3.10. Nuclear magnetic resonance spectroscopy

3.10.1 The nuclear magnetic resonance

An important part of the atomic nuclei have magnetic moment. If case of odd atomic mass (A) this magnetic quantum number (*I*) is odd mutiple of half. If A is even and the atomic number (Z) is is odd, the magnetic quantum is integer. If both A and Z are even, the magnetic moment and also the *I* nuclear spin quantum number is zero.

Table 3.18 contains some properties of the atomic nuclei those are important in NMR spectroscopy

Table 3.18
Properties of nuclei applied in NMR spectroscopy

Nucleus	*I*	Abundance (%)	Landé factor	Relative .000sensitivity
^{1}H	1/2	99.98	5.58540	1.000
^{2}H	1	0.016	0.85738	0.00965
^{13}C	1/2	1.108	1.40432	0.0159
^{14}N	1	99.63	0.40367	0.00101
^{15}N	-1/2	0.37	-0.56608	0.00104
^{19}F	1/2	100	5.2546	0.830
^{29}Si	-1/2	4.7	-1.10954	0,00784
^{31}P	1/2	100	2,2610	0.0663

The z component of the nuclear magnetic moment is in accordance with Eq. 2.30

$$\mathrm{M}_{\mathrm{I,z}} = \mathrm{g}_{\mathrm{a}} M \mu_{\mathrm{N}} \qquad M = -I, -I+1, ..., I-1, I \tag{3.99}$$

M is the magnetic nuclear quantum number; its values depend on the possible values of *I,* and according to Eq. 3.99 altogether 2*I*+1 different values are possible; g_a is the Landé factor of the nucleus; μ_N is the nuclear magneton.

The E energy of the nuclear magnetic moment is in a magnetic field **B**

$$\mathrm{E} = -\mathbf{M_I B} = -\mathrm{g}_{\mathrm{a}} \mu_{\mathrm{N}} M \mathrm{B} \tag{3.100}$$

The selection rule is deducable from the expression of the magnetic transition moment (Eq. 1.34)

$$\Delta M = \pm 1$$

Therefore

$$\Delta \mathrm{E} = \mp \mathrm{g}_{\mathrm{a}} \mu_{\mathrm{N}} \mathrm{B} \tag{3.101}$$

The energy transition is possible with the absorption of an electromagnetic wave having equal frequency of the Larmor one (see Subsection 1.6.2). This is a *resonance*. The resonance frequency is

$$\nu_0 = \frac{\gamma_a}{2\pi} B \qquad (3.102)$$

γ_a is the giromagnetic ratio of the nucleus. Fig. 3.68 shows the splitting of the nuclear levels in a magnetic field B.

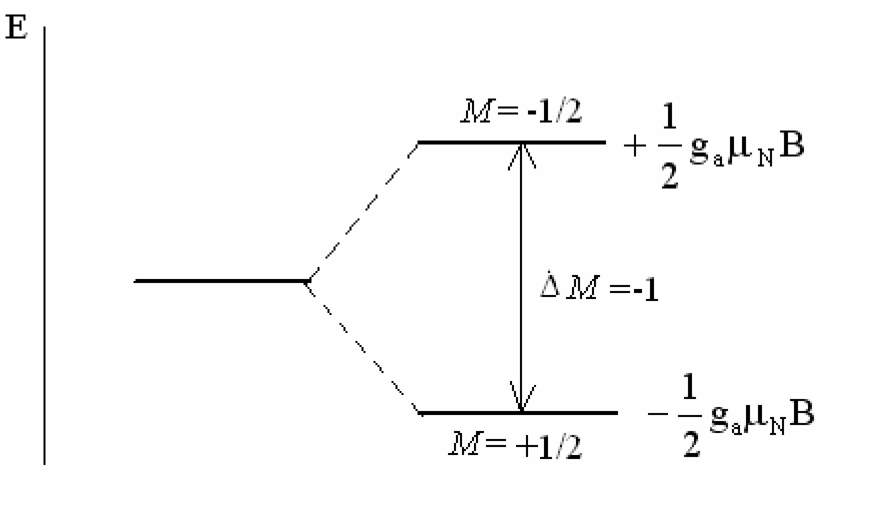


Fig. 3.68

In case if a molecule is placed in a magnetic field B then the chemical environment (the electron cloud) shields the magnetic field, and a so-called *local field* acts on the nucleus. This change is

$$\delta B = -\sigma B$$

σ is the *shielding factor*. The shielding factor is positive in diamagnetic environment (this is the general case). The diamagnetic field is generated by an external field (see Subsection 1.6.2). The local magnetic induction will be

$$B_l = B(1-\sigma)$$

Therefore the Larmor frequency changes to

$$\nu = \frac{\gamma_a}{2\pi} B_l = (1-\sigma)\frac{\gamma_a}{2\pi} B = (1-\sigma)\nu_r \qquad (3.103)$$

The nucleus, however, absorbes at ν_r frequency. There are two possibilities for solving this problem. Either, the frequency will changed to a value where B_l corresponds to ν, or the external B induction will increased up to ν will be equal to ν_r.

The ν_0 frequency is not measurable since a nucleus without environment does not exist. Therefore it was looked for a molecule that produce extremely large eletron cloud, i.e. extremely large diamagnetic field around the nuclei during the measurement. The molecule *tetramethylsilane* (TMS) has this property. The diamagnetism of the electron cloud around the protons exceeds the diamagnetism of all hydrogens connected to carbon atoms. The signal itself is very intense since it is produced from 12 protons in similar position. The TMS is applied as reference not only in ^{1}H measurements but also in ^{13}C ones. For ^{31}P measurements the 85% aqueous solution of phosphoric acid is used.

