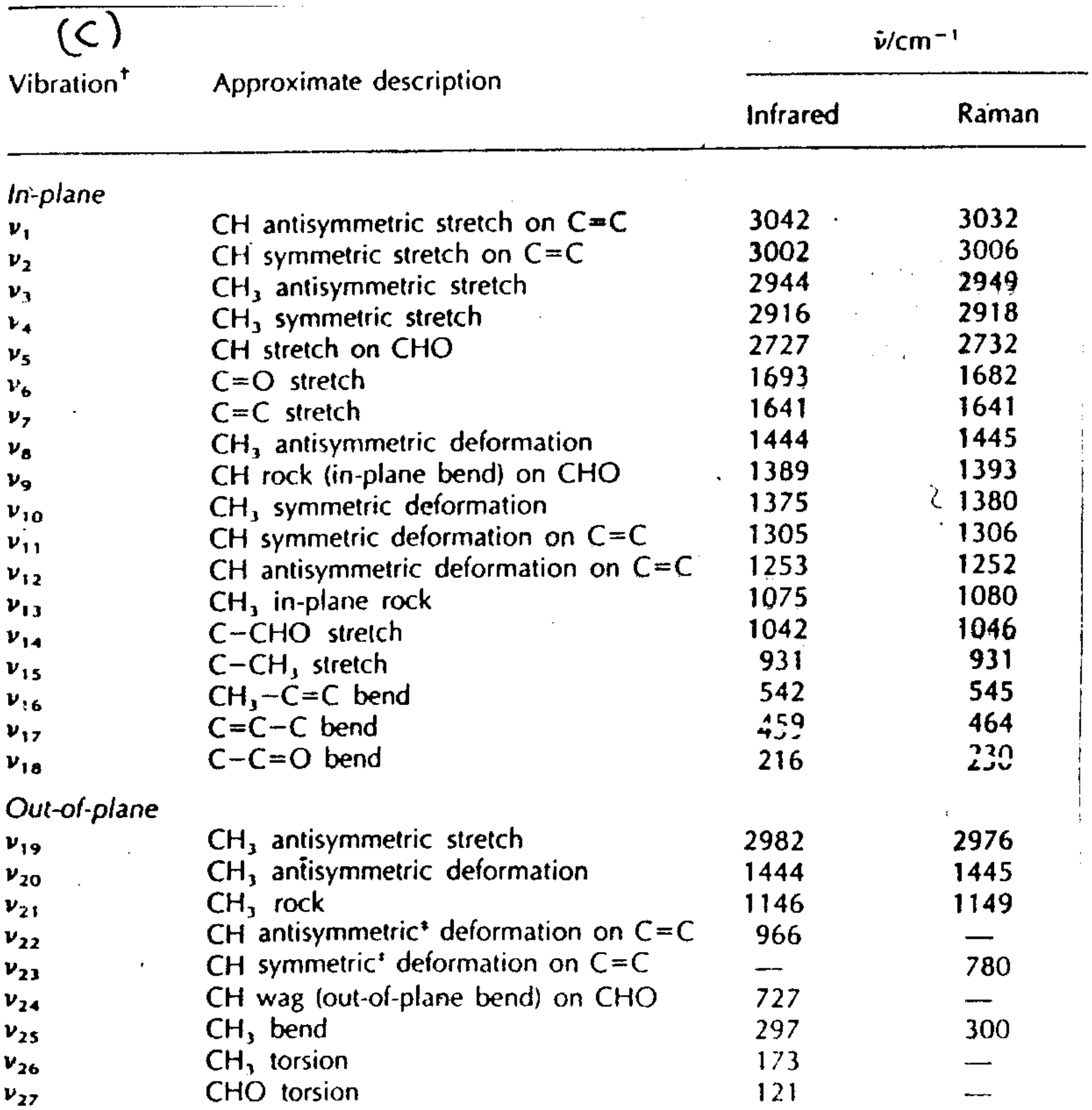
Raman spectrum





s-trans-crotonaldehyde

Vibrational wavenumbers of crotonaldehyde



(c)

Vibration[†]	Approximate description	$\tilde{\nu}/\mathrm{cm}^{-1}$	
		Infrared	Raman
In-plane			
ν_1	CH antisymmetric stretch on C=C	3042	3032
ν_2	CH symmetric stretch on C=C	3002	3006
ν_3	CH_3 antisymmetric stretch	2944	2949
ν_4	CH_3 symmetric stretch	2916	2918
ν_5	CH stretch on CHO	2727	2732
ν_6	C=O stretch	1693	1682
ν_7	C=C stretch	1641	1641
ν_8	CH_3 antisymmetric deformation	1444	1445
ν_9	CH rock (in-plane bend) on CHO	1389	1393
ν_{10}	CH_3 symmetric deformation	1375	1380
ν_{11}	CH symmetric deformation on C=C	1305	1306
ν_{12}	CH antisymmetric deformation on C=C	1253	1252
ν_{13}	CH_3 in-plane rock	1075	1080
ν_{14}	C−CHO stretch	1042	1046
ν_{15}	$C-CH_3$ stretch	931	931
ν_{16}	$CH_3-C=C$ bend	542	545
ν_{17}	C=C−C bend	459	464
ν_{18}	C−C=O bend	216	230
Out-of-plane			
ν_{19}	CH_3 antisymmetric stretch	2982	2976
ν_{20}	CH_3 antisymmetric deformation	1444	1445
ν_{21}	CH_3 rock	1146	1149
ν_{22}	CH antisymmetric[‡] deformation on C=C	966	—
ν_{23}	CH symmetric[‡] deformation on C=C	—	780
ν_{24}	CH wag (out-of-plane bend) on CHO	727	—
ν_{25}	CH_3 bend	297	300
ν_{26}	CH_3 torsion	173	—
ν_{27}	CHO torsion	121	—

Advantages of Raman spectroscopy

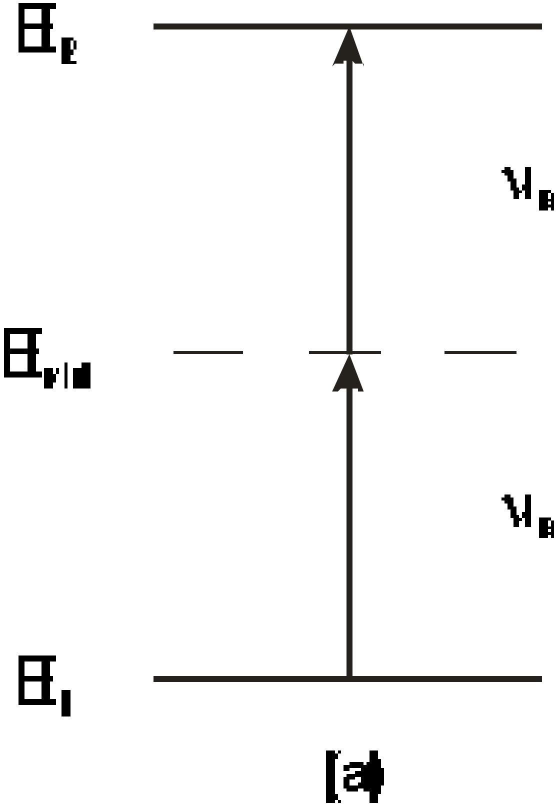
- aqueous solutions can be used (the absorption of water is strong over almost the entire IR range, but its Raman scattering is weak)
- non-destructive technique (The solid sample does not need to be ground with KBr and compressed to a pellet or to dissolve, only to place in the path of the light.)
- resonance Raman-effect (The wavelength of the exciting laser is within the electronic spectrum of a molecule. In that case the intensity of some Raman-active vibrations increases dramatically. Colorful components can be detected at low concentrations, e.g., in biological samples.)

Two-photon absorption

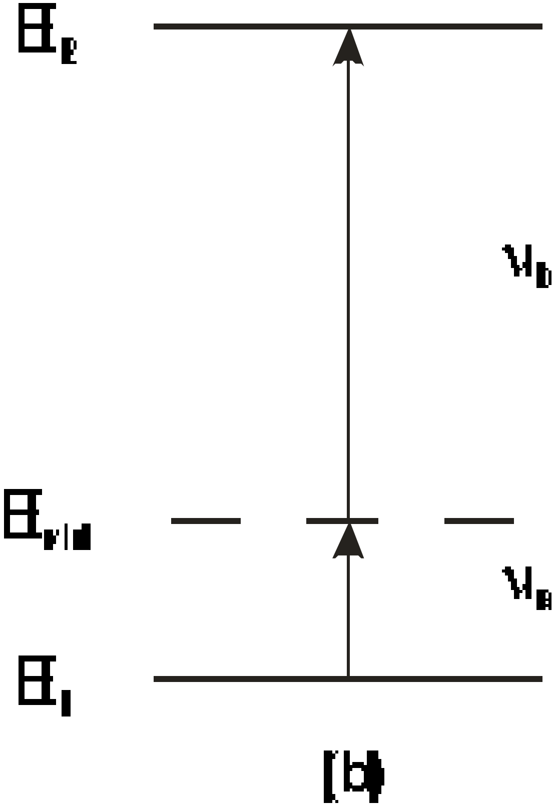
Rotational, vibrational, or electronic transitions when two photons are absorbed by the molecule. Its probability is sufficiently larger if the concentration of photons is high. It can be induced by pulse lasers, but not by conventional light sources, and continuous lasers.

Most often, the two-photon absorption is used in electronic spectroscopy.

Energy levels in two-photon absorption



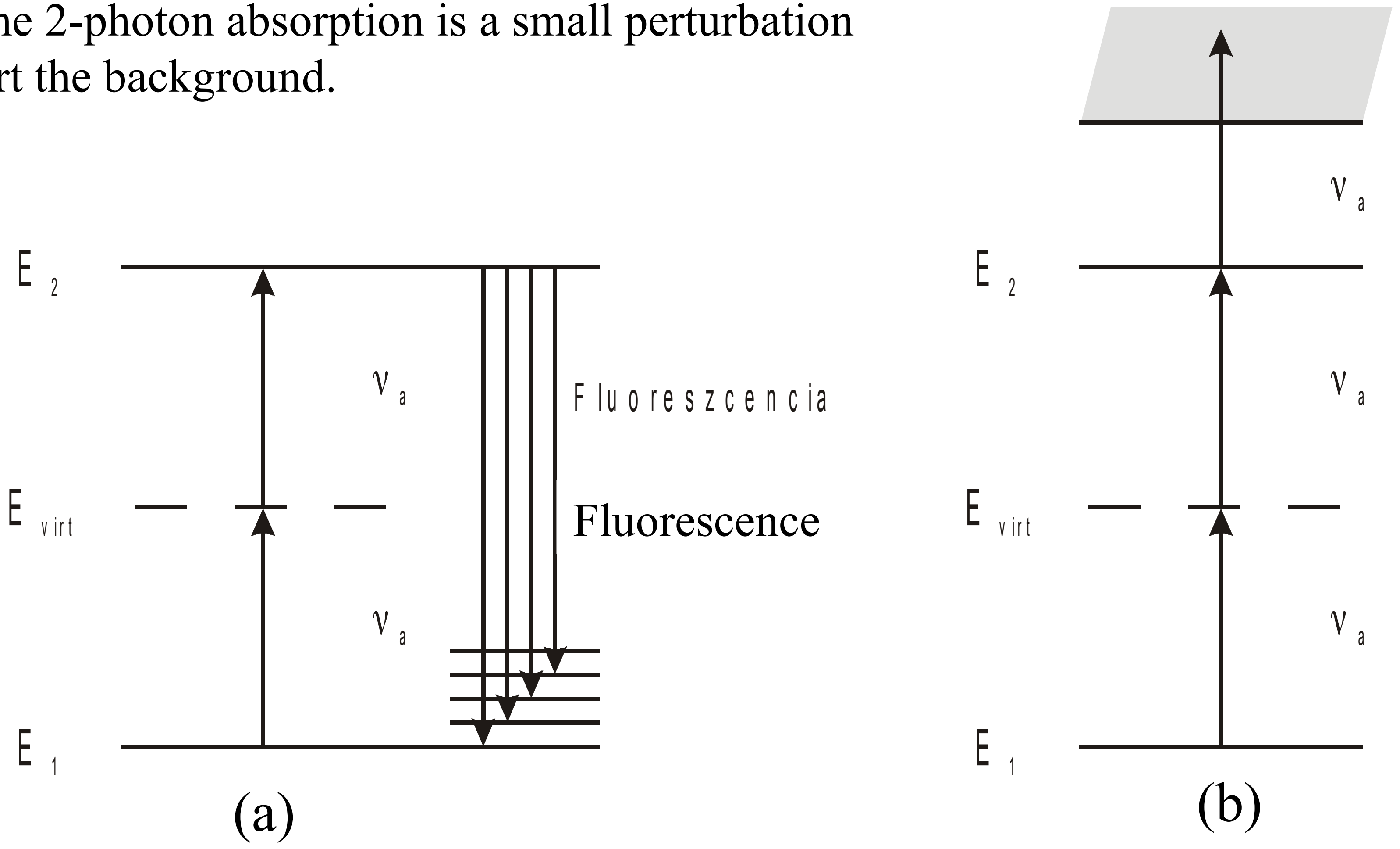
single tunable laser



two lasers

Detection methods for two-photon absorption

The 2-photon absorption is a small perturbation wrt the background.



Ionization continuum

Fluorescence

(a)

(b)

Either the total fluorescence intensity or the number of ions is proportional to the 2-photon absorption.

Selection rules

They are different from those of the one-photon absorption.

They are similar to those of the Raman scattering.

The irrep of the wave function of the final state must be identical to that of any component of α.

Explanation: $\left.\begin{array}{l}\text{Raman scattering}\\ \text{Two-photon absorption}\end{array}\right\}$ Two-photon processes

$\left.\begin{array}{l}\text{One-photon absorption}\\ \text{Spontaneous emission}\end{array}\right\}$ One-photon processes

Applications 1

1a) Investigation of transitions which are forbidden in one-photon absorption (because of the different selection rules)

1b) In the electronic spectrum transitions in the far UV range can also be observed. For instance, instead of the absorption of a photon of 150 nm, the transition can be induced by two photons of 300 nm.

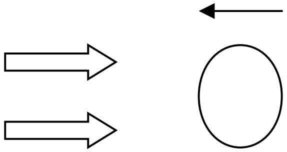
Applications 2

2) High-resolution spectroscopy: elimination of the Doppler broadening of spectral lines.

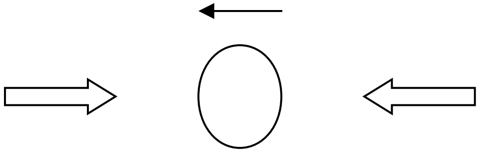
The consequence of Doppler effect:

$$\nu' = \nu\left(1 \pm \frac{v}{c}\right)$$

Elimination of Doppler broadening

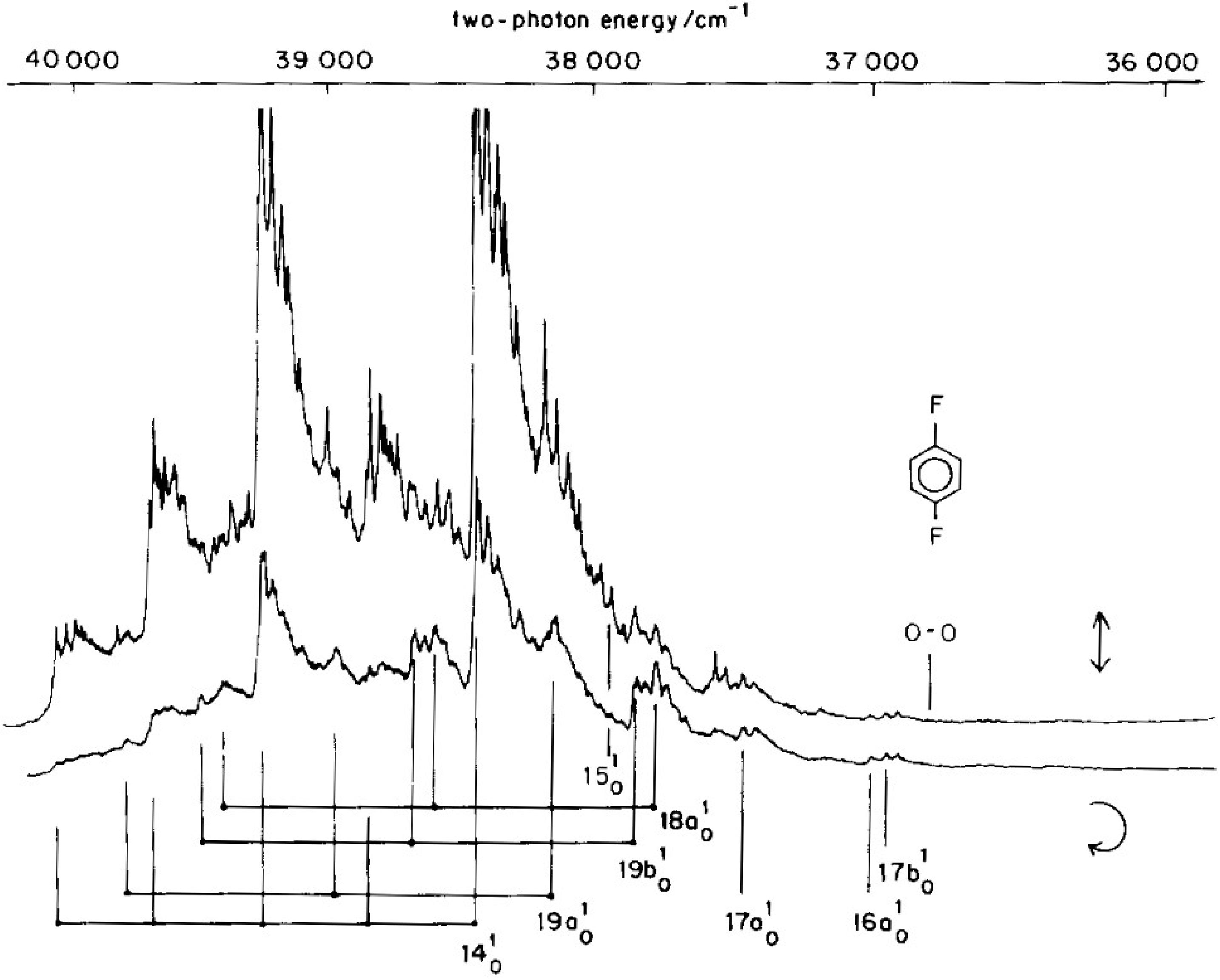


$$\Delta E = 2v\left(1 + \frac{v}{c}\right)$$



$$\Delta E = v\left(1 + \frac{v}{c}\right) + v\left(1 - \frac{v}{c}\right) = 2v$$

Two-photon spectrum of 1,4-difluorobenzene



Applications 3

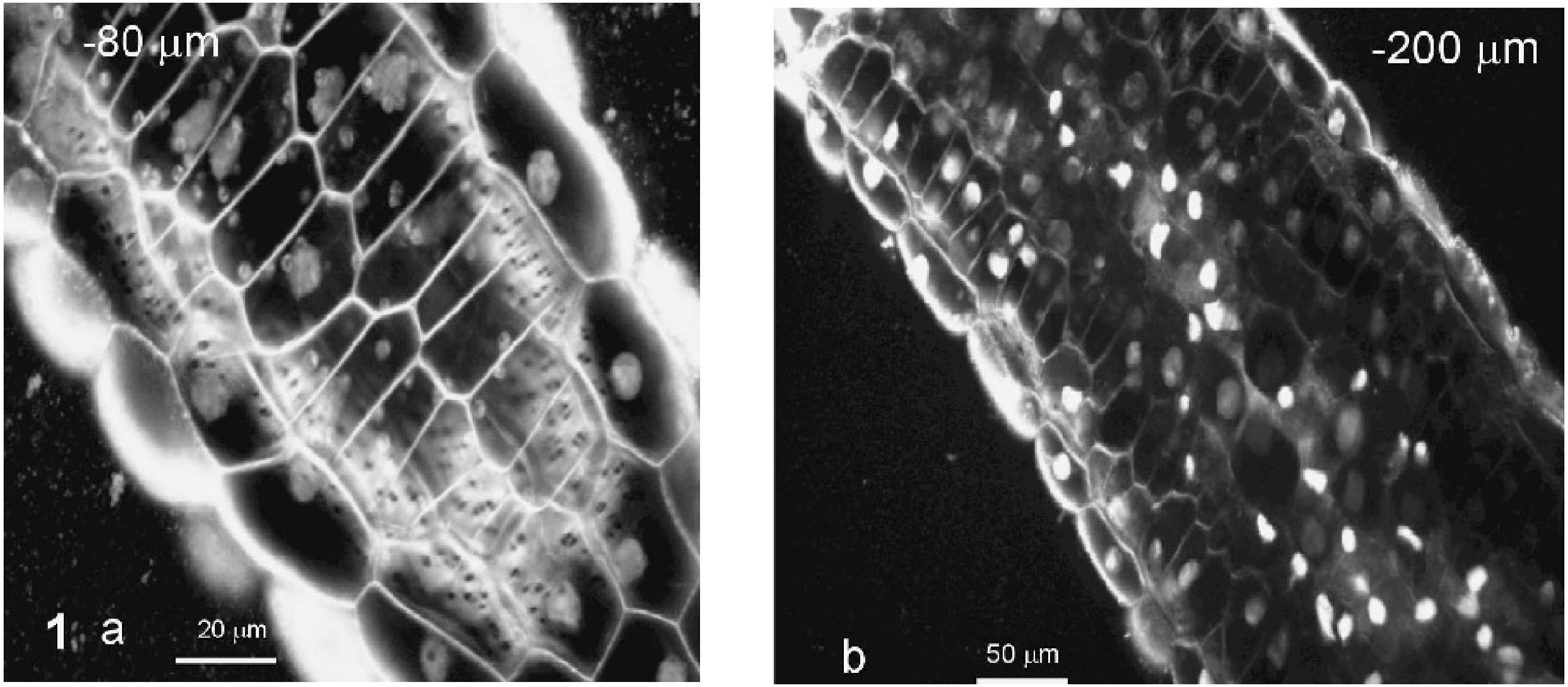
3. Two-photon microscopy

The laser beam is focused onto the sample, due to the high photon density, two-photon absorption takes place, which is indicated by fluorescence. This is what is detected.

