3.6.4 The electron excitation spectra and the substituent effect

An electronic transition may be forbidden neverthless the corresponding bands may appear in the spectrum since the joining vibrational transitions are allowed. Their superposition can make the transitions allowed and we can find these bands in the spectrum with different intensities.

The band intensities in the electron excitation spectra are given with the molar absorption coefficient (Eq. 3.63, Table 3.16).

Table 3.16
The intensities in the electron excitation spectra

$\alpha/\mathrm{dm^3 cm^{-1}/mol^{-1}}$	intensity	transition
$\alpha \le 10$	very weak	forbidden
$10 < \alpha < 10^3$	weak	slightly allowed
$10^3 < \alpha < 10^4$	medium	allowed
$10^4 < \alpha < 10^5$	strong	allowed
$\alpha \ge 10^5$	very strong	strongly allowed

The *integrated intensity* of a band is

$$A = \int_{\text{band}} \alpha(\nu) d\nu \qquad (3.64)$$

The oscillator strength is a quantum chemical quantity that also the characterizes the band intensity:

$$f = A \frac{4 m_e c \varepsilon_o}{N_A e^2} \ln(10) \approx 1.44 \times 10^{-19} \times A \quad \mathrm{dm^3\, cm^{-1} s^{-1} mol^{-1}} \qquad (3.65)$$

m_e is the electron mass, e is the absolute value of its charge. The oscillator strength is proportional to the square of the transiton moment:

$$f = \frac{4\pi m_e \nu}{3\hbar e^2} P^2 \qquad (3.66)$$

The average lifetime of the excited state is proportional to the reciprocal of f. The energy levels of electrons and the transition moments are calculable quantum chemically.

There are groups in the investigated compound that are responsible for the absorption in the UV or VIS regions. These groups are the *chromofors.* The transitions may be besides $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ also $\sigma^* \leftarrow n$. If the π electrons are localized the corresponding bands fall into the high frequency part of the UV region or in the far UV (see Table 3.17). Localized π systems are results of the hybridization, the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) come closer the band shows a bathochromic effect.

Table 3.17
Characteristic bands of some chromofors in solution

molecule	chromofor	$\tilde{\nu}/\mathrm{cm}^{-1}$	λ/nm	$\alpha/\mathrm{dm}^{-3}\mathrm{cm}^{-1}\mathrm{mol}^{-1}$	type
C_2H_4	-C=C-	61.700	162	16.000	$\pi^*\leftarrow\pi$
$(CH_3)_2O$	>C=O	35.800	270	18	$\pi^*\leftarrow n$
		54.100	185	1.000	$\pi^*\leftarrow\pi$
CH_3NO_2	$-NO_2$	47.600	210	15.800	$\pi^*\leftarrow\pi$
		37.000	278	10	$\pi^*\leftarrow n$
C_6H_6	C_6	39.000	255	220	$\pi^*\leftarrow\pi$
		49.300	203	7.400	$\pi^*\leftarrow\pi$
		54.600	183	46.000	$\pi^*\leftarrow\pi$
CH_3Cl	-Cl	57.800	173	200	$\sigma^*\leftarrow n$
CH_3Br	-Br	49.000	204	260	$\sigma^*\leftarrow n$
CH_3I	-I	38.750	258	380	$\sigma^*\leftarrow n$

The band positions are determined essentially by the chromofors but the substituent effects and the solvents have also influences on these.

The *inductive effect* is a direct electrostatic effect that influences the electron distribution in the molecule. The reason is the dipole character of the substituent. The character and strength of the effect depend on the direction and largenesse of the dipole moment. The electron attracting groups show a -I effect, the electron repulsing ones a +I effect.

The order of the groups with +I effect is

$$-CH_3 < -C_2H_5 < -CH(CH_3)_2 < -C(CH_3)_3 < -S^- < O^- \qquad (3.67)$$

The order of the groups with -I effects is

$$-F > -NO_2 > -OH > -Cl > -NH_2 - Br > -I > -C = O > -COOH > -CN > -SH > -R_3N^+ \qquad (3.68.)$$

The groups containing free electron pairs but no double bonds are called *auxochromic groups* if they join groups with conjugated double bonds.

Fig 3.47 shows the possible structures of substituted benzenes as results of the I effects.

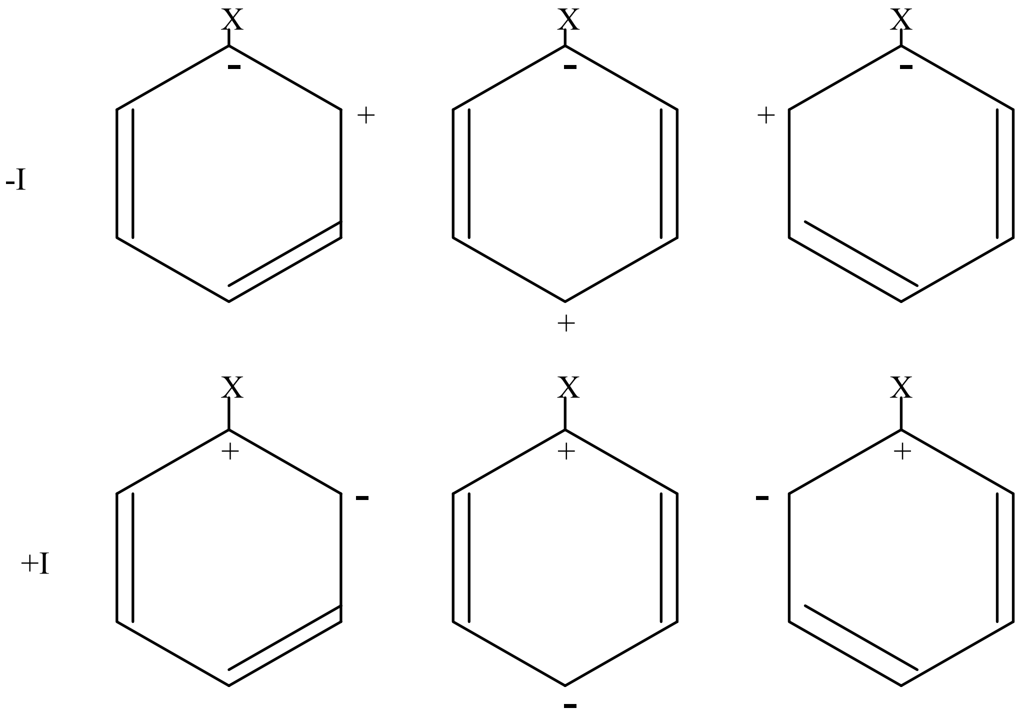

Fig. 3.47

The delocalized π electron system treats into conjugation with the groups containing double bond(s) and free electron pair(s). This *mesomeric effect* results also electron shifts.

The order of the groups with +M effect is

$$-\mathrm{F} < -\mathrm{Cl} < -\mathrm{Br} < -\mathrm{OH} < -\mathrm{OCH_3} < -\mathrm{NH_2} < -\mathrm{O^-} \qquad (3.69)$$

The order of the groups with -M effect is

$$-\mathrm{NO_2} > -\mathrm{CHO} > -\mathrm{COCH_3} > -\mathrm{COOH} > \mathrm{COO^-} \approx -\mathrm{CN} > -\mathrm{SO_2NH_2} \qquad (3.70)$$

Fig 3.48 shows the possible structures of substituted benzenes as results of the M effects.

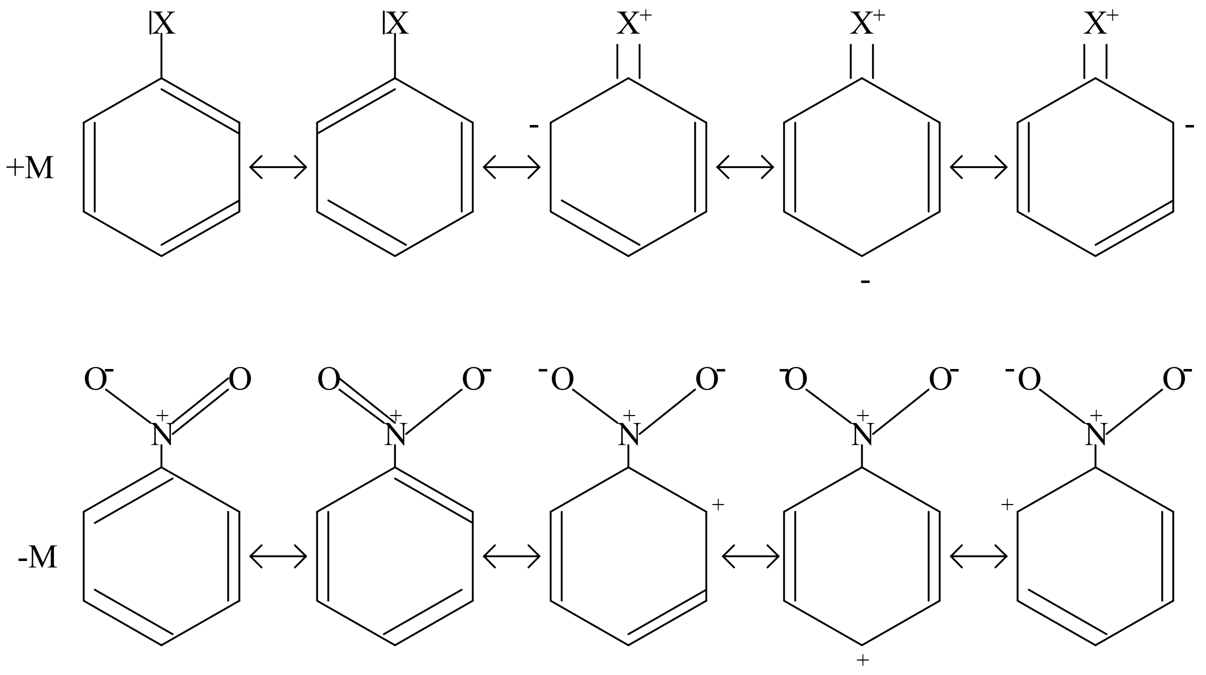

Fig 3.48

Investigating e.g. the substituent effect of aniline we find +M > -I, the positive effect dominates. For nitrobenzene, however, the substituent effect is -I, -M, i.e. the nitro group has a negative electron effect.

