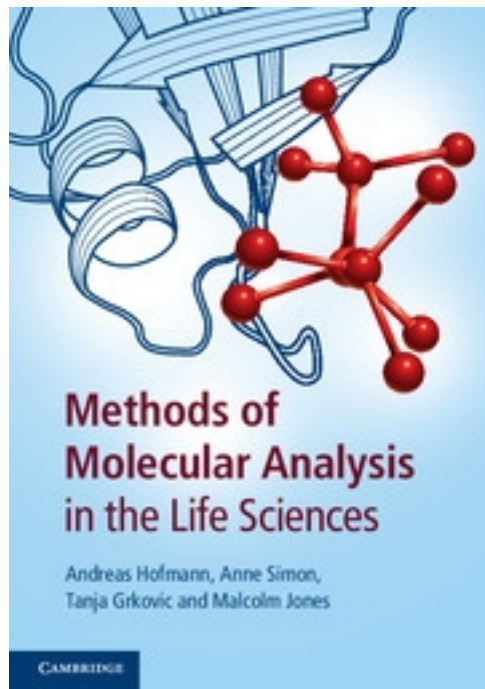


Part A.1

Interaction of light with matter

Recommended text book



Hofmann, Simon, Grkovic, Jones (2014) **Methods of Molecular Analysis in the Life Sciences**. 1st edt, Cambridge University Press.

ISBN: 9781107044708 (HB)

ISBN: 9781107622760 (PB)

eBook

Interaction of light with matter



Electromagnetic radiation

The electromagnetic spectrum

Photons

Constants, units and formulas

Energy at room temperature

Describing molecules by energetic states

Interaction of light with matter causes transitions in molecular states

Transitions give rise to a spectrum

Dipole momentum in chromophores

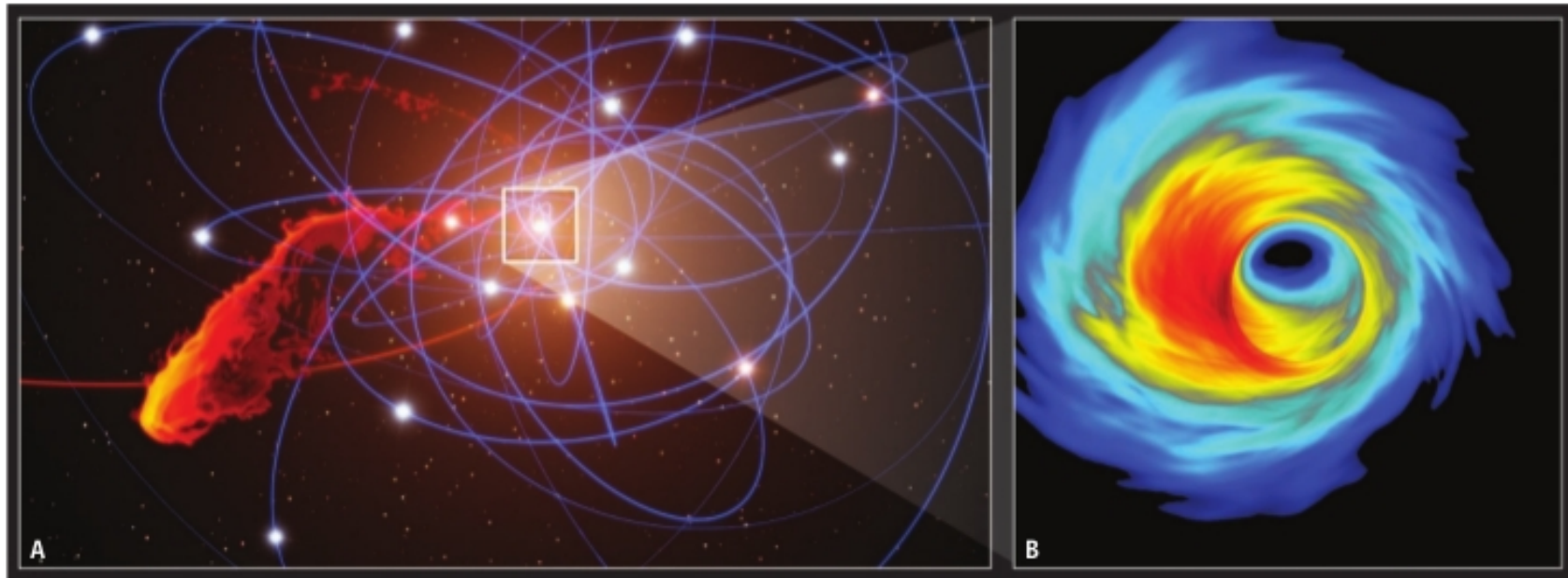
The transition dipole momentum

Electronic transitions: spin states

Molecular orbitals

Electromagnetic radiation: A crucial probe for astronomy

Dark matter: Because black holes are black, one can only infer properties by the light emitted from the hot gas surrounding the holes.

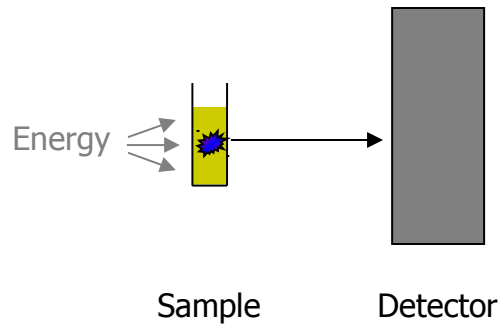


Orbiting within 1 light year distance:
Thousands of stars and gas clouds orbiting the black hole Sagittarius A-star.