Advantage: the sample does not absorb at the wavelength of the exciting light (in one-photon absorption), therefore

- thick layers can be studied,
- the destruction caused by the light is low

Example: two-photon microscope image of ant cells



Flash photolysis

The concentration of excited-state molecules most often decreases according to first-order kinetics:

$[M^*] = [M*]_0 \exp(-kt)$

$\tau = 1/k$ characteristic time

Triplet state

$\tau_{T_1} = 10^{-6}$-10^{0} s

there is time for chemical reactions

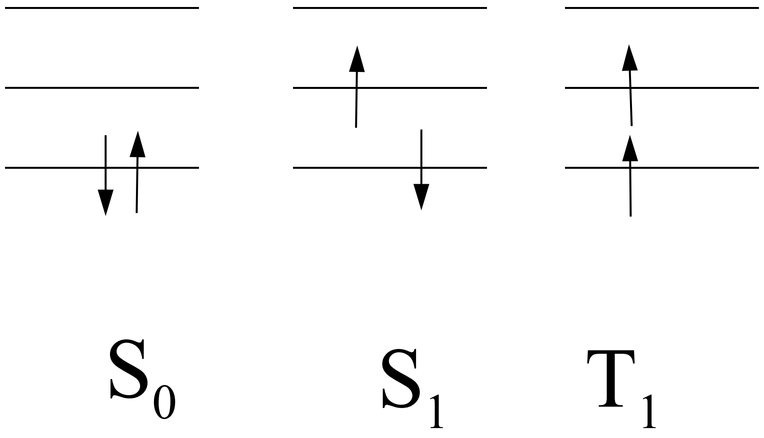
Instrument:

simple pulse laser

+ photodiode or photomultiplier

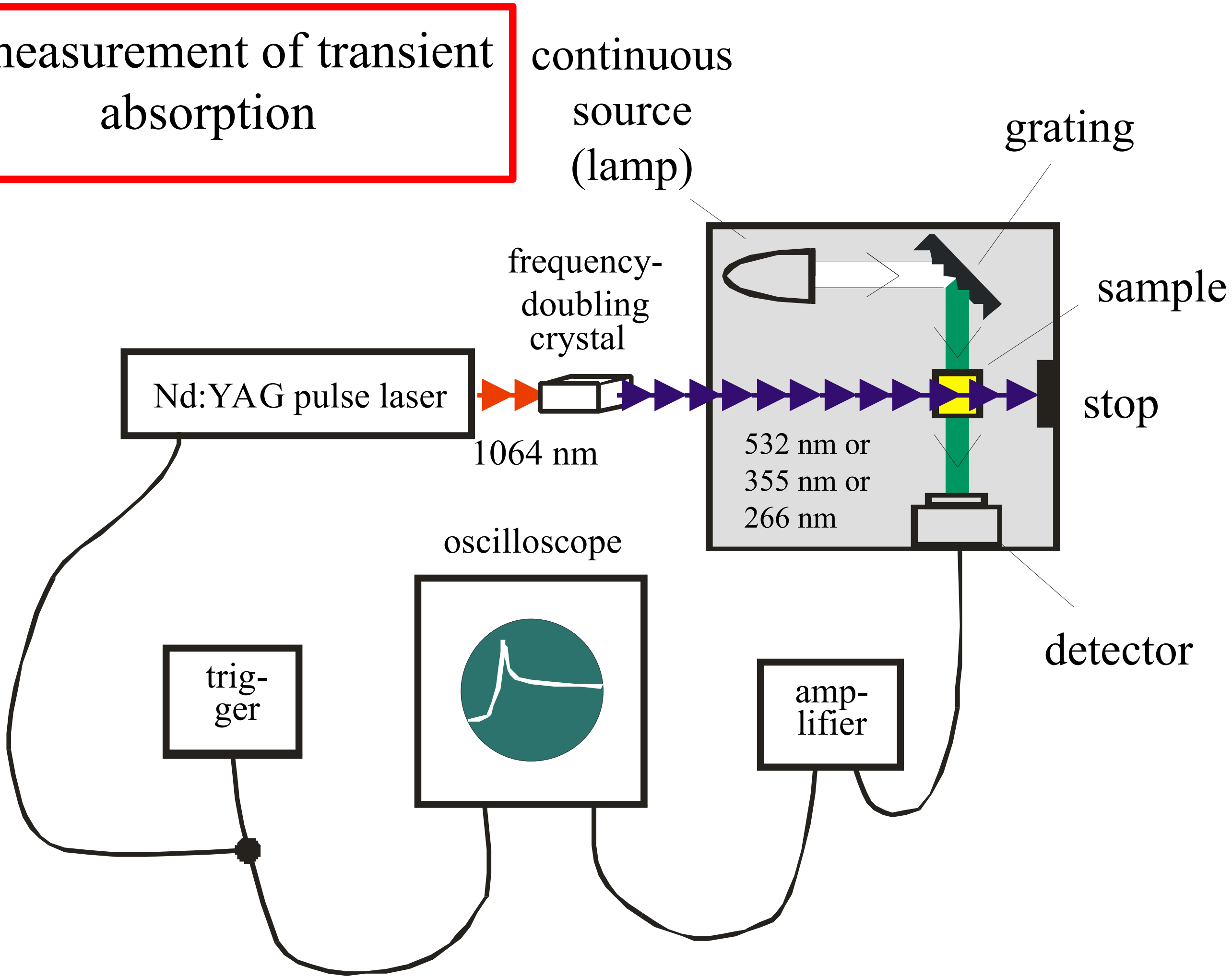
+ electronics (oscilloscope)

Experimental method: flash-photolysis



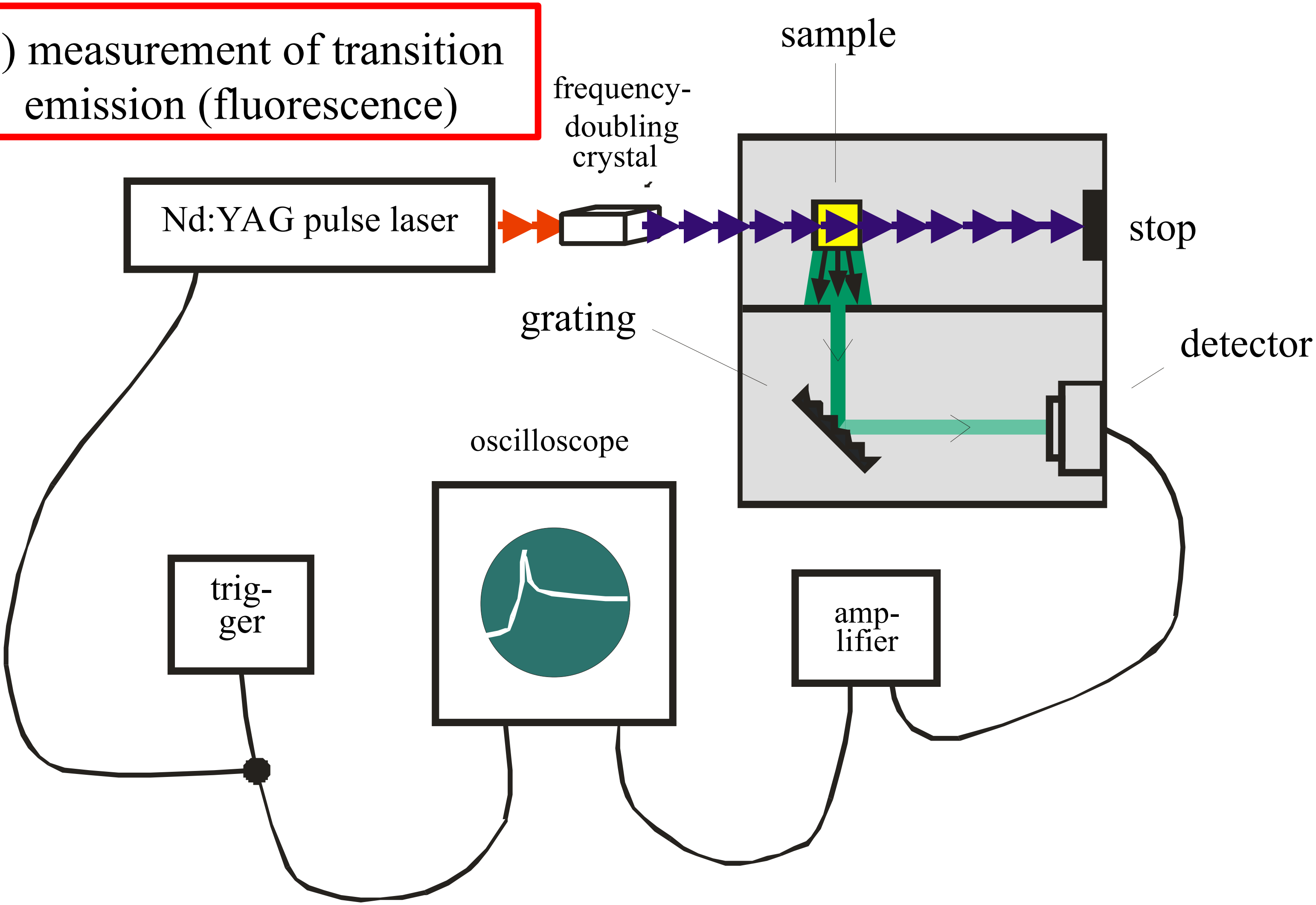
Flash photolysis I

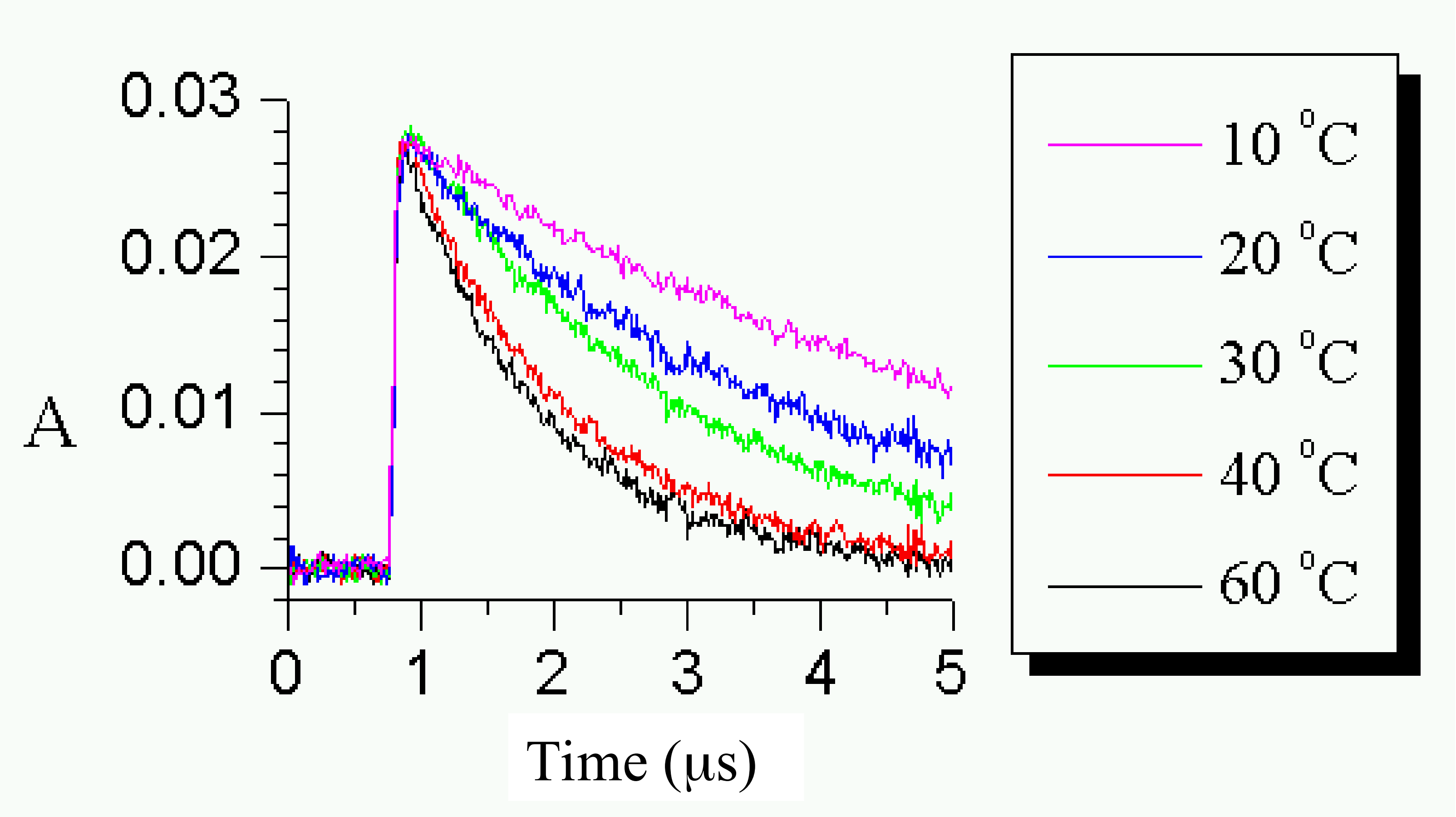
a) measurement of transient absorption



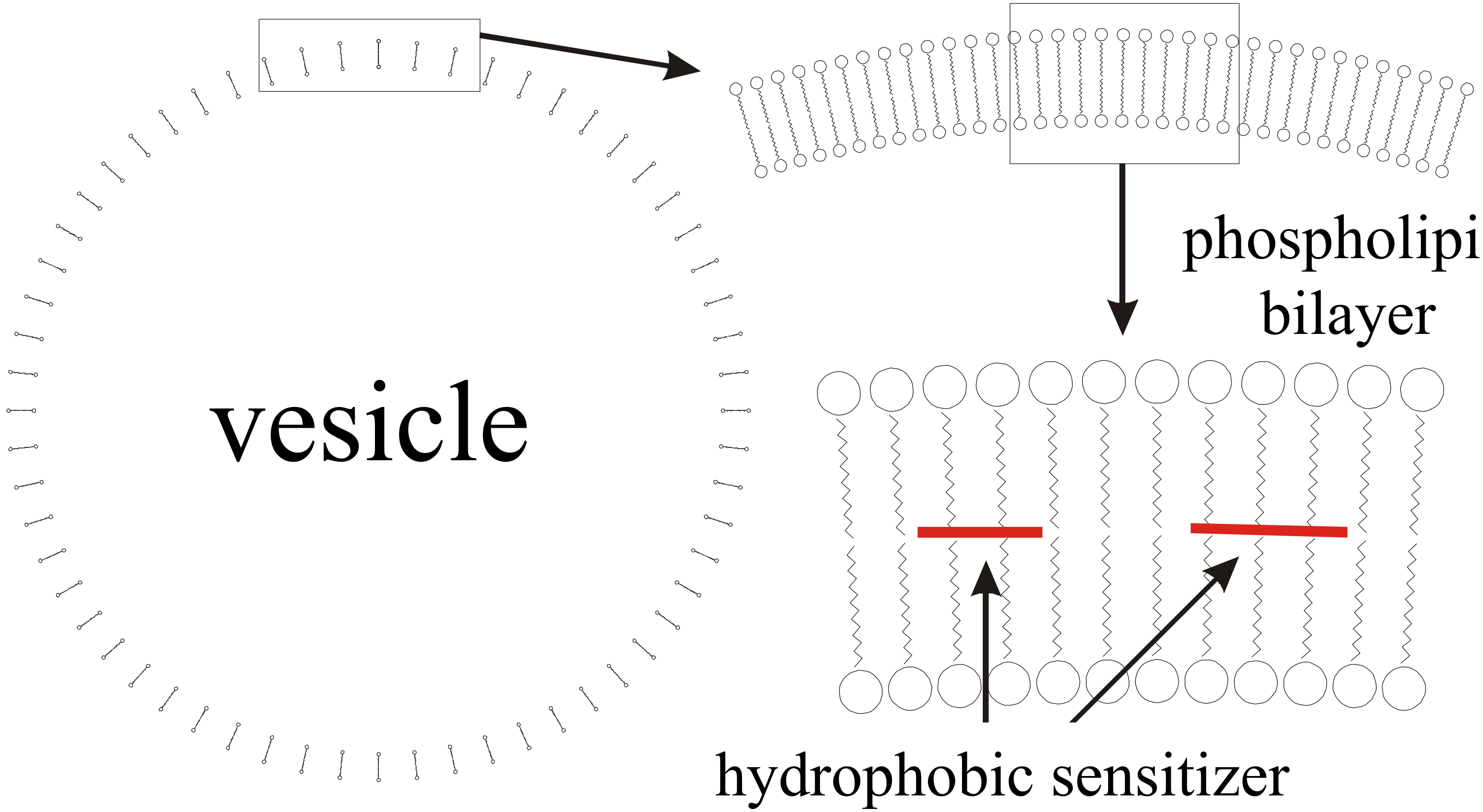
Flash photolysis II

b) measurement of transition emission (fluorescence)

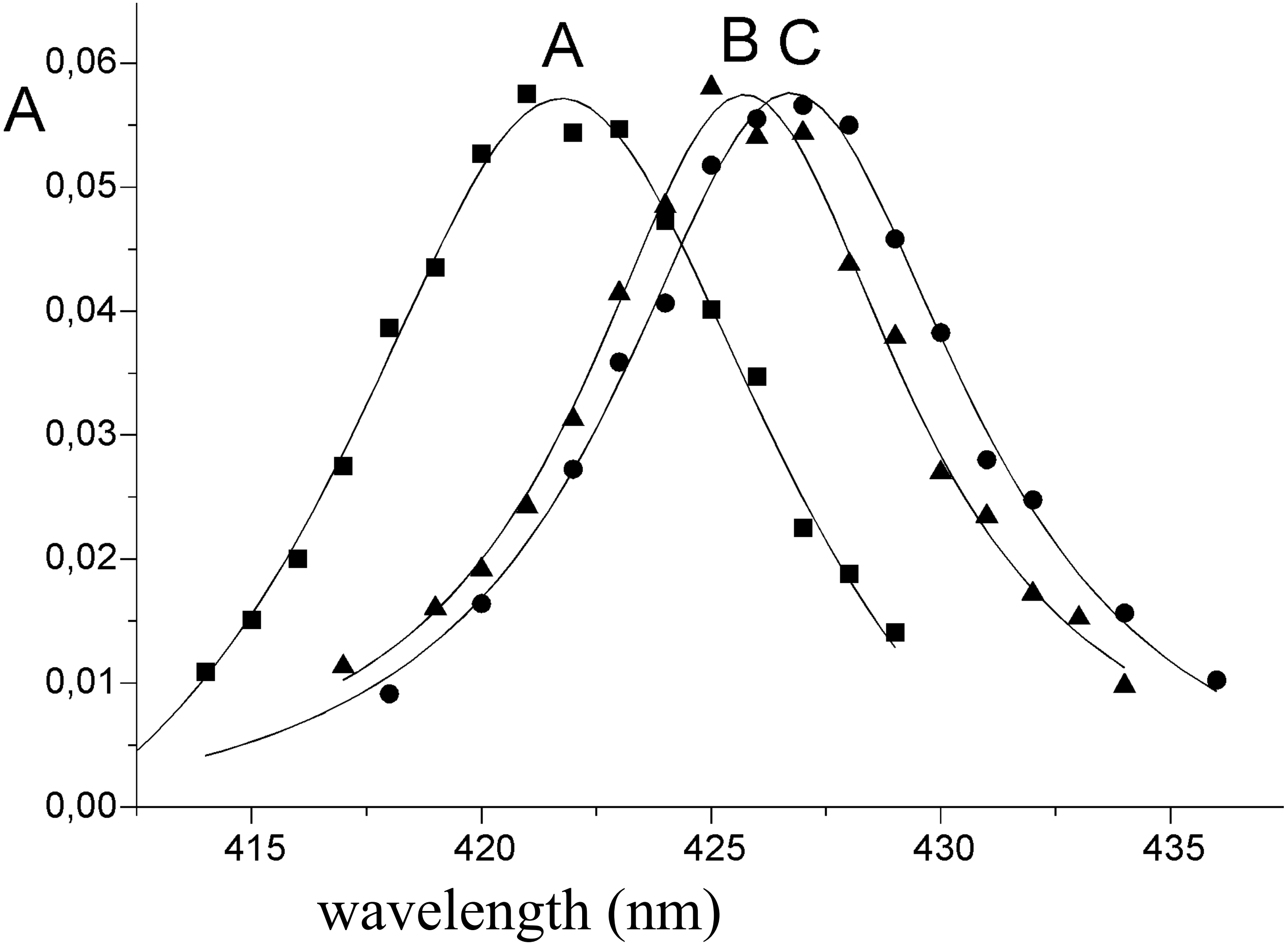




Decay of the triplet state of a porphyrin molecule dissolved in the lipid bilayer of a phospholipid vesicle in the presence of oxygen



Idealized structure of a phospholipid vesicle with the most probable location of the probe molecule.

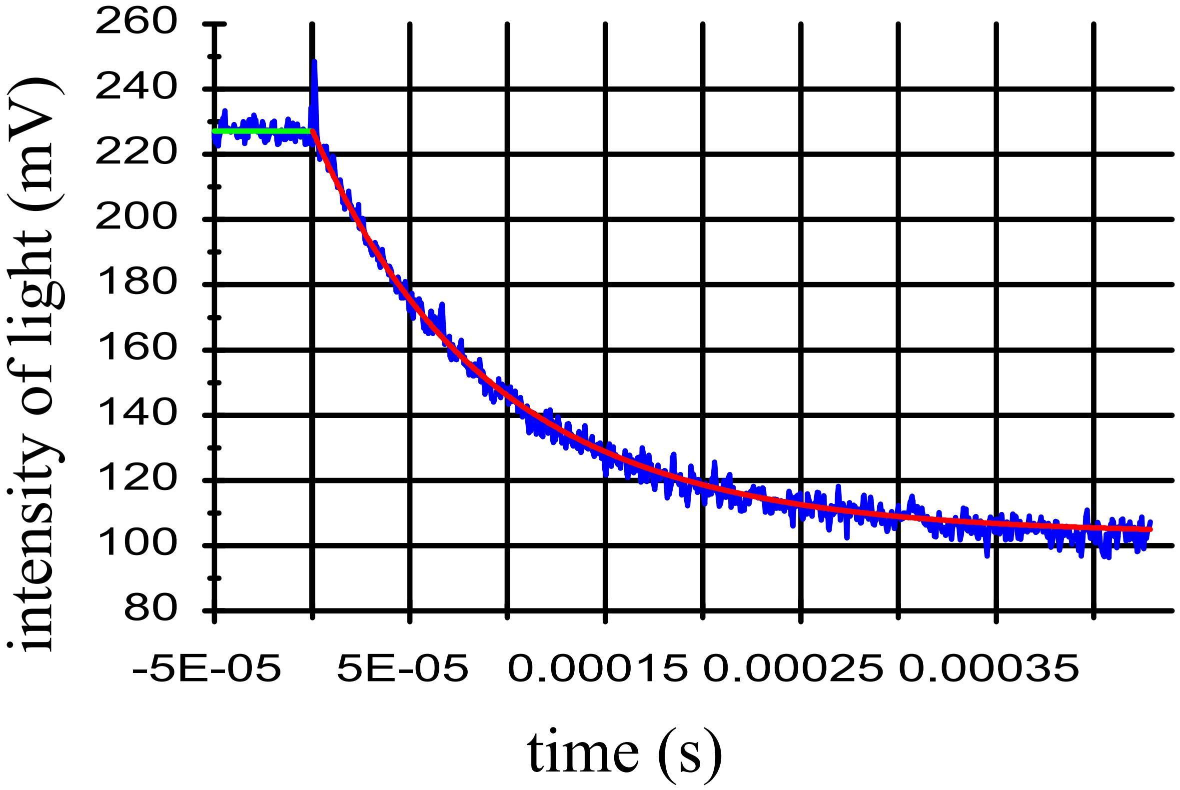


Absorption spectrum of triplet antracene

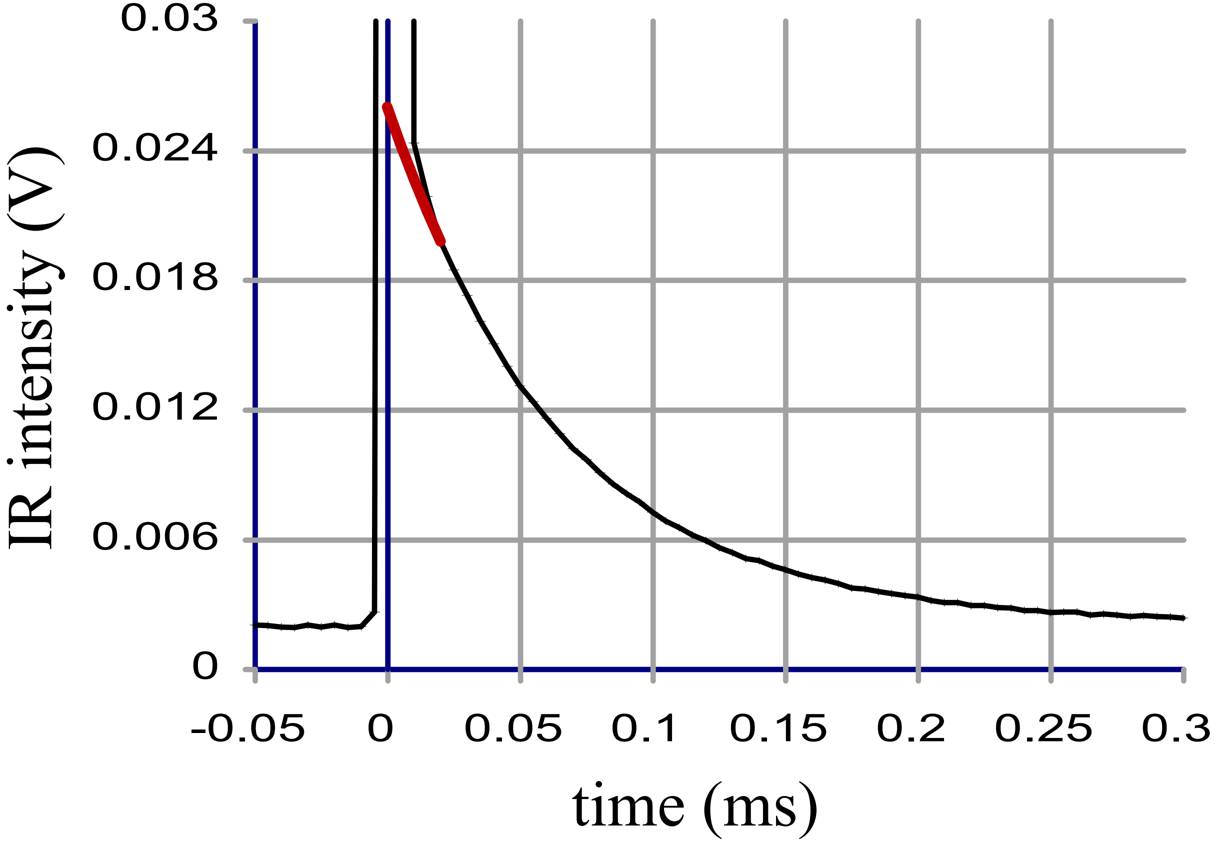
A: in hexane

B: in a phospholipid vesicle at 25 ^{o}C

C: in a phospholipid vesicle at 18 ^{o}C



Decrease of the acceptor reacting with singlet oxygen by measuring the absorbance of the acceptor



IR emission signal of singlet oxygen in the presence of hematoporphyrin sensitizer. (Thick line: extrapolation)