A quantitative measure of the substituent effect is its *Hammett constant.* This is the shift of the pK_a value of a substituted benzoic acid to the pK_a of the benzoic acid. The pK_a is the negative decimal logarithm of the ionization constant.

3.6.5 Measurement and application of electron excitation spectra

The UV and VIS spectrometers are dispersive instruments (Section 2.3.6). In the UV region the light source is a deuterium discharging lamp. The optics is made of quartz, the detector is a PMT with quartz window. The light source in the VIS is a tungsten or a halogen lamp, the optics is made of glass, the detector is a PMT. Since several spectrometers work in both UV and VIS, their optics is quartz and only the light sources are changed according the spectral region. These are double beam instruments, the sample and the reference are measured parallelly.

The recorded spectrum is the wavenumber or wavelength function of the absorbance. Since the accuracy of the absorbance is in these regions very good the UV and VIS spectrometry is applicable for quantitative analysis. Since there exist characteristic bands, also multicomponent analyses may carry out.

An interesting application of these measurements is the determination of the ionization constants. Recording the spectra as function of the solvent acidity we get a series of spectra. If in a given pH region the spectrum is constant this is a spectrum of an ion. With the knowledge of the spectra of the ions and their mixtures the ionization constant is calculable. Fig. 3.49 presents the acidity dependence of the pyrazine spectrum. The spectra cross one another in the same point. This is an *isobestic point:* at this wavelength is the absorbance independent of the solvent acidity.

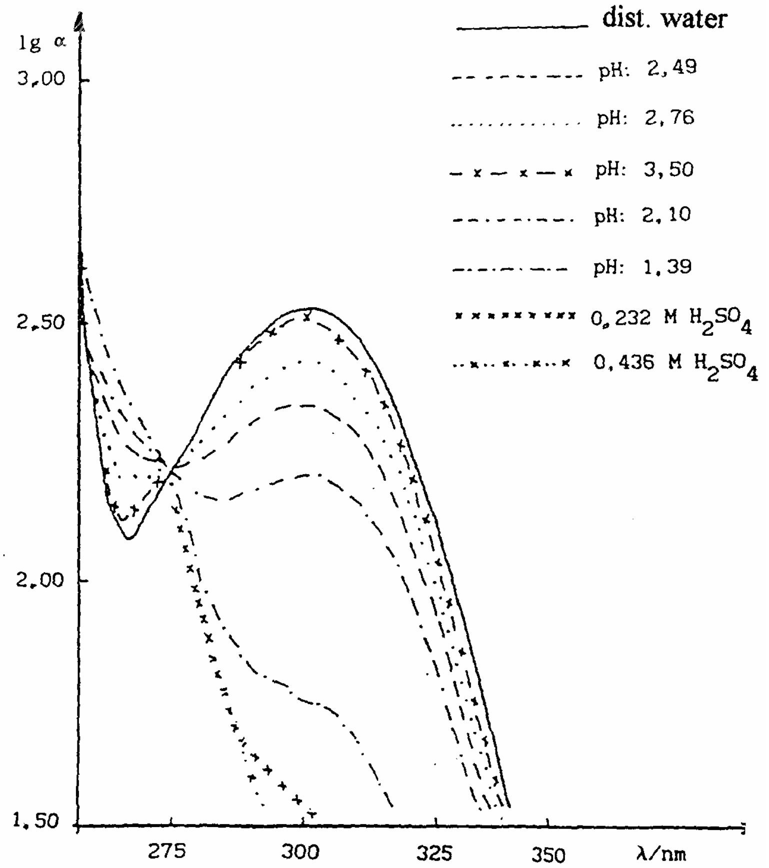

Fig. 3.49

3.6.6 Ultraviolet photoelectron spectroscopy (UPS)

The photoelectron spectroscopy is based on the inelastic scattering of a particle with particle change (Section 1.2). The high energy photon collides with the molecule in high vacuum and ionizes it. If the energy of the photon is greater than the ionization energy (I) of the molecule the difference appears as kinetic energy:

$$h\nu = \frac{1}{2}m_e v^2 + I \qquad (3.71)$$

The UV photons may have energy for the external ionization, for internal ionization X-ray photons (XPS) are necessary (Section 1.6). Since the electrons are situated on different orbitals there are several ionization energies. Besides, also the vibrational states may parallelly change. Therefore

$$h\nu = \frac{1}{2}m_e v^2 + I + \Delta E_v + \Delta E_r \qquad (3.72)$$

v labels the vibrational, r the rotational energy. The changes in the rotational energy are very small in comparison with I, the spectrometers cannot resolve these changes. If the vibrational state does not change during the ionization we speak about adiabatic ionization, all other are vertical ionizations.

According Koopman's theorem the absolute value of the ionization energy is equal to the orbital energy of the departed electron. This is a good approach and this is the basis of the interpretation of the photoelectron spectra.

The light source is a He discharging lamp, its 20.21 eV line is used (Fig. 3.50). The analyzer separates the electrons according to their velocity, the detector is a special PMT.

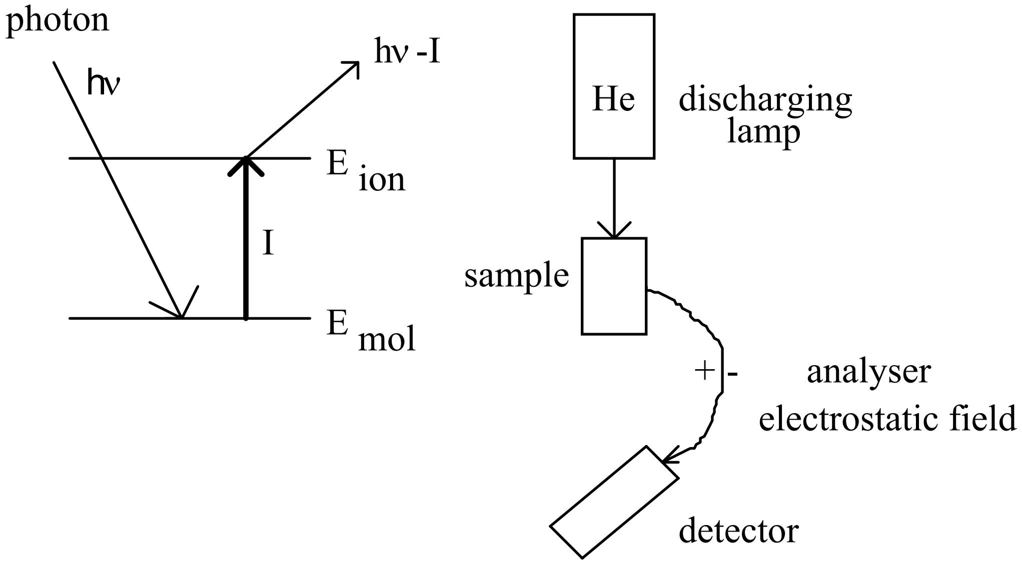

Fig. 3.50

The first derivative of the intensity - electron energy function has "spectrum like" shape. Fig. 3.51 shows the UPS spectrum of nitrogen completed with its XPS spectrum. The interpretation was based on Koopman's theorem.

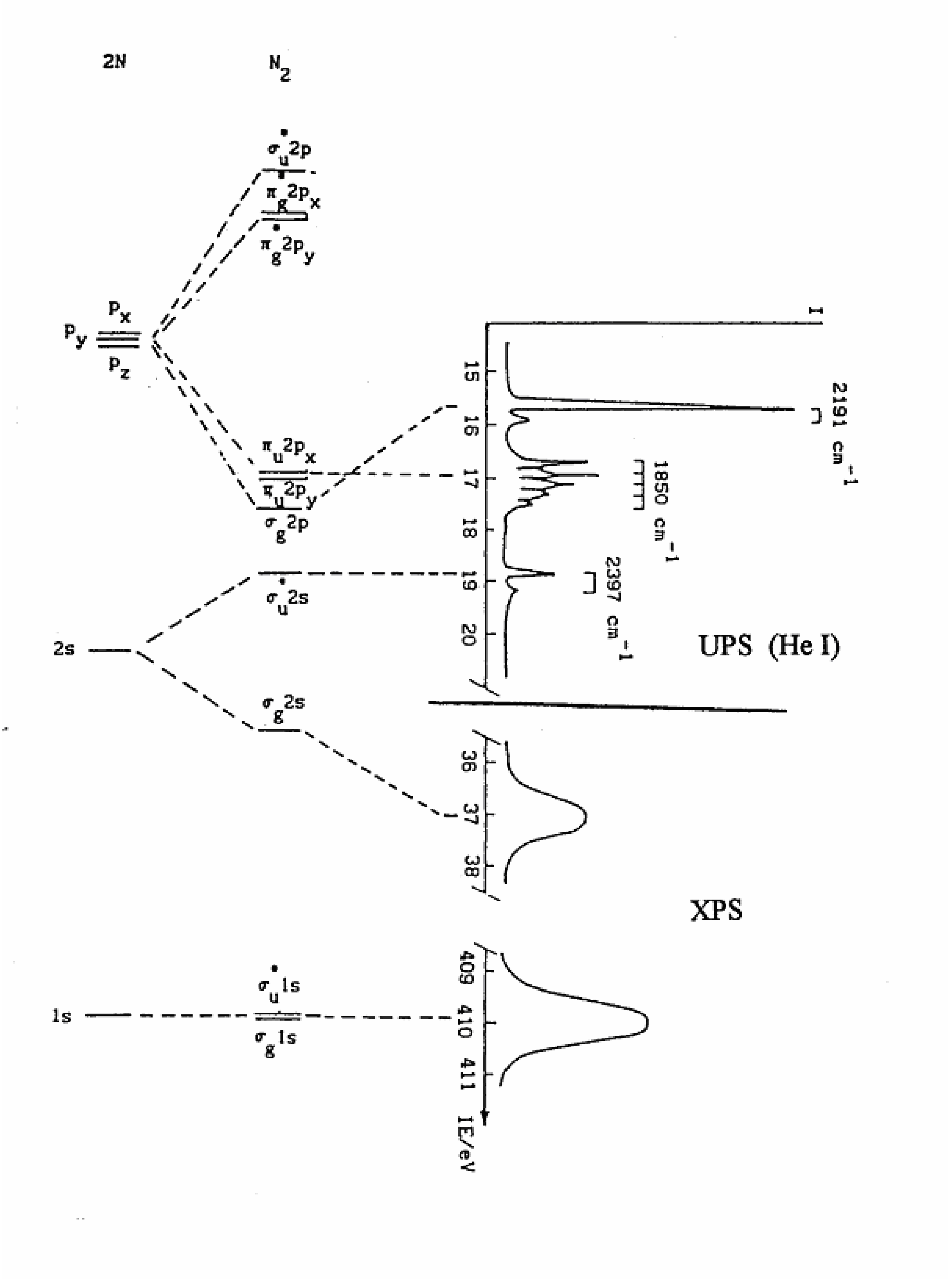
2N
N_2
$\sigma_u^* 2p$
$\pi_g^* 2p_x$
$\pi_g^* 2p_y$
p_x
p_y
p_z
$\pi_u 2p_x$
$\pi_u 2p_y$
$\sigma_g 2p$
$\sigma_u^* 2s$
2s
$\sigma_g 2s$
$\sigma_u^* 1s$
1s
$\sigma_g 1s$
I
15
16
17
18
19
20
2191 cm^{-1}
1850 cm^{-1}
2397 cm^{-1}
UPS (He I)
36
37
38
XPS
409
410
411
IE/eV