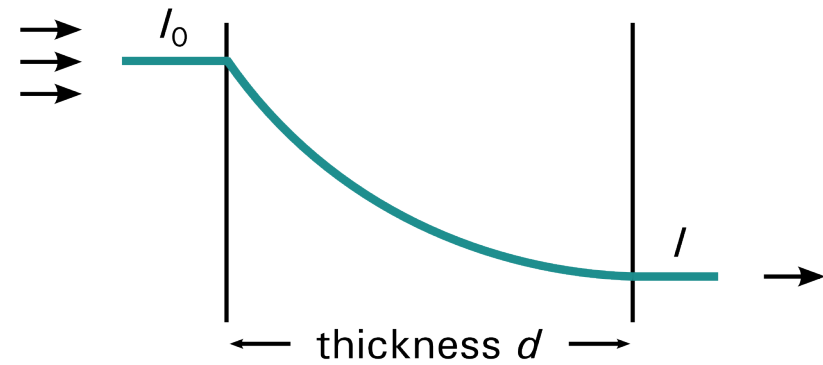
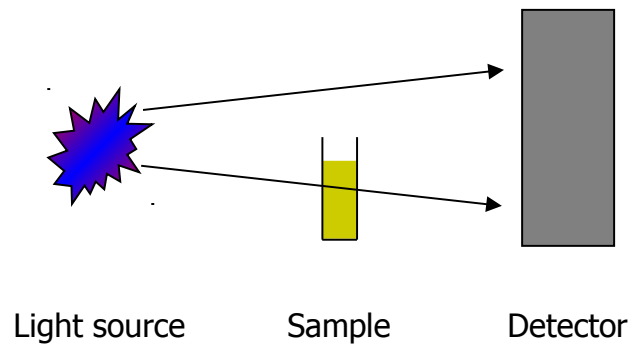
When gas gets within a distance of a few radii of a black hole, it forms a hot torus of highly magnetized relativistic plasma and emits a broad range of electromagnetic radiation from radio waves to X-ray light.

Light emission and absorption

Emission



Absorption

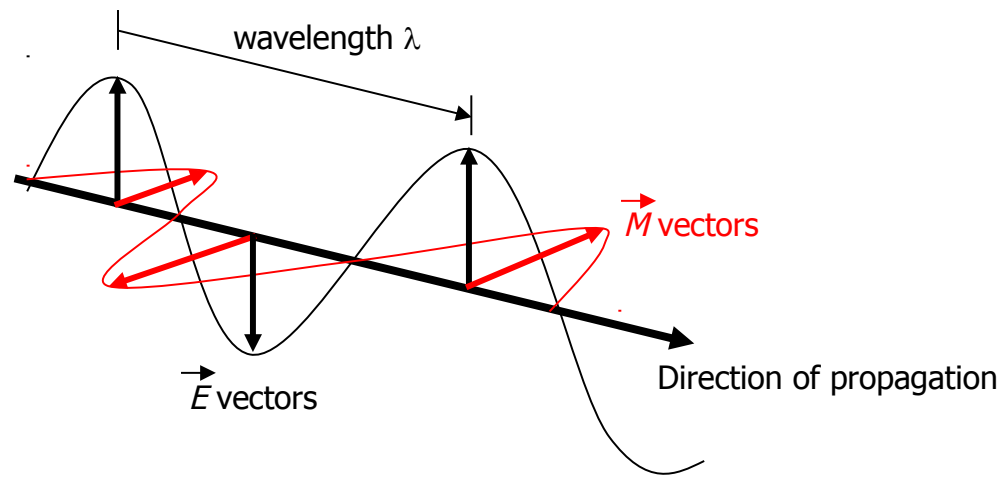


Interaction of electromagnetic radiation with matter

The interaction of electromagnetic radiation with matter is a **quantum phenomenon**.

It depends on: properties of the radiation
 appropriate structural parts of the sample

The **transitions** occurring within matter upon interaction with electromagnetic radiation are predictable in principle.



Electromagnetic radiation

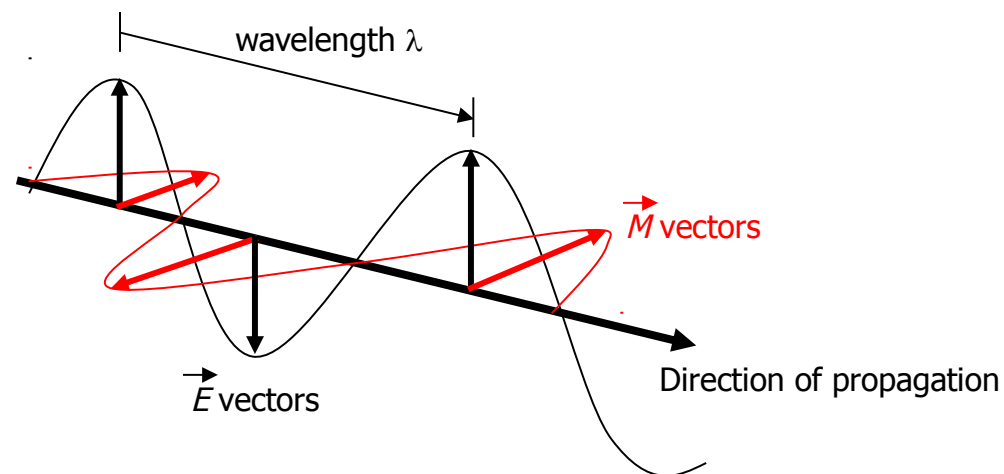
Light is electromagnetic radiation and can be described as a wave propagating transversally in space and time.

