BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS

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STRUCTURAL CHEMISTRY

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PREFACE

The structural chemistry deals with the interpretation of the physico-chemical properties of the substances at molecular level. It relies upon the general chemistry, applies the results of the quantum chemistry and provides for the theoretical background for the evaluation of the results yielded by the instrumental measurements of the analytical and organic chemistries.

This lecture note is based on mathematics, especially on the differential, integral, vector and matrix calculuses and on physics, especially on parts of electricity, magnetism and optics.

The aim of this course is to form a comprehensive conception about the structure of matter, about the methods of its investigation and description. This course deals with the theoretical backgrounds of the most important methods for the elucidation of the molecular structure, the theoretical set-up of the measuring systems and the principles of the interpretation of the results, surveies the different spectroscopic and diffraction methods. There is not possible, however, to deal with all these methods in detail since the period of the course is limited.

After a short introduction about the interaction of molecules and atoms with force fields the lecture note deals with the investigation and the description of the atoms and molecules.

Budapest, September 2008.

Ferenc Billes

INTERACTIONS OF ATOMS AND MOLECULES WITH PARTICLES AND EXTERNAL FIELDS

1.1. Research and its application

The aim of the scientific work is the application. On one hand the industry, the agriculture etc. raise questions and the researcher try to solve them. On the other hand the scientist finds new methods and theories and help with them the real life. Fig. 1.1. shows the diagram of the connections.

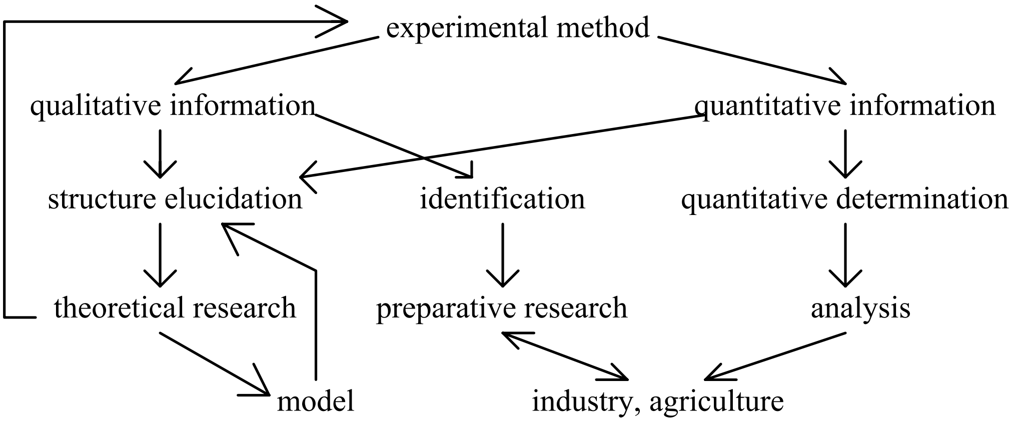


Fig. 1.1. Research and application

There are properties of the matter that belong to atoms (A), other belong to moleculs (M) and a lot to atomic or molecular sets (S). The environment of the atoms or molecules changes the A and M properties. These changes show the strength and quality of the interaction, see Table 1.1.

Table 1.1.
Types of properties

System	*Propety*	*Example*
atom	A	A: atomic spectrum
molecule	ΔA, M	M: vibrational spectrum
molecular ensamble	ΔA, ΔM, S	S: X-ray diffractogram

The theory give us a model of the system. It is, however, only an approach of the reality.

1.2. Interactions with particles

The experiment disturbs (perturbs) the investigated sytem. The perturbation can be

- a *collision* with particles
- an effect with *external* - electric
  - magnetic

-electromagnetic *fields.*

The *answer* of the *system* is
- the change of its properties
- or/and emission of one or more particles.

The *answer* of the *particle* is
- the change of one or more of its properties.

Collisions are in the overwhelming cases *not central.* It can be:

A) *elastic:* (theoterically) the energies of both the system and the particle(s) do not change: the wavelength or energy of the particle ramain; practically the energy change is negligable;
inelastic: the total energy of the particle increases the (internal) energy of the system;
partly inelastic: only a part of the particle energy increases the internal energy of the system;

B) *coherent:* the coherence of the particles does not change during the collision;
incoherent: the coherence changes during the collision.

Coherence describes a property of waves, that enables stationary (i.e. temporally and spatially constant) interference. Coherence describes all correlation properties between physical quantities of a wave. When *interfering*, waves add constructively or substract destructively, depending on their relative phase. Two waves are said to be *coherent* if they have a constant relative phase, which also implies that they have the same frequency.

The *collision cross-section* (σ) characterizes the effectivity of the collision. If N particles impact into a surface of the target with ρ particle surface density, the number of the produced reactions (collisions, absorptions, etc.) will be

$$s = \sigma.\rho.N \qquad (1.1.a)$$

or otherwise, if the particle stream (particle/cross-section unit) is Φ, and there are n particles on the target surface,

$$s = \sigma.n.\Phi \qquad (1.1.b)$$

The unit of the collision cross-section is called *barn,* 1 barn=10^{-28} m^2.

The *pulse of a photon* (velocity v=c) is

$$p = \frac{h\nu}{c}$$

The *pulse of a particle* with velocity v < c is (electron, ion, etc.)

$$p = mv \qquad (1.2)$$

p is the pulse, h is the Planck constant (6.62608×10^{-34}Js), ν is the frequency, c is the velocity of light in vacuum, m is the mass of the particle, v is the velocity.

The *energy of a photon is* The (kinetic) *energy of a particle* with v << c

$$E = h\nu \qquad E_k = \frac{mv^2}{2} \tag{1.3}$$

We regard the atom or the molecule fixed in the space during the collision and suppose an essentially smaller mass of the colliding particle than that of the atom or molecule. *Eight collision types* have interest in structural chemistry. The following notation will be used:

E_1	energy of the atom or molecule before the collision;
E_2	energy of the atom or molecule after the collision;
ε_1	energy of the particle before the collision;
ε_2	energy of the particle after the collision;
*	excited state of the atom or molecule.