Fig. 3.51

3.7 *The dispersion of light*

3.7.1 *The dispersion of the refractive index*

The dispersion of the light is the frequency dependence of the refractive index (n), that is the ratio of the light velocity in vacuum (c) and in a medium (v):

$$n = \frac{c}{v} \tag{3.73}$$

and

$$v = \nu\lambda \tag{3.74}$$

Otherwise the refractive index is a function of the relative permittivity and relative permeability of the medium (see Chapter 1):

$$n = \sqrt{\varepsilon_r \mu_r} \approx \sqrt{\varepsilon_r} \tag{3.75}$$

Let z the direction of the light and x the transversal elongation of the electric field vector E, the electric wave has the form

$$E = E_o \exp\left[i2\pi\nu\left(t - \frac{nz}{c}\right)\right] \tag{3.76}$$

i is the imaginary unit.

If the light penetrates into the medium, the wave amplitude decreases exponentially, therefore

$$E = E_o \exp\left(-2\pi\nu\frac{n_k z}{c}\right)\exp\left[i2\pi\nu\left(t - \frac{nz}{c}\right)\right] \tag{3.77}$$

n_k is a damping factor.

The complex refractive index is

$$\mathit{n} = n - in_k \tag{3.78}$$

Considering the definition of the absorbance and the Lambert-Beer low

$$I = I_0 \exp(-\alpha c z \ln 10)$$

from Eq. 3.77 since $I \sim E^2$,

$$I = I_0 \exp(-4\pi\tilde{\nu} n_k z)$$

therefore

$$n_k = \frac{c \ln 10}{4\pi\tilde{\nu}}\alpha \tag{3.79}$$

c is the concentration of the solution.

. The imaginary refractive index is proportional to the molar absorption coefficient and depends on the light frequency.

The real part of the complex refractive index depends also on the frequency. Let the frequency of the light absorption ν_o, and let Δp_o the amplitude of the light induced dipole moment, then a good approach is

$$\Delta p_o = \frac{a}{\nu_o^2 - \nu^2} \tag{3.80}$$

a is constant. Fig. 3.52 shows the form of the exact function.

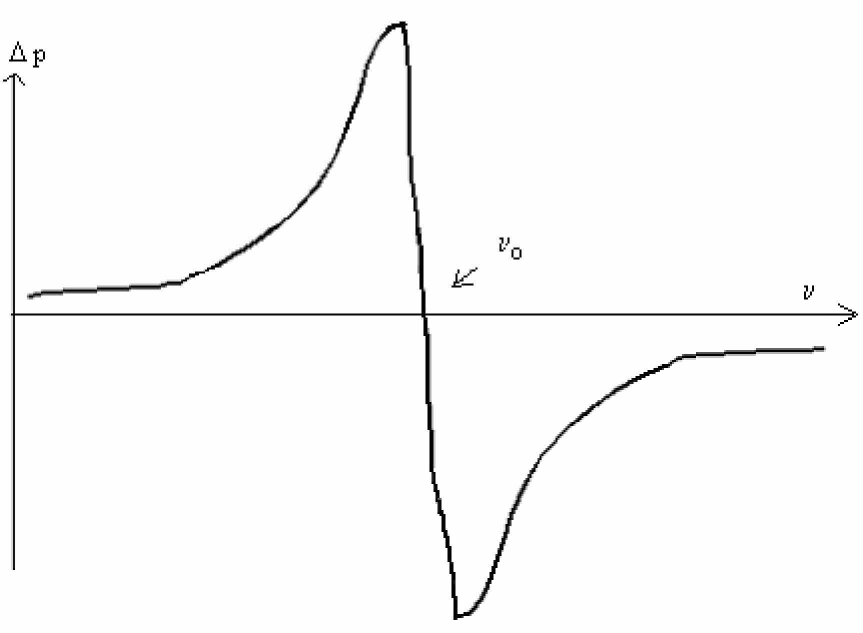

Fig. 3.52

According to Eq. 3.75 we have from Eq. 1.21 (molar polarization) the molar refraction:

$$R_M \equiv \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} \tag{3.81}$$

From Eqs. 3.80 and 3.81 we have the dispersional formula for n

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\rho_N}{3} \sum_i \frac{C_i A_i}{\nu_{o,i}^2 - \nu^2} \tag{3.82}$$

ρ_N is the particle density, i labels the absorption maxima, C_i's are constant, A_i is Einstein's absorption probability that is proportional to the square of the transition moment.

$$A_i = \frac{P_i^2}{6\varepsilon_o \hbar^2}$$

Fig. 3.53 is the dispersion curve of the real refractive index. If the refractive index increases with the frequency the dispersion is normal, if it decreases (at the absorption maxima) it is anomalous.

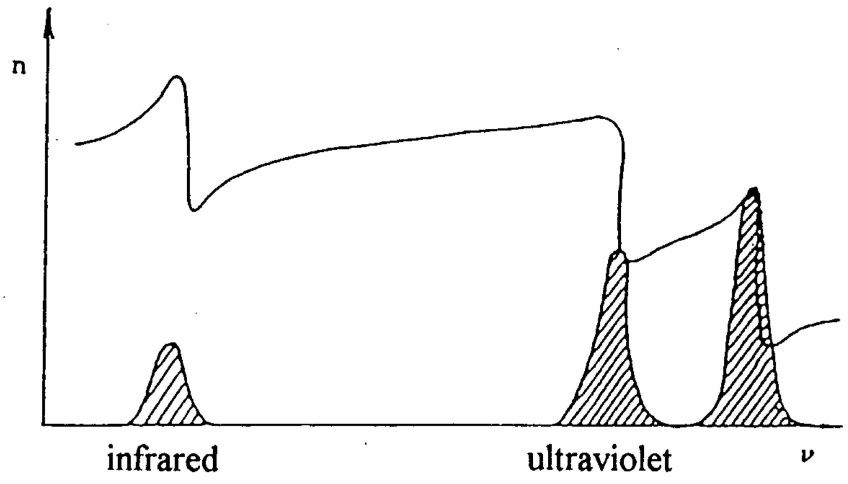

Fig. 3.53

3.7.2 Electron excitation with polarized light

A molecule (a substance) is *optically active* if it rotates the plane of the linearly polarized light. We regard this light as the result of two counter-rotating circularly polarized lights (L and R) having different velocity in the medium (see Fig. 3.54). Therefore the refractive indices are different, the plane of polarization rotates, the substance is birefringent. The angle of rotation characterizes the effect:

$$\Delta\vartheta = 2\pi\ell\frac{n_L - n_R}{\lambda} \tag{3.83}$$

Here if $n_L > n_R$, the substance rotates to right, ℓ is the length of the sample.

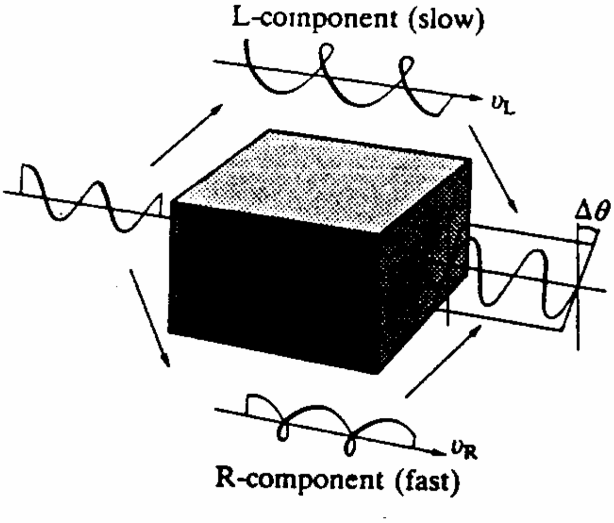

Fig. 3.54

The *specific rotation* is

$$[\alpha]=\frac{\Delta\vartheta}{\ell c} \tag{3.84}$$

c is the concentration. The molar rotation

$$[\mathrm{M}]=10^{-3}\mathrm{M}[\alpha] \tag{3.85}$$

M is the molar mass.

The *optical rotatory dispersion* (ORD) is the frequency dependence of the optical activity. If the rotational angle decreases with the frequency in the region of the anomalous dispersion of the optical activity , this is the positive *Cotton effect*, and the opposite case is called negative Cotton effect (see Fig. 3.55).