The chemical environment of the nucleus can be *theoretically* characterized by the frequency shift ($\Delta\nu$) that is necessary for shifting the constant frequency (ν_s, the standard reference frequency, e.g. that of TMS) from the signal of the investigated proton to ν_s. A relative frequency scale is applied in the *practice* since this is indpendent of the strength of the applied magnetic induction (this is usually some tesla):

$$\delta = 10^{6}\frac{\Delta\nu}{\nu_{0}} = 10^{6}\frac{\nu - \nu_{s}}{\nu_{0}} \tag{3.104}$$

Here ν_0 is the high frequency of the NMR spectrometer, some hundred MHz.The chemical shift (δ) increases with increasing paramagnetism relative to the reference (TMS), i.e. the local field increases with δ. There exsists also an other scale, with opposite direction

$$\tau = 10 - \delta \tag{3.105}$$

^{1}H-NMR chemical shitfts of several groups are listed in Table 3.19. The shifts depend on the solvents but they are independent of the applied frequency. Very strong eectronic effects may shift the chemical shifts over 10 ppm (see Table 3.19)

Table 3.19
^{1}H-NMR chemical shifts of some groups

Group	δ_H/ppm	Group	δ_H/ppm
CH_3-C<	0.6-1.9	Alkyl-CHO	9.4-9.8
CH_3-C=C-	1.6-2.1	Aryl-CHO	9.7-10.8
CH_3-aryl	1.1-1.5	Alkyl-OH	1.0-4.4
CH_3-CO-alkyl	1.9-2.3	Aryl-OH	4.2-9.0
CH_3-CO-aryl	2.3-2.6	R-COOH	9.2-13.2
CH_3-O-alkyl	3.1-3.4	R_2C=N-OH	8.3-10.4
CH_3-O-aryl	3.7-4.0	Alkyl-SH	1.0-2.7
CH_3-NH-alkyl	2.1-2.4	Aryl-SH	3.0-4.5
CH_3-NH-aryl	2.6-3.1	R-COSH	4.0-6.0
CH_3-Hal	1.3-1.9	Alkyl-NH_2	1.0-3.2
>C-CH_2-C<	1.3-2.1	Aryl-NH_2	2.8-5.6
-CH_2- (cyclic)	1.3-1.8	R-NH_3^+	6.6-8.8
-CH_2-C≡C- -CH_2-C≡N-	2.0-2.6	$R_2NH_2^+$	8.2-11.5
-CH_2-aryl	1.5-1,9	R_3NH^+	7.2-11.5
-CH_2-N<	3.06-3.8	R-CO-NH_2	5.5-9.6
aromatic	6.5-8.5	R-SO_2-NH_2	4.8-9.2
heteroaromatic	7.0-9.2	NH (saturated ring)	1.1-2.4

3.10.2 Spin-spin interaction

The magnetic fields of the spins interact with one another in external magnetic field (simlarly to the EPR, see Subsection 3.9.2 and Fig. 3.64). The energy levels of the nucleus split on the effect of the other nuclei of the molecule. Fig. 3.69 shows this effect for a diatomic (AB) system (B nucleus act on A).

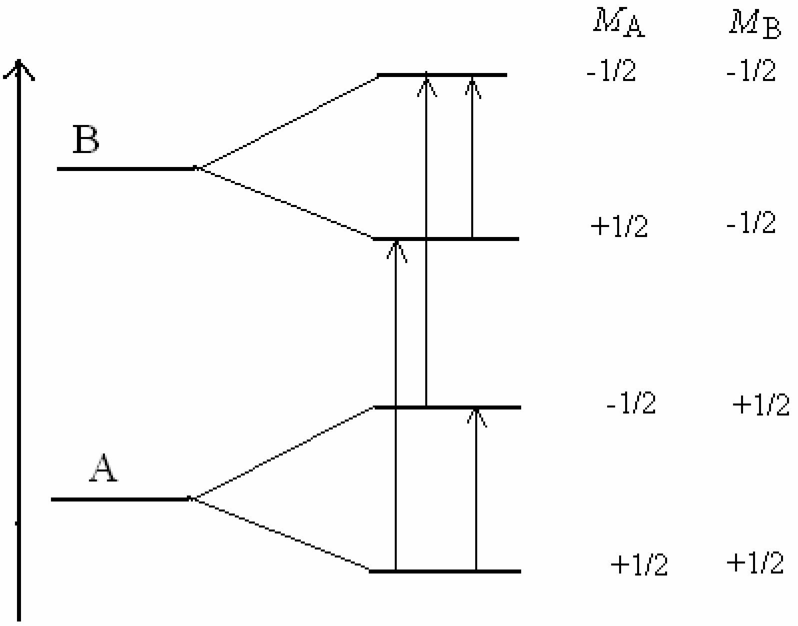


Fig. 3.69

If several equivalent nuclei act on a nucleus A (AB_n system) the splitting depends on the relative positions of the spins of the nuclei B (see Subsection 3.9.2, the analysis of an ESR spectrum). The weight of the states (the degree oöf ther degeneration) is determined for the k-th level by $\binom{n}{k}$.