The pump and probe experiment

Singlet states

τ_{S_1} 10^{-11}-10^{-8} s

there is no time for chemical reactions

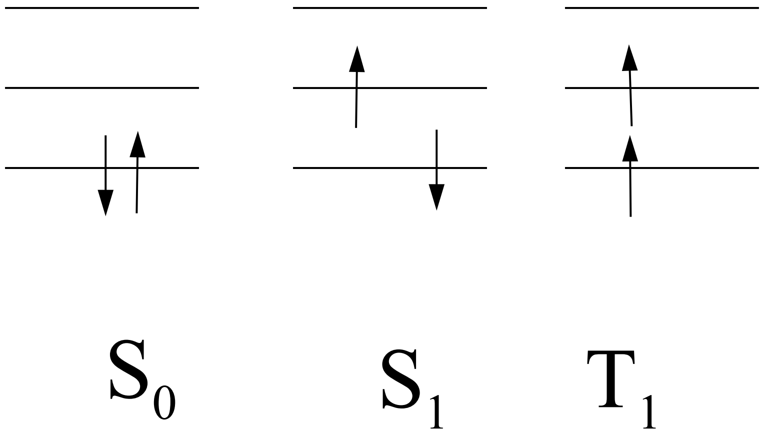
Instrument

mode-locked laser

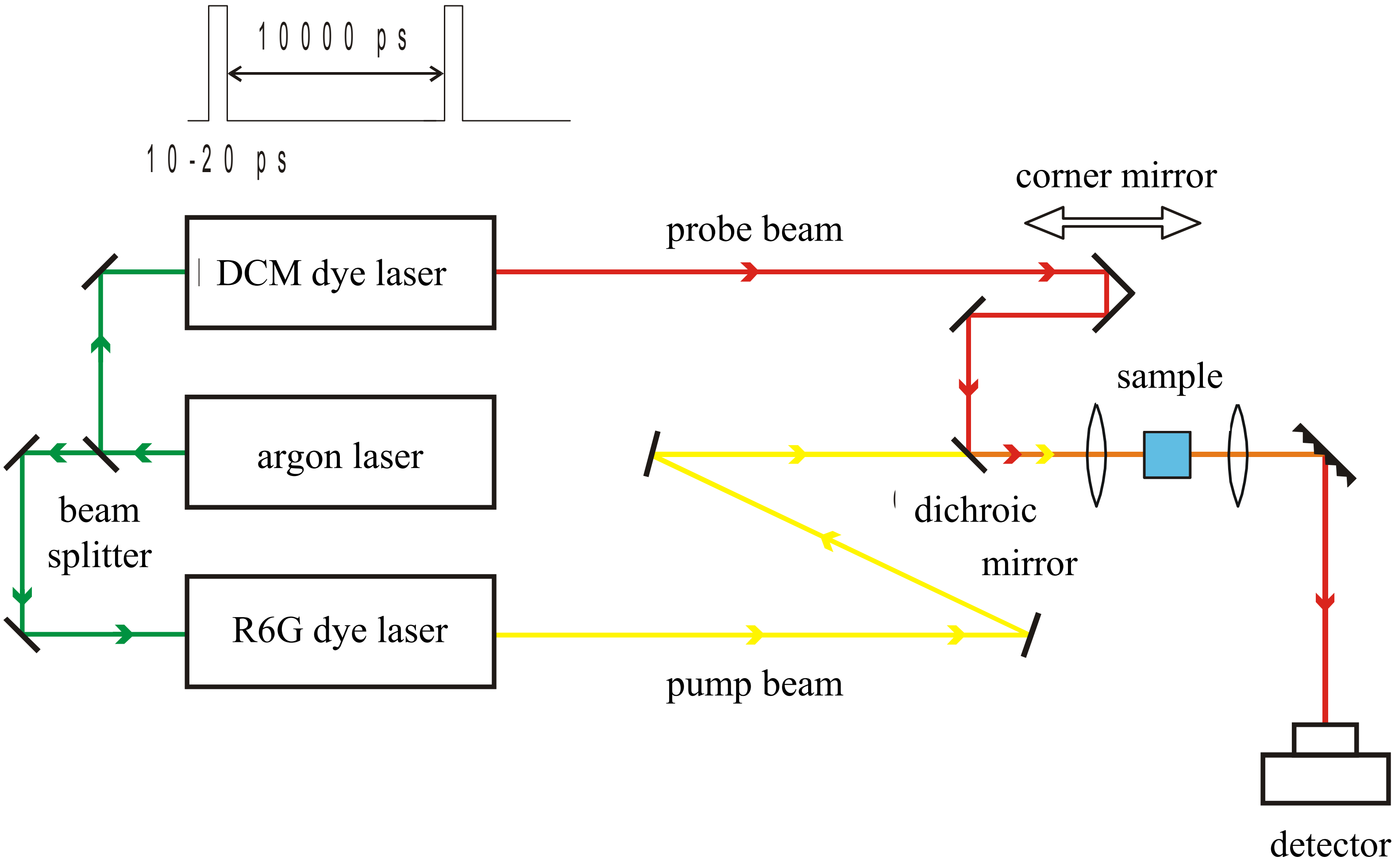
+ fast photodiode or photomultiplier

+ electronics (lock-in amplifier)

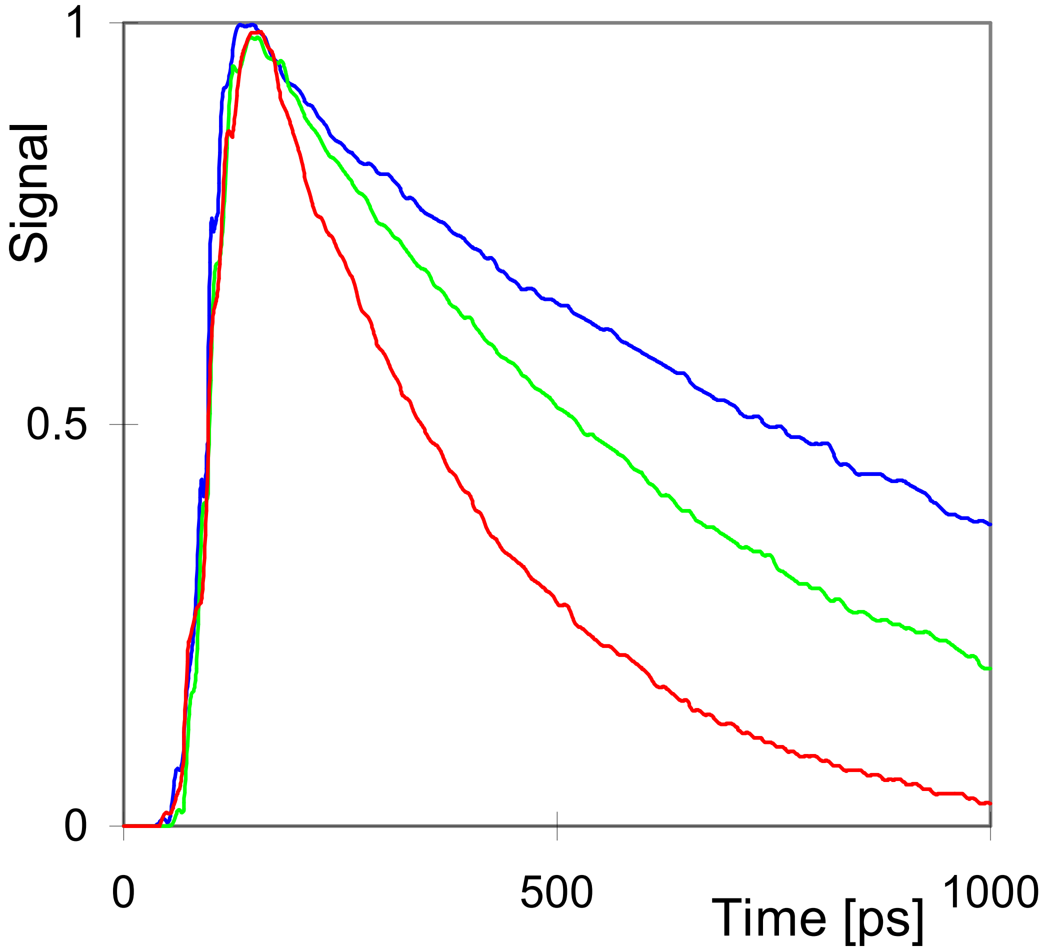
Experimental method: pump and probe experiment



The pump and probe experiment



Decay of the transient absorption of Nile Blue



solvent: ethyleneglycol

temperature: 20 °C

40 °C

60 °C

The transient absorption is the resultant of several factors:

- bleaching: decrease of the population of the S_0 state (the intensity of the probe beam increases)

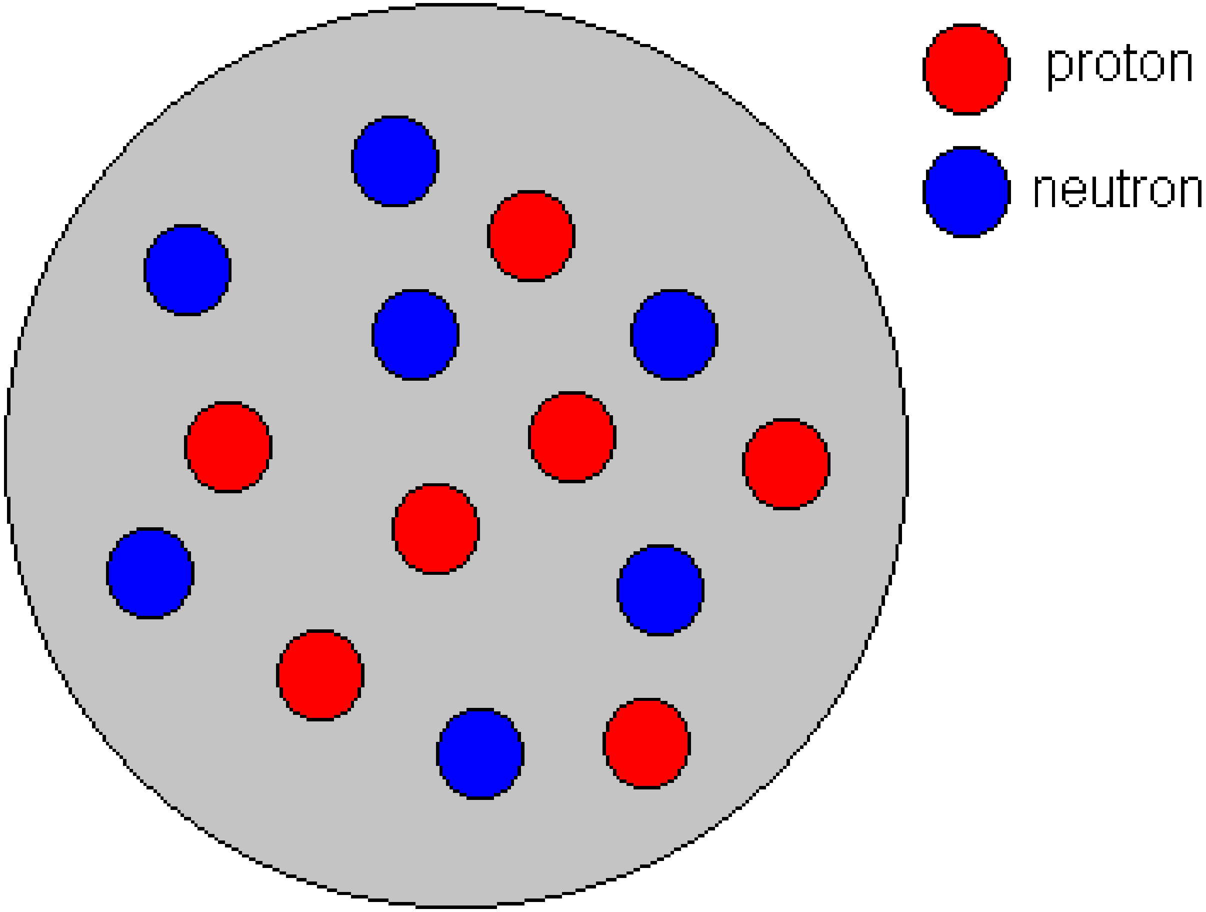
- stimulated emission: increase of the population of the S_1 state (the intensity of the probe beam increases)

- $S_1 \rightarrow S_2$ absorption: (the intensity of the probe beam decreases)

ENERGY LEVELS OF NUCLEI

The nuclear shell model

Nuclear shell model

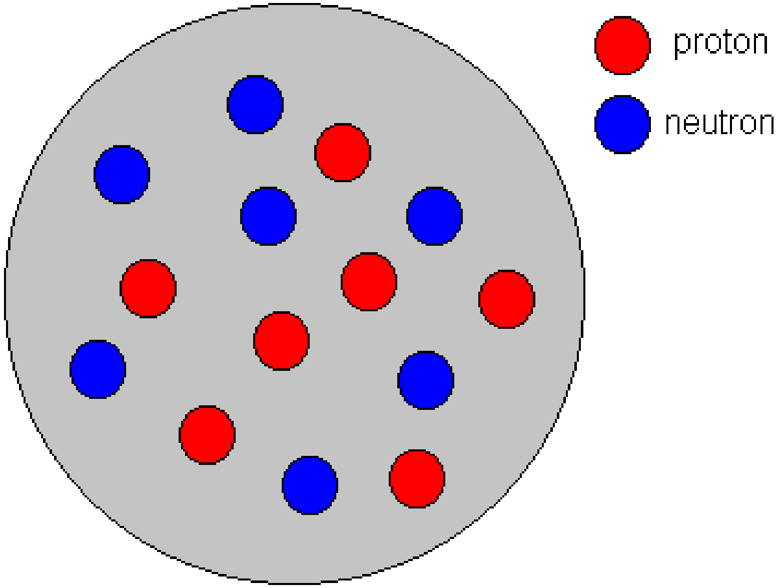


The angular momentum of nucleons due to spin

$$|\vec{S}(\text{proton})| = |\vec{S}(\text{neutron})| = |\vec{S}(\text{electron})| = \sqrt{S(S+1)}\hbar$$

$$S = 1/2$$

(Protons and neutrons are particles of 1/2 spin like the electrons.)



Nuclear shell model

- used for the description of quantum states of the nuclei
- it is similar to the model applied to polyatomic molecules, which introduces the electron shells. (It is more complicated, because there are two types of nucleons.)

Characterization of the quantum states of the nuclei
(Results of the nuclear shell model)

The states of the nuclei are characterized by two quantum numbers:

- I: nuclear spin quantum number
- M_I: nuclear magnetic quantum number

Nuclear quantum numbers

I: nuclear spin quantum number

I is defined by the atomic number and the mass number.

atomic number	**mass number**	**possible values of I**
even	even	it is zero
even	odd	half-integers (1/2, 3/2, 5/2…)
odd	even	integers (1,2,3…)
odd	odd	half-integers (1/2, 3/2, 5/2…)

M_I : values of the nuclear spin quantum number :

$$M_I = I, I-1, \ldots, -I.$$

Energy of nuclei

Without magnetic field it depends on I and it is degenerate (M_I-fold degeneracy).

In magnetic field this degeneracy is lifted.

Excitation of nuclei

- Mössbauer effect: I is modified, excitation with gamma-photon
- Nuclear magnetic resonance: M_I is modified (in magnetic field), excitation with radio-frequency pulse

Mössbauer-effect

- Transition involves the change of nuclear spin quantum number I.

- Large energy γ-radiation

- Recoilless nuclear resonance fluorescence

- Vary narrow linewidth → small energy shifts correspond to large changes in absorbance

Mössbauer effect

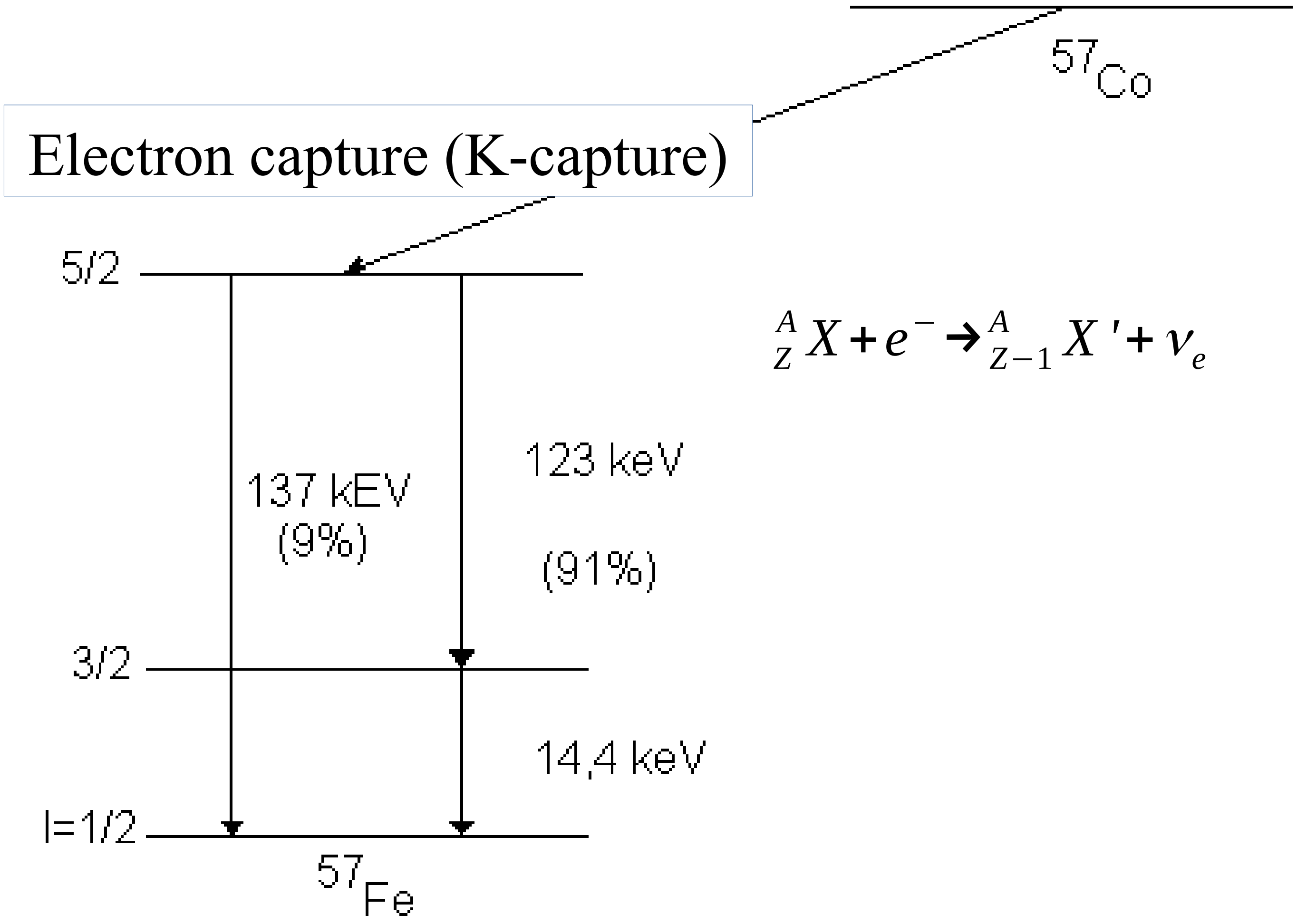
Radiation source:
compounds containing the same type of nuclei which are under investigation in the sample

ground state

excited state

Excited nuclei of the compounds serves as a radiation source appear from radioactive decay.

Example: Mössbauer-absorption of ^{57}Fe-nucleus using ^{57}Co isotop as the radiation source


Electron capture (K-capture)

$${}^{A}_{Z}X + e^{-} \rightarrow {}^{A}_{Z-1}X' + \nu_{e}$$

Mössbauer-spectroscopy

- Mössbauer-effect can be utilized in the structural chemistry.
- Roughtly the half of the chemical elements of the periodic system can be studied using the Mössbauer-spectroscopy.
- There is a need for a radioactive parent (nucleus with atomic number one unit greater) which dacays to the excited state of the investigated nucleus.
- Some frequently studed nuclei: ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{125}Te.

Experimental technique

Tuning of the source of γ-radiation using Doppler-effect: The radiation source is moved wrt the sample.

$$\nu' = \nu\left(1 \pm \frac{\mathrm{v}}{\mathrm{c}}\right)$$

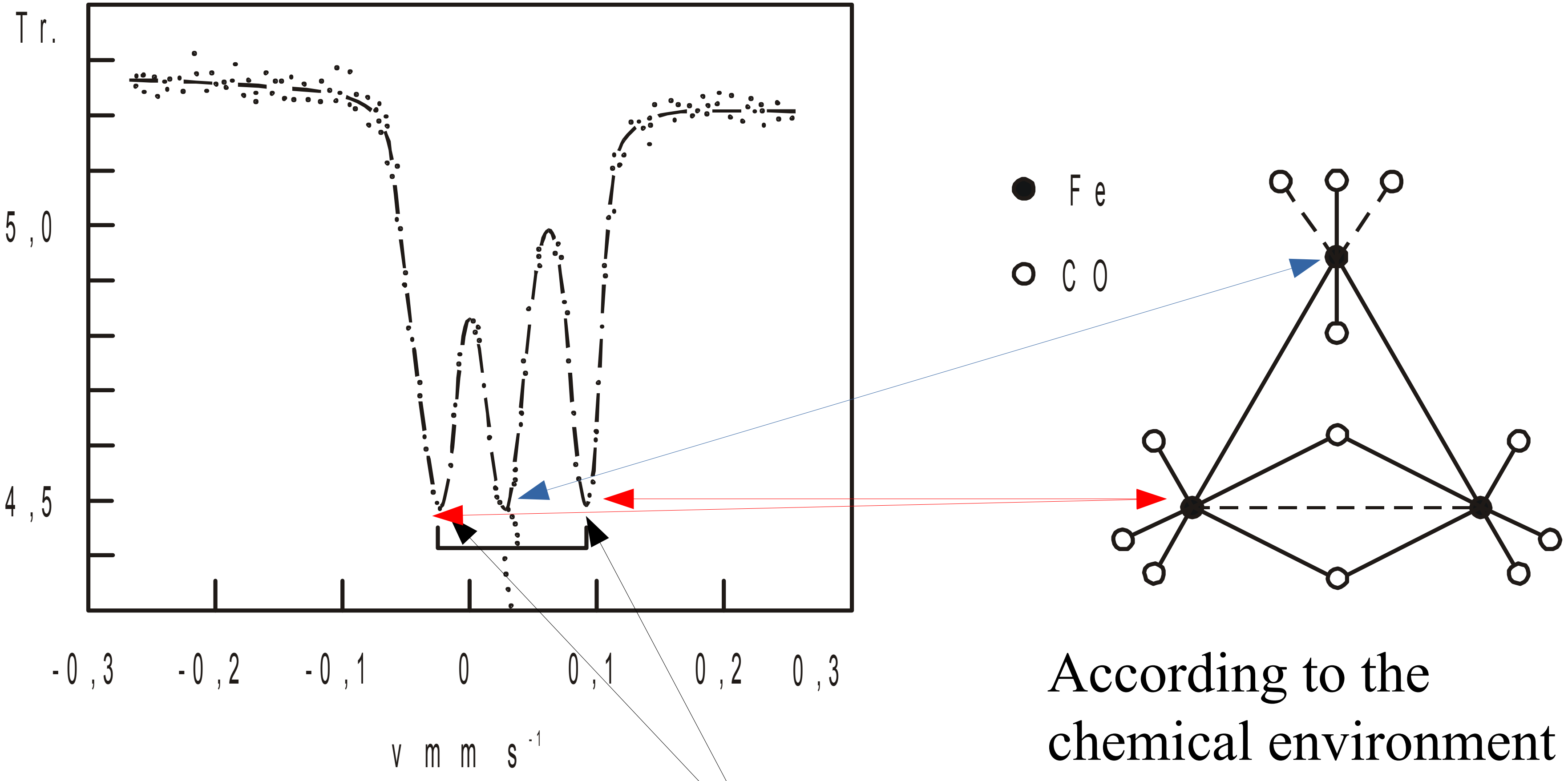
Absorption is measured while changing v systematically.

Detector: intenzity of the γ-radiation is measured by a NaI crystal. The γ-photon can strip an electron from one of the I^- ion of the NaI crystal. The current is detected. The current is amplified by an electron multiplier.

Properties of spectra

- **Chemical shift:** the absorbed frequency is characteristic to the nuclei but it also depends slightly on the electronic density of surrounding atoms, thus the spectrum contains information about the molecular structure as well.
- **Quadruple splitting**: the quadruple moment is a property of charge distribution. If the nucleus has a quadruple moment (the charge distribution is not spherically symmetric) than the energy levels (belonging to quantum number I) are split.
- **Magnetic splitting:** in magnetic field the energy of states characterized by quantum number I are broken according to M_I. Observable:
  - in external magnetic field
  - in internal magnetic field (e.g., in ferromagnetic material)

$Fe_3(CO)_{12}$ – Mössbauer spectra



Two excited levels due to the quadruple spitting

According to the chemical environment two peaks are expected with 2:1 intensity.