1. Elastic scattering

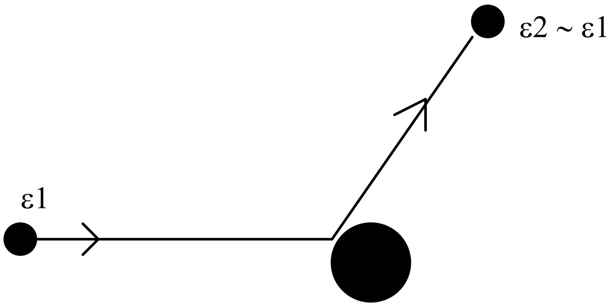


Fig. 1.2.

$$\varepsilon_1 + E_1 = \varepsilon_2 + E_2 \qquad [h(\nu_1 - \nu_2) << h\nu_1] \tag{1.3}$$

2. Inelastic scattering

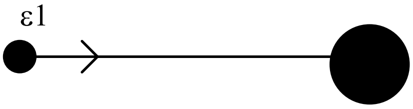


Fig. 1.3.

$$\varepsilon_1 + E_1 = E_2^* \tag{1.4}$$

This "scattering" is the annihilation of the particle, *absorption* of the photon, catching of the electron.

3. Induced scattering (coherent)

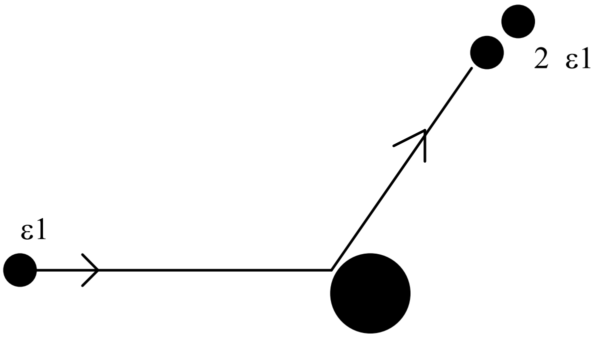


Fig. 1.4.

$$h\nu_1 + E_1^* = 2h\nu_1 + E_2 \qquad (1.5)$$

This is the so-called *induced emission*, the method of light amplification. This is the fundamental process in the function of lasers.

4. Partially inelastic scattering

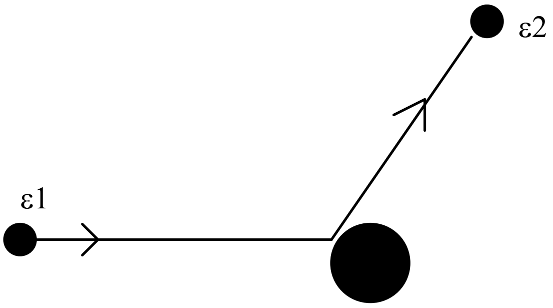


Fig. 1.5.

$$\varepsilon_1 + E_1^* = \varepsilon_2 + E_2 \qquad (\varepsilon_2 > \varepsilon_1) \qquad (1.6a)$$

or

$$\varepsilon_1 + E_1 = \varepsilon_2 + E_2^* \qquad (\varepsilon_2 < \varepsilon_1) \qquad (1.6b)$$

Since atoms and molecules are generally in ground state (according Boltmann's energy distribution) the second reaction is more probable. Such kind processes take place in the Raman and the inelastic neutron scatterings.

6. Induced partially inelastic scattering (coherent)

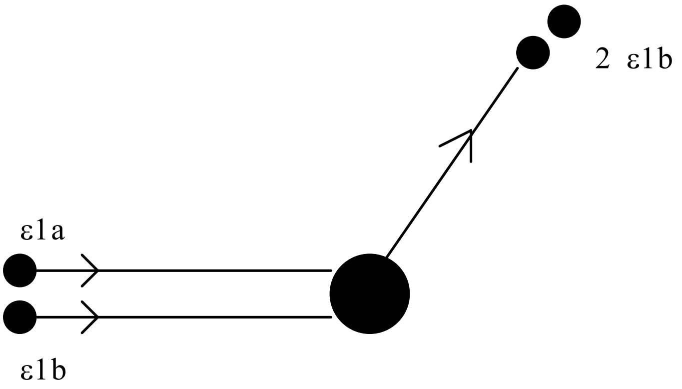


Fig. 1.6

$$\varepsilon_{1a} + \varepsilon_{1b} + E_1 = 2\varepsilon_{1b} + E_2^* \qquad (\varepsilon_{1a} > \varepsilon_{1b}) \tag{1.7}$$

Two photons of different frequency scatter on the molecule. If the energy difference of these photons equals the energy difference of the ground and an excited states then the result is an excited molecule and two photons of lower frequency. The frequency of one of the photons will be change. This is the fundamental process of the energy gain and loss spectroscopy.

7. Spontaneous scattering

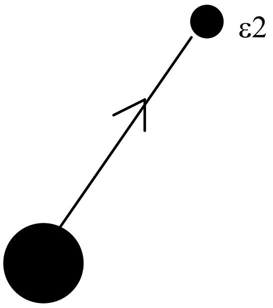


Fig. 1.8

$$E_1^* = E_2 + \varepsilon_2 \tag{1.8}$$

This is the spontaneous emission of light.

8. Ineleastic scattering with particle change

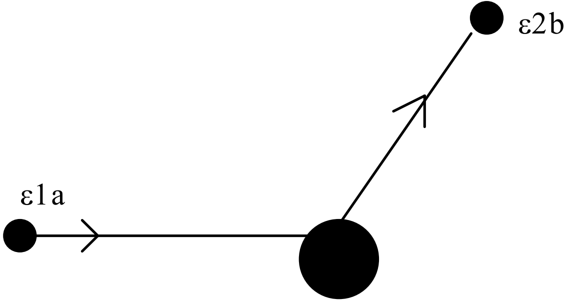


Fig. 1.9

$$\varepsilon_{1a} + E_1 = \varepsilon_{2b} + E_2^* \tag{1.9}$$

If particle 1a is a photon and particle 2b is an electron then

$$h\nu_{1a} = I + \frac{m_e v_e^2}{2} \qquad I = E_2^* - E_1 \tag{1.10}$$

I is the ionization energy of the atom or molecule, m_e is the mass of the electron and v_e is its velocity. This is the basic process of the photoelectron- and mass spectroscopies, E_2^* is the energy of the excited ion.