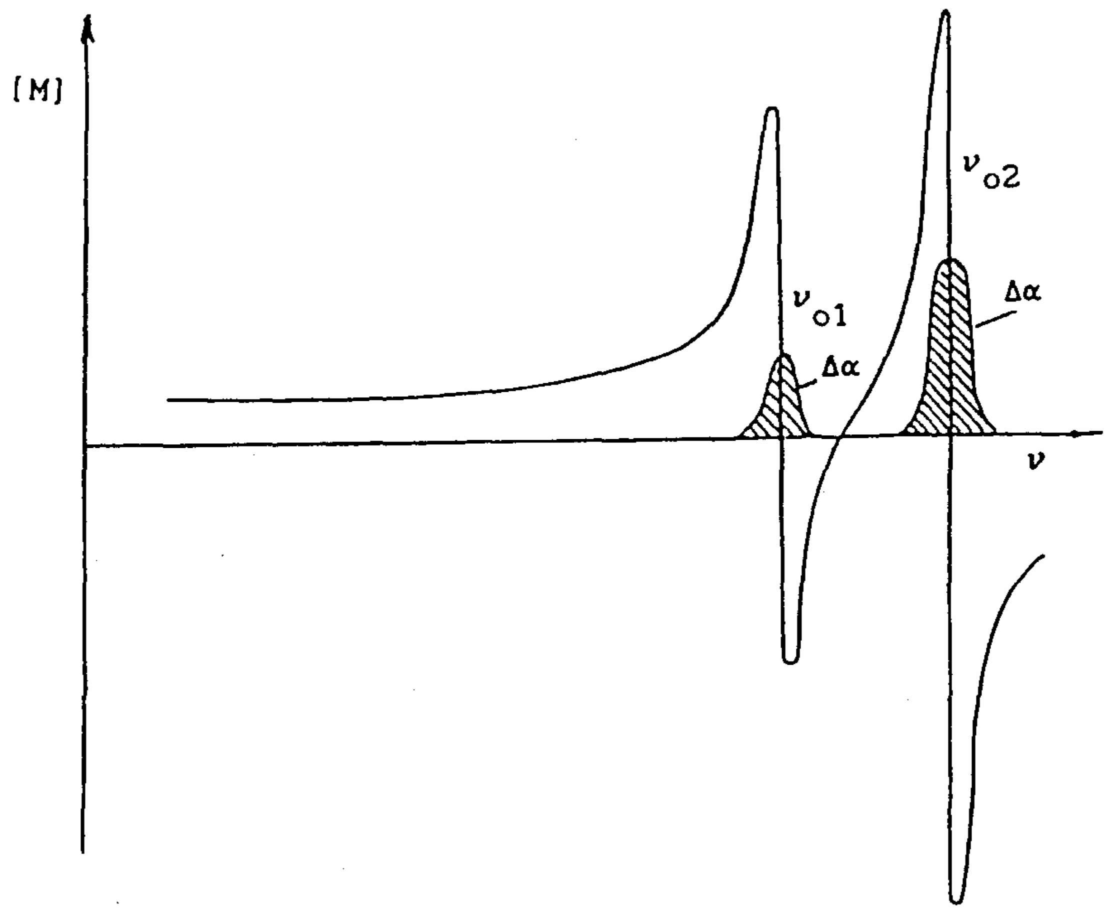

Fig. 3.55

The *circular dichroism* (CD) is observable if the molecule absorbs the L and R circularly polarized light with different intensity. This is the case of the asymmetric carbon (very often) and nitrogen (rarely) atoms and some asymmetric transition metal complexes. The measure of the CD is the difference of the two molar absorption coefficients:

$$\Delta\alpha = \alpha_R - \alpha_L \qquad (3.86)$$

The CD spectrum is the frequency dependence of $\Delta\alpha$, or the dependence of the molar ellipticity, $[\Theta] = 3300\Delta\alpha$ The form of the spectrium is affected by the chromofors, and also by the substituent effects of other groups.

Both ORD and CD give information about the symmetry centers of the molecule. The ORD gives information from all these centers, the CD only from the environment of the chromofors if there are optically active centers in it. Both methods help in the determination of the absolute spatial configuration of molecules.

ORD and CD spectra are recorded on spectropolarimeters. Fig. 3.56 shows the ORD spectra of molecules with negative (dashed) and positive (full) Cotton effect.

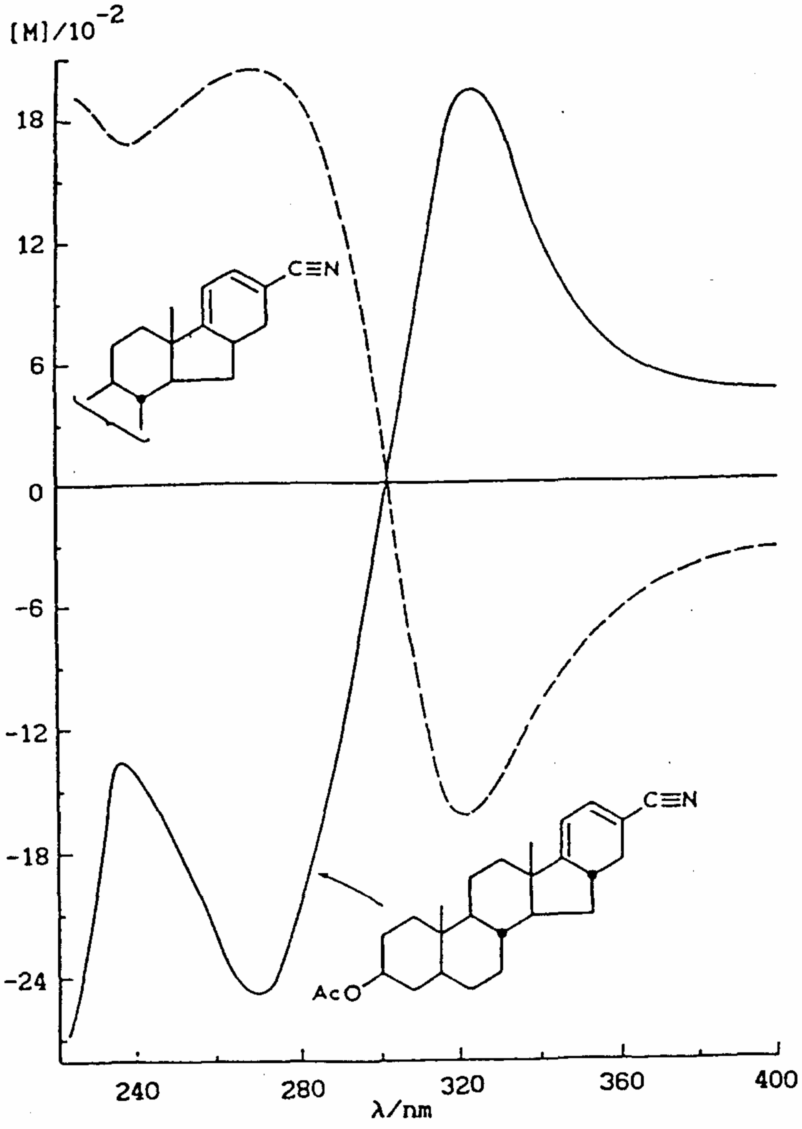

Fig. 3.56

Fig. 3.57 contains the CD spectra of molecules with negative (dashed) and positive (full) Cotton effect.

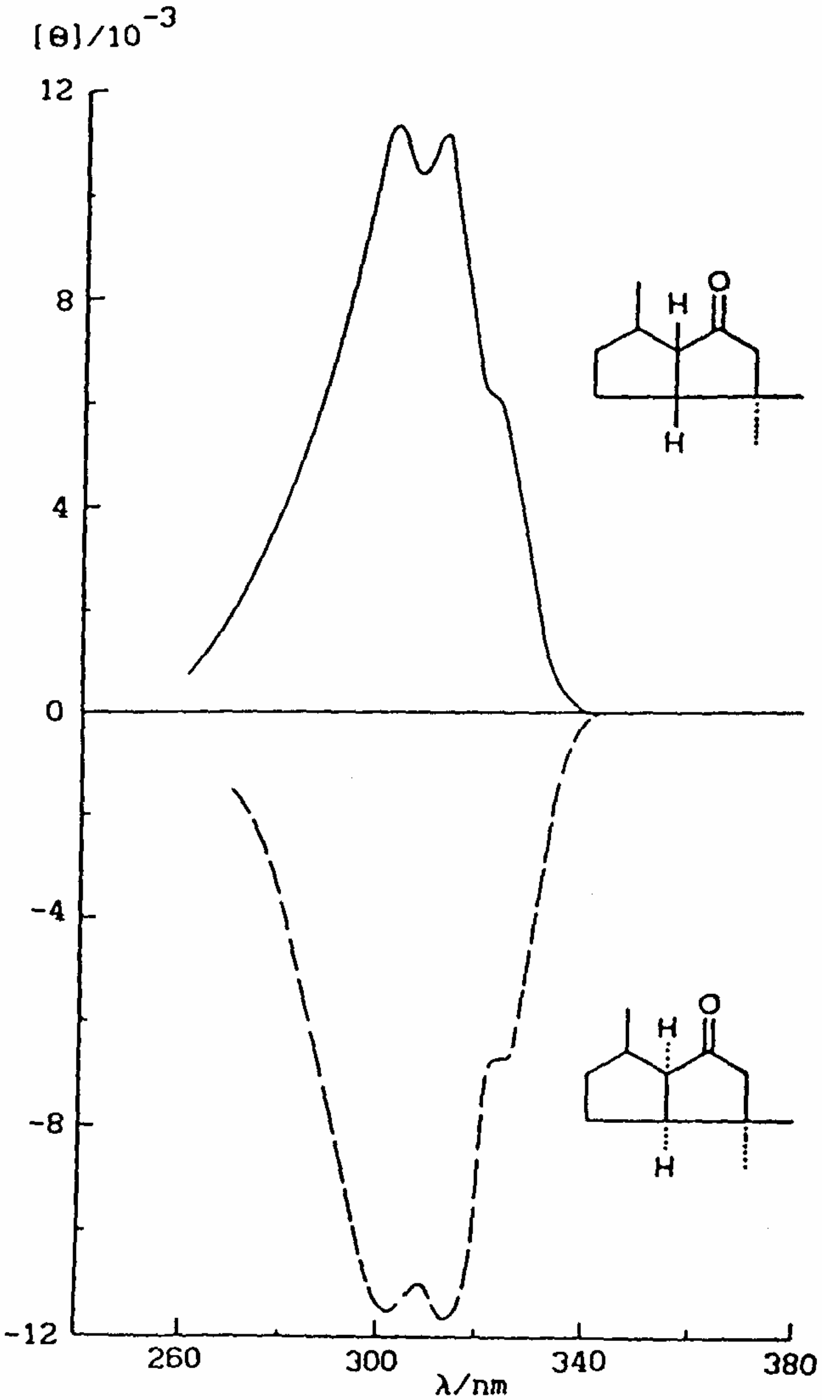

Fig. 3.57

Fig. 3.58 compares the electron excitation (UV), the ORD and the CD spectra of the same molecule.