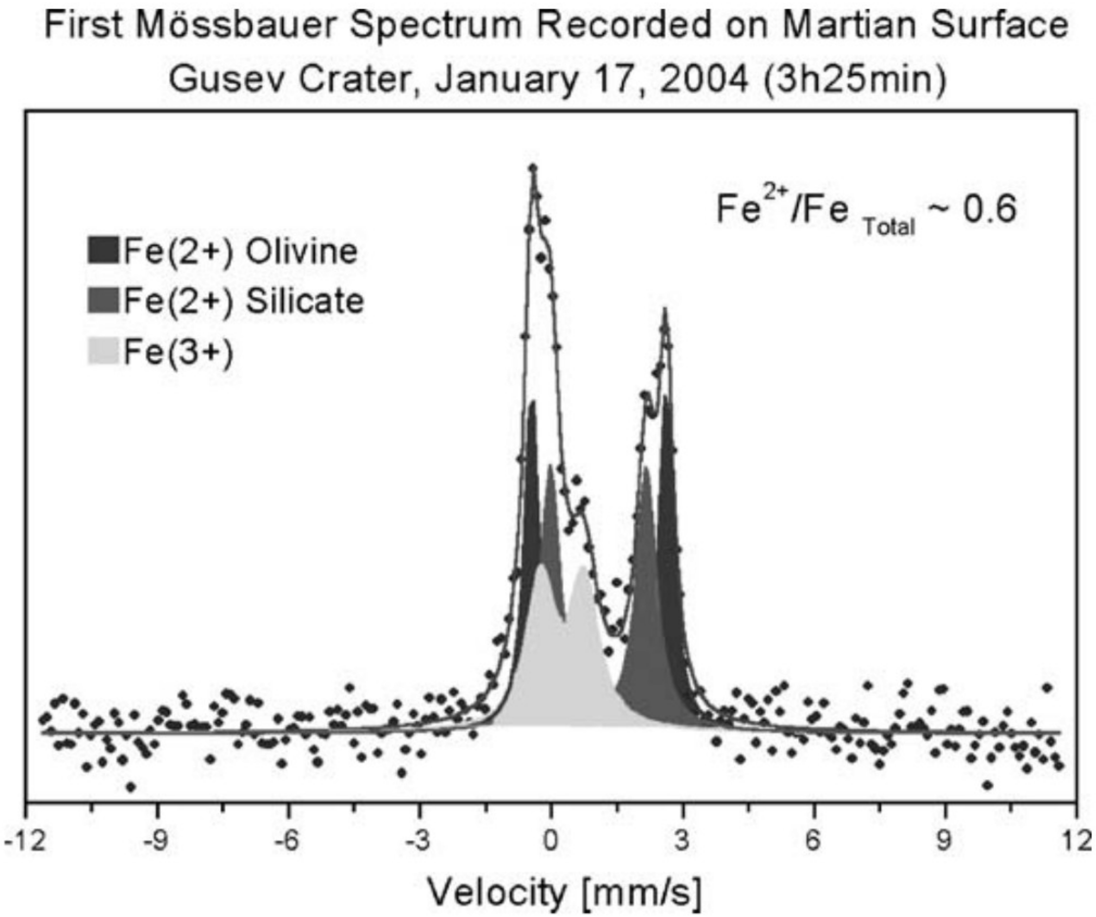


Figure 4. Very first Mössbauer spectrum ever taken on an extraterrestrial surface. The data from the Martian soil at the Spirit landing site were taken on sol (= Martian day) 13 of operations.

“With MIMOS II, besides other minerals the Fe silicate olivine has been identified in both soil and rocks at both landing sites. At the Meridiani site the Fe sulfate jarosite has been identified by MIMOS II which is definitive mineralogical proof of the presence of water at this site in the past.” (Hyperfine Interactions (2004) 158:117–124)

Applications in structural chemistry

- Metal complexes
- Corrosion – the atoms in the different oxidized state affected by different chemical shifts
- Magnetic alloys (internal magnetic field)

Nuclear magnetic resonance spectroscopy (NMR)

Absorption of nuclei in magnetic field

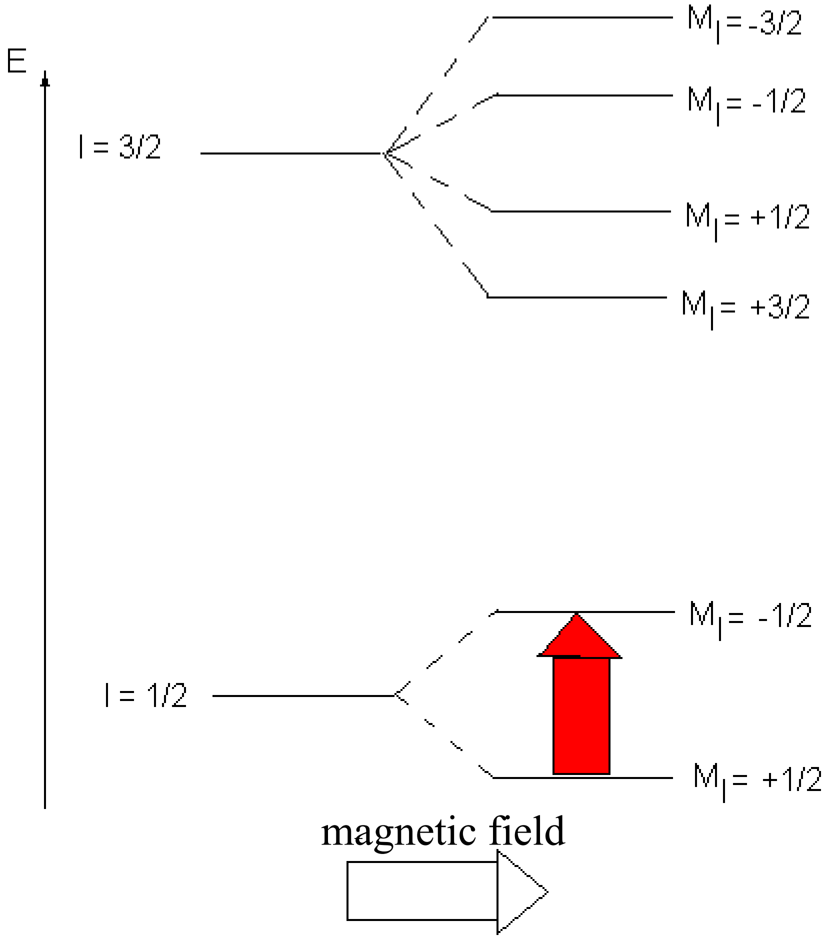
Mössbauer effect

Without magnetic field it is I dependent, degenerate according to M_I

Nuclear magnetic resonance

In magnetic field: energy of states depend on I and M_I

Magnetic nuclear resonance



Transition with changing M_I and constant I value.

Magnetic field is needed!

Absorption of radio wave radiation

Nuclear spin, angular momentum, and magnetic moment

Eigenvalues of the $\hat{L}^2$ and $\hat{L}_z$ operators: $\hbar^2 I(I+1)$ and $\hbar M_I$

$M_I=-I,-I+1,\ \dots\ ,I$

Nuclear spin ↔ Nuclear magnetic moment

g : „Lande-factor”

μ_n : Bohr-magneton of nucleus

(nuclear magneton)

m_n : mass of nucleus

$$\mu_n=\frac{e\hbar}{2m_n}$$

Eigenvalues of the $\hat{M}^2$ and $\hat{M}_z$ operators: $g^2 I(I+1)\mu_n^2$ and $g M_I \mu_n$

Potential energy of a particle with magnetic moment

Classical physics:

$$V = -\vec{M} \cdot \vec{B}$$

$\vec{B}$: magnetic induction

In magnetic field oriented in the direction of z axis,

$$V = -M^z |\vec{B}|$$

In quantum mechanics:

$$M^z = \mathrm{g} \mathrm{M}_I \mu_n$$

$$\boxed{V = -\mathrm{g} \mathrm{M}_I \mu_n |\vec{B}|}$$

Most frequently investigated nuclei in NMR spectroscopy: ^{1}H, ^{13}C

	Atomic number	Mass number	I (ground state)	M_I	g-factor
^{1}H					
	even	odd	1/2	+1/2, -1/2	5.586
^{13}C					
	even	odd	1/2	+1/2, -1/2	1.405

Splitting as a function of magnetic field

Energy of

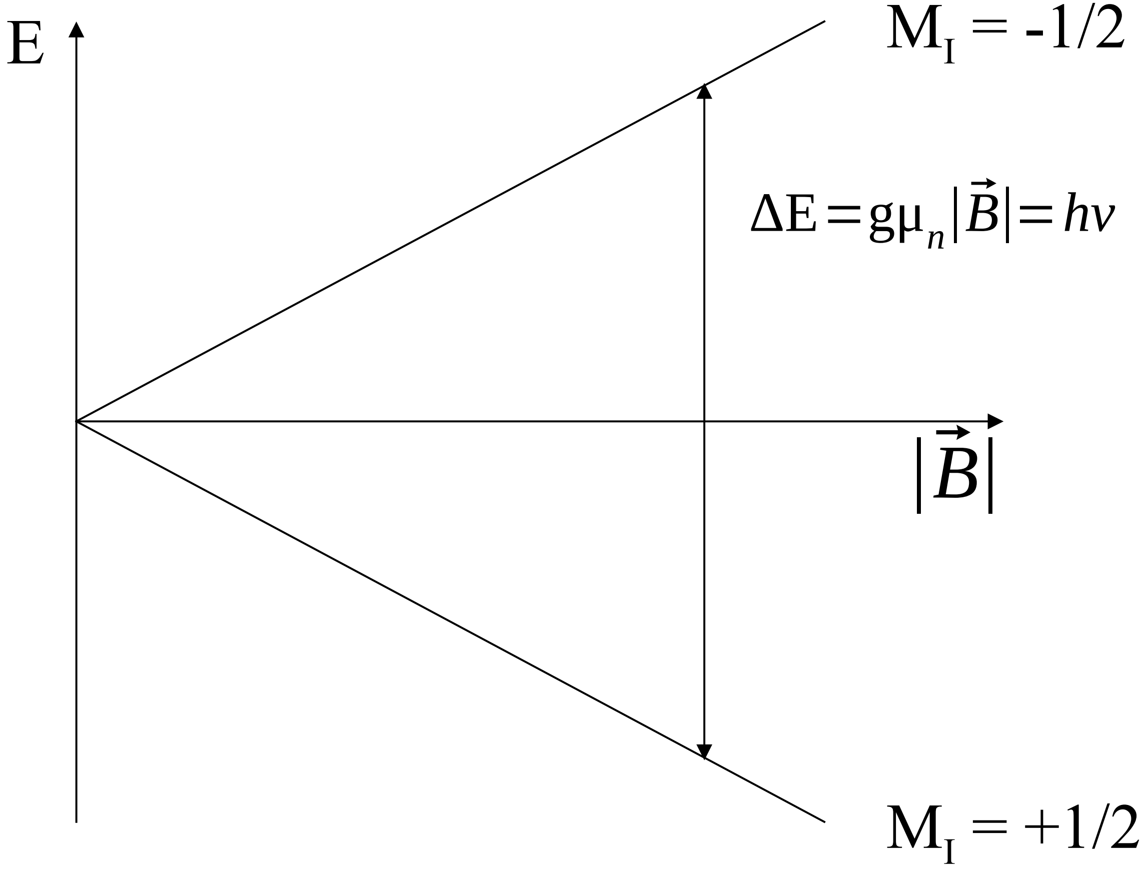
M_I = +1/2 state:

$$E_1 = -\frac{1}{2}\,\mathrm{g}\mu_n|\vec{B}|$$

Energy of

M_I = -1/2 state:

$$E_2 = +\frac{1}{2}\,\mathrm{g}\mu_n|\vec{B}|$$



Transitions between the nuclear states of ^{1}H and ^{13}C

$M_I = +1/2$ ↔ $M_I = -1/2$

The transition is allowed!

$$\Delta \mathrm{E} = \mathrm{g}\mu_n |\vec{B}| = hv$$

Energy of absorbed photon:

$$v = \frac{\Delta \mathrm{E}}{h} = \frac{\mathrm{g}\mu_n |\vec{B}|}{h}$$

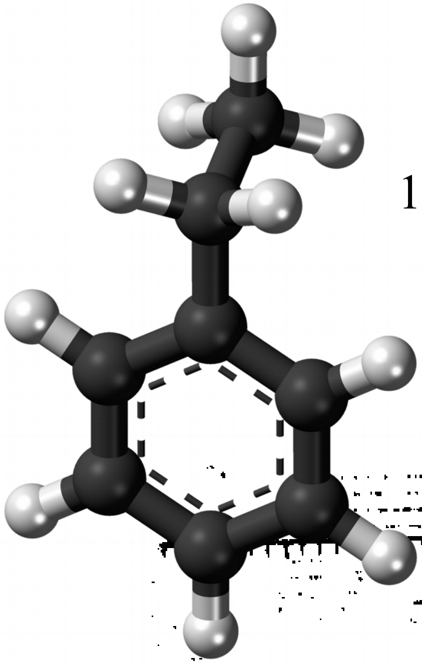
Absorption NMR frequencies of nuclei

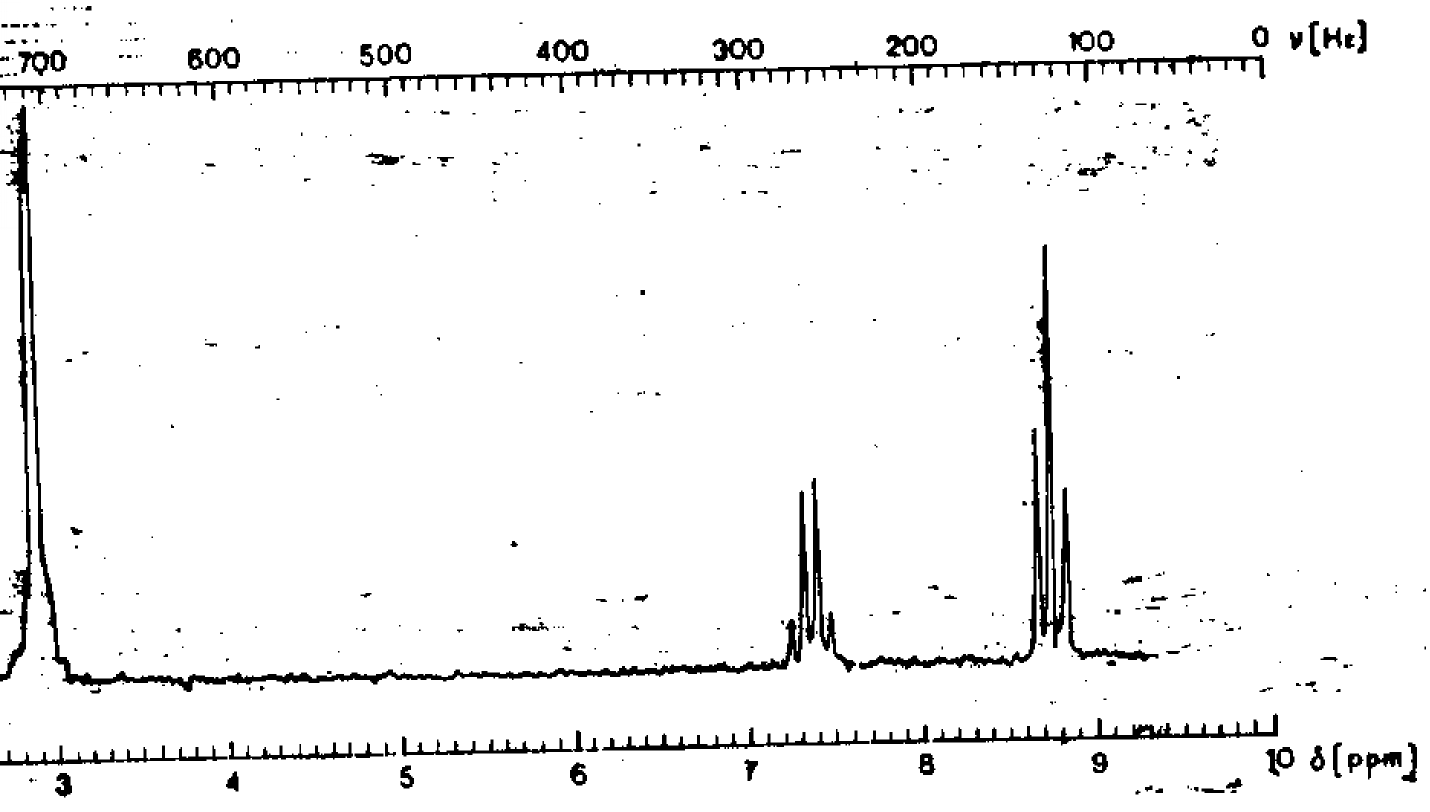
In $|\vec{B}|=1\,T$ magnetic field

Nucleus	Natural occurrence(%)	I (ground state)	ν (MHz)
^{1}H	99.98	1/2	42.58
^{11}B	81.17	3/2	13.66
^{13}C	1.11	1/2	10.70
^{19}F	100.0	1/2	40.06

Properties of NMR spectra I
Chemical shift

^{1}H NMR spectrum of Ethylbenzene





Chemical shift

Chemical shift: the characteristic atomic absorption (emission, ionization) frequency is slightly modified by surrounding molecular enviroment.

Detectable:

- XPS (ionization energy of atomic core)
- Mössbauer-effect (changing of nuclear energy due to the absorption of a γ-photon)
- Magnetic nuclear resonance (transition between magnetic energy levels due to absorption of radio wave radiation)

Chemical shift in the NMR spectrum

In the magnetic field electrons around a nucleus will circulate and create a secondary induced magnetic field.

$$\vec{B}_{\mathrm{lok}} = \vec{B}\left(1-\sigma\right)$$

σ : sheltering coefficient

σ positive: diamagnetic sheltering

σ negative: paramagnetic sheltering

Due to the chemical shift the absorption frequency is modified:

$$v' = \frac{\mathrm{g}\mu_n |\vec{B}| \left(1-\sigma\right)}{h}$$

In the NMR-spectrum the “relative change” wrt a reference absorption frequency is given:

$$\delta = \frac{\nu' - \nu_0}{\nu_0}$$

Choosing the ν_0

theoretical possibility: ν of an isolated nuclei

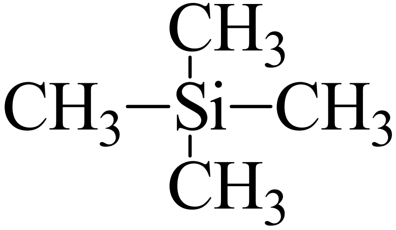
practical solution: ν of an atom of a chosen compound

Most frequently applied reference molecule: Tetramethylsilane (TMS)

advantage of TMS: single absorption signal for both ^{1}H and ^{13}C

δ : chemical shift (the phenomenon is also called chemical shift!)

Chemical shift δ is usually expressed in parts per million (ppm) by frequency

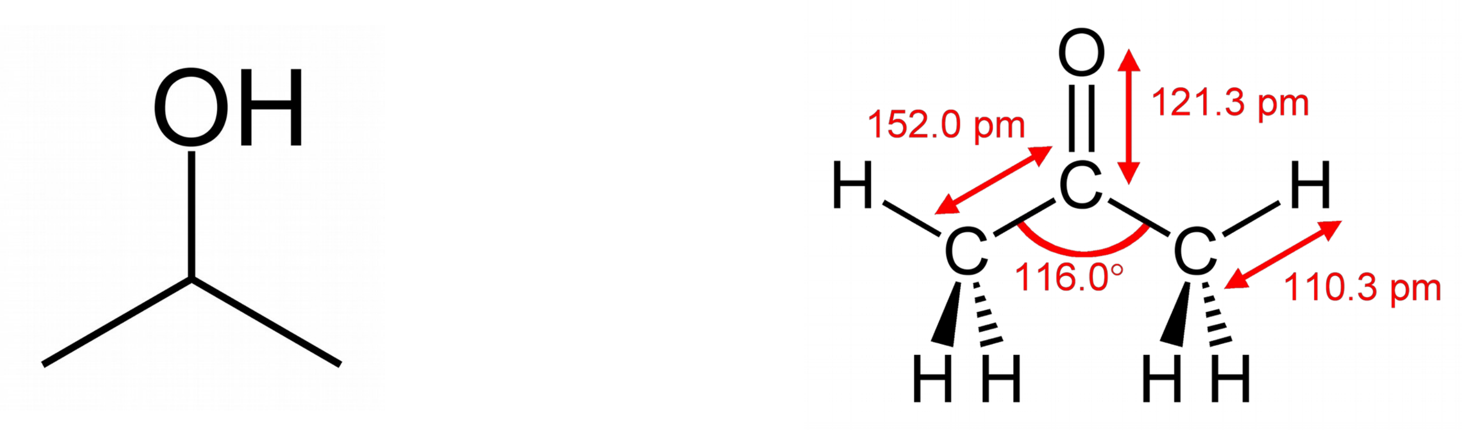


$$\begin{array}{c} CH_3 \\ | \\ CH_3-Si-CH_3 \\ | \\ CH_3 \end{array}$$

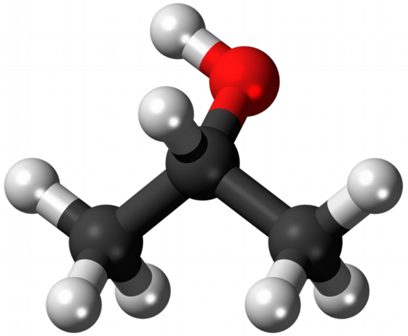
An advantage of δ to ν: it is independent of magnetic field

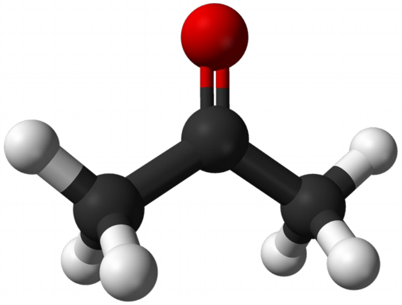
Examples:

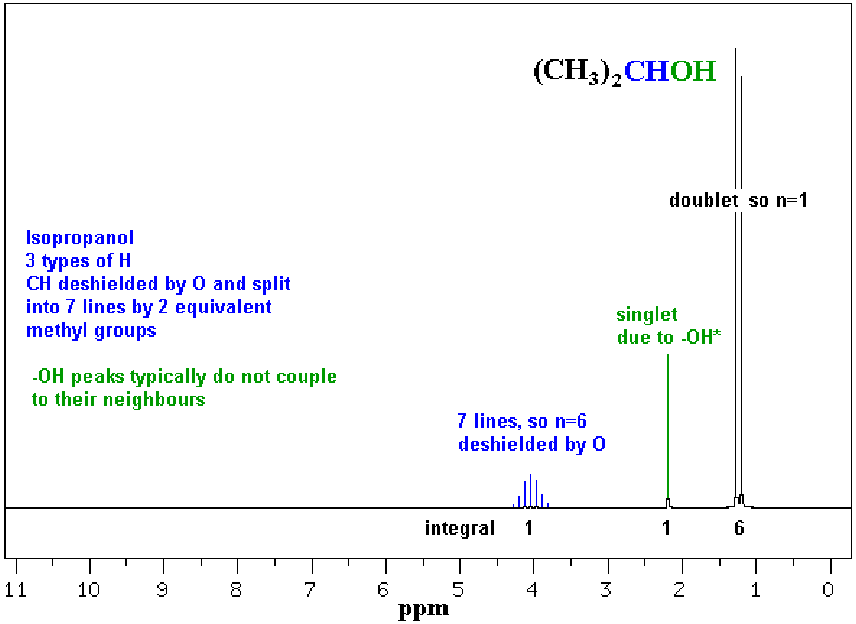
How many spectral lines can be found in the H^1 NMR spectrum of isopropanol or in the spectrum of acetone?



The set of chemical shifts of nuclei ^1H, ^{13}C is characteristic property of the functional groups.