The electric (\vec{E}) and magnetic (\vec{M}) field vectors are directed perpendicular to each other.

Light is characterised by its frequency (ν) and wavelength (λ).

The product of ν and λ is the speed of light (c).

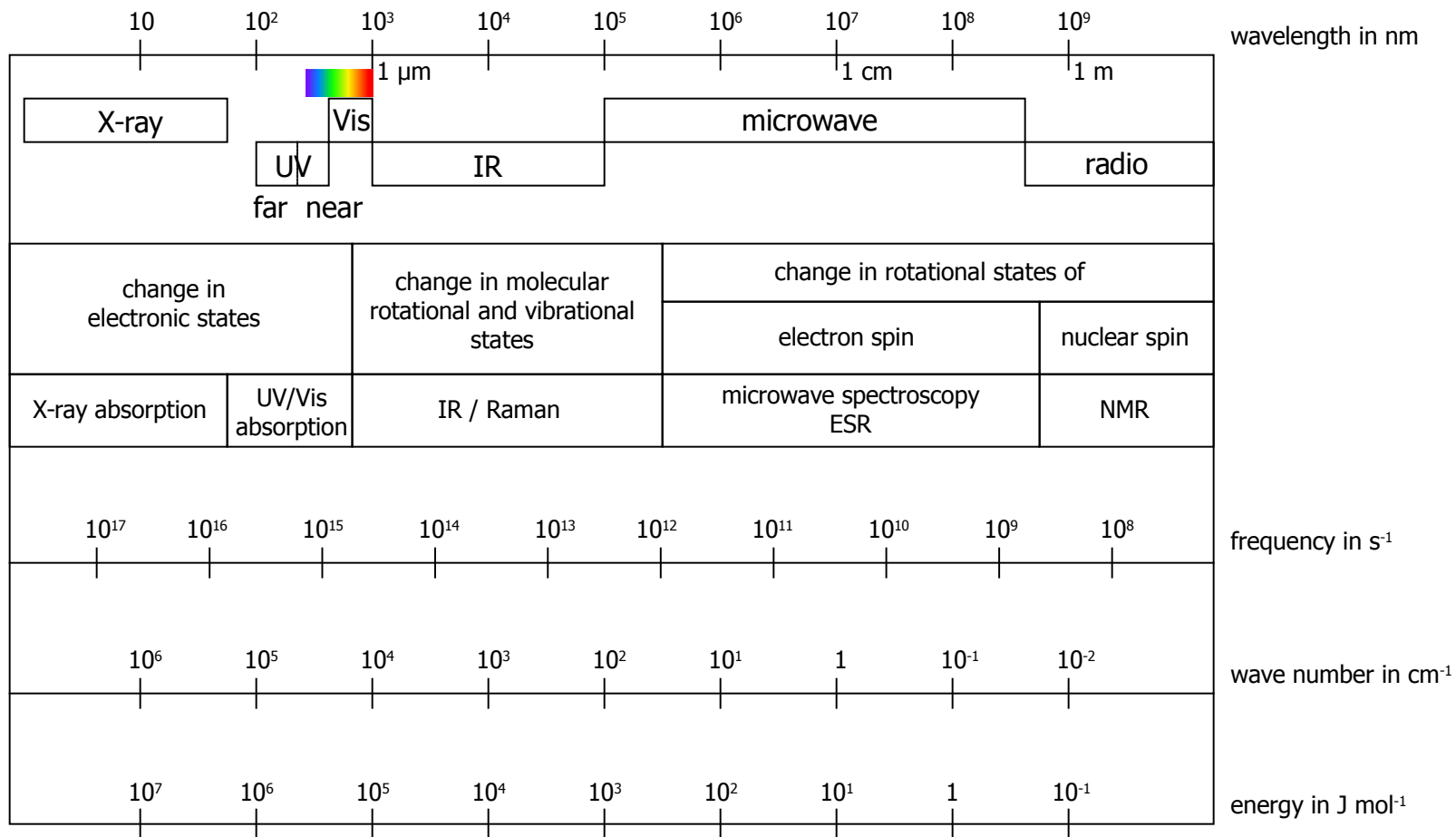
For UV/Vis, CD and fluorescence spectroscopy, the electric field vector \vec{E} is of most importance. For ESR and NMR spectroscopy, the emphasis is on the magnetic field vector \vec{M} .



$$\lambda = c / \nu$$

$$E = h \cdot \nu$$

The electromagnetic spectrum



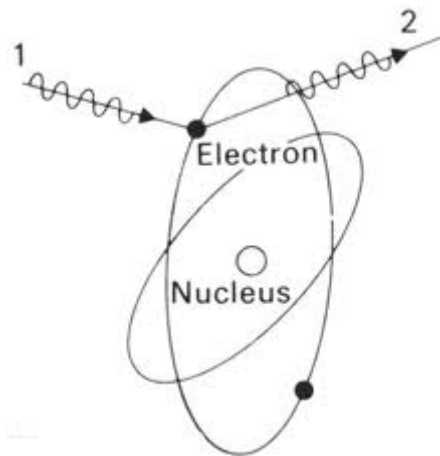
Photons

Electromagnetic phenomena are explained in terms of quantum mechanics.