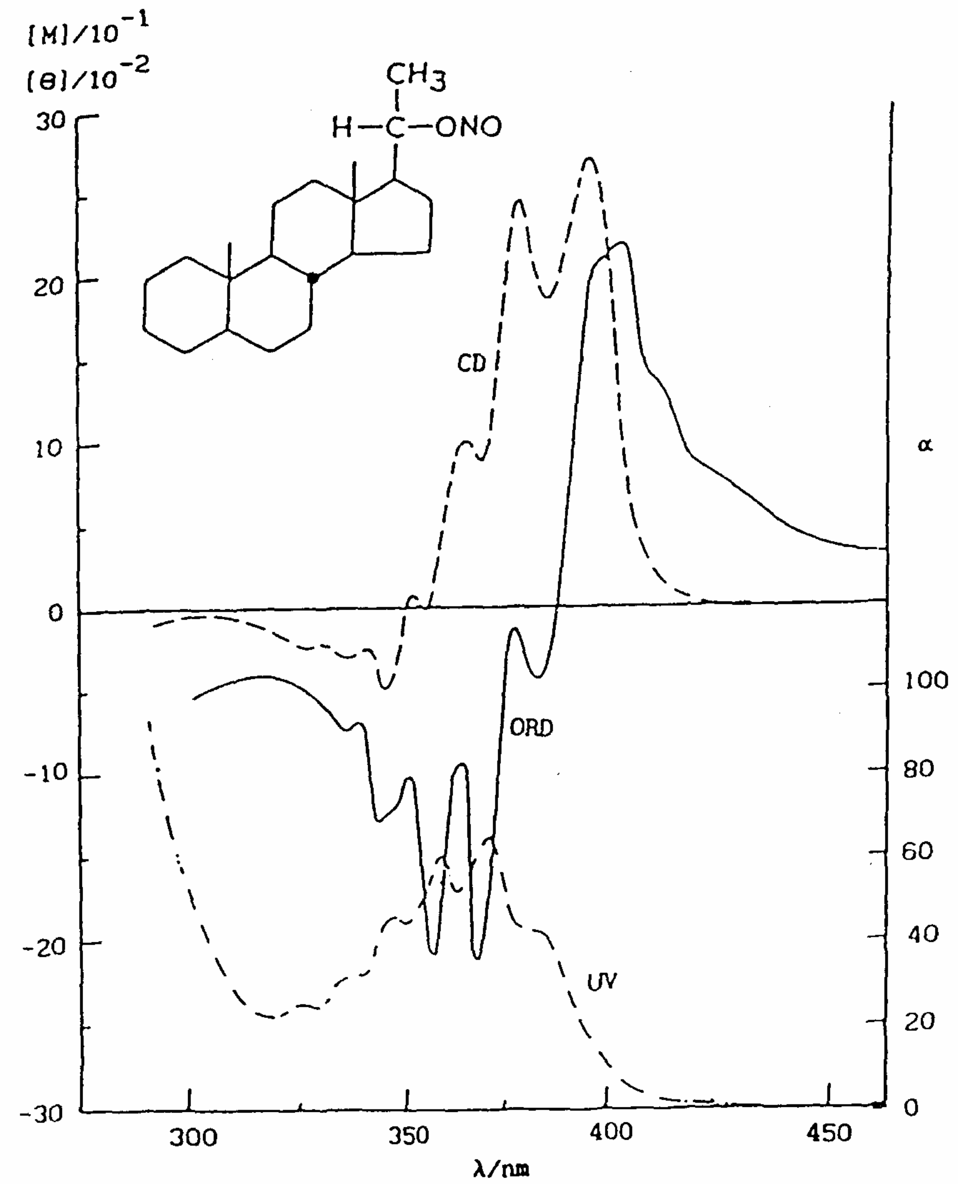

Fig. 3.58

The forms of the CD curves are influenced by the chromofores. Some other atomic groups act on the CD curves through their electronic effects since they influence the electron distributions of molecules. The effect of the optically active centers in the vicinity of the chromofors depends on their relative position. According to the *octant rule* the space around the chomofor is devided into eight octants. Depending on the octants of the substitents of the chiral carbon atom they add a positive or a negative member to the Cotton effect.

Let us compare the ORD and the CD methods! Both give us information about the asymmetric centers of the molecule. The ORD curve present information about all the asymmetric centers of the molecule, this is the beckground or skeleton effect, and also information about the stereochmical environment of the choromofors if they are bonded to active centers.

The CD curve presents information only about the nearest stereochemical environment of the chromofors, if there is an optically active center in this environment.

The ORD and CD measurents give very useful information about the conformation of the molecule. This is very useful for the determination of the structure of molecules of natural origin (see Figs. 3.56 and 3.58).

Special spectrometers are applied for the measurements of the ORD and CD curves, the *spectropolarimeters* working in the UV and VIS spectral regions.

ORD spectra of those compounds are preferred, that have not chromofors in the vicinity of asymmetric centers or the chromofor absorbs in the far UV region (below 200 nm).

On the effect of *external magnetic field* also those compounds rotate the plane of the linear polarized light, which are otherwise optically inactive. This is the *Faraday effect*. The corresponding magnetic methods (MORD and MCD) have not practical importance.

3.8 Mass spectroscopy

3.8.1 The principle and instrumentation of mass spectroscopy (MS)

The mass spectroscopy is based on the ionization of the molecules. It was applied for the separation of the atomic isotopes already in the second decade of the last century.

It has two important applications:

- the structure elucidation of the molecules,
- in the chemical analysis, coupled to chromatograph (GC-MS).

The mass spectrometers have three principal components: the ionizer, the analyzer and the detector.

The most popular method of the *ionization* (Section 2.4.1) is the *electron impact* (EI). The electrons are produced through thermal electron emission (W, Ta or Mo cathodes) and accelerated by an electric field (predominating +70 V). The kinetic energy of the electrons depends on the strength of this field.

The measurement is realizable only in high vacuum (10^{-4}-10^{-6} Pa). This vacuum is necessary for the collision of the electrons with the molecules. Low energy electrons only ionize the molecule, electrons having higher energy causing the dissociation of chemical bonds and ionize the new particles, the *fragments.* This is the process of *fragmentation.* The fragments characterize the molecule. There are multi-ionizations possible, fragments may have also negative charges or they may be also neutral.

In the process of *chemical ionization* (CI) the first step is the yielding of a high energy gas plasma (CI plasma) with electron impact. As plasma gas mostly ammonia, isobutane or methane are used. During the CI both positive and negative ions are produced. The pressure in the ionization chamber is about 10 Pa. A possible reaction is (if XH^+ is the bombarding ion, M is the molecule)

$$XH^+ + M = X + MH^+$$

As result a peak will appear at the mass of M+1 (M+1 peak).

The *fast atomic bombardment* (FAB). The molecules are bombarded with fast Ar or Xe atoms or Cs^+ ions. This is a soft ionization: only positive ions are yielded, fragments are not produced, $X^+ + M = X + M^+$.

Several other ionization methods are elaborated, some for the GC-MS coupling.

The most important *analyzer types* apply either electric and/or magnetic fields for the separation of the ions.

The *magnetic mass analyzer* is based on the effect of the magnetic field (B) on moving ions: the field B forces the ions on a ring orbital (Fig. 3.59), the detector is here PMT.

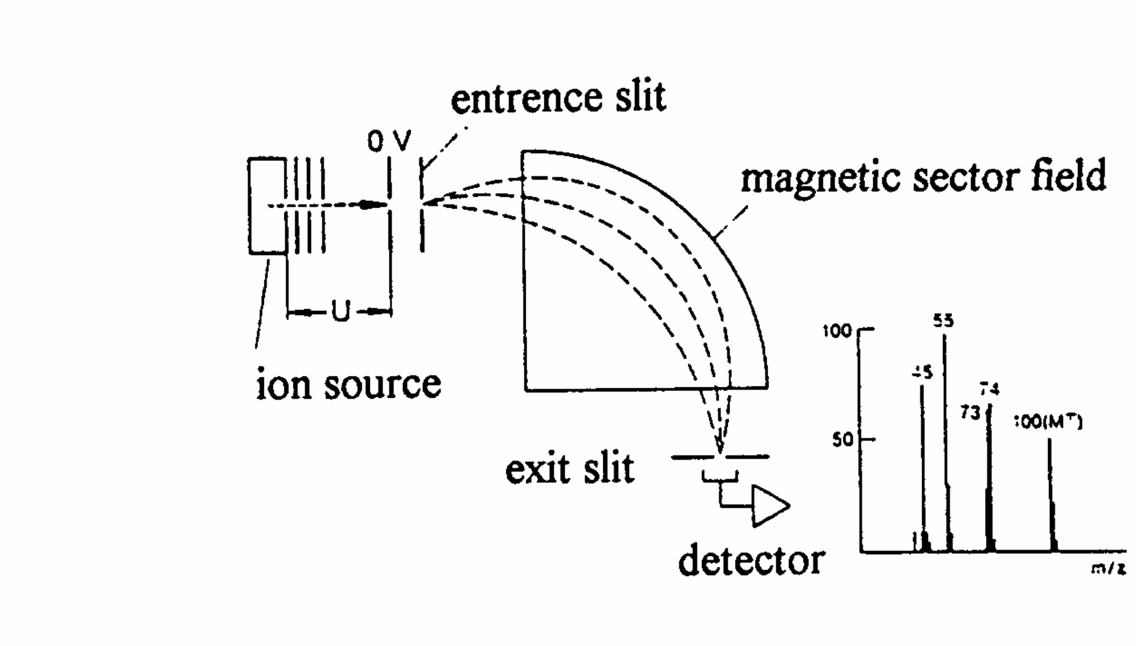

Fig. 3.59

Let the ion move with velocity v, mass m and charge z on a ring with radius r. The ions are accelerated with an electric field of U voltage. The force forced the ion on a ring orbital that is equal to the centripetal force:

$$zvB = \frac{mv^2}{r} \tag{3.87}$$

In this way the potential energy of the ion is transformed to kinetic energy:

$$zU = \frac{mv^2}{2} \tag{3.88}$$

The mass belonging to unit charge (i.e. the absolute value of the electron charge) is therefore

$$m/z = \frac{B^2r^2}{2U} \tag{3.89}$$

If both U and B are constant the ions with charge +1 (z=e) come to different orbitals according their masses. The detector is either photo plate, film or PMT. If the detector is a PMT the field strength B is changed to forced every ion after one other to the same orbital. Of course, in this case the signals of the ions appear separately, each after the other. The resolution of the instrument ($m/\Delta m$) is about 5,000, the upper limit of the measurement is m/e=1.500 dalton/charge unit.