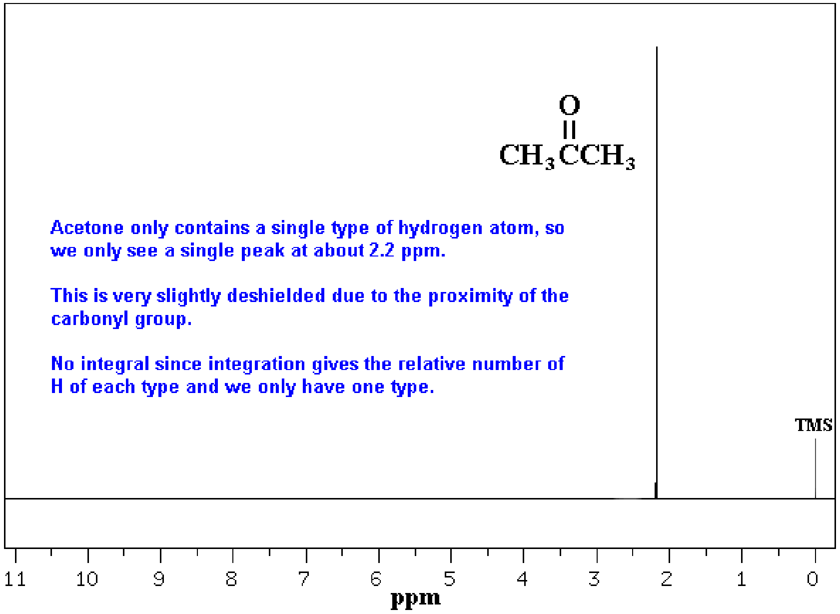






Isopropanol
3 types of H
CH deshielded by O and split into 7 lines by 2 equivalent methyl groups

-OH peaks typically do not couple to their neighbours



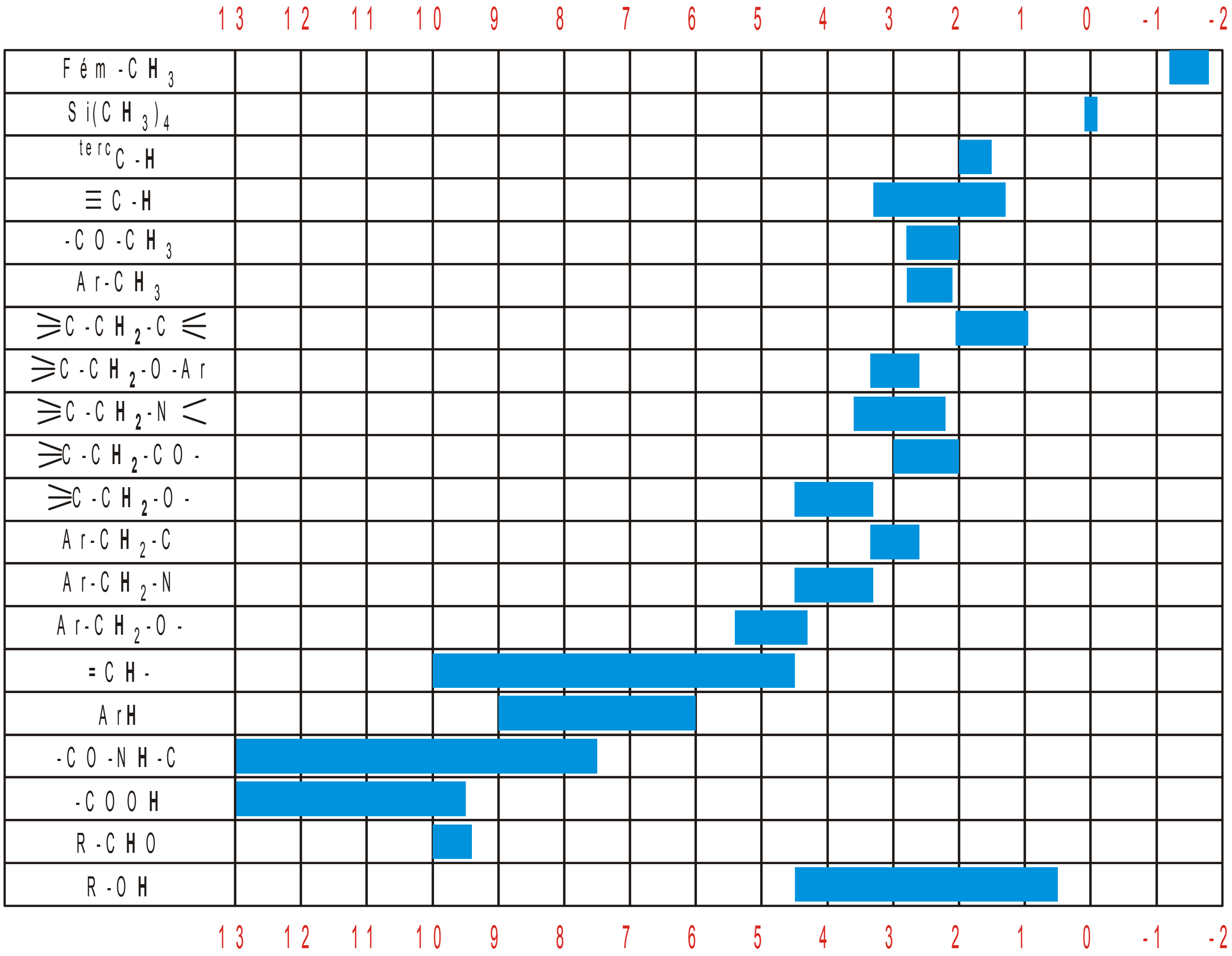
Acetone only contains a single type of hydrogen atom, so we only see a single peak at about 2.2 ppm.

This is very slightly deshielded due to the proximity of the carbonyl group.

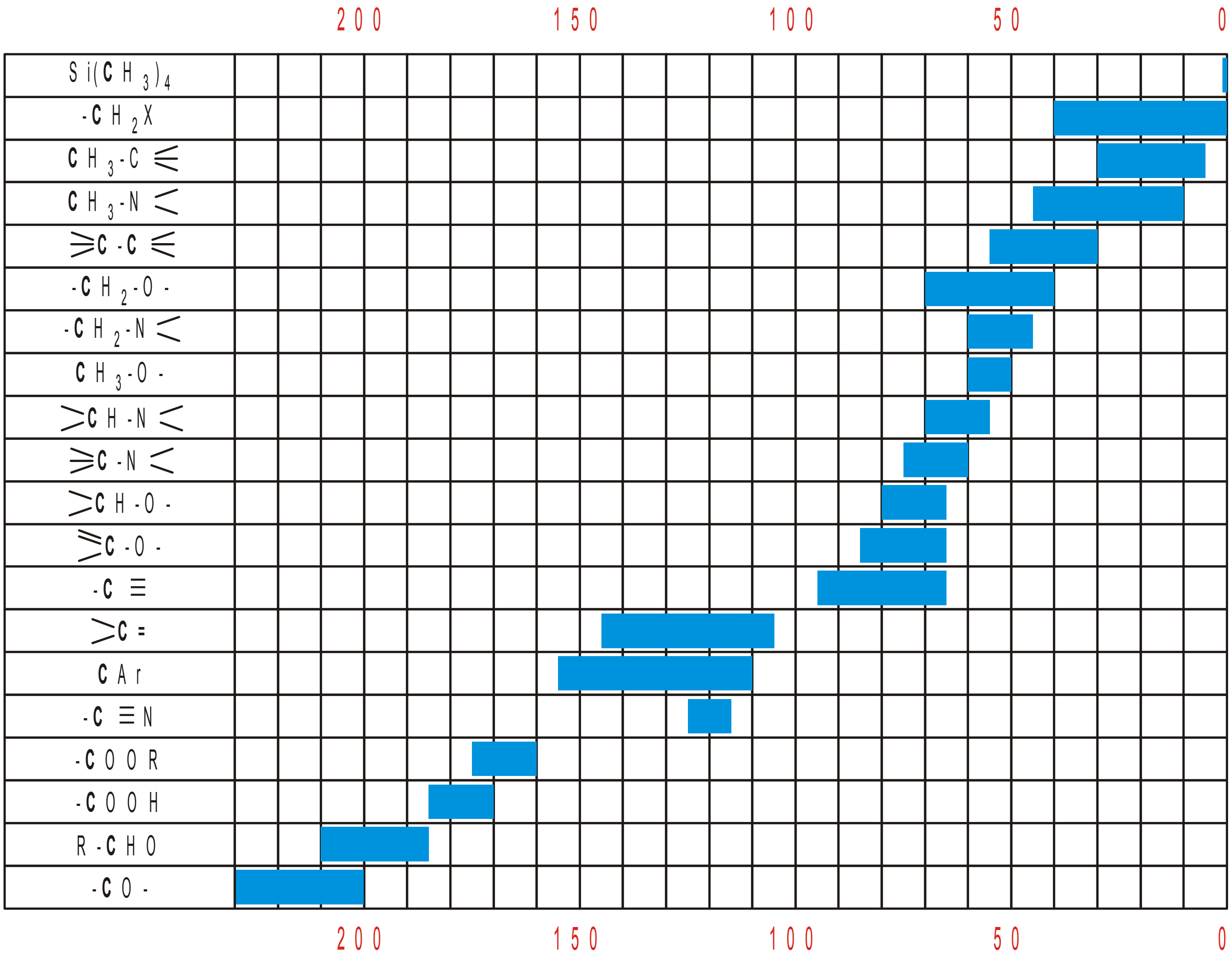
No integral since integration gives the relative number of H of each type and we only have one type.

http://www.mhhe.com/physsci/chemistry/carey/student/olc/graphics/carey04oc/ch13/figures/hiproh.gif

^{1}H chemical shifts



^{13}C chemical shifts

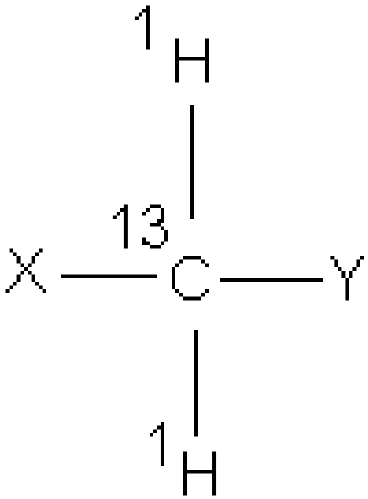


Properties of NMR spectrum II spin-spin coupling

Spin-spin coupling: interaction between the magnetic moments of the NMR-active nuclei of molecule.

→ Splitting of NMR bands.

Example:



In the ^{13}C spectrum peaks with 1:2:1 relative intensities due to the interaction of ^{13}C and the two ^{1}H nuclei.

The energy of ^{13}C in the CH_2 group with the spin-spin coupling:

$$E = -g^{^{13}C} M_I^{^{13}C} \mu_n^{^{13}C} |\vec{B}| + J^{\mathrm{CH}} M_I^{^{13}C} \left(M_I^{\mathrm{H}_1} + M_I^{\mathrm{H}_2} \right)$$

J^{CH} : C-H coupling constant

Excitation: $M_I^C = +\frac{1}{2} \rightarrow M_I^C = -\frac{1}{2}$

$$\Delta E = g^{^{13}C} \mu_n^{^{13}C} |\vec{B}| + J^{\mathrm{CH}} \left(M_I^{\mathrm{H}_1} + M_I^{\mathrm{H}_2} \right)$$

M_I^{H1}	M_I^{H2}	E^{CH}
+1/2	+1/2	+ J^{CH}
+1/2	-1/2	0
-1/2	+1/2	0
-1/2	-1/2	- J^{CH}

Coupling constant depends on

- the type of interacting atom pair (e.g., ^1H-^1H, ^1H-^{13}C, ^1H-^{19}F, ^{13}C-^{13}C coupling)
- the atomic distance
- the type of chemical bound

It does not depend on the magnetic field!

Units of coupling constant:

J^{CH}/h, J^{HH}/h, J^{CC}/h, etc.

[Hz]

Chemically equivalent nuclei:

- they are related by a symmetry operation of the molecule (same chemical shifts)

e.g., - 3 protons of CH_3,

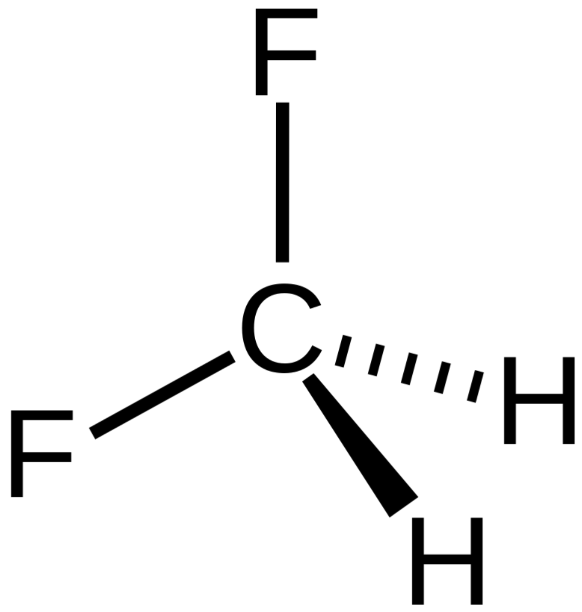
- 2 protons of CH_2.

Magnetically equivalent nuclei:

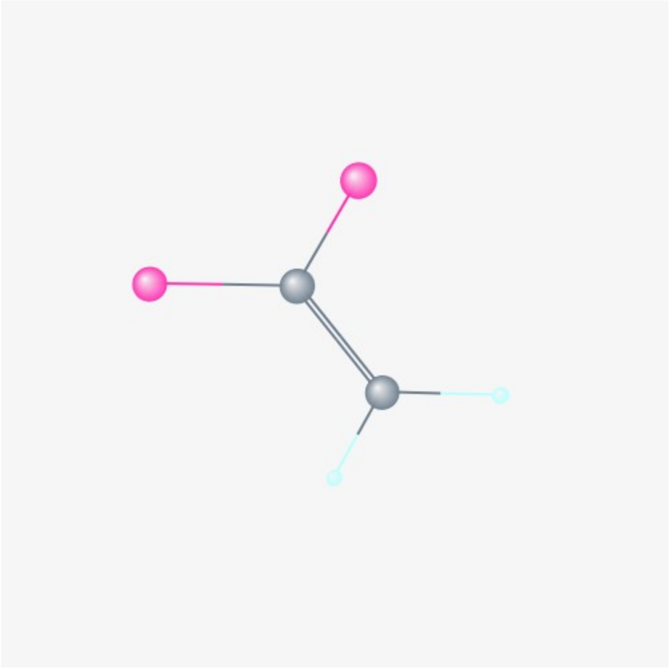
- Nuclei are magnetically equivalent if they have identical spin–spin interactions with any other nuclei in the molecule. Magnetically equivalent nuclei are chemically equivalent as well.

- Due to the rapid internal rotations the protons of the CH_3 group can be magnetically equivalent.

Difluoromethane and Vinylidene fluoride



The two H atoms are symmetrically connected to both F atoms, they are magnetically equivalent.



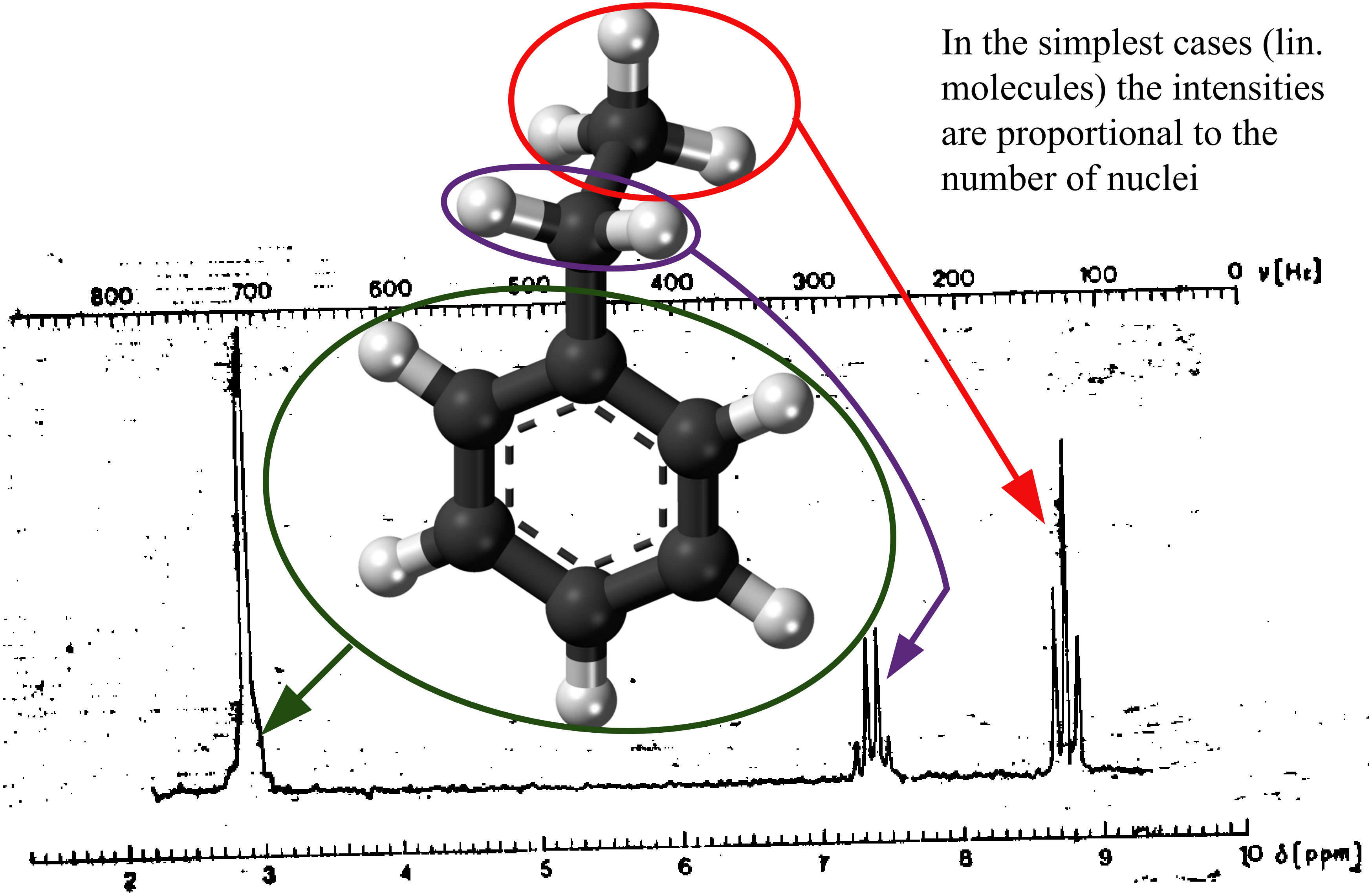
The two H atoms are chemically equivalent, but magnetically not.

Interpretation of NMR spectrum

Based on the chemical shifts and the spin-spin coupling

1st order spin-spin coupling: chemical shifts are much larger than the value of the spin-spin coupling constant. Simple interpretation.

^{1}H NMR spectrum of the Ethylbenzene



In the simplest cases (lin. molecules) the intensities are proportional to the number of nuclei

Rules of spin-spin coupling in the ^{1}H NMR spectra

- Interaction of magnetically equivalent protons bounded to the same carbon does not cause splitting.

- The spin-spin interaction between protons of neighboring carbons do cause well-detectable splitting.

- Interaction between protons far from each other is weak in the case of aliphatic compounds. The splittings due to these weak interactions are detectable only in high resolution measurements. Interactions of protons connected by conjugated C-C bounds is stronger.

^{1}H NMR spectrum of Ethylbenzene

Splittings in the spectrum of the CH_3 group (due to the CH_2 group)

$$\Delta E = g^{^1H} \mu_n^{^1H} |\vec{B}| + J^{H_1 H_2} \left(M_I^{H_1} + M_I^{H_2} \right)$$

M_I^{H1}	M_I^{H2}	E^{HH}
+1/2	+1/2	J^{HH}
+1/2	-1/2	0
-1/2	+1/2	0
-1/2	-1/2	$-J^{HH}$

1:2:1

^{1}H NMR spectrum of Ethylbenzene

Spitting of the band of CH_2 group (due to CH_3 group)

$$\Delta E = g^{^1H}\mu_n^{^1H}|\vec{B}| + J^{H_1H_2}\left(M_I^{H_1} + M_I^{H_2}\right)$$

M_I^{H1}	M_I^{H2}	M_I^{H3}	E^{HH}
+1/2	+1/2	+1/2	+3/2 J^{HH}
+1/2	+1/2	-1/2	+1/2 J^{HH}
+1/2	-1/2	+1/2	+1/2 J^{HH}
-1/2	+1/2	+1/2	+1/2 J^{HH}
+1/2	-1/2	-1/2	-1/2 J^{HH}
-1/2	+1/2	-1/2	-1/2 J^{HH}
-1/2	-1/2	+1/2	-1/2 J^{HH}
-1/2	-1/2	-1/2	-3/2 J^{HH}

→ **1:3:3:1**

The chemical formula of molecule can be obtained from the NMR spectrum.

Spin-spin interactions in the ^{13}C spectra

$$\Delta E = g^{^{13}C}\mu_n^{^{13}C}|\vec{B}| + J^{\mathrm{CH}}\left(M_I^{\mathrm{H}_1} + M_I^{\mathrm{H}_2}\right)$$

The bands of ^{13}C atoms are splitted by their hydrogen neighbors.

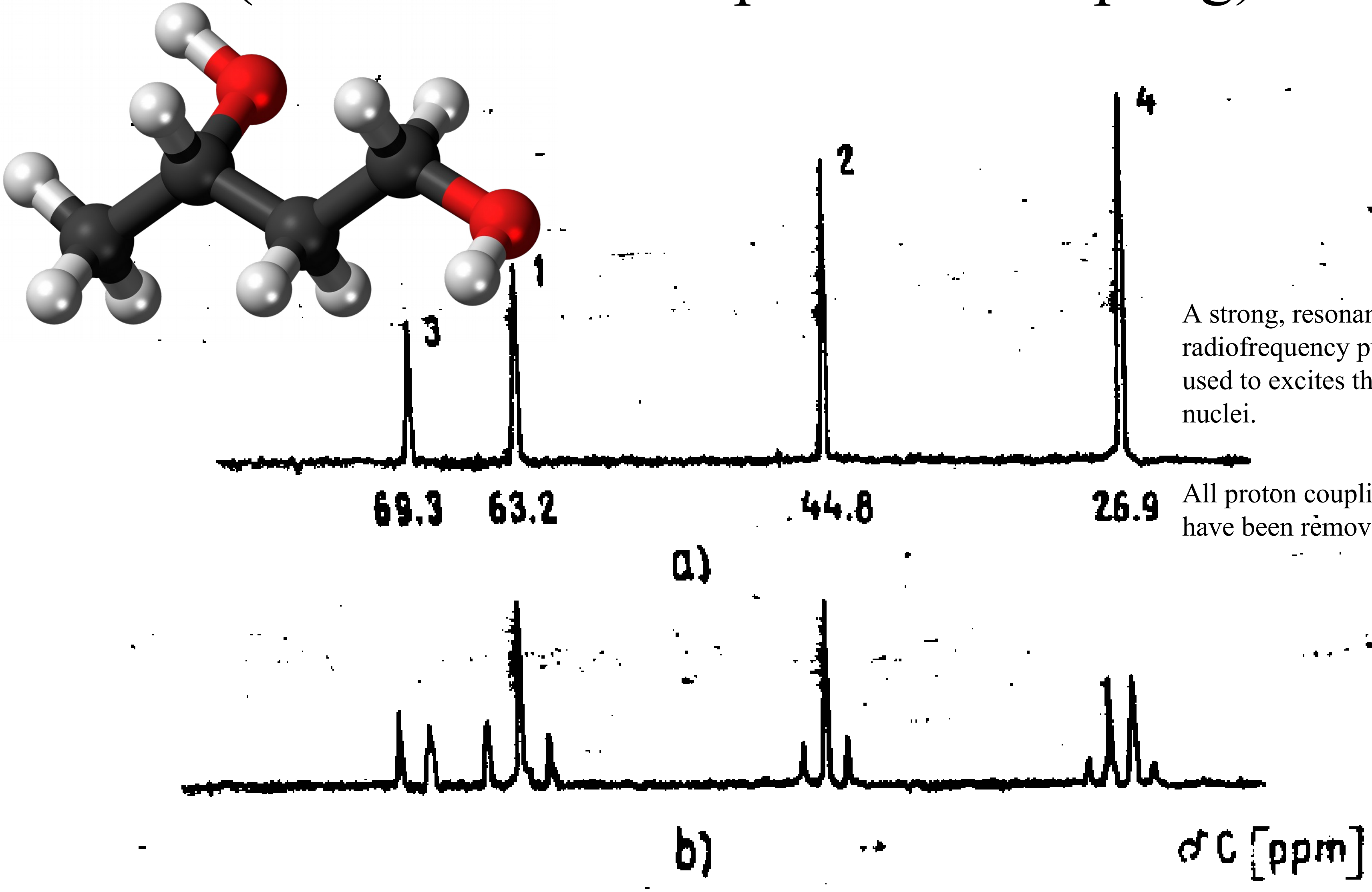
CH group 1:1 doublet

CH_2 group 1:2:1 triplet

CH_3 group 1:3:3:1 quartet

M_I^{H1}	M_I^{H2}	E^C
+1/2	+1/2	J^{CH}
+1/2	-1/2	0
-1/2	+1/2	0
-1/2	-1/2	$-J^{CH}$

^{13}C NMR spectrum of 1,3-butanediol (with and without proton decoupling)



A strong, resonant radiofrequency pulse is used to excites the H nuclei.

All proton couplings have been removed

NMR spectroscopy

In most of the cases solutions are studied.

Deuterated solvents: chloroform-d ($CDCl_{3)}$, aceton-D_6 (To avoid the absorption of protons, ^{1}H of the solvent are replaced by deuterium.)

TMS is also added.