1.3. Interactions with electric field

The atom consists of a positively charged nucleus and negatively charged electrons. Molecules consist of atoms. If in a charge system the centers of the positive and negative charges differ from each another, the molecule has a *dipole moment.*

The charge system of charges Q_i with position vectors $\mathbf{r}_i$ affect on a charge at the point P with position vector **R** with the electric potential

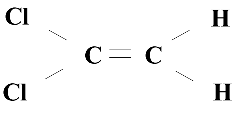
$$U = \frac{1}{4\pi\varepsilon} \sum_i \frac{Q_i}{|\mathbf{R} - \mathbf{r}_i|} \tag{1.11}$$

ε is the permittivity of the medium. Expanding into series U around the point P the coefficients contain the different moments. The first term contains the sum of charges, this is the 0th moment. The second term contains the *dipole moment*:

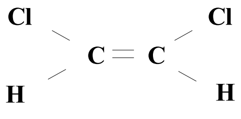
$$\mathbf{p} = \sum_i Q_i \mathbf{r}_i \tag{1.12}$$

The *quadrupole moment* is part of the next term. This moment characterizes the asymmetricity of the charge distribution.

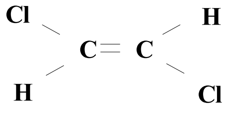
Examples:



I



II



III

Molecule I and II have dipole moments but in different directions: vertical and perpendicular to the C=C bond, respectively. The molecule III has not dipole moment but since the charge distribution is asymmetric it has quadrupole moment (like also I and II).

The electric field acts on the charges with the force

$$\mathbf{F} = Q\mathbf{E} \tag{1.13}$$

E is the electric field strength. This force shifts the electric charges, changes their relative positions in the molecule and in this way distort the molecule. This effect is called *distorsion polarization.*

The total dipole moment can be expand into series according **E**

$$\mathbf{p} = \mathbf{p}_o + \alpha\mathbf{E} + \frac{1}{2}\beta\mathbf{E}^2 + \ldots \tag{1.14}$$

$\mathbf{p}_o$ is the permanent dipole moment, α is the *polarizability tensor*, β is the *hyperpolarizability*.

In molecular systems the molecular dipoles are disoriented. An external field orients these dipoles. The field acts with a torque on the dipoles

$$\mathbf{T} = \mathbf{p} \times \mathbf{E} \tag{1.15}$$

The result is the *orientation polarization.* The sum of the dipole moment vectors is no more zero. The *vector of polarization* characterizes the situation:

$$\mathbf{P} = \frac{\sum_i \mathbf{p}_i}{V} \tag{1.16}$$

V is the volume of the sample.

For weak electric fields the vector of polarization is proportional to the field strength:

$$\mathbf{P} = \varepsilon_o \chi_e \mathbf{E} \tag{1.17}$$

ε_o is the *permittivity of vacuum* (8.85419 x 10^{-12}AsV^{-1}m^{-1}), χ_e is the *dielectric susceptibility* of the molecule.

The *dielectric induction* is a vector that characterizes the surface charge density:

$$\mathbf{D} = \varepsilon\mathbf{E} \tag{1.18}$$

The permittivity is in weak fields a proportionality factor. In strong fields **D** and **E** are not collinear, so the permittivity becomes a tensor. The permittivity and the susceptibility are not independent:

$$\mathbf{D} = \varepsilon_o\mathbf{E} + \mathbf{P} = \varepsilon_o(1 + \chi_e)\mathbf{E} \tag{1.19}$$

Using the Eqs. 1.18 and 1.19 the relative permittivity is

$$\varepsilon_r \equiv \frac{\varepsilon}{\varepsilon_o} = 1 + \chi_e \tag{1.20}$$

The *molar polarization* characterizes the polarization state of the substance. According to Clausius and Mosotti

$$P_M \equiv \frac{\varepsilon_r - 1}{\varepsilon_r + 2}\frac{M}{\rho} \tag{1.21}$$

M is the molar mass, ρ is the density of the substance.

$$P_M \equiv \frac{\varepsilon_r - 1}{\varepsilon_r + 2}\frac{M}{\rho} = \frac{N_A}{3\varepsilon_o}\left(\overline{\alpha} + \frac{\mathbf{p}^2}{3kT}\right) \qquad (1.22)$$

N_A is the Avogadro constant (6.0214 x 10^{23} mol^{-1}), $\overline{\alpha}$ is the average polarizability, k is the Boltzmann constant (1.38066 x $10^{-23}JK^{-1}$), T is the absolute temperature. The first term in the parentheses represents the distorsion polarisation, the second one the orientation polarisation. Measuring the temperature dependence of the relative permittivity and using Eq. 1.22 one can separate the two types of polarization.

There exists an other possibility for the separation of the different types of polarization. The relative permittivity and so the molar polarization is frequency dependent. At high frequencies, in the visible region of the spectrum (5 x 10^{14}Hz) only the electron can follow the vibrations and we can measure the *electronic polarization.* At lower frequencies, in the infrared region (5 x 10^{12} Hz) also the atoms can follow the vibrations. So the total distorsion polarization (*atomic polarization* and electronic one) will be measured. In the microwave region (10^{10} Hz) also the molecules can follow the vibrations. At this frequency the total polarization is measurable. Carrying out these three measurements the different polarization types are determinable.

1.4. Interactions with the magnetic field

1.4.1. Elementary magnets

The external magnetic field **B** acts on the moving charged particules by the force (Lorentz force)

$$\mathbf{F} = Q\mathbf{v} \times \mathbf{B} \qquad (1.23)$$

B is called *magnetic induction* (or *magnetic flux density*), **v** is the velocity of the particle. The elementary magnets are magnetic dipoles. The field turns these dipoles:

$$\mathbf{T} = \mathbf{m} \times \mathbf{B} \qquad (1.24)$$

m is the *magnetic (dipole) moment*. Electrons have magnetic moment from their nature and from their position (orbit) in the atom or molecule. Nuclei may have magnetic moment from their nature.

The magnetic moment of the particle is always coupled with an angular moment.