The *twice focused spectrometer* improves the uncertainty in the ionic velocity (Boltzmann distribution). An electric field energy is applied before the magnetic field (energy focusing, Eq. 3.88). The velocity distribution according to the different orbit radius is compensated in this way. Therefore the resolution increases to over 100,000, the limit to m/e= 50,000.

The *quadrupole mass spectrometer* consists of four parallel metal bars (Fig. 3.60).

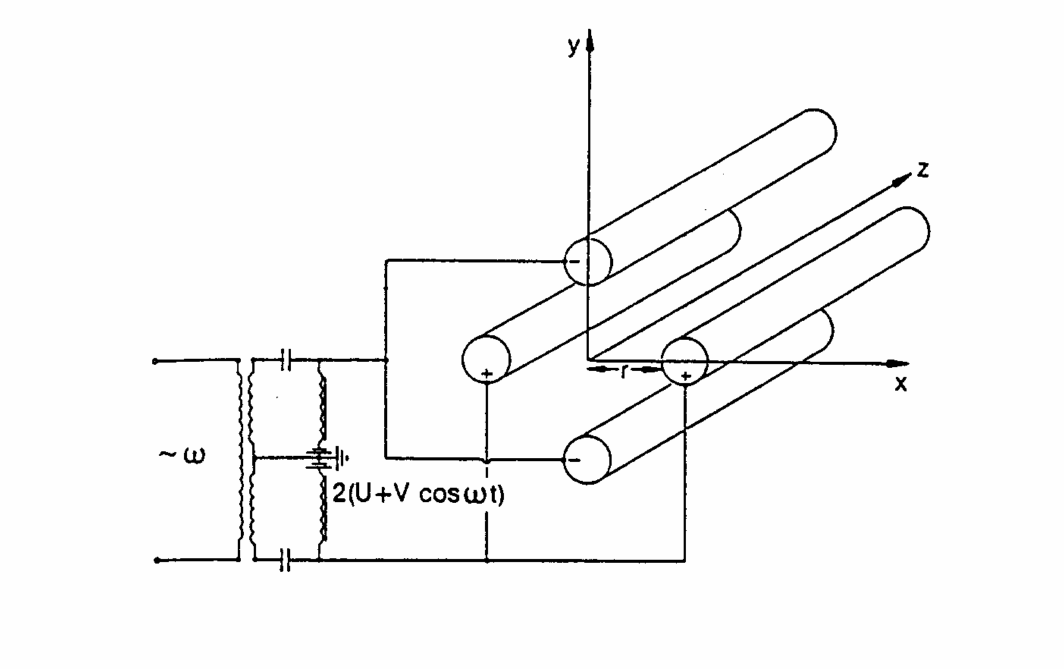

Fig. 3.60

Opposite bars are equally, neighbouring are differently charged (+ or -) under dc. voltage U. An ac. voltage (V) is superimposed on U having frequency ν. The particle moves between the bars parallelly to them. If its velocity is enough to across the system during a half period, it moves further:

$$m/z = \frac{5.7V}{4\pi^2 \nu^2} \tag{3.90}$$

This is a typical mass filter. The resolution is low, only 1, the mass limit is m/e=4,000. It is very often applied in GC-MS.

The *time-of-flight analyzer* (TOF) accelerates all ions with the same U dc. voltage. The time of covering the distance s depends on the mass (from Eq. 3.87)

$$m/z = \frac{2U}{s^2} t^2 \tag{3.91}$$

The time-of-flight is measured. The resolution is about 10,000, the mass limit is m/e>200,000.

The *ion-cyclotron mass spectrometer* (ICR-MS) or *Fourier transform MS* (FT-MS) is based on the effect that the B field forced the ions on ring orbitals. Irradiating these ions with a wide range radio frequency perpendicular to B, they receive selectively energy from the radiation. Therefore the orbital radius increases and the rotation become in phase with the radiation. The result is an induced voltage that can be detected with the electrodes standing perpendicularly to the direction of both B, and also the irradiation (Fig. 3.61). The Fourier transform of the detector signal gives the mass spectrum. For small fragments the resolution is very high (over 10^6).

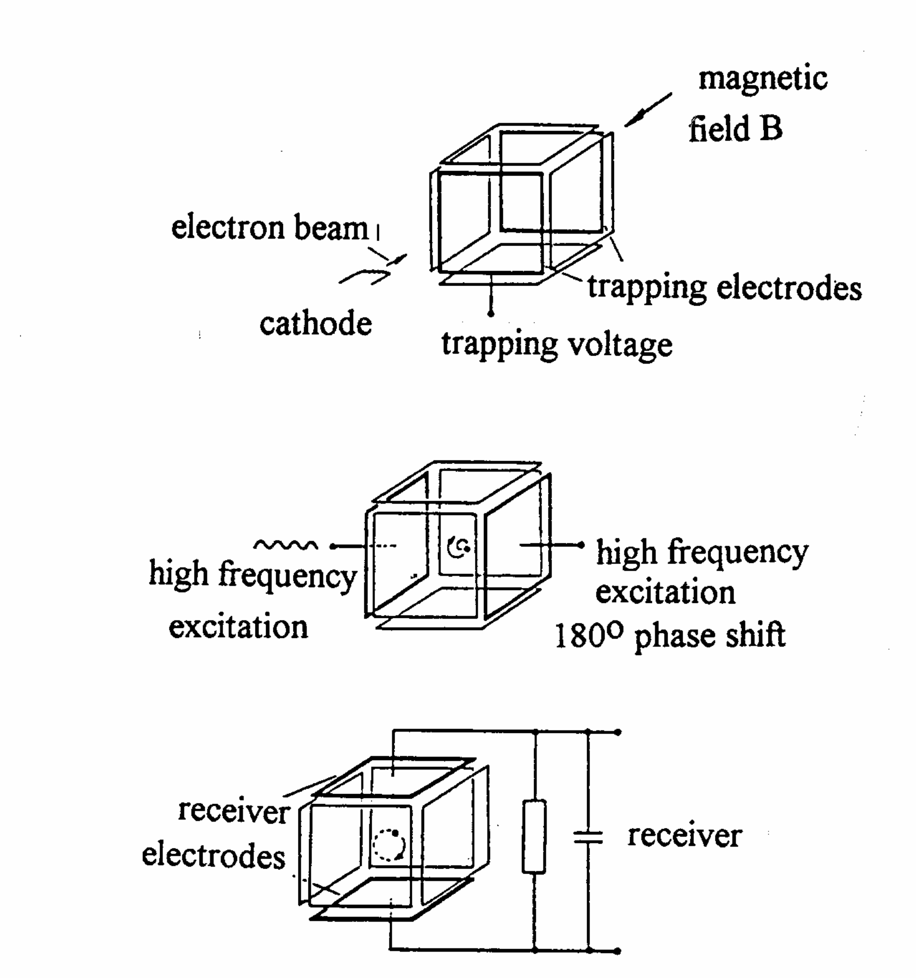

Fig. 3.61

The *tandem mass spectrometers* consist at least of two coupled mass spectrometers (MS/MS). One ion is selected from the fragment ions of the first MS and led to the second one. Here a second fragmentation can follow for the better identification of the primary fragment. This can be important in the environmental analysis and in metabolism studies.

3.8.2 Applications of the mass spectroscopy

The following *peak types* may appear in a mass spectrum:

- molecule peak M/e, if the field energy is at least equal to ionization energy of the ion;
- fragment peaks: they indicate the fragments of the molecule ion but as results of possible rearrangings in the molecule also peaks of groups may appear that are originally not present in the molecule;
- multi-peaks: they belong to m/z ($z>e$) and give the possibility of measuring molecules having very high molecular masses;
- metastable peaks: the peaks of ions having shorter lifetime than the time-of-flight from the ion source to the detector. If an ion with mass m_2 is formed from the ion with mass m_1 a diffuse peak appears at

$$m^* \approx \frac{m_2^2}{m_1} \tag{3.92}$$

An important application of the MS is the *chemical structure elucidation.* The formation of the predominant part of the fragments is interpretable with chemical reactions since during the reaction functional groups split from the molecule. In this way we can draw conclusions on the structure of the molecule. Fig. 3.62a presents the mass spectrum of 2-methylpentane, Fig. 3.62b is the mass spectrum of its isomer the n-hexane. Both molecules have the molar weight 86 dalton.