The photon is the elementary particle responsible for these phenomena.

It carries the electromagnetic radiation and has properties of a wave, as well as of a particle; its mass is zero.

As a particle, it interacts with matter by transferring its energy E :



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

Planck's constant $h = 6.63 \cdot 10^{-34} \text{ J s}$

Constants, units and formulas

Energy of a photon

$$E = h \cdot \nu$$

$$[E] = 1 \text{ J}$$

h: Planck's constant

$$h = 6.63 \cdot 10^{-34} \text{ J s}$$

ν : Frequency

$$[\nu] = 1 \text{ s}^{-1}$$

Wavelength

$$\lambda = c / \nu$$

$$[\lambda] = 1 \text{ m}$$

c: speed of light

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

$$\Rightarrow E = h \cdot \nu = h \cdot c / \lambda$$

Wave number

$$\nu = 1 / \lambda$$

$$[\nu] = 1 \text{ m}^{-1}$$

Number of complete wave cycles per distance,
e.g. $\lambda = 3.33 \mu\text{m} \Rightarrow \nu = 3000 \text{ cm}^{-1}$

$$280 \text{ nm: } E = h \cdot c / \lambda = 7.1 \cdot 10^{-19} \text{ J} = 4.4 \text{ eV}$$

$$1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$$

$$1 \text{ mol: } E \cdot N_A = 428 \text{ kJ mol}^{-1}$$

N_A : Avogadro's constant

$$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$$

Thermal energy

$$E = k_B \cdot T$$

k_B : Boltzmann's constant

$$k_B = 1.38 \cdot 10^{-23} \text{ J K}^{-1}$$

$$1 \text{ mol: } E = R \cdot T$$

R: gas constant

$$R = 8.2144 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{At } 20^\circ\text{C: } E = 4.0 \cdot 10^{-21} \text{ J} \Rightarrow \lambda = 50 \mu\text{m}$$

$$E = 2.4 \text{ kJ mol}^{-1}$$

Energy at room temperature

We can calculate the energy provided by ambient environment, i.e. room temperature (20°C = 293 K), using the following formula

$$E = k_B \cdot T$$

k_B is the Boltzmann constant, $k_B = 1.38 \cdot 10^{-23} \text{ J K}^{-1}$

The thermic energy is thus

$$E = 1.38 \cdot 10^{-23} \text{ J K}^{-1} \cdot 293 \text{ K} = 4.04 \cdot 10^{-21} \text{ J}$$

This energy corresponds to light of a particular wavelength according to

$$E = h \cdot \nu = h \cdot c / \lambda \Rightarrow \lambda = h \cdot c / E, \quad h \text{ is the Planck constant} \quad h = 6.63 \cdot 10^{-34} \text{ J s}$$

$$\lambda = 6.63 \cdot 10^{-34} \text{ J s} \cdot 2.998 \cdot 10^8 \text{ m s}^{-1} / (4.04 \cdot 10^{-21} \text{ J}) = 4.91 \cdot 10^{-5} \text{ m} \approx 50 \mu\text{m}$$

Which type of light?

Describing molecules by energetic states

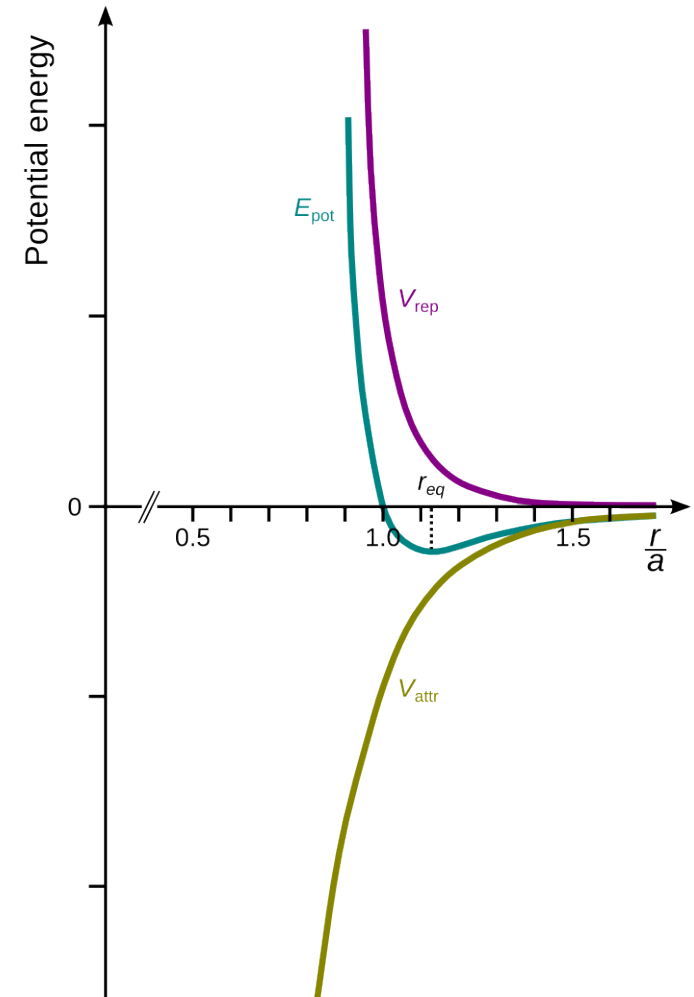
Molecules can be described conceptually by states on the energy scale.