The electrons have from their nature the angular moment called *spin* (**s**). This is coupled with a spin magnetic moment $\mathbf{m}_S$:

$$\frac{e}{m_e}\mathbf{s} = -\mathbf{m}_S \qquad (1.24)$$

e is the elementary charge (absolute value of the electron charge, 1.60218 x 10^{-19}As), m_e is the mass of the electron (9.10939 x 10^{-31}kg). According to the *correspondence principle* of quantum mechanics in the quantum mechanics the quantities of the classical physics arte substituted by operators that act on wavefunctions; at high quantum numbers the quantum mechanical laws reaches the classical ones. Applying this principle the Eq. 1.24 has the form

$$\mu_B \hat{\mathbf{s}} = -\frac{\hbar}{2}\mathbf{m}_s \qquad (1.25)$$

$\hbar = \frac{h}{2\pi}$, h is the Planck constant (6.62618 x 10^{-34} Js) and

$$\mu_B = \frac{e\hbar}{2m_e} \qquad (1.26)$$

is the Bohr magneton (9.2740 x10^{-24}Am^2), the magnetic moment unit in quantum mechanics, ^ labels the operator.

An electron on an atomic orbit has the *orbital angular moment* **l** and the corresponding *orbital magnetic moment* **m**. Their connection is

$$\frac{e}{m_e}\mathbf{l} = -2\mathbf{m} \qquad (1.27)$$

Compair Eqs. 1.24 and 1.27 and find the difference, the factor 2 on the right side of Eq. 1.27. The corresponding quantum chemical equation has the form

$$\mu_B \hat{\mathbf{l}} = -\hbar\mathbf{m} \qquad (1.28)$$

The *total orbital angular moment* **L** (for several electrons) is coupled to the *total orbital magnetic moment* **M** (**L** and **M** are vector sums of the individual moments, respectively):

$$g\mu_B \hat{\mathbf{L}} = -\hbar\hat{\mathbf{M}} \qquad (1.29)$$

g is a proportionality factor, the *Landé factor* (see Chapter 2).

Similar equation is valid for the *nuclei*. A nucleus has magnetic moment ($\mathbf{M}_I$) if its atomic number is odd (e.g. ^{1}H) or if its atomic number is even and its mass number is odd (e.g. ^{13}C). So

$$g_N\mu_N \hat{\mathbf{I}} = \hbar\hat{\mathbf{M}}_I \qquad (1.30)$$

g_N is the Landé factor of the nucleus, μ_N is the nuclear magneton:

$$\mu_N = \frac{e\hbar}{2m_p} \qquad (1.31)$$

m_p is the mass of the proton. Pay attention on the positive sign on the right side of Eq. 1.30! Nuclei have positive charges.

1.4.2. Diamagnetism

This type of magnetism exists for all molecules independently of other magnetic effects. It is weak, therefore the stronger effects cover it.

Switching on a magnetic field **B**, the change in the magnetic flux induces an electric field **E**. This field induces **p** dipoles (1.14) and acts on this dipole with a torque **T** (1.15). Since the torque is the time derivative of the angular moment **l**, also this will change. According Eq. 1.27, **l** is coupled with the magnetic moment **m**. In this way a diamagnetic moment will be induced.

$$\Delta\mathbf{B} \to \Delta\mathbf{E} \to \Delta\mathbf{p} \to \Delta\mathbf{T} \to \Delta\mathbf{l} \to \Delta\mathbf{m}$$

The induced diamagnetic moment is

$$\Delta m = \frac{e^2 r^2}{4 m_e} B \qquad (1.32)$$

r is the orbit radius of the electron.

1.4.3. Precession of the magnetic moment

According to Larmor's theorem the magnetic dipoles move in a field **B** like in the abscence of the field plus they precession around the direction of **B** (see Fig. 1.9).

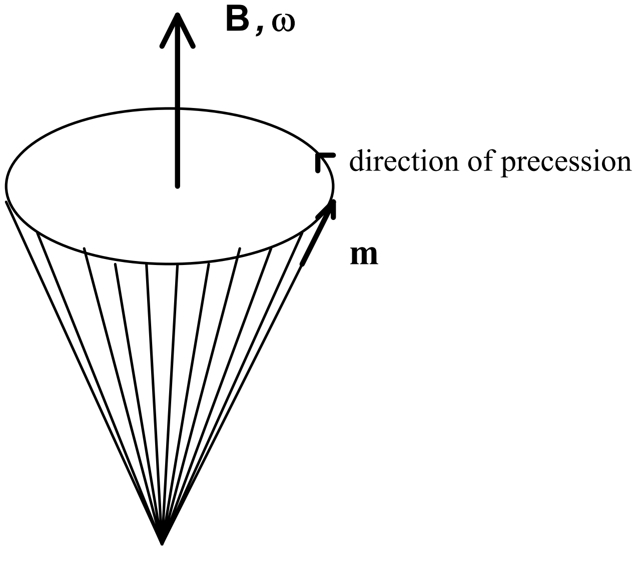


Fig. 1.10

The direction of **B** (or other external field) is always chosen as direction z. The frequency of the precession around the direction of **B** is proportional to **B**, the angular velocity **ω** and the **B** are collinear:

for electrons

$$\omega = g\frac{\mu_B}{\hbar}B = \gamma_e B \qquad (1.33)$$

for nuclei

$$\omega = g_N\frac{\mu_B}{\hbar}B = \gamma_N B \qquad (1.34)$$

γ_e and γ_N are the *magnetogyric ratios* for electrons and nuclei, respectively.

An other external magnetic field perpendicular to the first can disturb the stationary state and the magnetic moments. It changes the diractions but continues the precession. If the second field is an electromagnetic wave and its frequency corresponds to the energy difference of two magnetic levels the molecule, the molecule absorbs the wave. The relaxation process is well observable.

These magnetic effects are very important since these are the theoretical bases of the very important structure elucidation methods NMR (nuclear magnetic resonance), and ESR (electron spin resonance).

The magnetic transition is possible if the *magnetic transition moment* is not zero:

$$M = \int \psi_i^* \Delta\mathbf{m}\psi_j d\tau \qquad (1.35)$$

ψ is the wavefunction, i stands for the magnetic excited, j for the magnetic ground state, the complex conjugate is starred, the integration is extended to the full space τ.