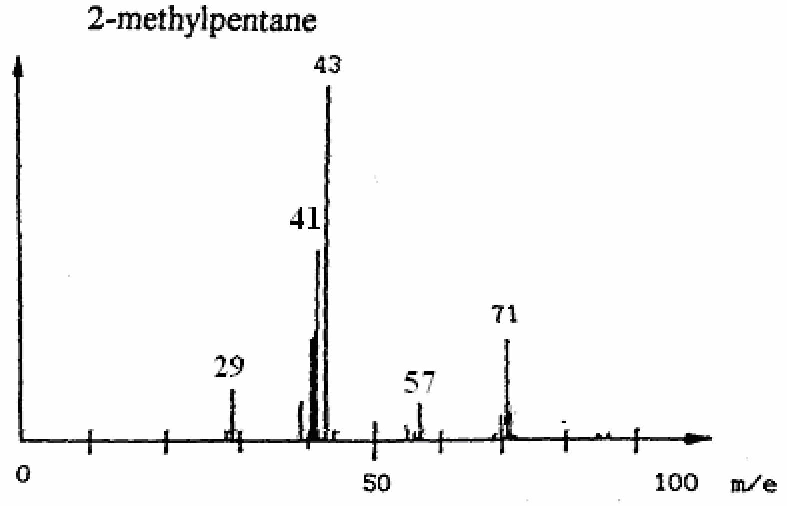

Fig. 3.62a

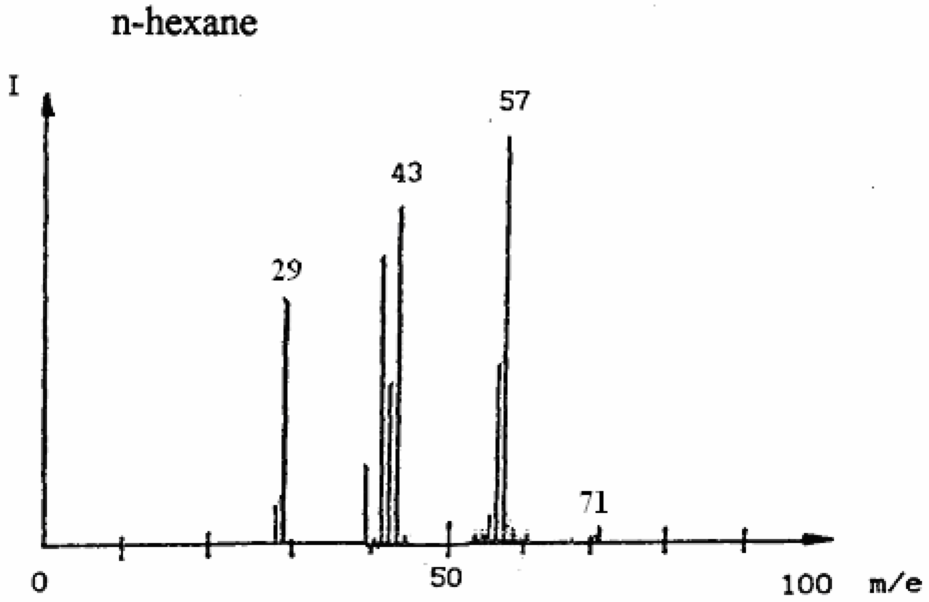

Fig. 3.62b

The peaks m/e=43 and m/e=57 dominate in the mass spectrum of 2-methylpentane. The first peak shows the splitting of the molecule into two 2-propyl (CH_3-CH-CH_3) radicals: 43+43=86, the C2-C3 bond splits in this case. Besides, the stronger m/e=57 peak shows the splitting of the molecule into an ethyl group and a t-butyl group (86-29=57).

The peaks m/e=71 and m/e=43 dominate in the mass spectrum of n-hexane. The first peak shows the splitting of the molecule into a methyl group (m/e=15) and an n-amyl group (m/e=71). The second peak refers to the splitting of the molecule into two equal parts. Both spectra contain also the peak of the ethyl group (m/e=29).

Fig. 3.63 presents the mass spectrum of thiophen together with the corresponding reactions. The processes can be easily followed.

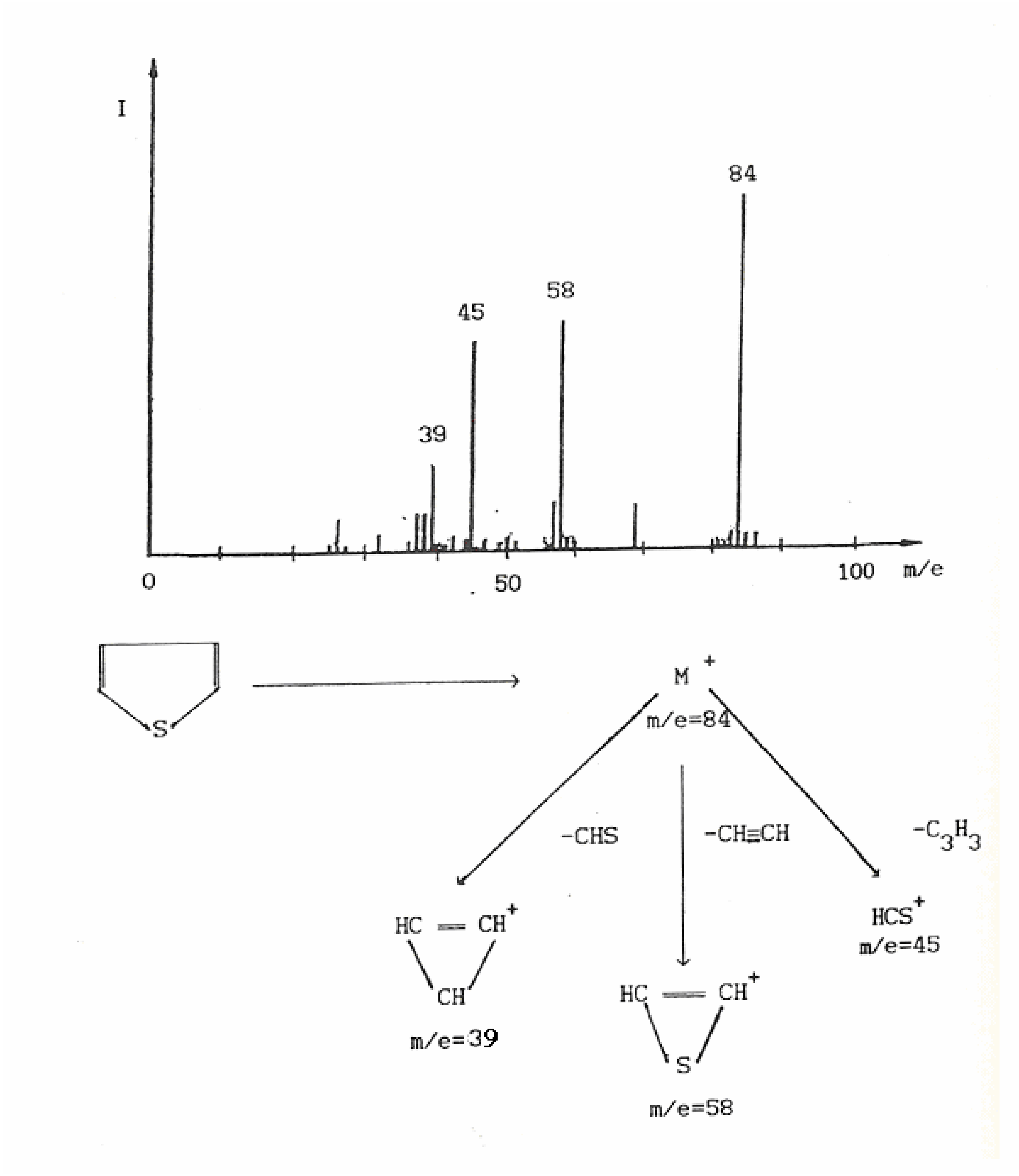

Fig. 3.63

The *ionization energy* is determinable with mass spectroscopy. In this case electrons with very low energy dispersion are necessary for the ionization. So the molecule peak becomes more intense. Also dissociation energies, heats of formations of ions and radicals are determinable. The mass spectrometers give always vertical energies (Section 3.6.6). Since also negative ions are produced in mass spectrometers the electron affinities are also determinable.

The MS has the advantage of high sensitivity and the fastness. Its drawback is that it is only in gas phase applicable. The newer ionization methods (electrospray, thermospray, etc.) and sample preparation methods remove this drawback. These methods extended the applicability of the MS to *substances with high molar masses*: MS is very often used in biochemistry (biopolymers) and in the plastic research (synthetical polymers).

High resolution ($m/\Delta m > 1{,}000$) mass spectra are used in the environmental analysis for the determination of the *isotopic composition* of the compounds. This analysis gives the possibility to determine the origin of the substance.

3.9 Paramagnetic properties of molecules

3.9.1 Paramagnetic molecules

Section 1.4.4 dealt with the paramagnetism. The spin and orbital magnetic moments of molecules were mentioned. If these moments are not balanced the molecule shows paramagnetism. From the viewpoint of chemistry the unbalanced spin magnetic moment is important. Free radicals, triplet state molecules (Section 3.6.3), transiton metal complexes with unpaired d electrons are paramagnetic.

A good example of the paramagnetic compounds is the oxygen molecule having two unpaired electrons, i.e. it is a biradical. The high spin complexes (Section 3.3.5) are examples of paramagnetic transition metal complexes.

Radicals are formed during several chemical reactions (e.g. polymerization). The measurement of the paramagnetism helps in the investigation of reaction mechanisms.

The paramagnetic balance is used for the paramagnetic measurements. This is a very sensitive balance. An external magnetic field (electromagnet) acts on the paramagnetic substance. This force is compensated through an other electromagnet that acts on an iron bar. The necessary current is measured.

The result is suitable to decide about the paramagnetism of the substance but it does not give information about the reason of the paramagnetism. This is only possible with the method of electron spin (electron paramagnetic) resonance.

3.9.2 Electron spin resonance (ESR)

The essence of the magnetic resonance is the following. The molecule having a magnetic moment **m** and precessing with angular velocity ω around the constant magnetic induction vector **B** (Section 1.4.3) is irradiated in the direction perpendicular to **B** with an electromagnetic wave having frequency ν.