Fig. 3.70 shows the ^{1}H-NMR spectrum of ethylbenzene. One can observe on this figure three line groups. The ratio of the total intensities of the line groups is 5:2:3. Since the signal intensities of all the protons is equal, the first very intense line belongs to the five protons of the phenyl group. The quartet is the signal of the methylene group, while the triplet belongs to the methyl group. According to the spectrum there is not coupling between the protons of the phenyl group and the other protons of the molecule under the condition of the measurement. The chemical shifts of the phenyl protons are approximately the same. Looking at quartet of the methylene group it reflects the effect of the methyl group. The effect on all protons of the CH_2 equivalent (AB_3 system). Therefore n=3, and according to $\binom{n}{k}$ the relative intensities of the lines are 1:3:3:1. The coupling of the methylene and methyl group is mutual. Therefore we have an AB_2 system investigating the CH_2 group action on the CH_3 one. Therefore the line intensity ratio for the methyl signal group is 1:2:1.

The freqeuncy shift affected by the spin-spin coupling is independent of the applied frequency and magnetic induction. Therefore applying an NMR spectrometer of higher ν_0 frequency, the frequency shifts seem smaller on the δ scale (see Eq. 3.104).

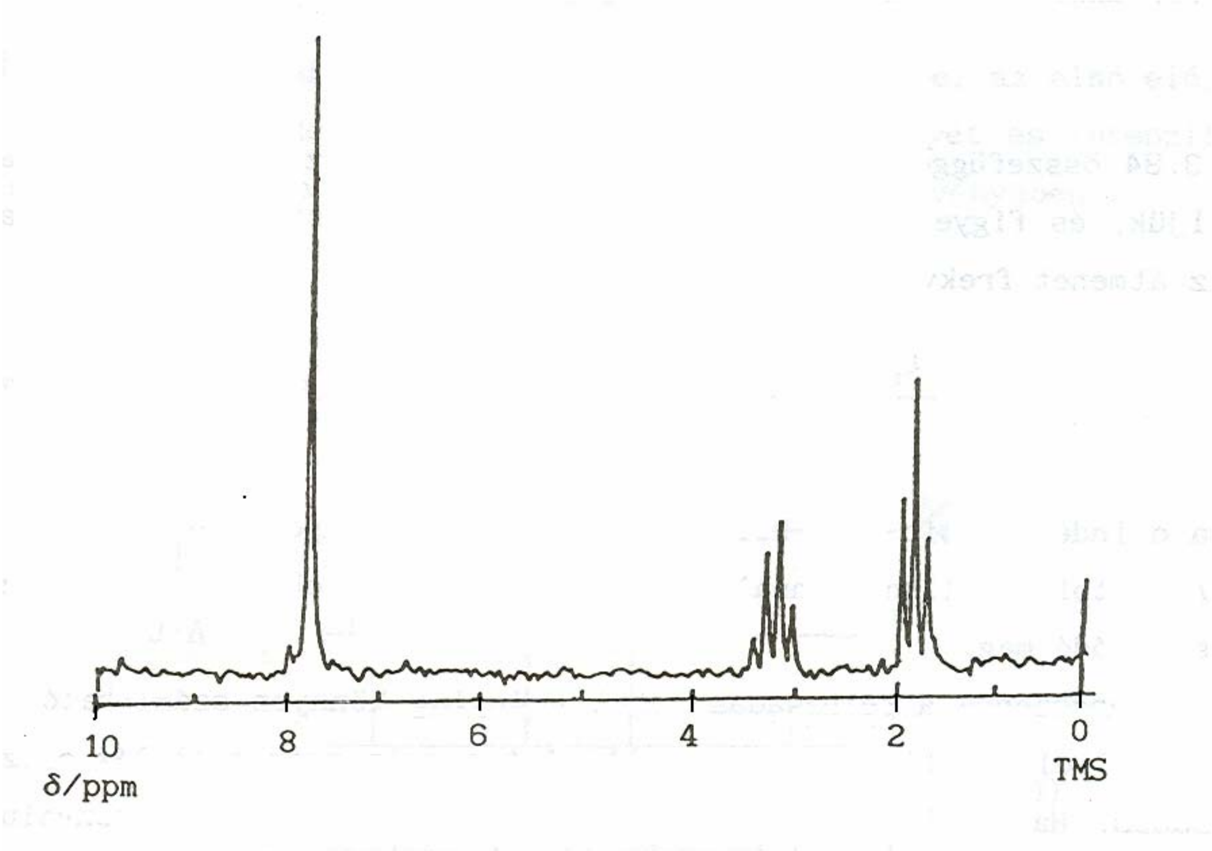


Fig. 3.70

The interactions between the different moments and magnetic moment are characterized with coupling constants. The interactions between the nuclear spins are represented with *spin-spin coupling constants*. For an AB system they are symmetric, $J_{AB}=J_{BA}$. The unit is the Hz. The energy of such a coupled system is in case if the chemical shifts are far higher than the split caused by the spin-spin coupling

$$E = E_0 - g_a \mu_N B \sum_i (1-\sigma_i) M_i - \frac{h}{2} \sum_i \sum_j J_{ij} M_i M_j \qquad (3.106)$$

E_0 stands for the energy of the magnetic field free state. If Eq. 3.106 is valid, the selection rules are for an AB_n system

$$\Delta M_A = \pm 1 \qquad \Delta M_{B_i} = \pm \qquad i = 1,2,\ldots,n \qquad (3.107)$$

In case of commensurable chamical shifts and spin-spin coupling caused splits, the selection rule is

$$\Delta \sum_i M_i = \pm 1 \qquad (3.108)$$

Referring Eq. 3.106 to one nucleus and and regarding the selection rule Eq. 3.107, the frequency of the magnetic transition will be

$$\nu_i = \frac{g_a \mu_N B(1-\sigma_i)}{h} + \sum_{j \neq i} J_{ij} M_j = \nu_i^0 + \sum_{j \neq i} J_{ij} M_j \qquad (3.109)$$

the zero superscript refers to the state without spin-spin coupling.