1.4.4. Paramagnetism

If a molecule (atom) has resulting magnetic moment the *vector of magnetization* shows the stregth of magnetization, it is the magnetic dipole density (like the vector of polarization for electric dipoles):

$$\mathbf{M} = \sum_i \frac{\mathbf{m}_i}{V} \qquad (1.36)$$

The vector of magnetization is proportional (in case of weak fields) to the magnetic field strenght **H** (attention! the field strength is determined by **B** and not by **H**)

$$\mathbf{M} = \mu_o \chi_m \mathbf{H} \qquad (1.37)$$

μ_o is the *permeability* of vacuum (1.25664 x 10^{-6} $VsA^{-1}m^{-1}$), χ_m is the *magnetic susceptibility,* and

$$\mathbf{B} = \mu\mathbf{H} \qquad (1.38)$$

Similarly to Eq. 1.20 we have from Eqs. 1.37 and 1.38

$$\mu_r = 1 + \chi_m \tag{1.39}$$

μ_r is the relative permeability related to the permeability of vacuum.

If the field is strong, the linear eqations are no longer valid, the two vectors are no more parallel and instead of the constant permittivity we have a tensor. If the relative permittivity is large, the substance is *ferromagnetic.* If

μ_r	i.e.	χ_m	the substance is
<1		<0	diamagnetic
>1		>0	paramagnetic
>>1		>>0	ferromagnetic

In the case of ferromagnetic substances we have a magnetization curve (Fig. 1.11).

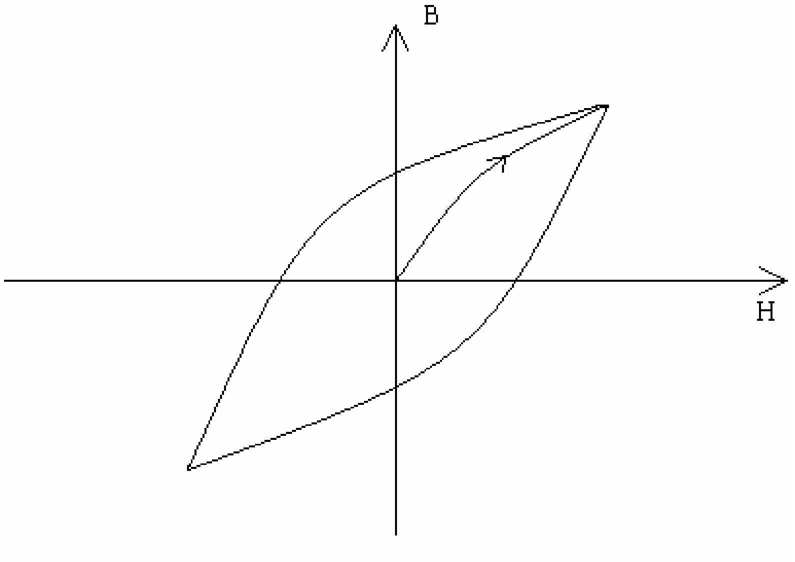


Fig. 1.11

This curve show the magnetic hysteresis. The area of the loop is proportional to the power of the magnetization cycle. A good magnetic tape or diskette need a magnet with large magnetization area.

Ferromagnetic substances change their magnetic susceptipility with the temperature according Curie's law:

$$\chi_m = \frac{A}{T} + B \tag{1.40}$$

A>0 and B are constants, T is the absolute temperature. With increasing temperature the susceptibility approaches zero, the magnetic state of the substance changes from ferro- to paramagnetism. This effect is applicable to switch on and out the electric power (e.g. for soldering irons).

1.5. Interactions with electromagnetic waves

A wave is periodic in time and space and propagates in space. Electric (**E**) and magnetic (**H**) waves propagate in an electromagnatic wave. Both **E** and **H** are perpendicular to the direction of the propagation (transversal waves) and they are also perpedicular to each other.

The electric field perturbs the atom or the molecule. If the energy difference between two energy levels of the atom (molecule) is equal to the energy of the photon propagating in the electromagnetic wave

$$\Delta E \equiv E_i - E_j = h\nu \equiv \hbar\omega \tag{1.41}$$

the absorption of the photon is possible (inelastic collision).

The light absorption depends on

- the probability of absorption;
- the relative population of the excited state;
- the average lifetime of the excited state.

A) The *probability* of the process must be larger than zero. The experession of the probability is

$$a_{i\leftarrow j} = \frac{1}{\hbar^2}\left|\int_0^{t_p} K_{ij}(t)\exp(i\omega_{ij}t)dt\right|^2 \tag{1.42}$$

t is the time, t_p is the time of perturbation, the first factor under exp i is the imaginary unit and

$$K_{ij} = \int \psi_i^* \hat{K}\psi_j d\tau \tag{1.43}$$

The $\hat{K}$ operator is the operator of perturbation, here the potencial energy operator that is simply the multiplication with the potential energy. The potential energy is

$$V = \Delta\mathbf{p}\mathbf{E} \tag{1.44}$$

$\Delta\mathbf{p}$ is the change of the dipole moment during the perturbation. Using Eq. 1.44

$$K_{ij} = \mathbf{E}\int \psi_i^* \Delta\mathbf{p}\psi_j d\tau \tag{1.45}$$

supposing local **E** (vibration) that is independent of the coordinates. The integral in Eq. 1.45 is called *transition moment*

$$\mathbf{P} = \int \psi_i^* \Delta\mathbf{p}\psi_j d\tau \tag{1.46}$$

If the transition moment is not zero, the absorption is possible. The square of **P** is proportional to the *transition probability of absorption.*

B) The effect of *population.* According to Boltzmann's distribution law

$$\frac{N_i}{N_j} = \exp\left(-\frac{E_i - E_j}{kT}\right) = \exp\left(-\frac{h\nu}{kT}\right) \qquad (1.47)$$

N is the population of the state. The relative populations depend on the frequency (Table 1.2)

Table 1.2
Frequency dependence of populations

ν /Hz	N_i/N_j
10^8	$1- (2 \times 10^{-5})$
10^{10}	0.99
10^{12}	0.85
10^{13}	0.30
10^{14}	10^{-7}

The process is determined by the relative population difference of the two states $(N_j-N_i)/N_j$. If it is large, then the excited state is far from the saturation, if it is small, the driving force of the process is very low. In the case of small energy differencies the saturation of the excited state at ambient temperature has reality.