The NMR signal is weak

^{1}H

$$|\vec{B}| = 1\,\text{T}$$

$$\frac{N\left(M_I = -\frac{1}{2}\right)}{N\left(M_I = +\frac{1}{2}\right)} = 0{,}999993$$

t = 25^{o}C

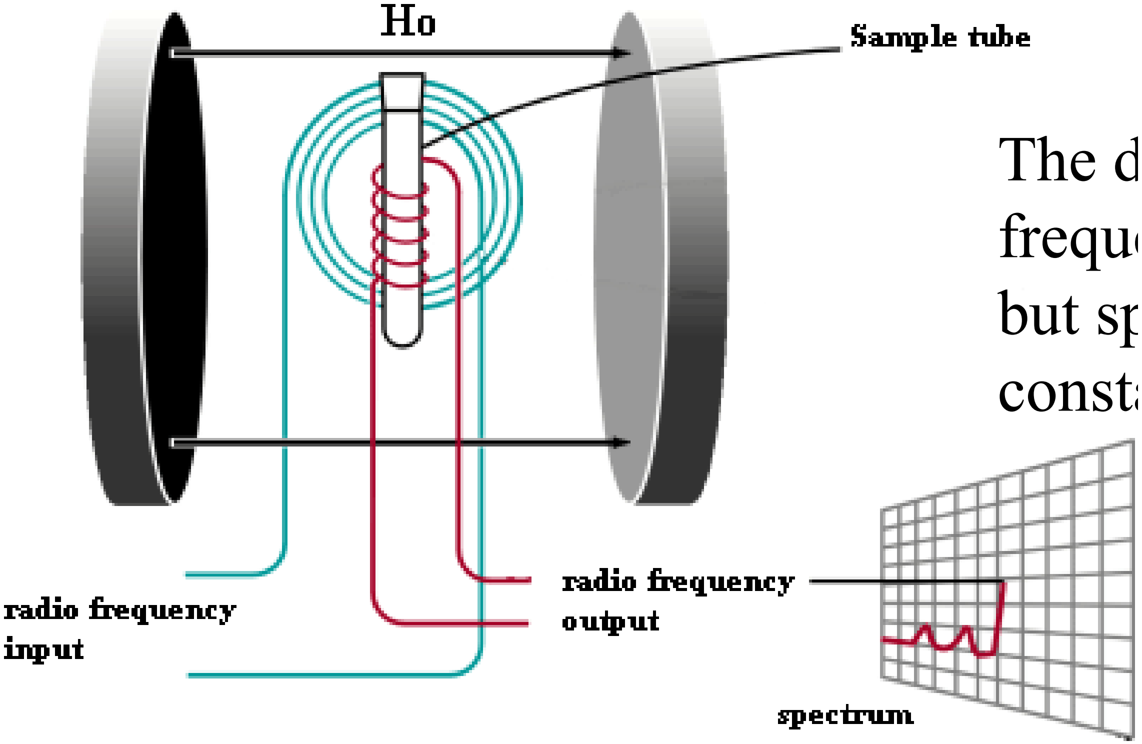
Reason: small excitation energy

The probability of the absorption and induced emission is almost the same.

Due to the excitations during the measurement shift this ratio closer to one.

Relaxation processes: nuclei return to the ground state in non-radiative processes.

NMR spectrometer

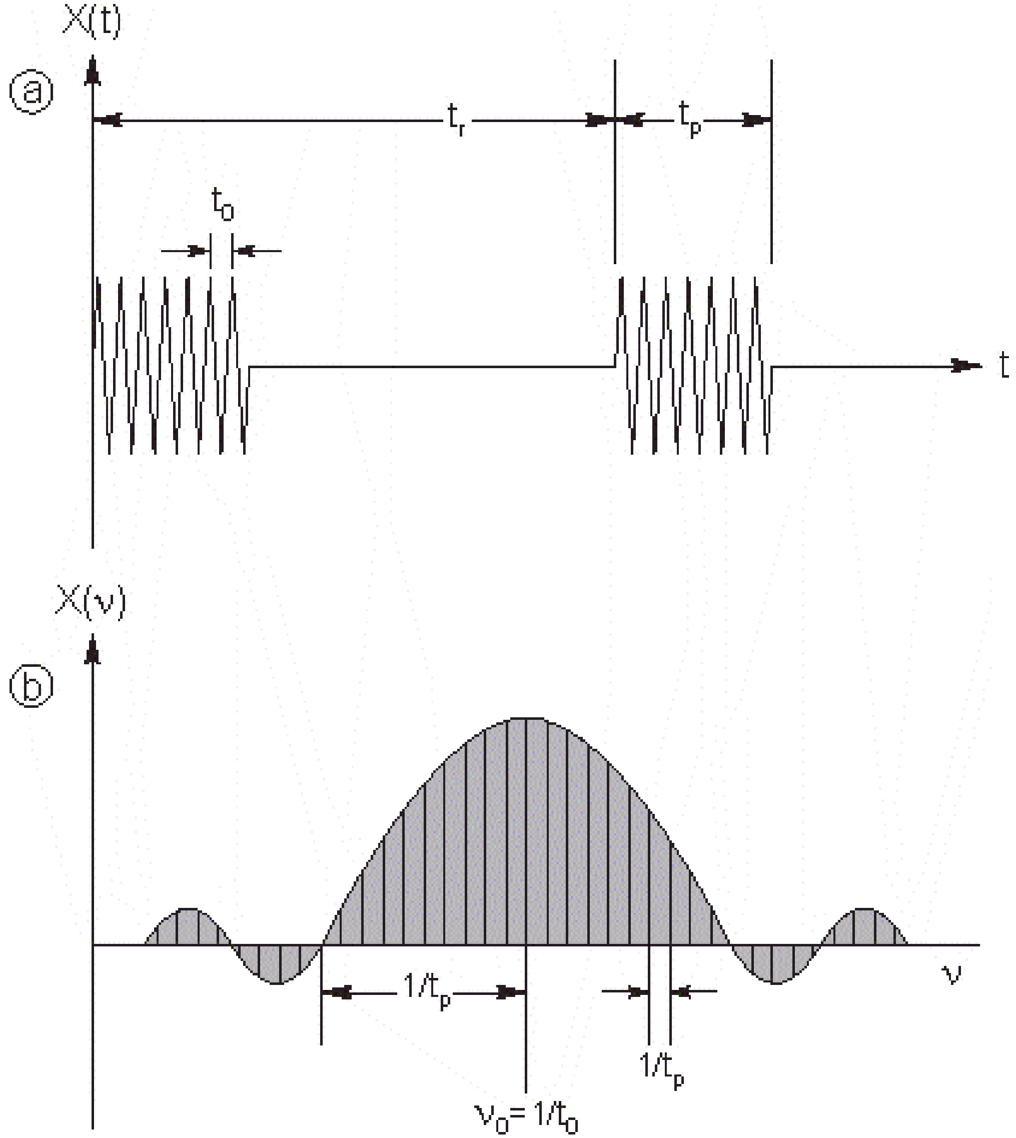


The difference in resonance frequencies increases with B, but spin–spin coupling constants are independent of it.

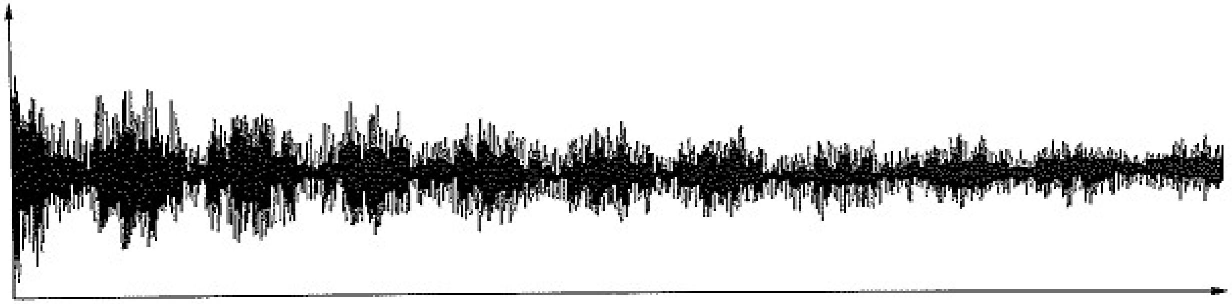
Strong magnetic field:
Many 1st order details

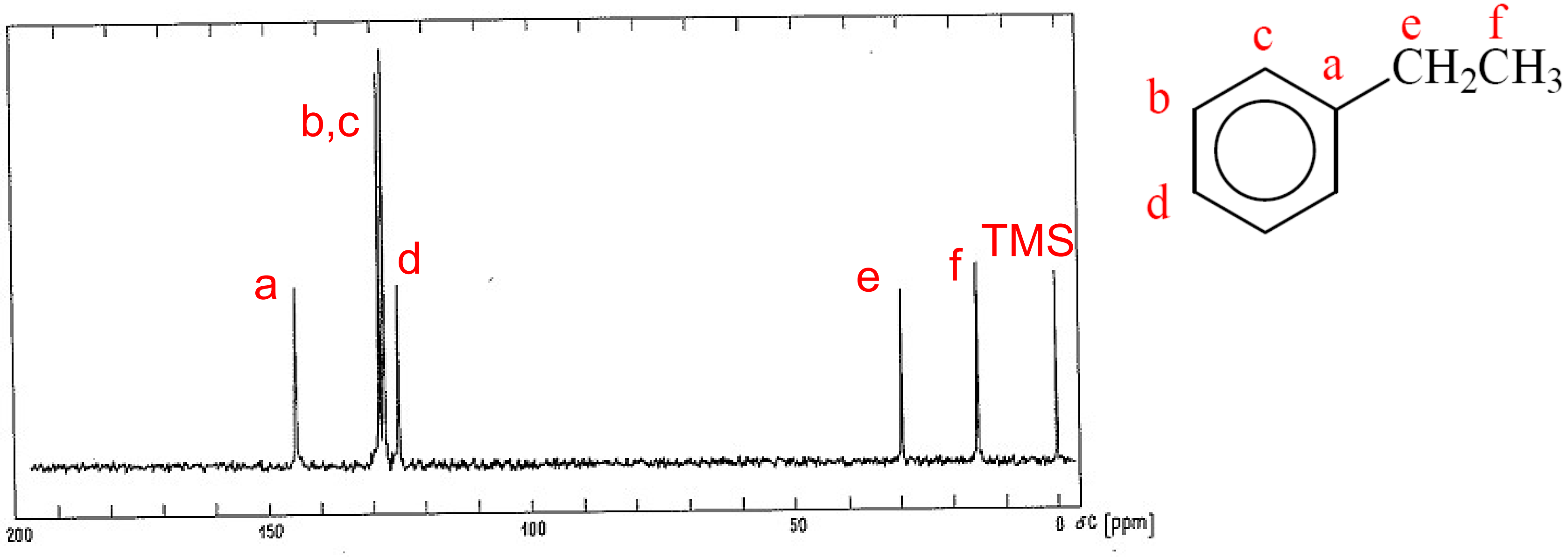
Pulse techniques in NMR:
FT-NMR

Excitation pulse sequence and its Fourier transform in FT-NMR

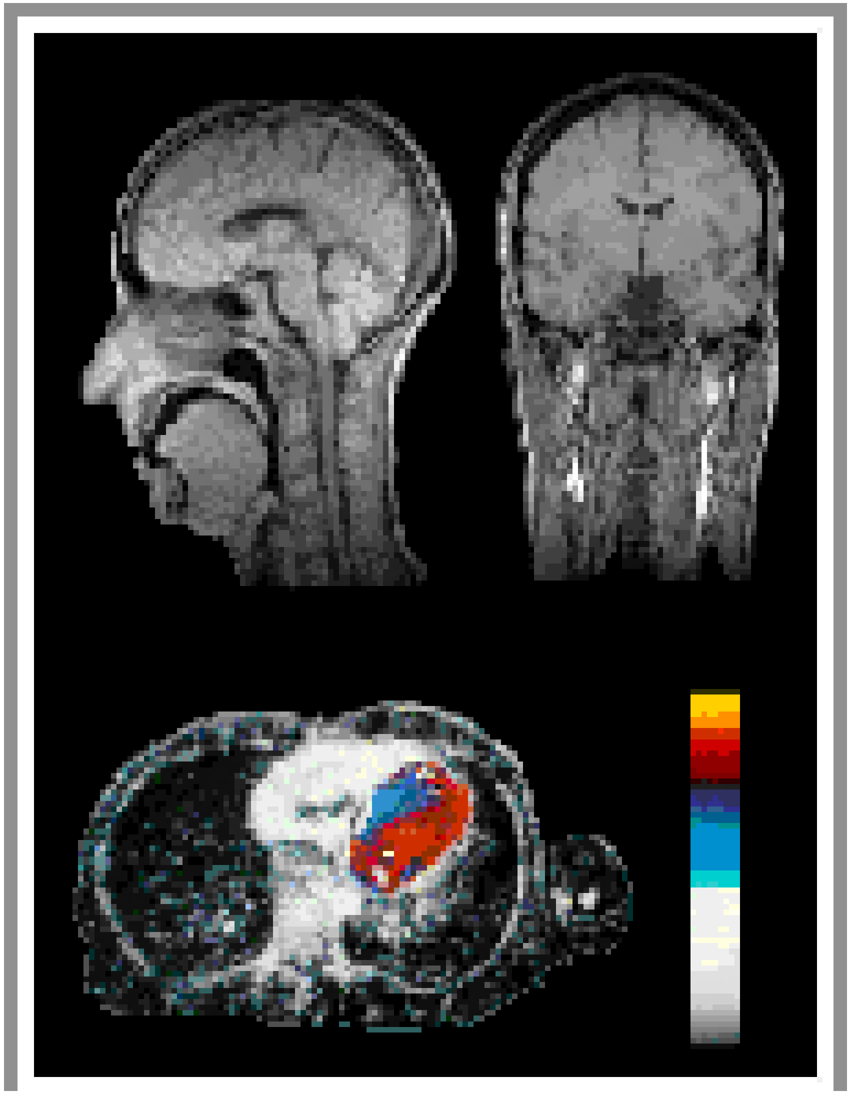


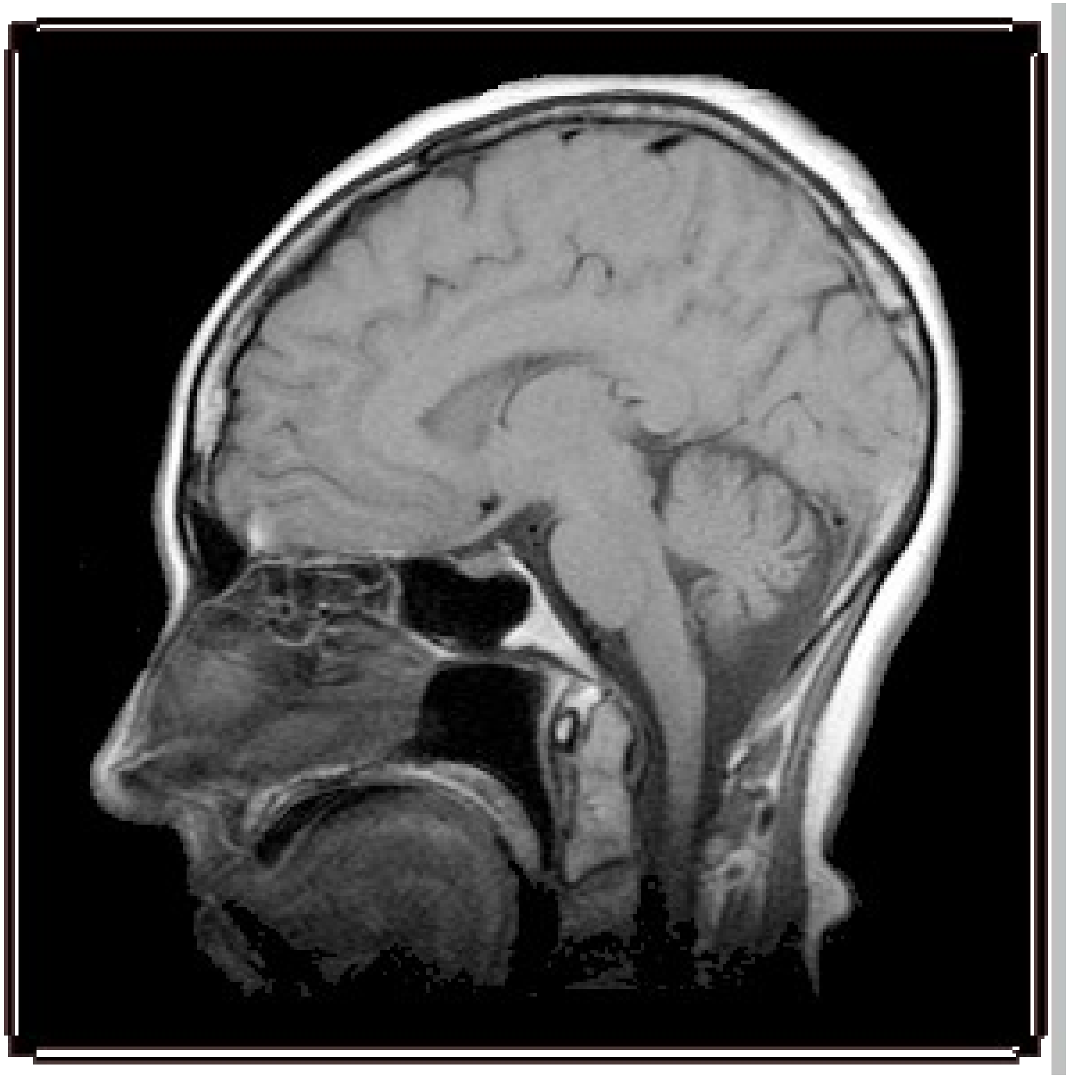
a) Free induction decay (FID) courve of ethylbenzene in deuteroacetone solution b) Fourier transform ^{13}C-NMR spectrum





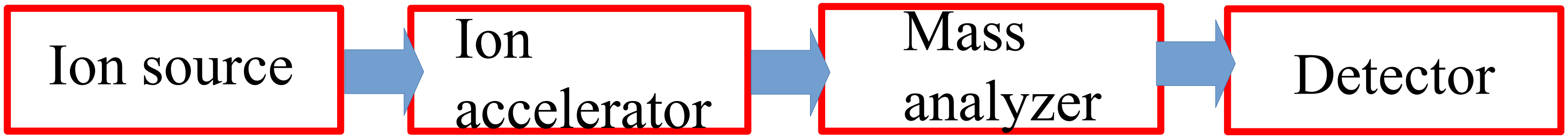
Magnetic resonance imaging



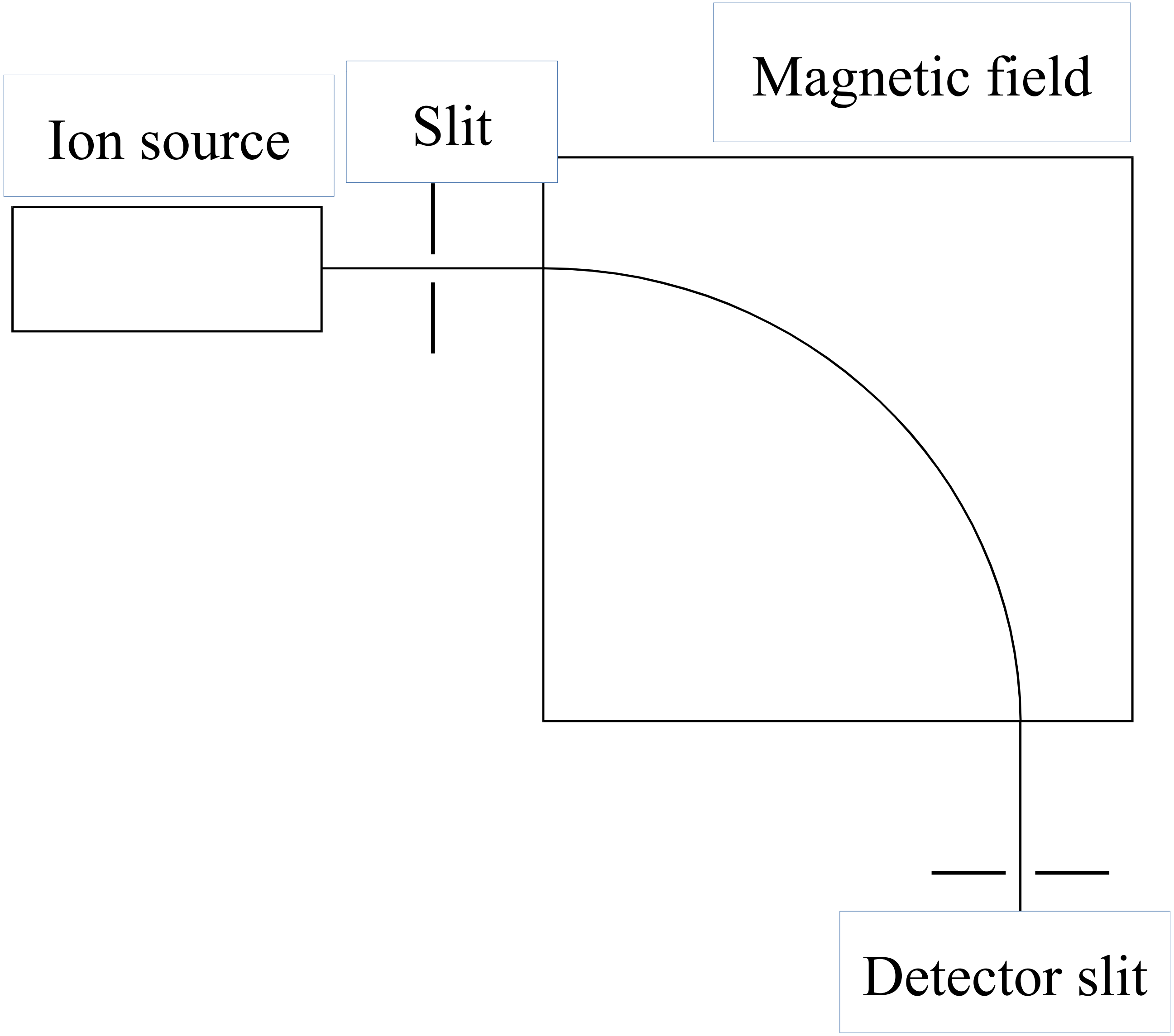


Mass spectrometry (MS)

- Separation of isolated, ionised particles according to the mass/charge ratio
- Main elementes of the mass spectrometer:



Single-focus mass spectrometer



Single-focus mass spectrometer:

Sample is ionized, ions are accelerated in electric field than separated in magnetic field.

Mass and charge of particles: m, e.

Voltage of acceleration: U

A kinetic energy: $\frac{1}{2}\mathrm{mv}^{2}=\mathrm{eU}$ ⇒ $v^{2}=\frac{2\mathrm{eU}}{m}$

Magnetic field is homogeneous

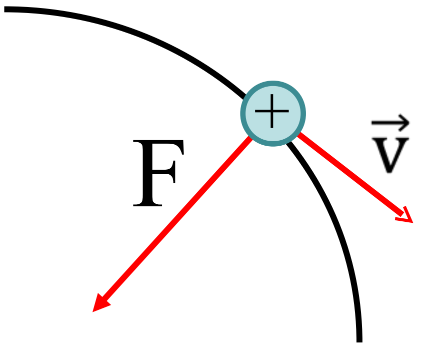
(The magnetic field is perpendicular to the velocity of entering particles.)

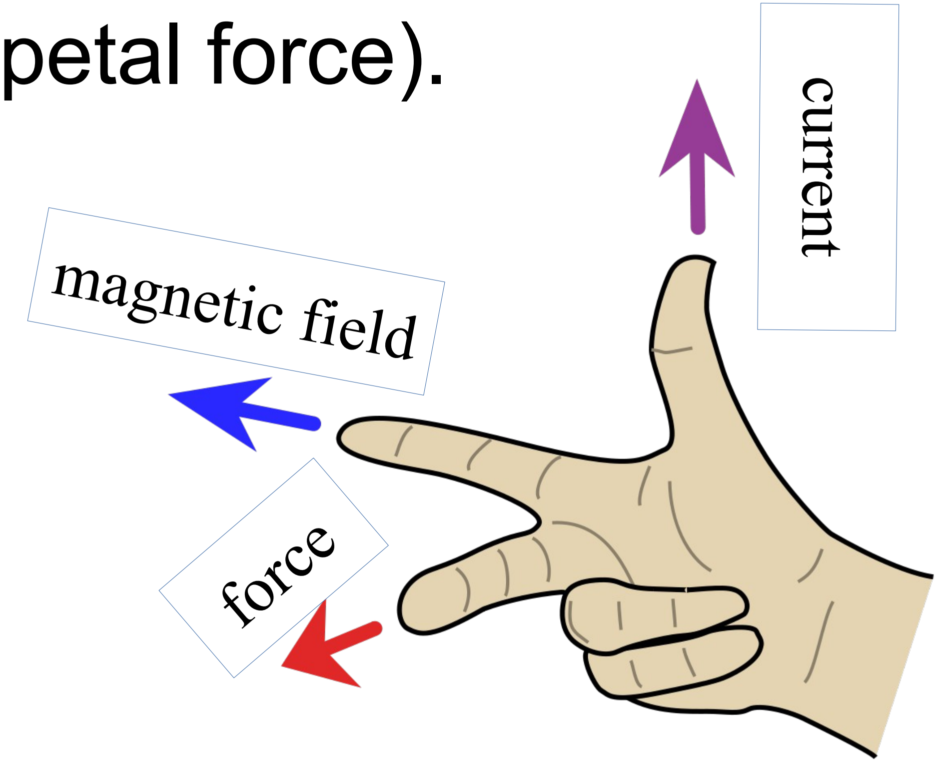
Lorentz force:

$$\vec{F} = e \cdot \vec{v} \times \vec{B}$$

e [As]: ionic charge
v [m/s]: speed of the ion
B [Tesla = N/Am = Vs/m^2]: magnetic field

Circular motion due to the force perpendicular to the velocity (centripetal force).