The closer the coupled nuclei the greater the spin-spin coupling constant.

The calculation of the splitting is relatively easily calculable for an AB system if Eq. 3.106 is valid (otherwise the calculation is very complicate). Let

$$\Delta = \nu_A^0 - \nu_B^0 \qquad \Sigma = \nu_A^0 + \nu_B^0 \qquad J = J_{AB} \qquad q = \sqrt{J^2 + \Delta^2}$$

The energy levels are with these

M_A	M_B	E
$1/2$	$1/2$	$E_1 = \frac{h}{2}(-\Sigma - J/2)$
$1/2$	$-1/2$	$E_2 = \frac{h}{2}(-q + J/2)$
$-1/2$	$1/2$	$E_3 = \frac{h}{2}(+q + J/2)$
$-1/2$	$-1/2$	$E_4 = \frac{h}{2}(+\Sigma - J/2)$

The observable frequencies are ($\Delta M_A = \pm 1 \qquad \Delta M_B = \pm 1$)

$$\nu_{A1} = \frac{1}{2}(q + \Sigma + J)$$

$$\nu_{A2} = \frac{1}{2}(q + \Sigma - J)$$

$$\nu_{B1} = \frac{1}{2}(-q + \Sigma + J)$$

$$\nu_{B2} = \frac{1}{2}(-q + \Sigma - J)$$

If $\Delta >> J$, then $q \approx \Delta$, if $\Delta \approx 0$, then $q \approx J$. The first case results two doublets, the second one result s triplet with the intensity ratio 1:2:1. The line intensities are in general case

$$I = 1 \pm \frac{2qJ}{q^2 + J^2} \qquad (3.110)$$

the upper sign refer to the two inner lines, while the lower one to the two outer lines. Fig. 3.71 intoduce the positions of the lines and their intensities as function of J/Δ, i.e. the relation of the spin-spin coupling constant to the frequency difference in couplingless state.

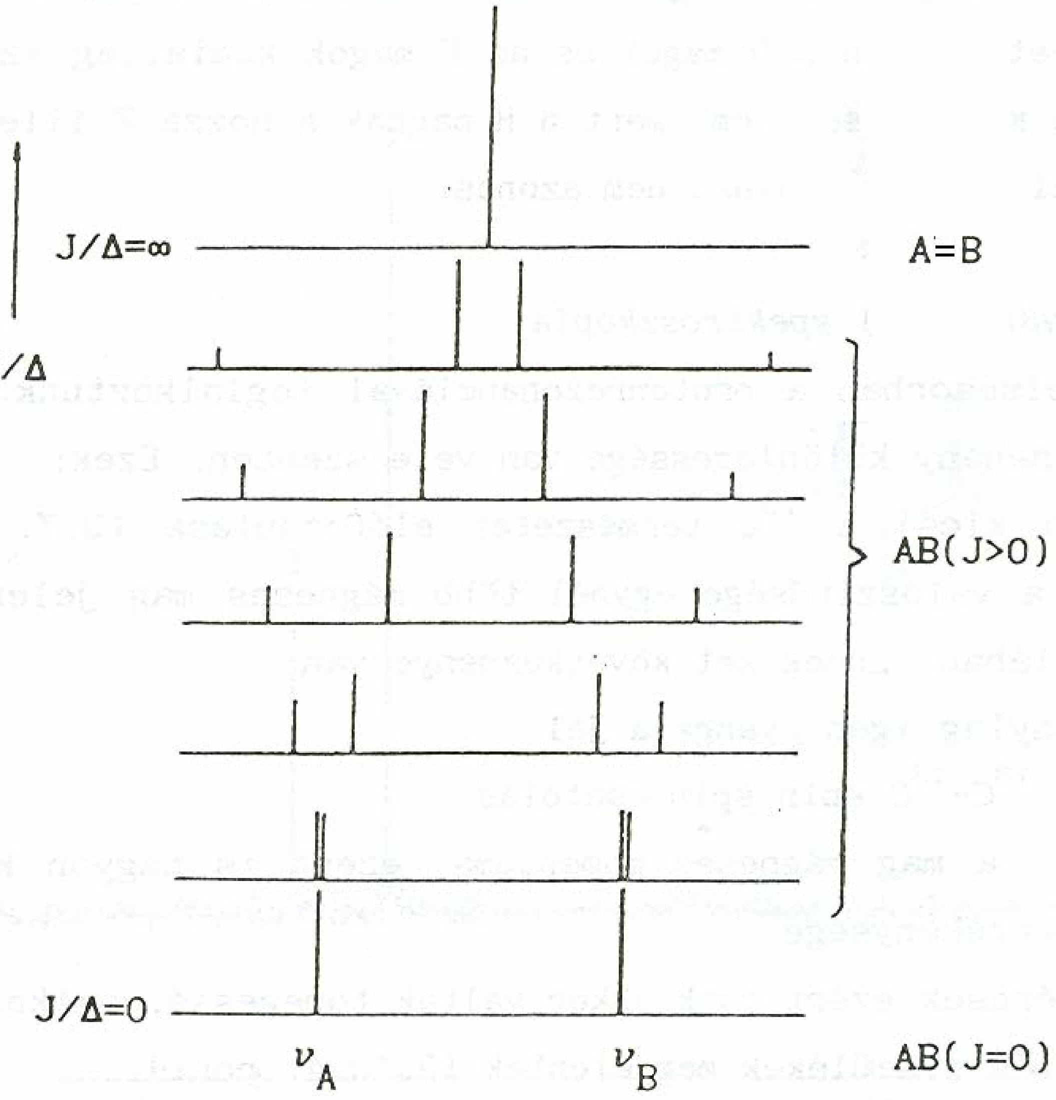


Fig. 3.71

The value of the J coupling constants does not exceed 25 Hz in ^{1}H-NMR spectroscopy. Hower, in case of other nuclei it can be even 1000 Hz. The values of the coupling constants (like the chemical shifts) are findable in the special NMR literature or on the internet.