C) The *average lifetime* of the excited state. This is the average period of the particles in the excited state. If this is long, the saturation of the excited state is easy, if it is short this is difficult. Some average lifetimes of different excited states are presented in Table 1.3.

Table 1.3.
Average lifetimes

type of the excited state	average lifetimes (s)
rotational	$10^{-10} – 10^{-11}$
vibrational	$10^{-7} – 10^{-8}$
electronic (singlet)	10^{-5} - 10^{-6}
electronic (triplet)	10^{-2} - 10

1.6. The electromagnetic spectrum

The *spectrum* is an intensity versus energy (frequency) curve. The spectra are recorded with *spectrometers.* Fig 1.12 presents the regions of the electromagnetic spectrum: the names (and colours) as functions of the frequency.

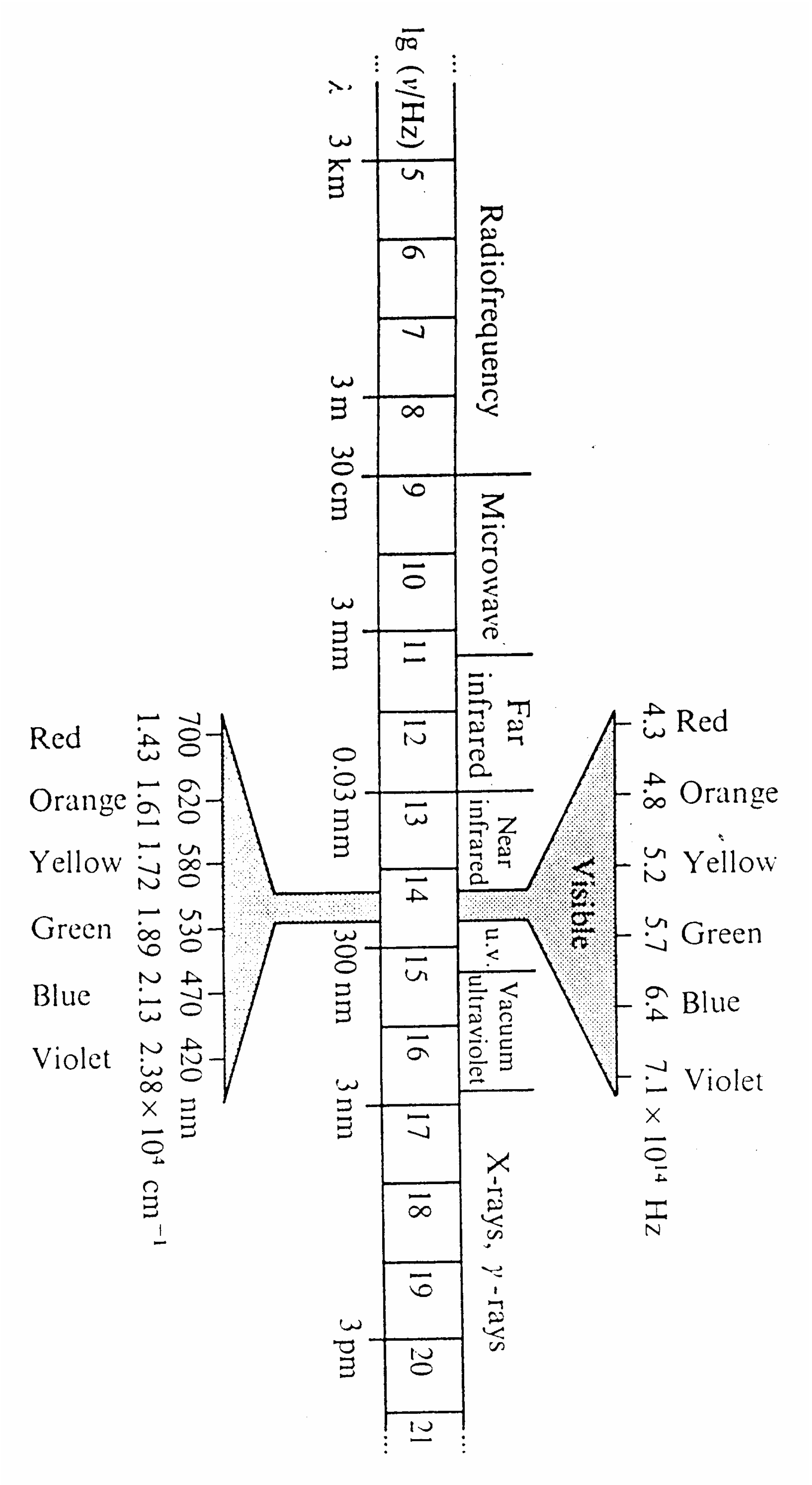

lg (ν/Hz)
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
λ
3 km
3 m
30 cm
3 mm
0.03 mm
300 nm
3 nm
3 pm
Radiofrequency
Microwave
Far infrared
Near infrared
Visible
u.v.
Vacuum ultraviolet
X-rays, γ-rays
Red
Orange
Yellow
Green
Blue
Violet
4.3 4.8 5.2 5.7 6.4 7.1 × 10^14 Hz
700 620 580 530 470 420 nm
1.43 1.61 1.72 1.89 2.13 2.38 × 10^4 cm^-1

Fig. 1.12

Two types of spectrometers are used in the optical spectroscopy: the dispersive and the Fourier transform (FT) one.

The *dispersive spectrometer* (Fig. 1.13). The light of the light source crosses the input slit. This is the input of the light resolving part. In this part, in the monochromator, the grating is the dispersive element. Turning the grating with the help driving motor different parts of the spectrum fall on the output slit. The light falls on the detector that transforms the optical signal to electric one. Two optical beams are used, a measuring and a reference one. These fall alternating into the monochromator. The electronics balances the two beams and amplifies the difference signal. The resulting signal appears on the screen of a computer and/or on the printer. The sample or the reference is placed on one of the starred positions: in infrared (IR) spectrometers after the light source, in ultraviolet (UV) an visible (VIS) spectrometers before the detector.