The two, originally degenerated electron spin levels split in the field **B** (Fig. 3.64). The spin magnetic moment in the favoured direction z may be either $-\mu_B$ or $+\mu_B$ (μ_B is the Bohr magneton, Eq. 1.26). Since the energy of the dipole in magnetic field is **-mB**, the splitting of the two levels is (3.93)

$$\Delta E = +\mu_B B - (-\mu_B B) = 2\mu_B B \qquad (3.93)$$

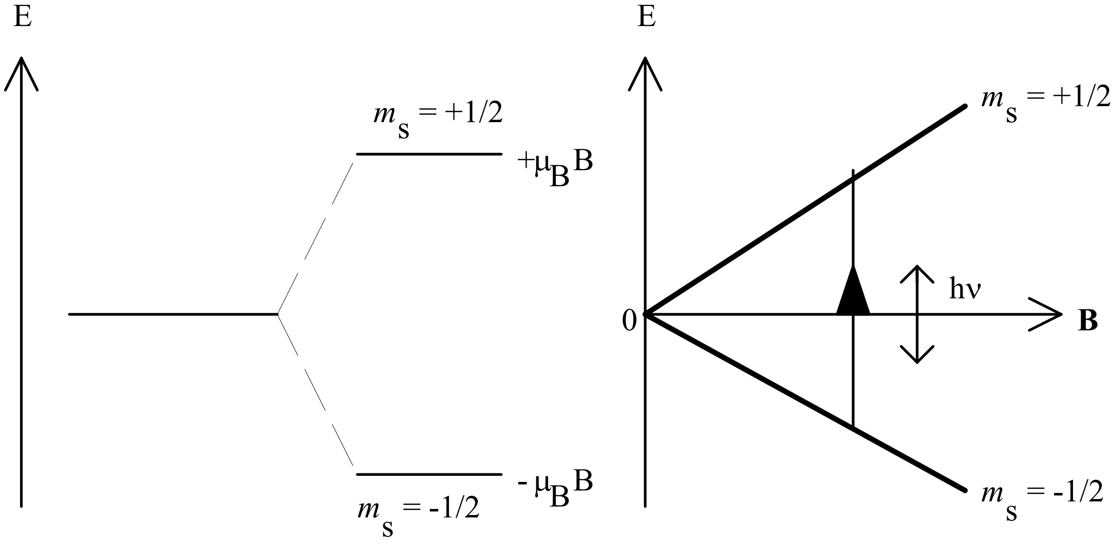

Fig. 3.64

If this energy difference is equal to the energy of the radio frequency photon then the molecule absorbs it (resonance):

$$h\nu = 2\mu_B B \tag{3.94}$$

The *selection rule* is

$$\Delta m_S = \pm 1 \tag{3.95}$$

The molecule is excited from the lower (m_S=-1/2) to the higher (m_S=+1/2) state. The induction B and the frequency ν are proportional according Eq. 3.94:

$$B = \frac{h}{2\mu_B}\nu \tag{3.96}$$

as it may be seen on Fig. 3.64. We have absorption if only the magnetic transiton moment (Eq. 1.35) is not zero and its direction is the same then that of the external **B**.

If any atom has paramagnetic nucleus, the magnetic field of the nuclear magnetic moment is added to or subtracted from the field **B**. Therefore the original spin levels split if the unpaired electron has finite density on the place of the nucleus. If the magnetic moment of the nucleus has two possible values (e.g. hydrogen) the number of the levels will be doubled (Fig. 3.65).

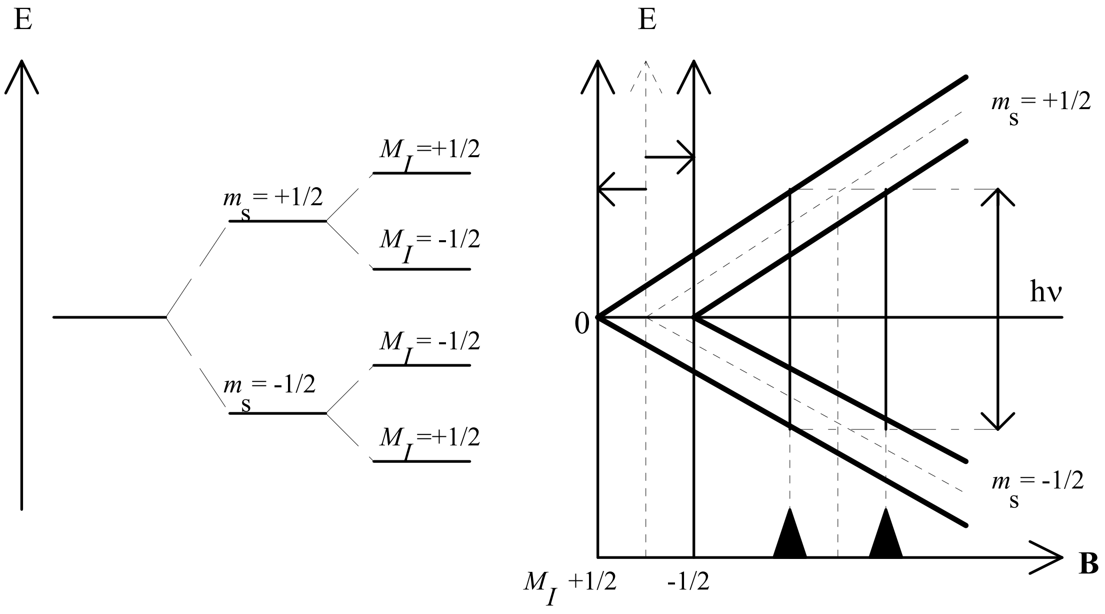

Fig. 3.65

The nuclear magnetic moment decreases the external field:

$$B - aM_I = \frac{h}{2\mu_B}\nu \tag{3.97}$$

a is the hyperfine coupling constant, the M_I nuclear magnetic quantum number. The possible values of M_I are for the hydrogen atom $\pm 1/2$. The real situation is more complicate. The external field indicates a counter field. The local field

$$B' = (1 - \sigma)B \tag{3.98}$$

interacts, $\sigma < 1$ is the shielding factor. In Eqs. 3.95 and 3.96 B must be substituted by B'.

Fig. 3.66 is the block diagram of an ESR spectrometer. The sample (S) is positioned between the poles of a constant magnet (M). The value of the field is changable through changing the electric current in the coil C. The radiofrequency source (about 10 GHz) is a klystron (K) producing fixed frequency and the magnetic field is changed. D is the radiofrequency detector.

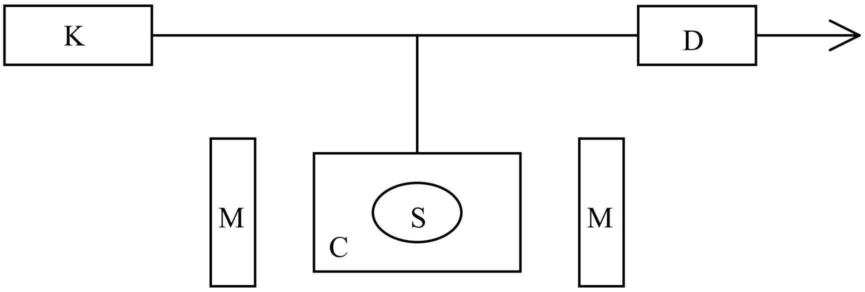

Fig. 3.66

Fig. 3.67 is the ESR spectrum of the free radical ion of 1,4-benzoquinone in solution. An unpaired electron is on both oxygens. The structure is symmetrical (point group D_{2h}, see Section 3.5.3). There are 16 possible configurations of the four hydrogen protons: 1

configuration with M_I=2, 4 with M_I=1, 6 with M_I=0, 4 with M_I=-1 and 1 with M_I=-2, i.e. like $\binom{n}{k}$, k=1,2,...,n. The number of possible configurations gives the statistical weight (relative intensity) of the levels. Fig. 3.67 shows the molecule and the ESR spectrum, the relative intensities are well seen.

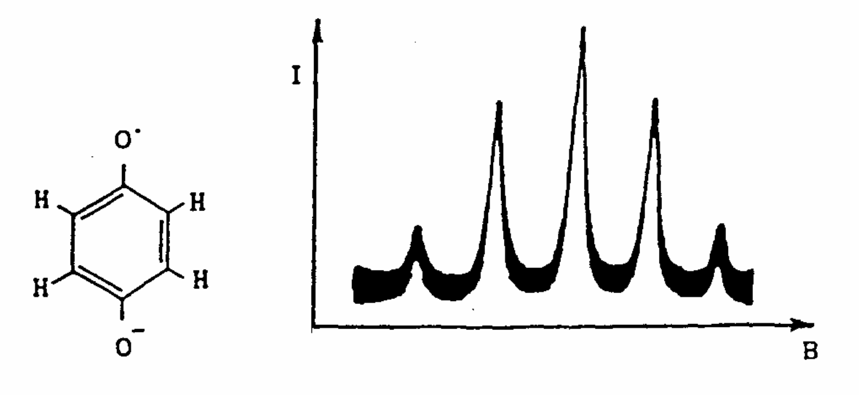

Fig. 3.67

The nuclear spin effect and the hyperfine structure must be taken into account at the interpretation of the ESR spectra. Since not all the nuclear spin quantum numbers are 1/2, one has to act also on the number of splitted levels. E.g. ^{14}N has the nuclear spin quantum number +1, therefore three projections are possible, M_I = 1, 0 or -1.

The most important application of the ESR spectroscopy is the discovery of free radicals. Since in reactions with radical mechanism the radicals are very active their concentrations may be very low. Nevertheless their discovery is important since it gives information about the reaction mechanism. Therefore the ESR spectroscopy is important in the investigation of polymerization and the oxidative reactions (through peroxides) of conjugated compounds.

A great deal of free radicals is formed under high energy irradiation (X ray or γ ray) of solid substances. The lifetimes of the free radicals increase at low temperatures embedded in solid matrices since their mobilities decrease. The matrix, however, influences the spectrum.

Free radicals are formed in catalysis on the surface of the catalyst. Similarly, free radicals are formed also in the fermentation processes.

Free radicals are coupled to the molecules in biological investigations. From differences between ESR spectrum of the "spin-marked" and the free molecule conclusions can be drawn about the structure of the molecule.

At fuorescence processes (Section 3.6.3) triplet states exist and in homogenous magnetic field the energy levels split according the spin quantum numbers. Three levels appear: ↑↑, ↑↓ and ↓↑, ↓↓. The formation of these levels was proved by ESR.