An individual electronic state of a molecule is described by its potential energy which takes the form of a Lennard-Jones Potential.

The Lennard-Jones potential results from a combination of the attractive **van der Waals potential** and the repulsive **Pauli term**:

$$V_{LJ} \sim \frac{A_{ij}}{r^{12}} - \frac{B_{ij}}{r^6}$$

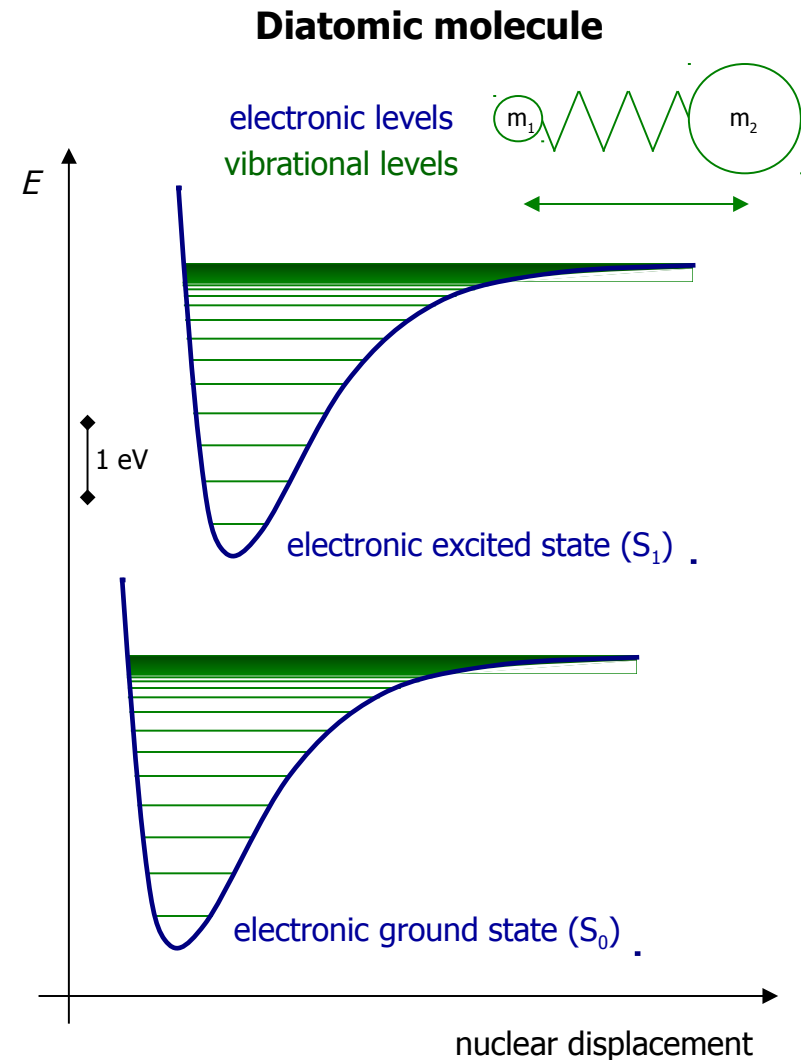
Diatomic molecule



Interaction of light with matter causes transitions in molecular states

The interaction of radiation with matter can cause transitions between the energy levels of atoms or molecules.

The possible energy of an **electronic orbital**, **molecular vibration or rotation** is restricted to well-defined energies (quantum mechanics!).



Interaction of light with matter causes transitions in molecular states

Type of radiation	Wavelength range	Type of transition
γ -rays	< 1 pm	nuclear
X-rays	1 nm - 1 pm	inner electron
ultraviolet	400 nm - 1 nm	outer electron
visible	750 nm - 400 nm	outer electron
near infrared	2.5 μ m - 750 nm	outer electron, molecular vibrations
infrared	25 μ m - 2.5 μ m	molecular vibrations
microwaves	1 mm - 25 μ m	molecular rotations, electron spin flips
radio waves	> 1 mm	nuclear spin flips

Interaction of light with matter causes transitions in molecular states

For a **transition** to occur, energy must be absorbed.