The magnetic nuclei having the same spin-spin coupling constant with other magnetic nuclei are called *equivalent nuclei.*

The symmetrically equivalent nuclei are *chemically equivalent*. *Magnetically equivalent* are the nuclei those have only the same kind spin-spinp coupling constants with the groups in their vicinity.

Nuclei are *isochronic*, if their chemical shits are identical. The chemically equivalent nuclei are at the same time also isochronic, however, the magnetic equivalent atoms are not by all means.

The difluoroethane (CH_2F_2) has two isochronic ^{1}H and two equivalent ^{19}F nuclei. The two ^{1}H nuclei are both chemically or magnetically equivalent with one another, similarly to the two ^{19}F nuclei. All J_{HF} coupling constants are identical.

In 1,1-difluoroethylene the ^{1}H atoms are chemically equivalent, similarly to its ^{19}F atoms. However, the are magnetically not equivalent, since the ^{1}H atoms have not the same coupling constants with the ^{19}F atoms in Z and E positions.

3.10.3 ^{13}C-NMR spectroscopy

The ^{13}C resonance has some pecularities in comparison with the ^{1}H-NMR spectroscopy.

1. The nattural abundance of the ^{13}C nucleus is low (1.1%), therefore the signal is small and ^{13}C -^{13}C coupling does not exist.

2. The magnetic moment of the ^{13}C nucleus is small, therefore its relative NMR sensitivity is also small.

The ^{13}C-NMR measurements became popular only with the appearance of the Fourier transform NMR spectrometers (see next section). The ^{13}C-NMR measurement has some advances in comparision with the ^{1}H-NMR ones.

1. It gives direct information about the carbon skeleton of the molecule.

2. The spin-spin coupling does not disturb the spectrum, the inductive and mesomeric effects are easier observable.

3. The ^{1}H-NMR spectrum is confused in the case of large molecules with several hydrogen atoms, the ^{13}C-NMR spectrum gives separated signals of every carbon atoms.

4. If the molecule does not contain hydrogen atoms this spectrum gives even in this case structural information.

5. ^{13}C-^{13}C coupling does not exist, the ^{13}C-^{1}H couplings are easily eliminable using the method of the *wide range double resonance* (spin decoupling). The ^{13}C neighbouring protons are irradiated with a second wide range radiofrequency radiation in the region of the proton absorptions. As result the multiplet bands become singlets.

Fig. 3.72 presents the ^{13}C-NMR spectrum of imidazole. The signal of the carbon atom 2 is the line 1, the atoms 4 and 5 are equivalent (there is a fast proton exchange between the two tautomers), their signal is denoted by 2. The spectrum was reorded with spin decoupling.