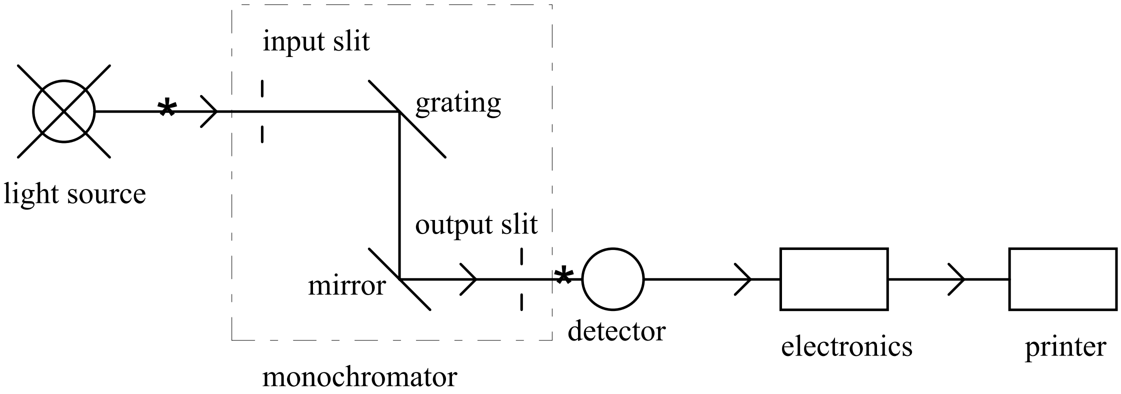


Fig. 1.13

The *Fourier transform spectrometer* (Fig. 1.14). The light of the light source falls on a beam splitter that divides the light into two beams. The first crosses the beam splitter and reflects from mirror M1, the second reflects first from the beam splitter and then from mirror M1. The two beams interfere on the beam splitter. The detector transforms the optical signals to electric ones. Through an ADC the data enter the computer. Mirror M1 will be moved. Since the optical path difference between the two interfering beams changes, the result is an intensity versus position M1 function, the interferogram. The computer carries out the Fourier transformation of the interferogram. The result is a one-beam spectrum. Independently also the spectrum of the reference must be recorded. The ratio of the sample and the reference spectrum is the usually used double-beam spectrum. The samples are placed on the starred positions.

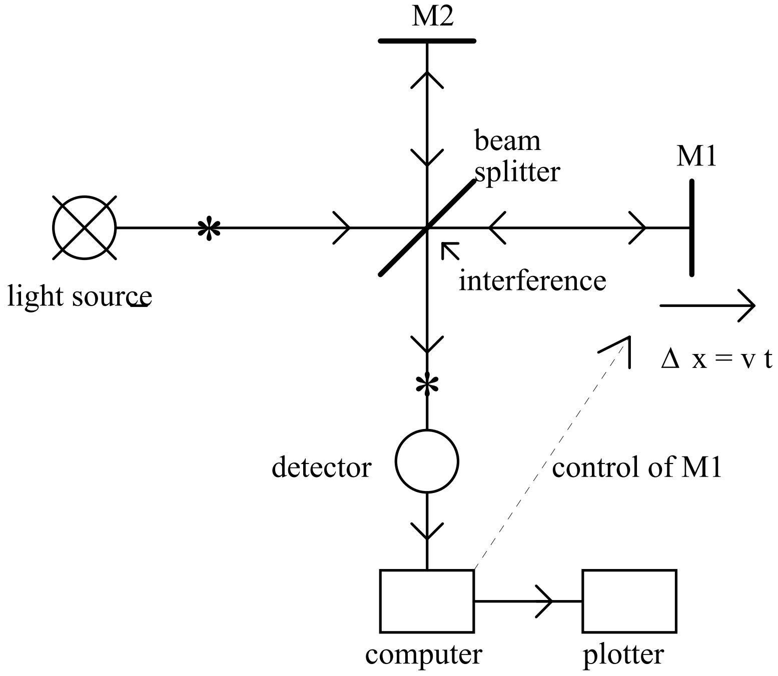


Fig. 1.14

The incident light partly reflects (reflectivity, r) from the surface of the sample, partly will be absorbed by the sample (absorptivity, a), the remaining part transmits the sample (transmittivity, t):

$$r + a + t = 1 \tag{1.48}$$

The *spectrum* consists of lines and bands. The *spectral line* is the signal of one transition. Practically it is the picture of the input slit (in case of dispersive spectrometer).

The *spectral band* (Fig. 15) belongs

- either to a series of transitons of the same origin but the environvent affected unequally on the molecules;
- or the frequencies of the transitons are very close to each other and the resolving power of the spectrometer is not sufficient to resolve the individual lines (e.g. rotational structure of rotational-vibrational transitions).

The *linewidth* is very important for the spectroscopist. The *natural linewidth* is determined by Heisenberg's uncertainty law:

$$\delta E . \delta t \geq \frac{h}{2\pi} \tag{1.49}$$

δ labels the uncertainty. In case of electromagnetic waves the energy uncertainty is $\delta E = h\delta\nu$, the time uncertainty is $\delta t = \tau$, the average liftime of the excited state. So we have for the natural linewidth

$$\delta\nu \geq \frac{1}{2\pi\tau} \tag{1.50}$$

The *Doppler effect.* An atom or a molecule approaches the detector with the velocity v and emits light with the frequency ν_0 and wavelength λ. The observed number of waves *increases* by v/λ if it approaches the atom or molecules. If the atom or molecule moves away from the detector, the number of observed waves *decreases* by v/λ. Since $\lambda=c/\nu_0$ (c is the velocty of light in vacuum) the frequency shift is

$$\Delta\nu = \nu - \nu_0 = \nu_o \frac{v}{c} \qquad (1.51)$$

The velocity v is positive, if the source approaches the target, and it is negative, if the source movees away. Since in gas phase the velocity distribution follows Maxwell-Boltzmann law, the spectral line becomes a well-defined profile.