Right-hand rule

B: perpendicular to the sheet.

$$\frac{mv^2}{r} = B \cdot e \cdot v$$

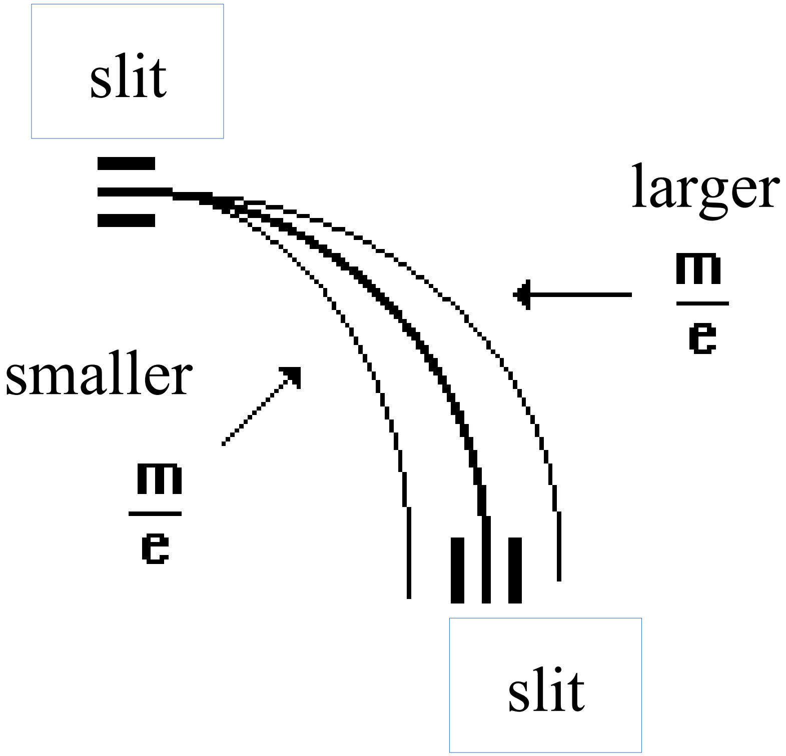
$$v = \frac{\mathrm{Ber}}{m}$$

$$v^2 = \frac{B^2 e^2 r^2}{m^2}$$

$$v^2 = \frac{2\mathrm{eU}}{m}$$

$$\boxed{\frac{m}{e} = \frac{B^2 r^2}{2U}}$$

Separation of charged particles in magnetic field



slit

larger $\frac{m}{e}$

smaller $\frac{m}{e}$

slit

Methods of ionization

a) Electron collision ionization

$$M + e^{-} \rightarrow M^{+} + 2\mathrm{e}^{-}$$ (positive ion)

$$M + e^{-} \rightarrow M^{-}$$ (negative ion)

The positive ions are more stable.

Fragmentation

The ions can further dissociate in parallel and consecutive reactions:

$$M^{+} \rightarrow A^{+} + B + \ldots$$

b) Chemical ionization: large quantity reagent gas (CH_4, NH_3, isobutan).

Mainly the reagent gases are ionized (most of the are MH^+) and collide the investigated molecules.

The spectrum is relatively simple.

c) Secondary Ion Mass Spectrometry, SIMS

Solid sample is bombarded by Ar^+ or O_2^+ ions.

Atoms and ions leave the surface. ➡

Method for investigation of surfaces.

d) Fast Atomic Bombardment (FAB)

Non volatile sample

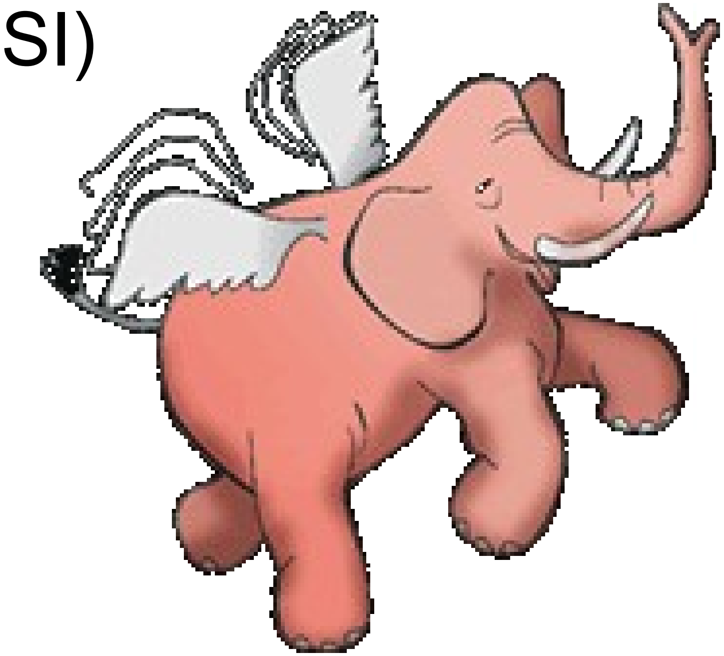
The sample is dissolved (e.g., in glycerol).

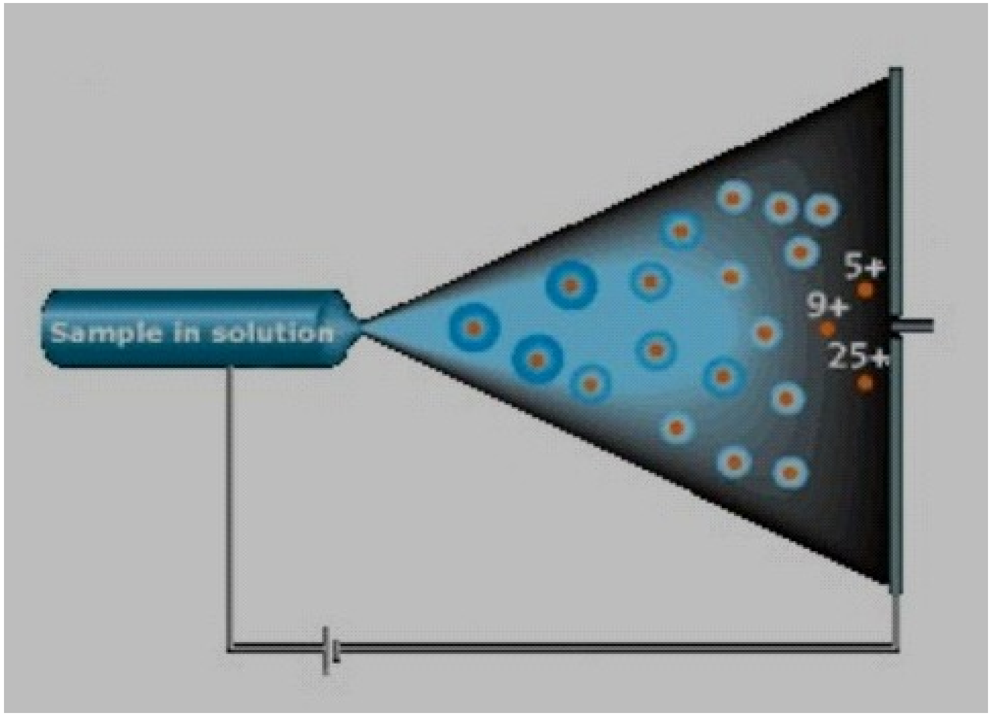
Bombardment with neutral atoms (Ar, Xe)

FAB can be applied for the study of biological and medical sample.

e)

Electrospray Ionisation (ESI)





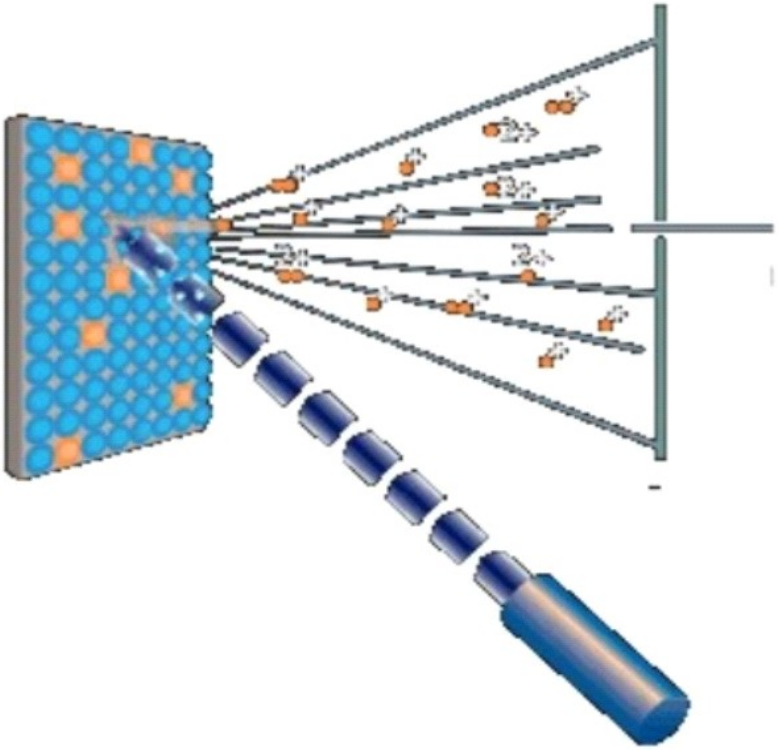
3000 V

Biological macromolecules in ionic vapor

Ion formation involves extensive solvent evaporation.

MALDI = matrix-assisted laser desorption-ionisation

matrix: aromatic acid



The sample is dissolved in a matrix material and applied to a metal surface.

A pulsed laser irradiates the sample, triggering ablation and desorption of the sample and matrix material.

The target molecules are Ionized.

resolution: $\frac{M}{\Delta M}$

M is the molar mass of ion, ΔM is the smallest detectable difference between two atomic mass values.

E.g., if the resolution is 500 than
  molecules with 1000 and 1002 atomic mass values can be separately detected, but the difference between 1000 and 1001 atomic mass values can not be seen.

Mass spectrometer configurations

Typical mass analyzers

a) Single-focus mass spectrometer (res:~100-1000)
b) Tandem mass spectrometry (res:~10000-100000)
c) Quadropul mass analyzers (fast!, res:~1000)
d) Time-of-flight spectrometry

Detector: electron multiplier

Applications of MS

a) Analytical tool

Molar mass

Quantitative analysis of gas mixes.

Identifying unknown compound

Isotopic composition

Can be combined with gaschromatograpy (GC-MS)

b) Structure of molecules

Types of peaks:

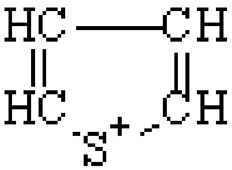
Molecular peaks

Fragment peaks $M^+ \rightarrow A^+ + B$

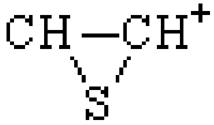
Multiply charged peaks $\frac{M}{2e}$ $\frac{M}{3e}$

Metastabe peaks (short living ions)

Thiophene

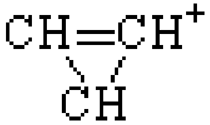


$-CH\equiv CH$



58

$-CHS$



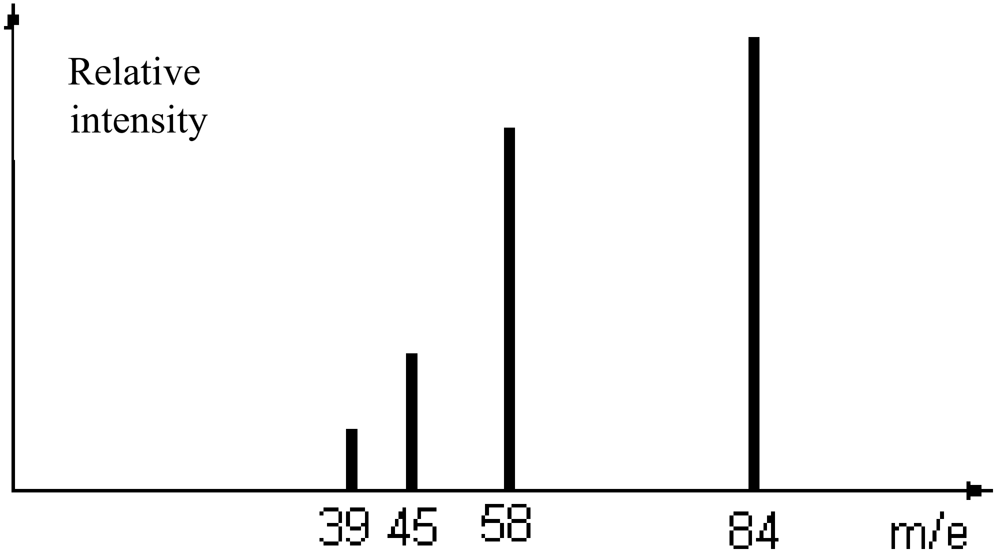
39

4*1+4*12+32=84

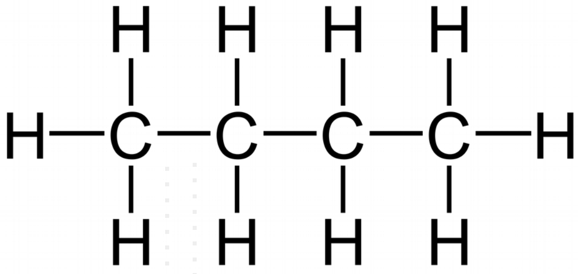
$-C_3H_3$

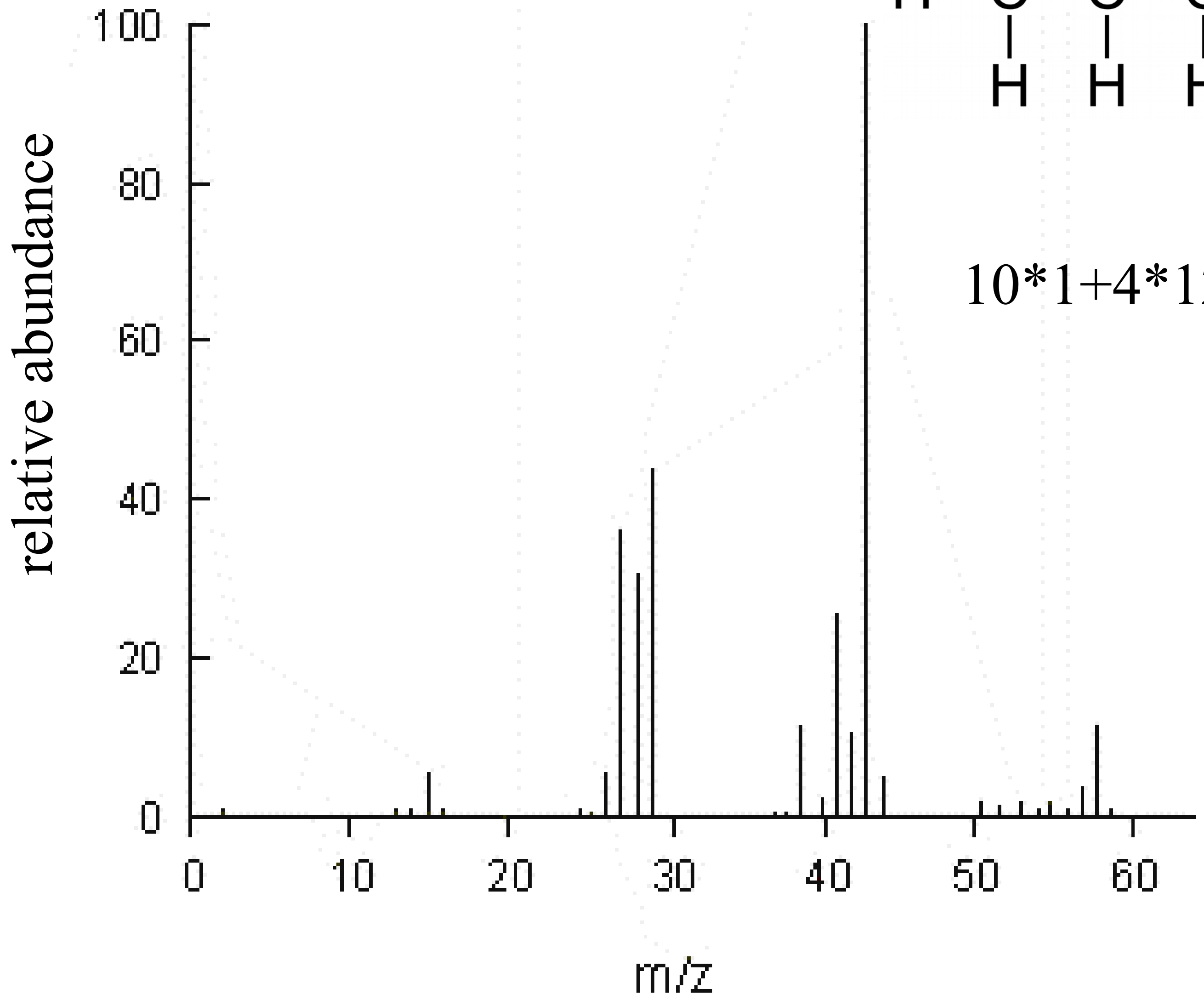
HCS^+

45



n-butane





10*1+4*12=58

n-butane

1) peak at m/e=58 has a relativelly small intensity

2) peak at m/e = 43 has the highest probability:
58-43 = 15, i.e., the CH_3 group has removed and the $C_3H_7^+$ ion is detected

3) small peak at m/e = 59, it is caused by the ^{13}C or ^{2}H isotopes (satelite peaks)

4) $C_2H_5^+$ / $C_4H_{10}^{2+}$ have the same m/e=29 value

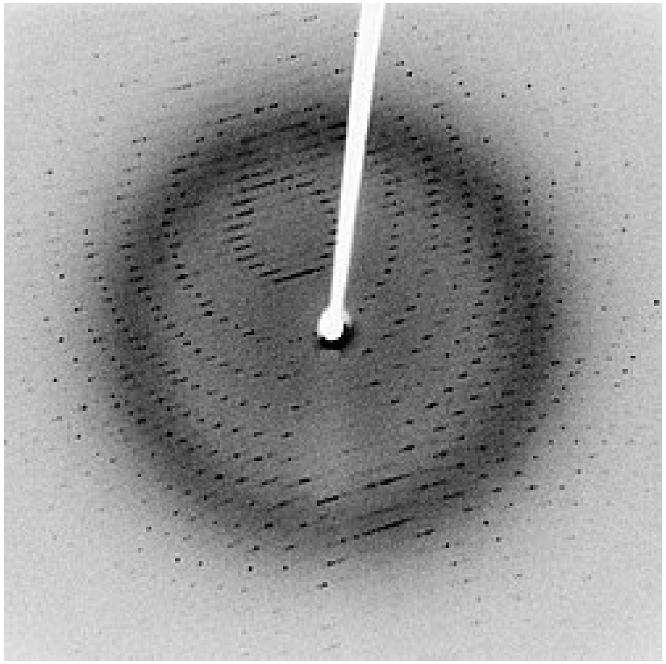
5) m/e = 25.5, 2*25.5=51, doubly charged ion.

c) Application in physical chemistry

Ionization potentials, molar heat of fragments, dissociation energies, reaction kinetics

Intensity is measured as a function of the energy of the bombarding electrons.

X-ray diffraction



X-ray diffraction pattern (reflections), protein sample (crystal)[wikipedia]

Molecular geometry

- Bound distancies, bound angles
- Conformation
- Configuration of chiral centers

Methods for determining molecular geometry

- Gas sample: microwave spectroscopy

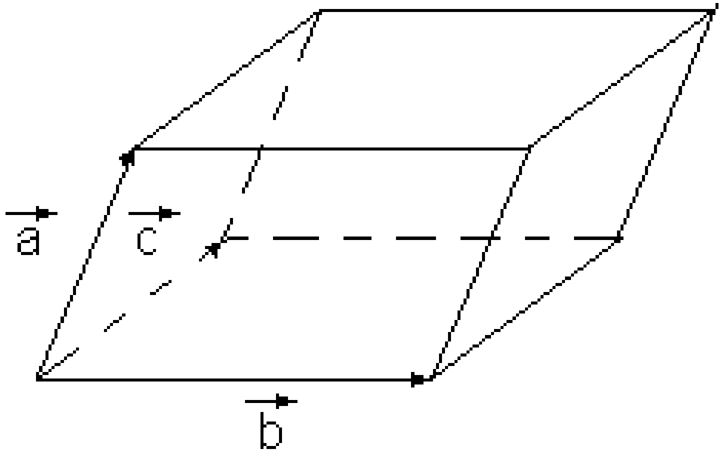
  rotational Raman-spectroscopy
- Solution: (NMR, conformation)

  (CD-spectroscopy, chiral centrums)
- Crystals: X-ray diffraction

Perfect crystals

Primitive cell

Parallelepiped



Lattice parameters:

a, b, c : edges

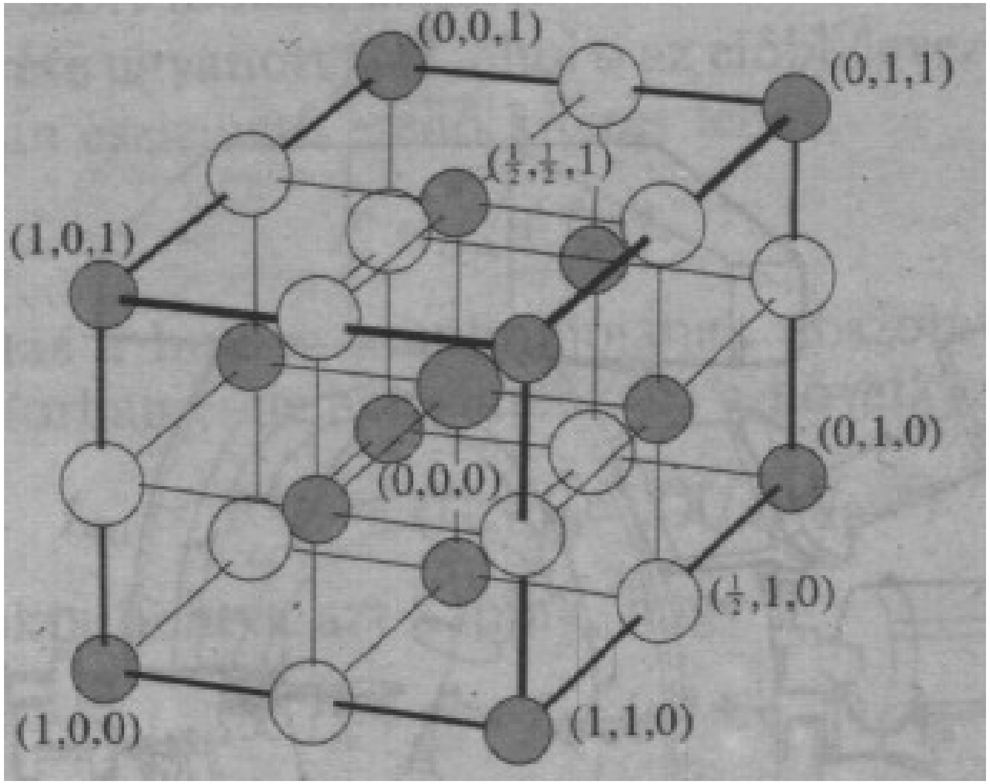
α, β, γ: angles.

Crystal structures

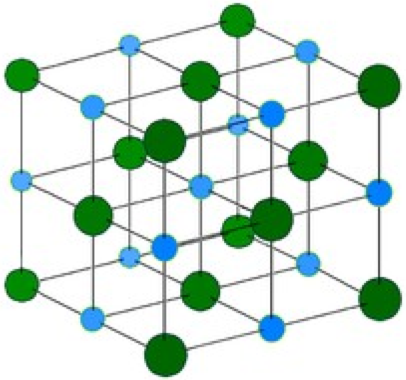
Crystal structures	Num. of independent parameters	Parameters
triclinic	6	$a \neq b \neq c, \alpha \neq \beta \neq \gamma$
monoclinic	4	$a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$
orthorombic	3	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
tetragonal	2	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
rhombohedral	2	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$
hexagonal	2	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$
cubic	1	$a = b = c, \alpha = \beta = \gamma = 90^\circ$

Position of an atom in the primitive cell

$$\vec{r}_n = x_n \vec{a} + y_n \vec{b} + z_n \vec{c}$$



NaCl crystal



Crystal lattice

Lattice point: assigned to one or more atoms, molecules, or ions.

Translation vectors which shift the lattice points to equivalent lattice points:

$$\vec{t} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

$\vec{a}, \vec{b}, \vec{c}$: elementary translation vectors which keep the lattice invariant.

n_1, n_2, n_3 : integers

The X-ray diffraction experiment

Aim of a X-ray diffraction measurment:

to obtain the crystal structures, i.e, to access

- the parameters of the primitive cell
- the positions of atoms in the primitive cell

The X-ray diffraction

On the crystal sample the X-ray radiation scatters ellastically. The interference of scattered radiation can be detected.

(The wavelenght of the X-ray radiation is comperable to the lattice parameters a, b, c leading to interference picture.)