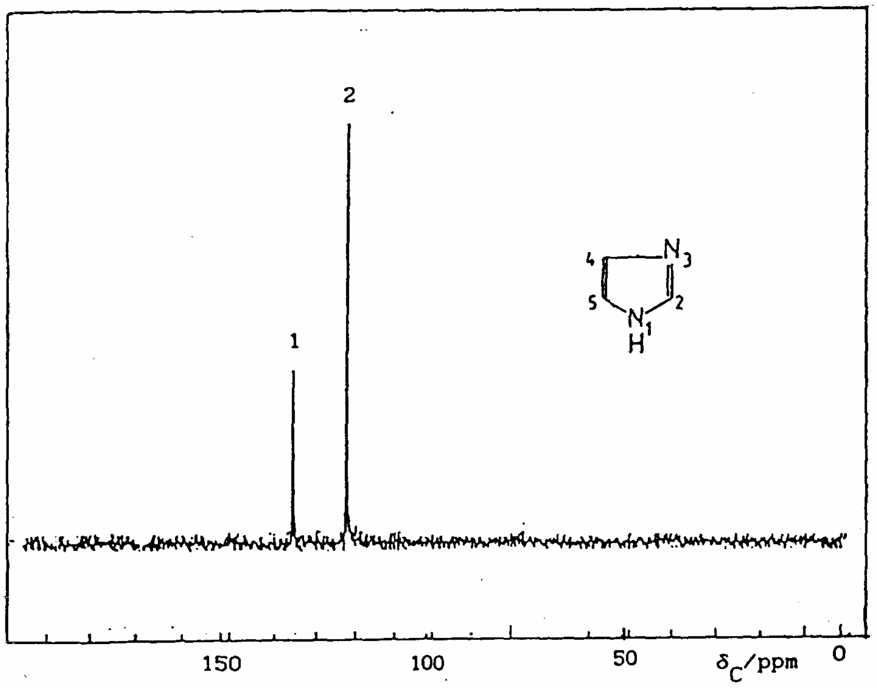


Fig. 3.72

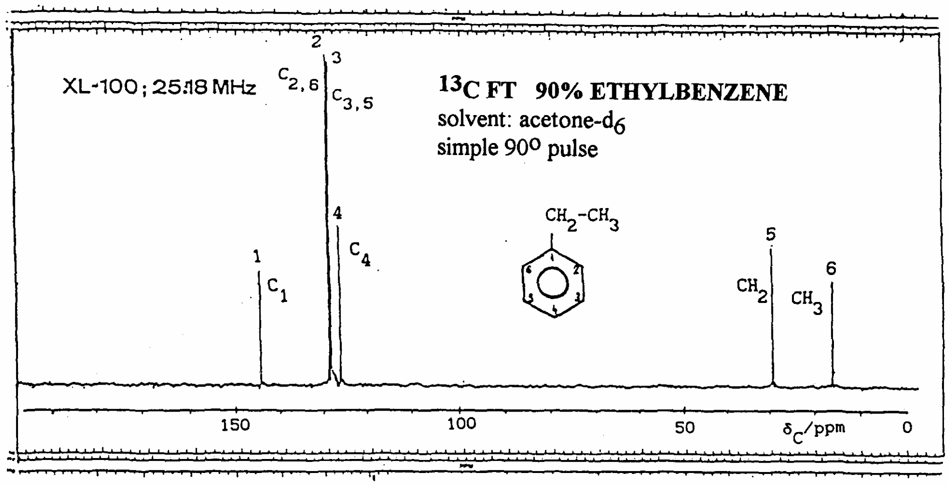


Fig. 3.73

Fig. 3.73 shows the ^{13}C-NMR spectrum of ethylbenzene. In contrary to its ^{1}H-NMR spectrum it consists of singlets only. The assignment of the lines is the following. 1: C_1, 2: C_2 and C_6, 3: C_3 and C_5, 4: C_4, 5: CH_2, 6: CH_3. The +I effect of the ethyl group is well observable on the shifts of the benzene carbon lines (for benzene δ_C=128.9 ppm).

The lines in Fig. 3.72 have different intensities. The intensities depend on the difference in the populations of the ground and excited states (Section 1.4) and their relaxation time (T_1, Section 3.10.6) is decisive.

Table 3.20. contains some ^{13}C-NMR shifts. The shift increases with incresing polarity of the functional group (similarly to the ^{1}H-NMR shifts, Table 3.19). Extraordinary high in the shift of the ^{13}C in -COOH and =C= groups.

Table 3.20
Some ^{13}C-NMR shifts in functional groups

group	δ_C/ppm	group	δ_C/ppm
C (cyclopropane)	0 - 10	>**C**-O-	65 - 85
CH_3X	0 - 20	$-$**C** ≡	65 - 95
-**C**H_2X	0 - 40	>**C**=	105 - 145
>**C**HX	30 - 65	=**C**=	200 - 220
≡ **C**X	35 - 80	**C**$_{ar}$	110 - 140
CH_3-C(sp^2)	5 - 30	**C**$_{ar}$ (benzene)	128.9
-**C**H_2-C(sp^2)	20 - 45	$-$**C** ≡N	115 - 125
>**C**H-C(sp^2)	30 - 60	**C**$_{het\ ar}$ -C(sp^2)	115 - 145
CH_3-S-	10 - 20	**C**$_{het\ ar}$ -N(sp^2)	145 - 155
CH_3-N<	10 - 45	>C=O	200 - 230
CH_3-O-	50 - 60	-CHO	185 - 210
-**C**H_2-O-	40 - 70	-COOH	170 - 185

3.10.4 Recording NMR spectra

The early instruments applied the *continuous wave (CW) technique*. They used fixed radio frequency (RF) and the magnetic induction (B) was changed. In this way the individual transitons were maesured each after one another.

The new instruments apply the *Fourier transform method (FT-NMR)*, i.e. excitation with pulses + Fourier transformation (PFT). The nuclear spins precessing in a field B in direction z with frequency ν_0 are excited with a wide range ($\Delta\nu$) RF radiation for a short (some μs) time t_r. The pulses are repeated in a period time t_p.

The high frequency pulse creats a rotating field B_i, the effective field at the nucleus is B_{eff}. This induction turns the magnetic moment from z to y direction (see Fig. 3.74a). The detected signal is the y component of the magnetic moment **M**, M_y. This signal contains all the possible frequency components - depending on the type and position of the nucleus in the molecule. During the decay of **M** (Fig. 3.74b) the y component decreases.

The signal detected in time is called *free induction decay* (FID, Fig. 3.74c). Ceasing the pulse the magnetic moments relax and M_y's trend to zero. The meaurement are repeated to get a better signal-to-noise ratio (accumulation of the signals).