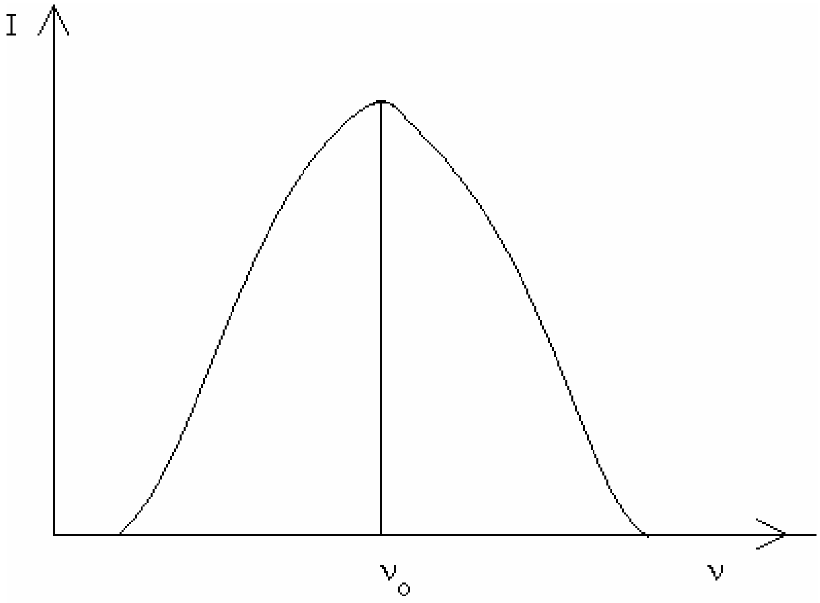


Fig. 1.15

Theoretically the change in the nuclear spin influences the electronic energy levels of the atom. Practitically, however, this effect is so small, that its influence is very rarely observable.

The measuring intrument influences the line profile, too. It broadens the lines and bands.

The *intensity* of the experimental spectra is measured

- either as the *transmittance* of the sample:

$$T \equiv \frac{I}{I_o} \qquad (1.52)$$

I is the trasmitted light intensity, I_O is the incident one, T is given in percents;

- or as *absorbance*

$$A \equiv \lg\left(\frac{I_o}{I}\right) = -\lg(T) \qquad (1.53)$$

The the intensity of the reflected light is measured as *reflectance*

$$R \equiv \lg\left(\frac{I_o}{I_r}\right) = -\lg(r) \qquad (1.54)$$

I_r is the intensity of the reflected light.

The independent variable of the spectra is either the frequency, or the *wavenumber*

$$\tilde{\nu} \equiv \frac{\nu}{c} \qquad (1.55)$$

or the wavelength.

The most important characterics of a band are presented in Figs. 1.16 and 1.17.

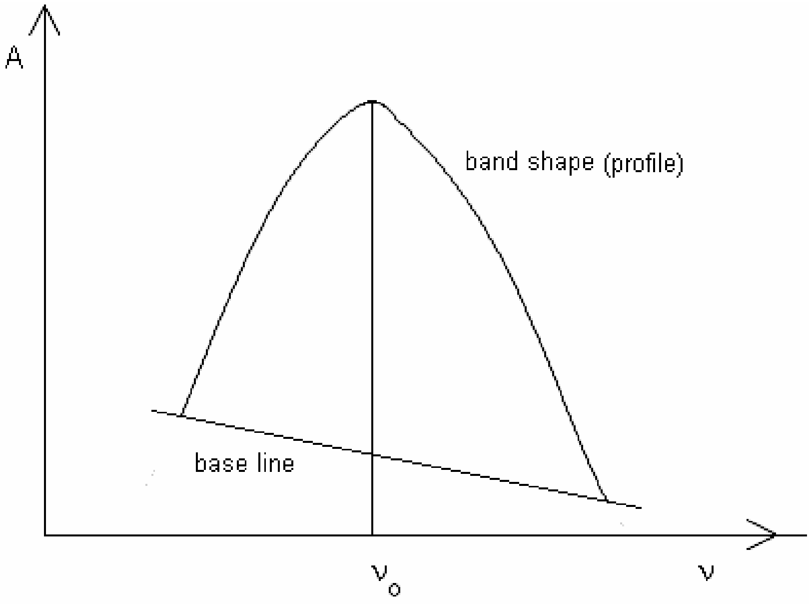


Fig. 1.16

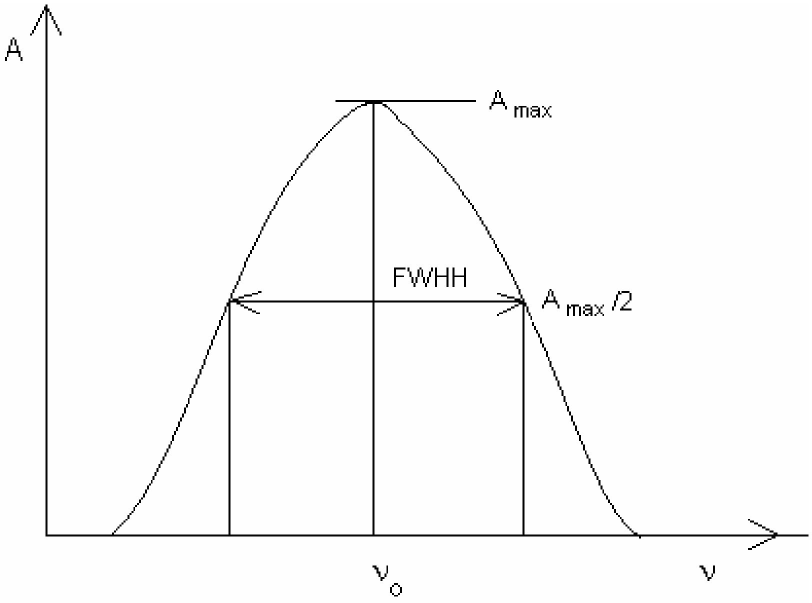


Fig. 1.17

A_{max} is the maximal absorbance at the nominal frequency ν_o , FWHH is the full width at half higth of the band.