Most important methods:

- methods to obtain the lattice parameters:

  - Debye-Scerrer method : monochromatic radiation scatters on powder sample
  - Laue method: polychromatic radiation scatters on powder sample

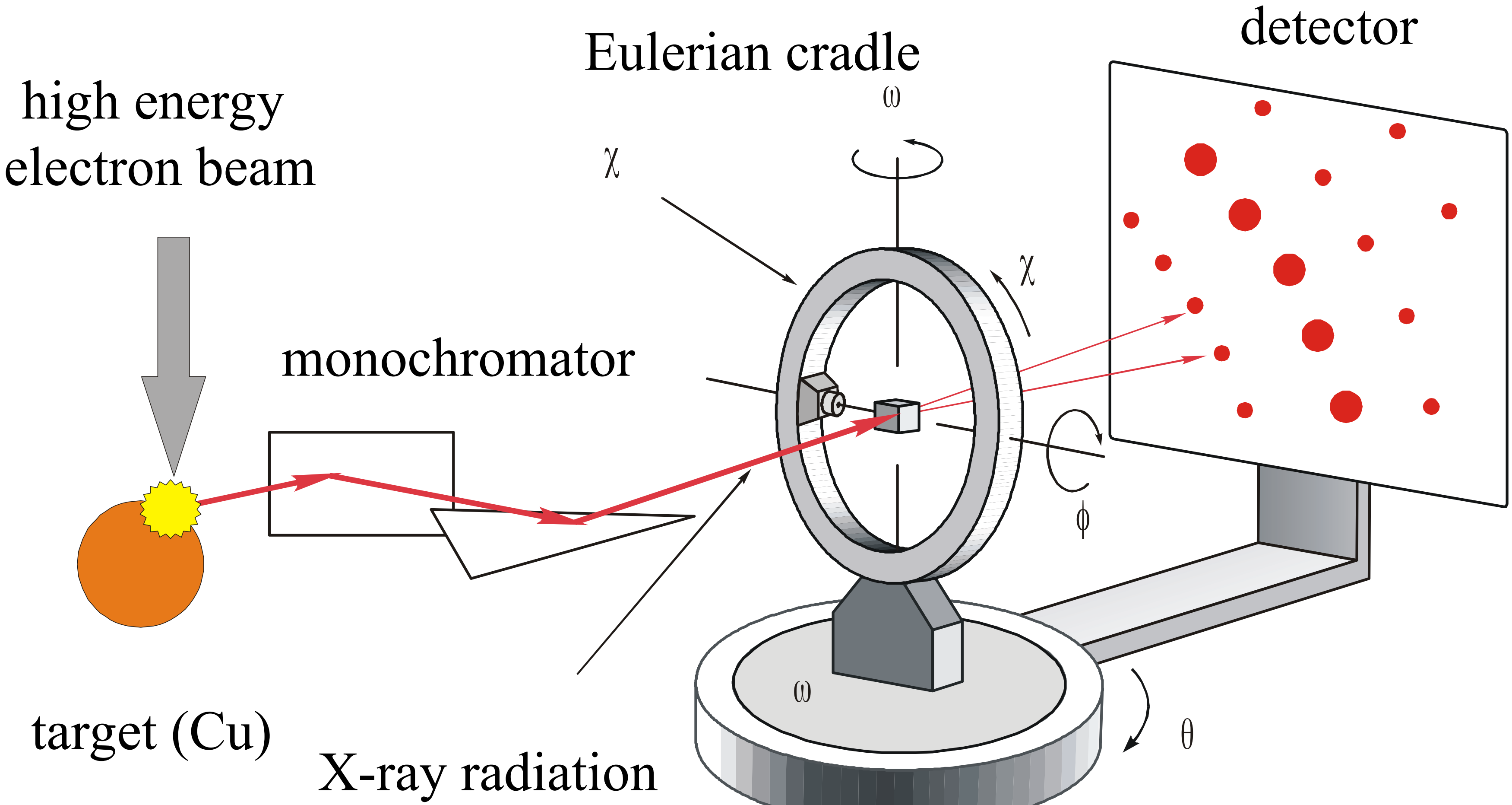
- to have the lattice parameters and the atomic positions

  - rotating crystal method: monochromatic radiation scatters on crystals

The X-ray radiation scatters on the electrons.

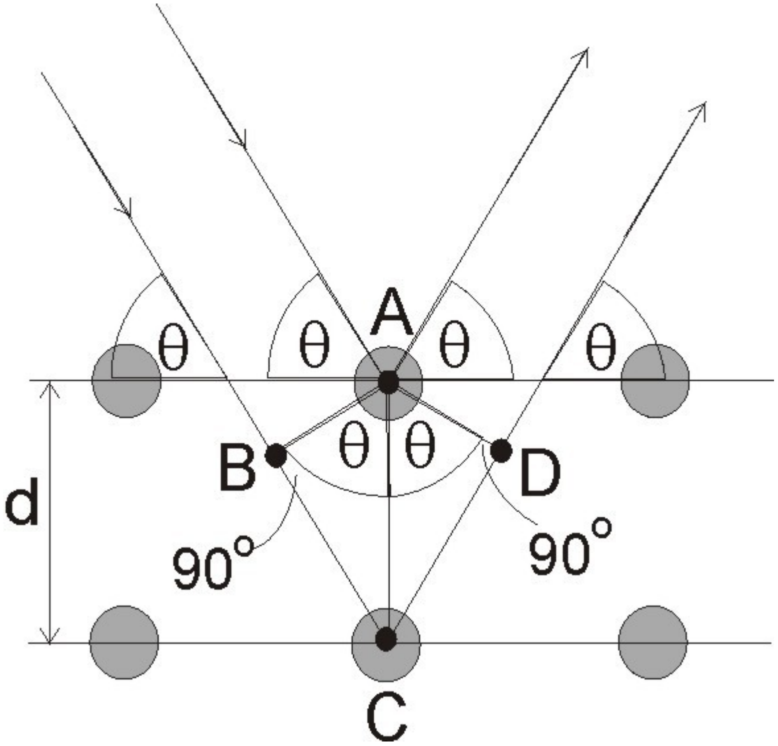
Scattering on the nuclei is negligible.

X-ray diffraction instrument for rotating crystal experiments



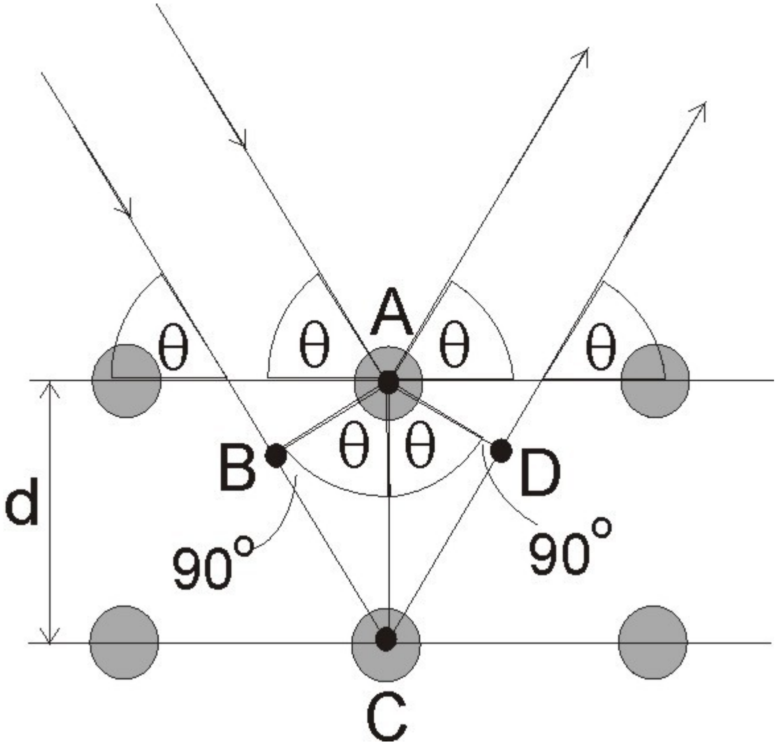
Lattice parameters

Reflection from two atomic crystal layers



$$\overline{BC}=\overline{CD}=d\sin\theta$$

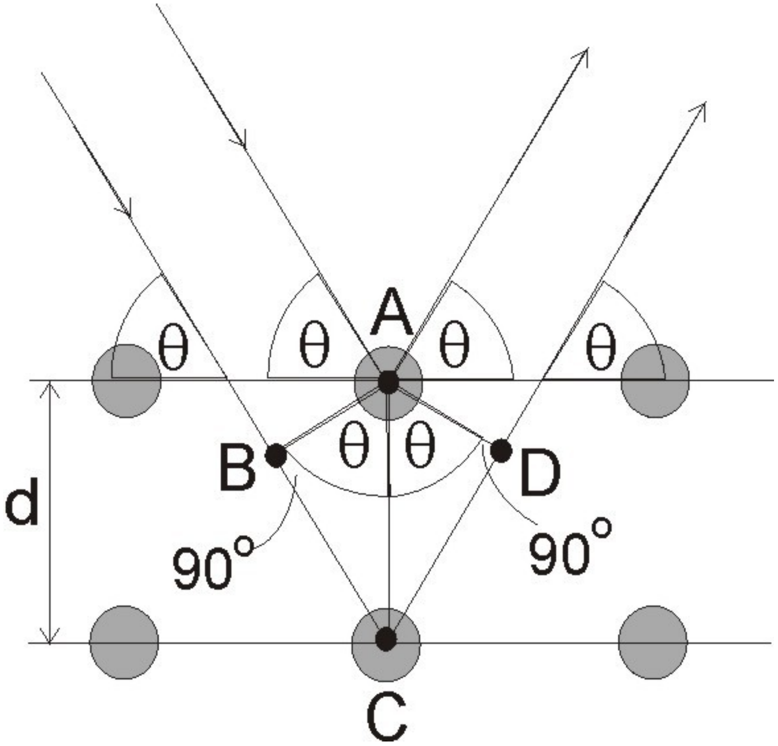
Condition of constructive interference



$$\overline{BC}+\overline{CD}=2d\sin\theta=n\lambda$$

Bragg equatition

Example: orthorombic crystal



d = a

$$2a\sin\theta_1^a = \lambda$$

$$2a\sin\theta_2^a = 2\lambda$$

$$2a\sin\theta_3^a = 3\lambda$$

….

Example: orthorombic crystal

Bragg equation

d = a

$$2a\sin\theta_1^a = \lambda$$

$$2a\sin\theta_2^a = 2\lambda$$

$$2a\sin\theta_3^a = 3\lambda$$

….

d = b

$$2b\sin\theta_1^b = \lambda$$

$$2b\sin\theta_2^b = 2\lambda$$

$$2b\sin\theta_3^b = 3\lambda$$

….

d = c

$$2c\sin\theta_1^c = \lambda$$

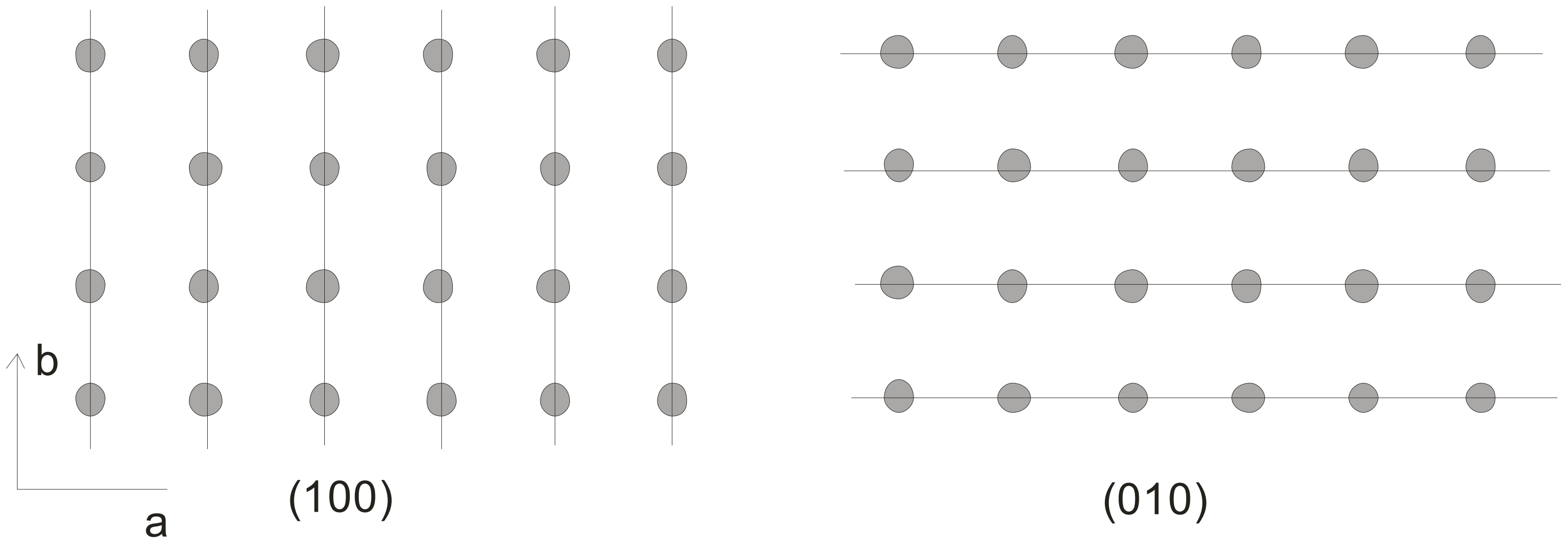
$$2c\sin\theta_2^c = 2\lambda$$

$$2c\sin\theta_3^c = 3\lambda$$

….

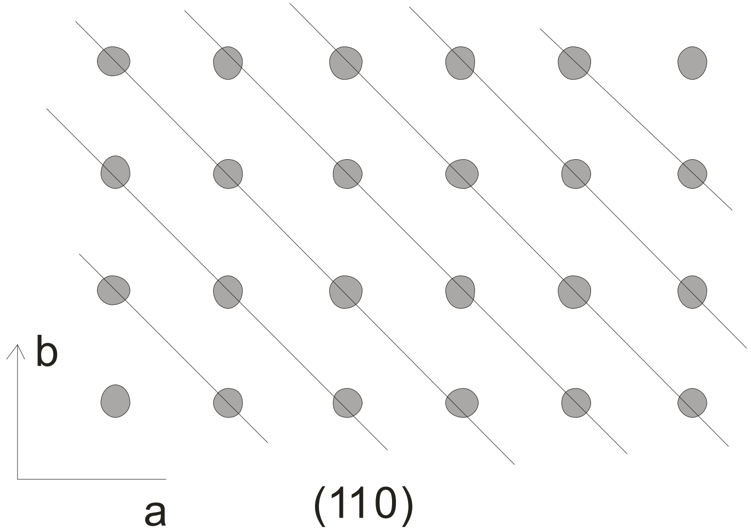
Example: orthorombic crystal

Lattice plain I.
(Miller indices)



Example: orthorombic crystal

Lattice plain II.
(Miller indices)



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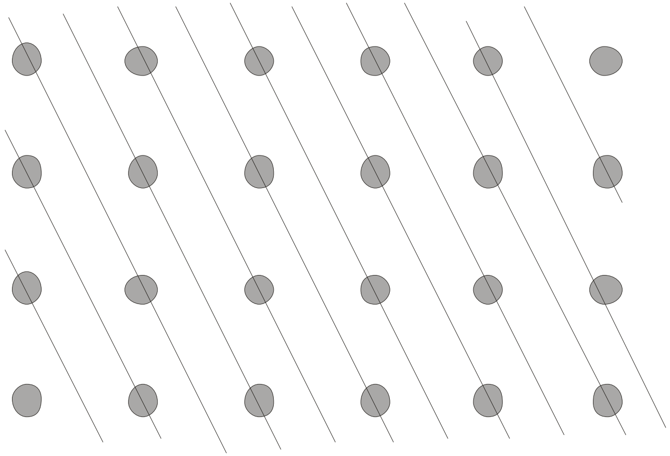


(210)

Example: orthorombic crystal

Distance of lattice plains

$$\frac{1}{d_{\mathrm{hk}\,\ell}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{\ell^2}{c^2}$$

$$\boxed{2\,d_{hkl}\sin\theta = \lambda}$$

When not all the lattice angles are 90° than dhkl depents on the lattice angles too.

The lattice parameters can be obtained from the directions of the diffraction maxima (reflections).

At most 6 parameters: 6 reflections is enough to determine the lattice parameters.

Atomic positions

The atomic positions can be obtained from the relative intensities of reflections.

Intensities

1. Model: spherically symmetric atoms (effect of valence electrons is neglected).
Steps of derivation:

 1.a Scattering on an isolated atom

 1.b Scattering on primitive cell

 1.c Scattering on 3D crystal

2. Model: distribution of electrons is not spherically symmetric

Intensity of the scattering on a crystal of spherically symmetric atoms

$$I = |F_{\mathrm{hk}\ell}|^2$$

$\mathrm{F}_{\mathrm{hk}\ell}$ is (hkℓ) scattering amplitude of the plain, it is the so-called structure factor.

For a set of particle it is a sum of scattering amplitudes times a phase factors: $F = \sum_i f_i \exp(i\phi_i)$

ϕ_i quantities describe the phase differences due to the different optical path lengths.

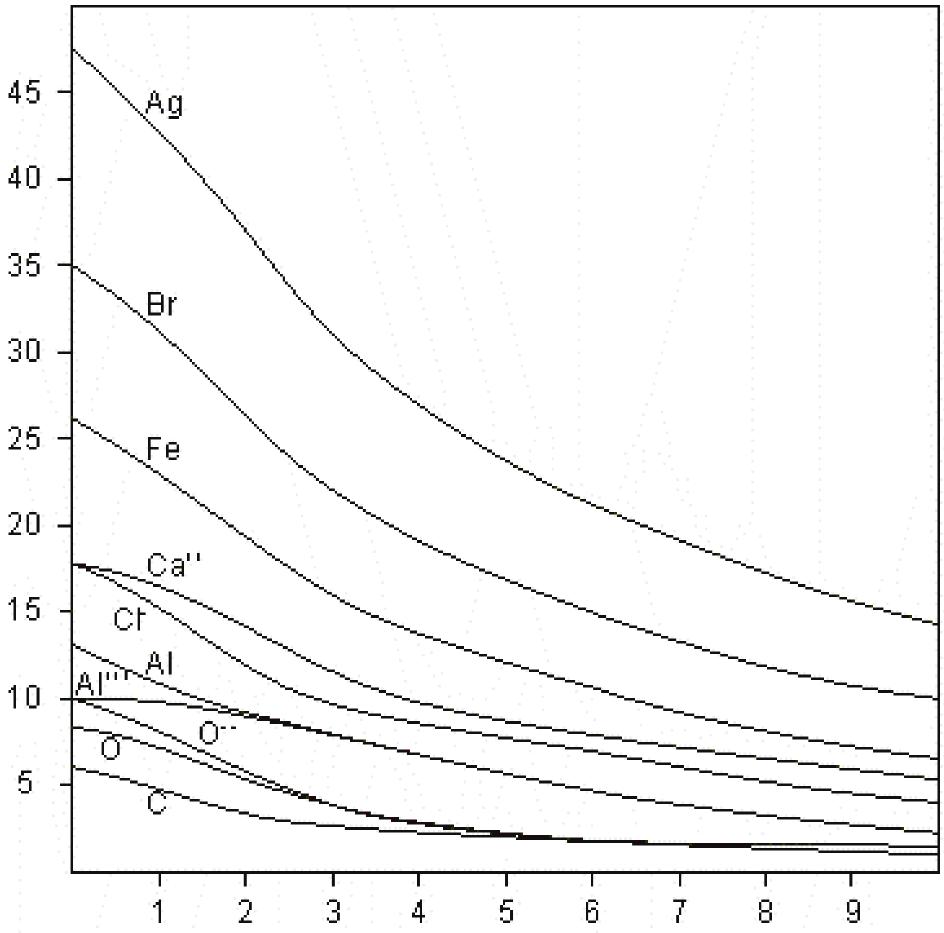
Structure factor

$$F_{\mathrm{hk}\ell}=\sum_n f_n \exp\left[2\mathrm{i}\pi\left(\mathrm{h}\mathrm{x}_n+\mathrm{k}\mathrm{y}_n+\ell \mathrm{z}_n\right)\right]$$

x_n, y_n, z_n are the atomic coordinates of the primitive cell

f_n is the scattering factors of the n^{th} atom.

Atomic scattering factor



$$f=\int \rho(\boldsymbol{r})\exp(\mathrm{i}\,\phi(\boldsymbol{r}))\,d\tau$$

Spherically symmetric charge distribution is supposed

$$f(\theta)=4\pi\int_0^\infty \rho(r)\frac{\sin(\mathrm{kr})}{\mathrm{kr}}r^2\,\mathrm{dr}$$

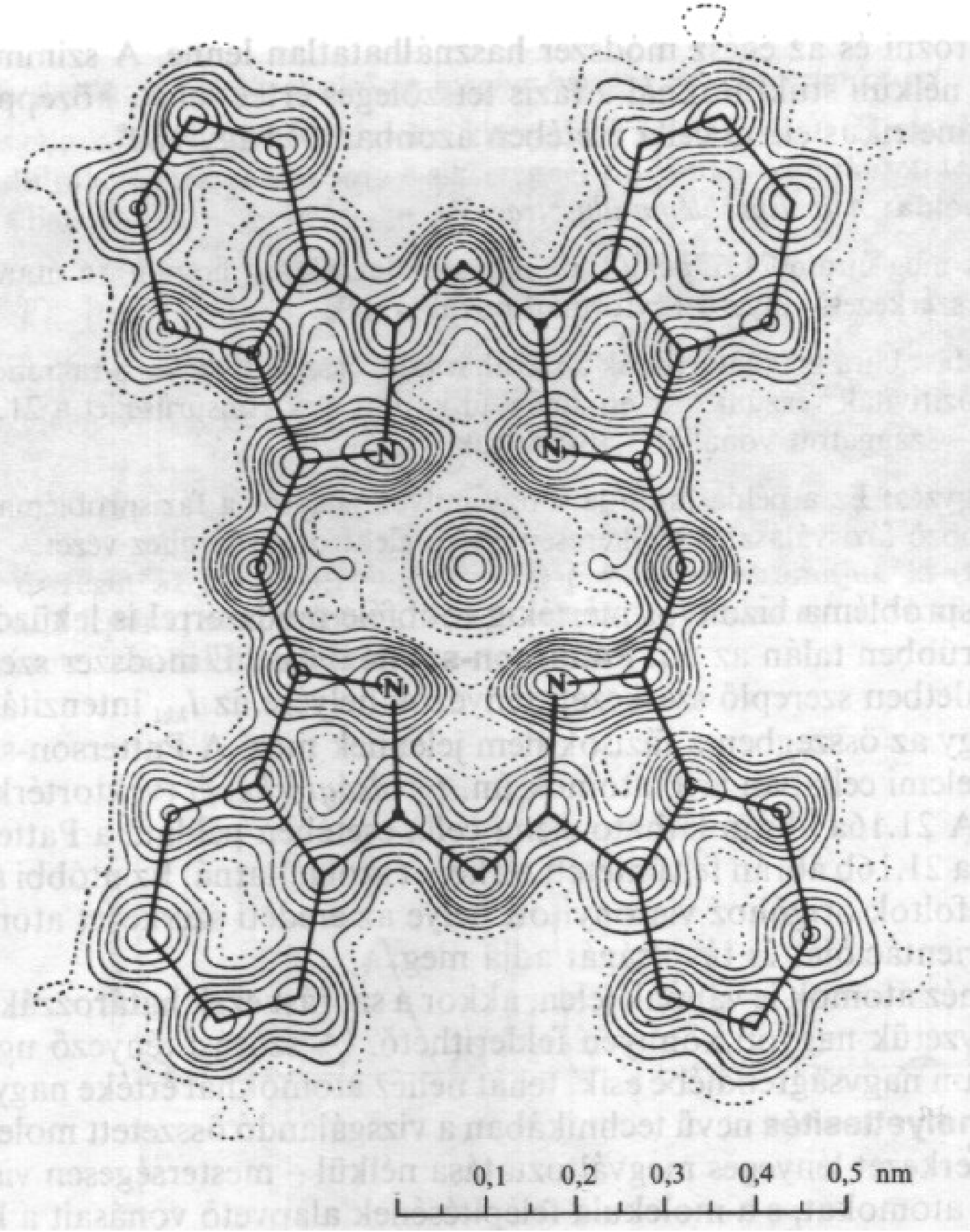
$$k=\frac{4\pi}{\lambda}\sin\theta$$

atomic scattering factors as functions of $\sin(\theta)/\lambda$

Scattering intensity of primitive cells with contiguous electron density

$$I = \left| F_{\mathrm{hk}\ell} \right|^2$$

$$F_{\mathrm{hk}\,\ell} = \frac{V}{a \cdot b \cdot c} \int_0^a \int_0^b \int_0^c \rho\left(\mathrm{x,y,z}\right) \exp\left[2\mathrm{i}\pi\left(\mathrm{hx} + \mathrm{ky} + \ell\mathrm{z}\right)\right] \mathrm{dxdydz}$$



Ni-Phthalocyanine electron density map