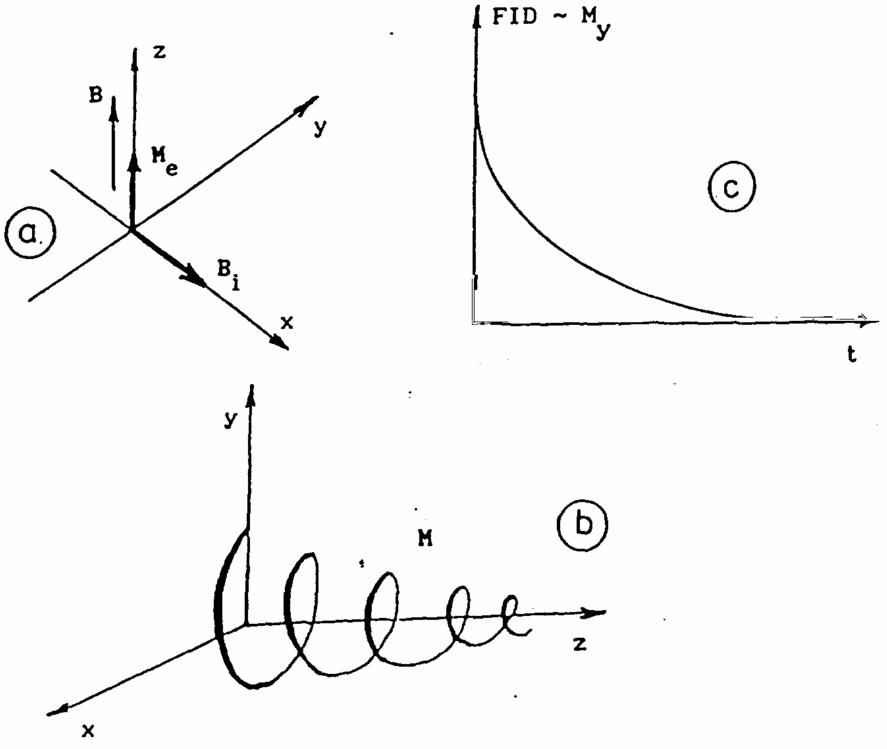


Fig. 3.74

The principle parts of an FT-NMR spectrometer (Fig. 3.75) are the radio frequency source (RFS), the pulse amplifier (PA), the pulse programmer (PP), the superconducting magnet (SM), the radio frequency receiver (RFR), the memory for accumulation (MA), the computer for control, data acquisition and data elaboration (PC) and the plotter (P). The applied RF is some hundred MHz.

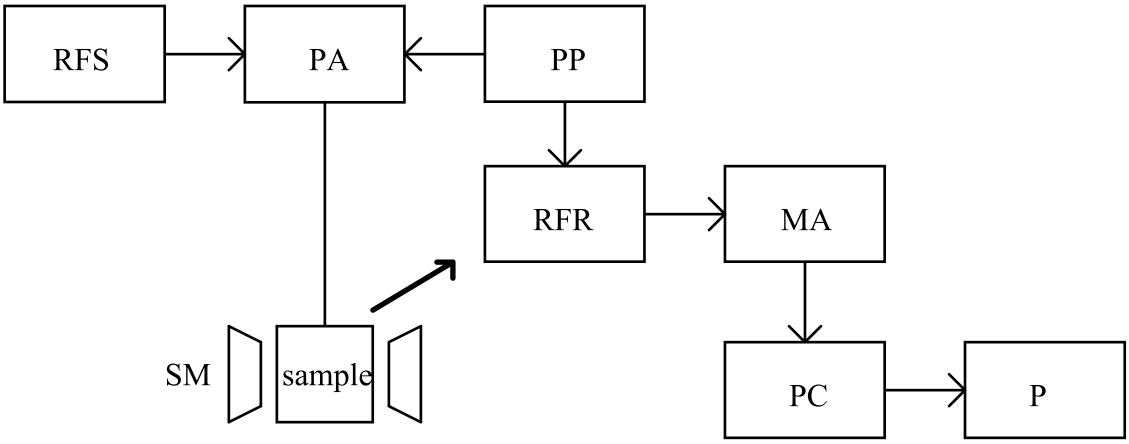


Fig. 3.75

The samples are overwhelming liquids, solutions. The solvents are in ^{1}H- and ^{13}C-NMR spectroscopy deuterated liquids. Also solid state NMR measurements are possible.

3.10.5. The Overhauser effect

The NMR spectroscopy is a very effective, flexible and versatile method. One of its special method is the mentioned wide range double resonance for spin decoupling. Some other methods will be introduced in the next sections.

The essence of the *nuclear Overhauser effect (NOE)* is the following. If we saturate a nucleus (turn its magnetic moment) this effect accelerates the relaxation processes of nuclei coupled to it. Therefore the resonance line of the second nucleus becomes sharper, it may absorb more energy from the B_1 field without getting saturated. Such kind nuclei are e.g. ^{1}H and ^{13}C.

It is important to eliminate all external paramagnetic contaminants from the sample (e.g. dissolved oxygen).

The ^{13}C-^{1}H coupling offers four possibilities for the spins (α labels the ground state, β the excited one): 1: $\alpha\alpha$, 2: $\alpha\beta$, 3: $\beta\alpha$ and 4: $\beta\beta$. The spins of the protons are saturated through double resonance and therefore the originally forbidden 4←1 and 3←2 transitions become allowed with P_{41} and P_{32} finite probabilities. Let be the probabilities of the originally allowed transitions P_o. The intensities of the ^{13}C resonance lines increase according to the equation 3.111

$$I_{NOE} = I\left(1 + \frac{P_{32} - P_{41}}{P_{32} + P_{41} + 2P_o}\frac{\gamma_H}{\gamma_C}\right) = I(1+\eta) \tag{3.111}$$

I is the original intensity, γ is the magnetogyric ratio, η is the NOE factor. If the two magnetogyric ratios are of different signs the intensity decreases.

3.10.6 Relaxation processes

The FT technique gives the possibility of the determination of the relaxation times of both the individual nuclei (T_1) and the chemically equivalent nuclei (T_2). These relaxation times give information about the chemical structure of the molecule, beside the chemical shift, the coupling constants and the line intensities. Since the carbon nuclei are in closer connection with the skeleton of the organic compounds, their relaxation is of higher interest.