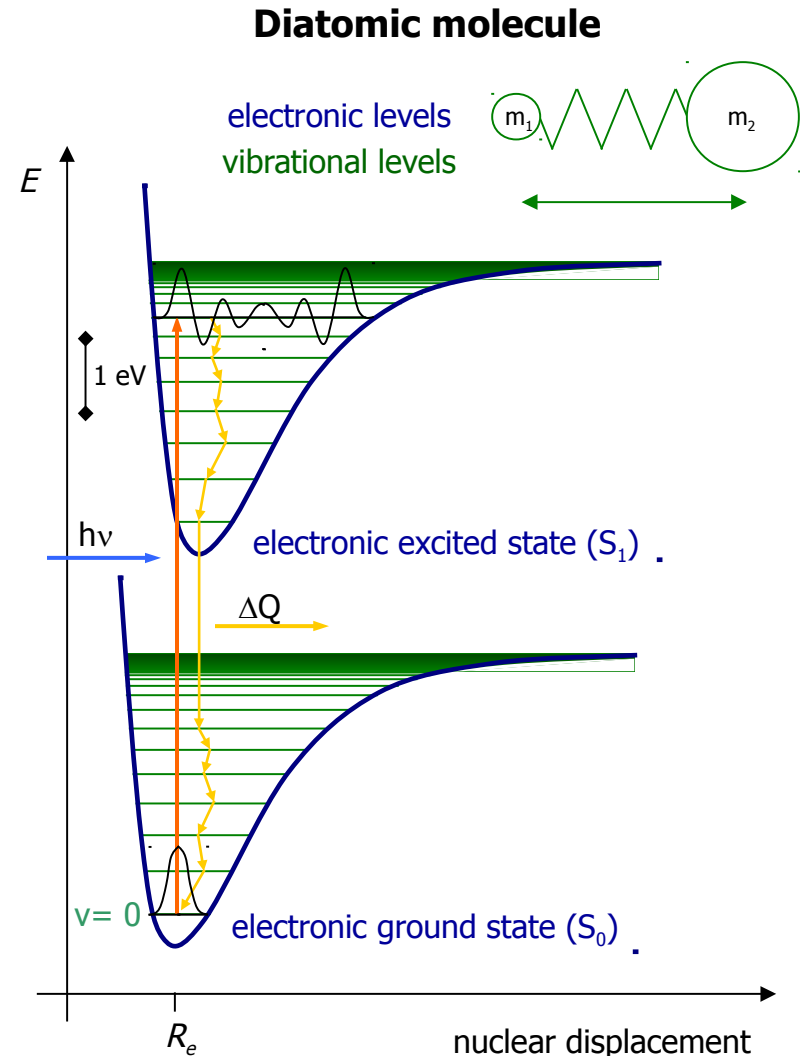
The energy change is defined in quantum terms by difference in absolute energies:

$$\Delta E = E_{\text{final}} - E_{\text{start}} = h \cdot \nu$$

If an incoming photon provides the appropriate energy, an electron is promoted from the ground to an excited state, and light is **absorbed**.

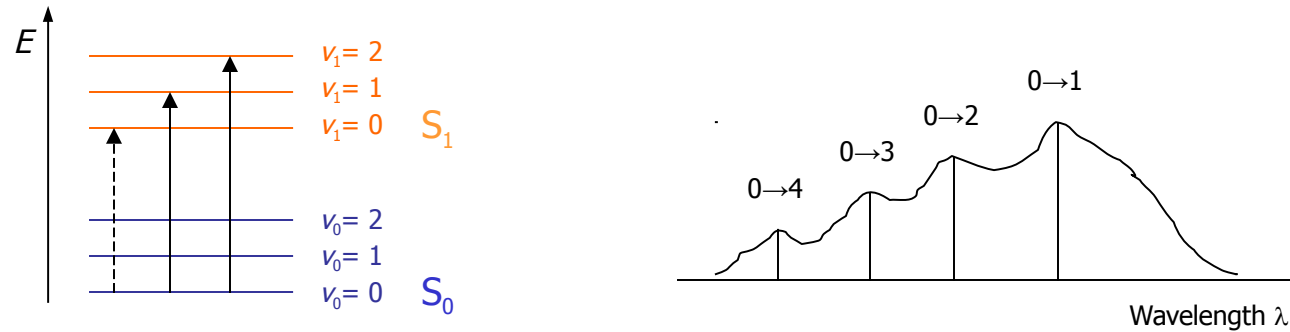
Subsequent **relaxation** of the molecule into the vibrational ground state of the excited state will occur.

The electron can then revert back to the electronic ground state. For non-fluorescent molecules, this is accompanied by emission of heat (ΔQ).



Transitions give rise to a spectrum

Vibration states are superimposed on electronic states. Depending on how the potential curves are situated, different transitions are possible:

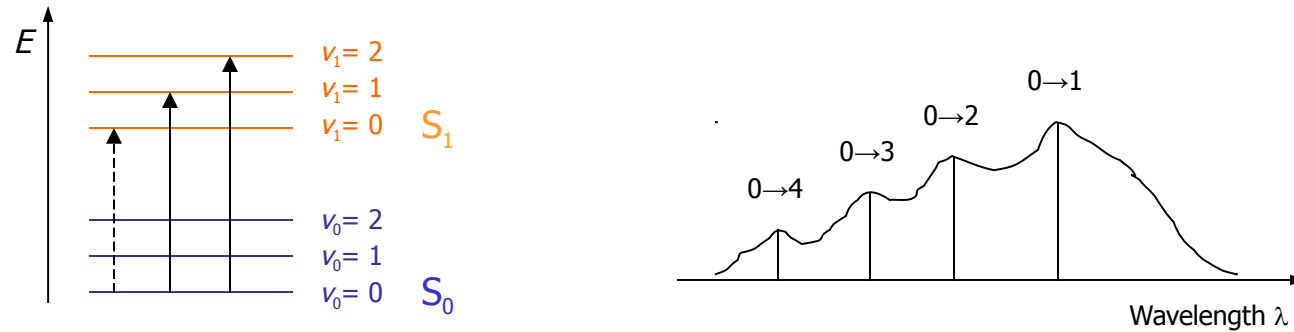


Starting point for all transitions is always the electronic ground state S_0 . Transitions can be made to $v_1 = 1$, $v_1 = 2$, etc.

The plot of absorption probability against wavelength is called **absorption spectrum**. The spectrum displays a molecule-specific structure due to the different vibration states. These transitions are denoted as $0 \rightarrow 1$, $0 \rightarrow 2$, etc.

In a **Jablonski diagramme**, electronic and vibrational states are schematically drawn as horizontal lines, while vertical energetic lines depict possible transitions.

Line spectrum – Band spectrum



Because of the existence of vibrational and rotational energy levels in the different electronic states of molecules, molecular spectra appear as **band spectra**.

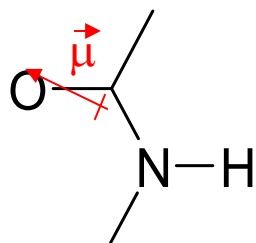
In the simpler case of single atoms (no vibrational and rotational levels), spectra are observed as **line spectra**.

Dipole momentum in chromophores

Chromophores are the light absorbing moieties within a molecule.

The chromophore possesses a spatial distribution of electric charge due to differences in electronegativity between individual atoms.

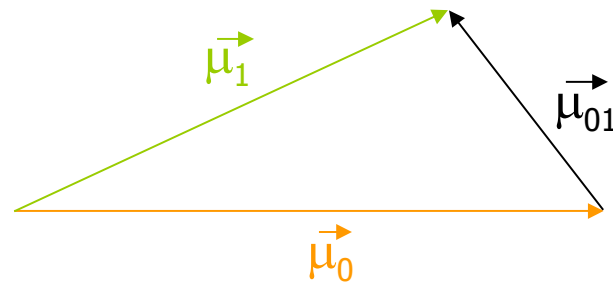
This results in a **dipole momentum μ** ; e.g. permanent dipole momentum of peptide bond:



The transition dipole momentum

Absorption of light excites the chromophore and changes distribution of electric charge; the dipole momentum changes accordingly.

The **transition dipole momentum** is the vector difference between the momentum in the ground and the excited state.

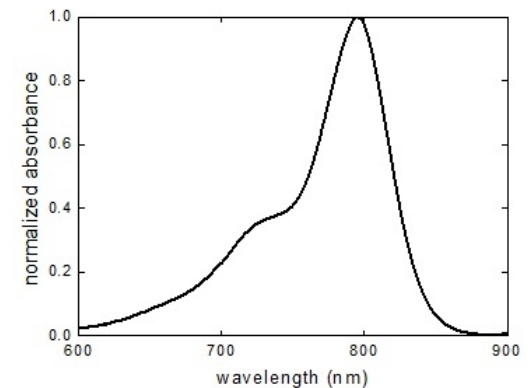


Dipole strength: $D_{01} = |\mu_{01}|^2$

The transition dipole momentum is a measure for transition probability.

$D_{01} \rightarrow 0$: forbidden transitions

$D_{01} \rightarrow 1$: allowed transitions



The plot of absorption probability against wavelength is called **absorption spectrum**.

Electronic transitions: spin states

For electronic transitions, the spin states of electrons need to be considered.

Electrons in binding orbitals are usually paired with anti-parallel spin orientation:

Total spin $S = (+1/2) + (-1/2) = 0$

Multiplicity $M = 2 \cdot 0 + 1 = 1$

=> Singlet state ("S")

The ground state of a molecule is usually a singlet state: S_0

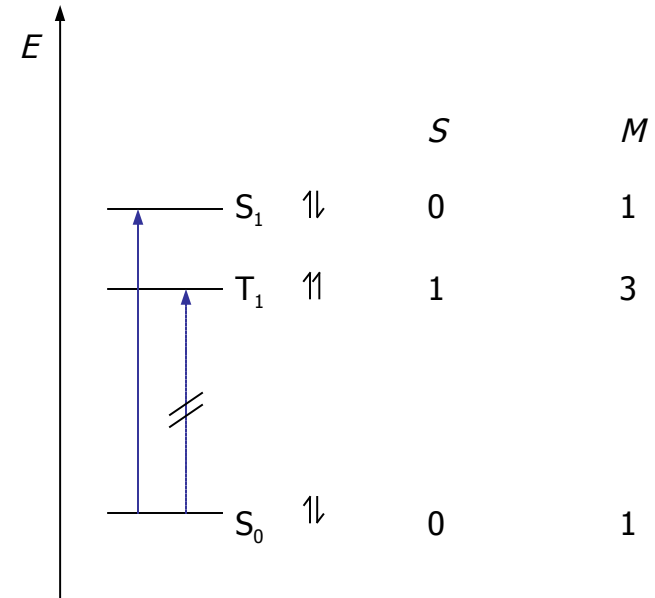
For parallel spin orientation:

Total spin $S = (+1/2) + (+1/2) = 1$

Multiplicity $M = 2 \cdot 1 + 1 = 3$

=> Triplet state ("T")

Triplet states are typically excited states of molecules.



Total spin:

$$S = s(\text{electron 1}) + s(\text{electron 2})$$

Multiplicity:

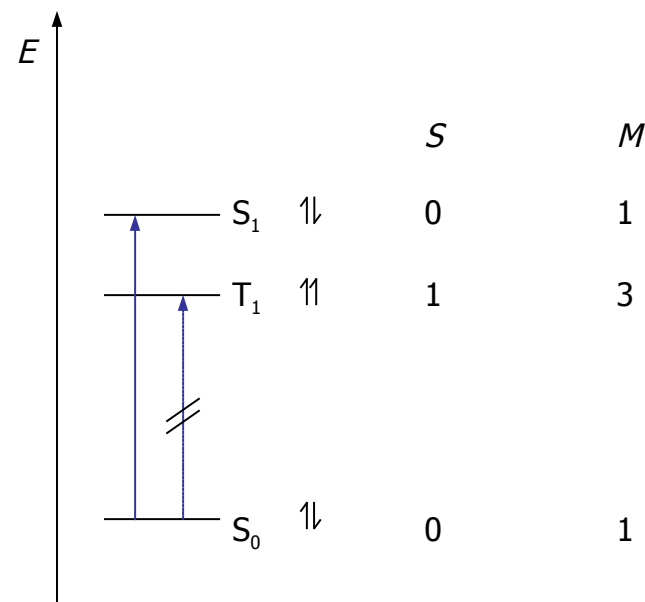
$$M = 2 \cdot S + 1$$

Electronic transitions: spin states

According to **transition rules**, the **multiplicity M and the total spin S must not change** during a transition.

Thus, the $S_0 \rightarrow S_1$ transition is allowed and possesses a high transition probability. In contrast, the $S_0 \rightarrow T_1$ is not allowed and has a small transition probability.

The transition probability is proportional to the intensity of absorption bands!



Molecular orbitals

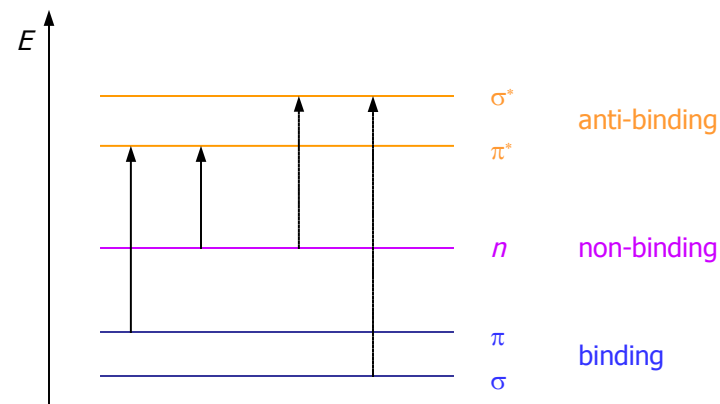
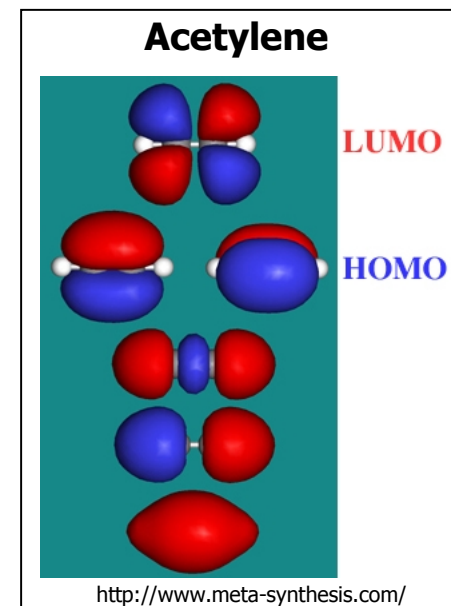
Electronic transitions can be classified according to participating molecular orbitals.

Orbitals are states of electrons, which have two properties: a geometry function and a probability function. Each orbital can be occupied by a maximum of two electrons.

The ground state has binding σ and π orbitals, as well as non-binding n orbitals.

While the single bonds of a molecule constitute the σ orbitals, the double bonds make up the π orbitals.

With hetero atoms, like e.g. N and O, there are also non-binding n orbitals.



Further reading

Textbooks

Banwell, C.N. & McCash, E.M. (1994) Fundamentals of molecular spectroscopy. 4th edition, McGraw-Hill, London. (A readable account of spectroscopic principles.)

Cantor, C.R. & Schimmel, P.R. (1980) Biophysical Chemistry. 1st edition, Freeman, New York. (A comprehensive reference in three parts.)

Hofmann, A., Simon, A., Grkovic, T. & Jones, M. (2014) Methods of Molecular Analysis in the Life Sciences. Cambridge University Press. Chapter 1.

Hoppe W., Lohmann W., Markl H. & Ziegler H. (1982) Biophysik. 2nd edition, Springer Verlag, Berlin, Heidelberg, New York. (A rich and authoritative compendium of the physical basics of the life sciences.)

Web sites

Physics 2000: an interactive journey through modern physics, including topics such as waves, quantum mechanics, etc.

<http://www.colorado.edu/physics/2000/>

Applet: Spectrum

<http://lectureonline.cl.msu.edu/%7Emmp/applist/Spectrum/s.htm>

Useful databases

Spectral Database for Organic Compounds, SDBS

http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

free site organized by National Institute of Advanced Industrial Science and Technology (AIST), Japan

NMR: T.Yamaji, T.Saito, K.Hayamizu, M.Yanagisawa and O.Yamamoto

MS: N.Wasada

ESR: K.Someno

IR: S.Kinugasa, K.Tanabe and T.Tamura

Raman: K.Tanabe and J.Hiraishi