The relaxation is the result of the local magnetic fields induced by the disordered molecular motions. From the viewpoint of NMR only the frequency components in magnitudes of some MHz to some hundred MHz are important. The disordered motions are characterizable by their *correlation times* (τ_c). This is the average lifetime of a type of motion. For translations this is the average time between two collisions, for rotations the time of a turning. The correlation times of small molecules are in the magnitude of 10^{-12} - 10^{-13} s, for medium size molecules (100 - 300 daltons) 10^{-10} s. The corresponding frequencies are the reciprocals of these values.

We shall deal with two types of relaxation: the spin-lattice relaxation and the spin-spin relaxation.

1. *The spin-lattice relaxation* (longitudinal relaxation). The motions in the environment (in the "lattice") of the nuclear spins have influence in the field B on the saturation of the levels splitted according to the magnetic quantum number *M*. If *M* has only two possible values (+1/2 and -1/2), i.e. *I*=1/2, the differential equation of the relaxation process is (Eq. 3.112)

$$\frac{dn}{dt} = 2P(n_e - n) \qquad n = N_+ - N_- \tag{3.112}$$

N_+ is the population of the *M*=+1/2 (the lower) level, N_- is that of *M*=-1/2, the subscript e refers on the equilibrium, P is the average probability of the processes there and back, the coefficient 2 refers to the fact that whenever a spin turns, the difference in the populations changes with 2. The solution of Equ. 3.112 is

$$n_e - n = (n_e - n)_o \exp\left(-\frac{t}{T_1}\right) \qquad T_1 = \frac{1}{2P} \tag{3.113}$$

T_1 is the time constant of the spin-lattice relaxation.

The nuclear spins turn in the inducing field B_i during the pulse time t_r with the angle

$$\vartheta = \frac{\gamma B_i t_r}{2\pi} \tag{3.114}$$

The amplitude of the pulse is $\gamma B_i/2\pi$, the angle of the rotation depends on the pulse length t_r.

2. *The spin-spin relaxation* (transverse relaxation).

The precessions of the chemically equivalent nuclei may induce vibrating magnetic fields at their places to one another. The frequencies of the fields are equal to the Larmor frequencies of the inducing nuclei. The result is the mutual change in the direction of the nuclear magnetic moments relatively to the polarizing field B. Their energies, however, remain unaltered. Exciting the nuclear spins with short B_i magnetic pulses their phases become coherent (all spins are of equal both in values and directions). This state remains only for a short time, the spins relax with a time constant T_2. The local B_l fields affect on this process therefore the measured effective time constant is

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{\gamma_a}{2\pi}(B - B_\ell) \tag{3.115}$$

The relaxation causes line broadening, the average FWHH is

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2^*} \qquad T_2^* \le T_2 \le T_1 \tag{3.116}$$

3.10.7 Measurement of the relaxation effects

1. *The measurement of the spin-lattice relaxation*

The relaxation is influenced by several facts:

- the viscosity (temperature and concentration effect),
- the paramagnetic compounds (e.g. oxygen) must be eliminated,
- molecular diffusion from the "effective area" into the ineffective one and vice versa,
- the evaporation (T_1 of vapours is smaller, low temperature is necessary).

The measurements are carried out periodically. The periods are called *sequences.* The description of the sequence means the detailing of the period.

The inversion recovery technique (Fig. 3.76).

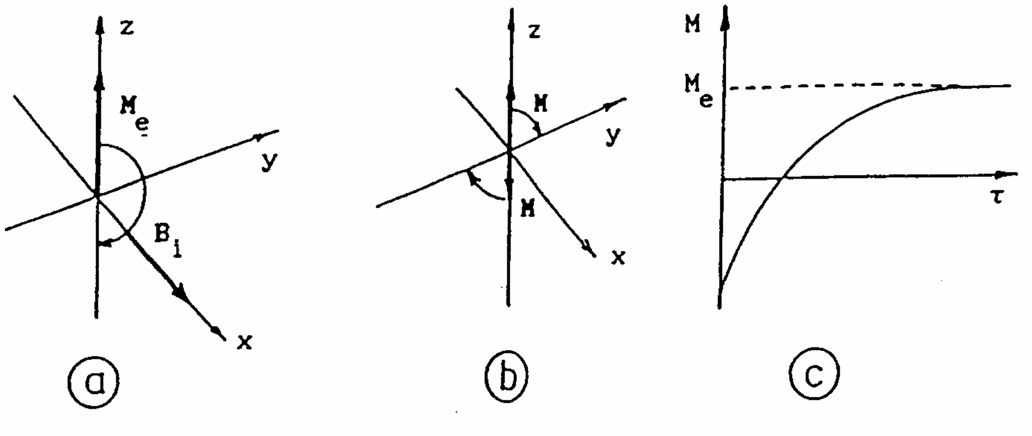


Fig. 3.76

The sequence is: *180°* - *τ* - *90°*. This means: the first pulse turns the nuclear spins 180° from the direction of the vector B (Fig. 3.75a). After the pulse, the time τ is the waiting period. During this time the spins relax partly into the starting direction. After this time a pulse in direction x turns the remained z component of the magnetic moment in direction y (Fig. 3.75b) and so it becomes measurable (M_y). Changing the time τ we get the decay curve (Fig. 3.75c). If $\tau < T_1$, the FID is negative, if the FID=0, that is the halftime $\tau = T_1 \times \ln 2$, at $\tau \approx 5T_1$ the starting state is practically restored ($M_e = M_z$).

A modification of this technique uses the sequence *90^o - t - 180^o - τ - 90^o - t*. The spins are turn first in direction y and the difference of this signal and the end signal is measured. The difference signal starts from $2M_e$and finishes at zero (see Fig. 3.77).

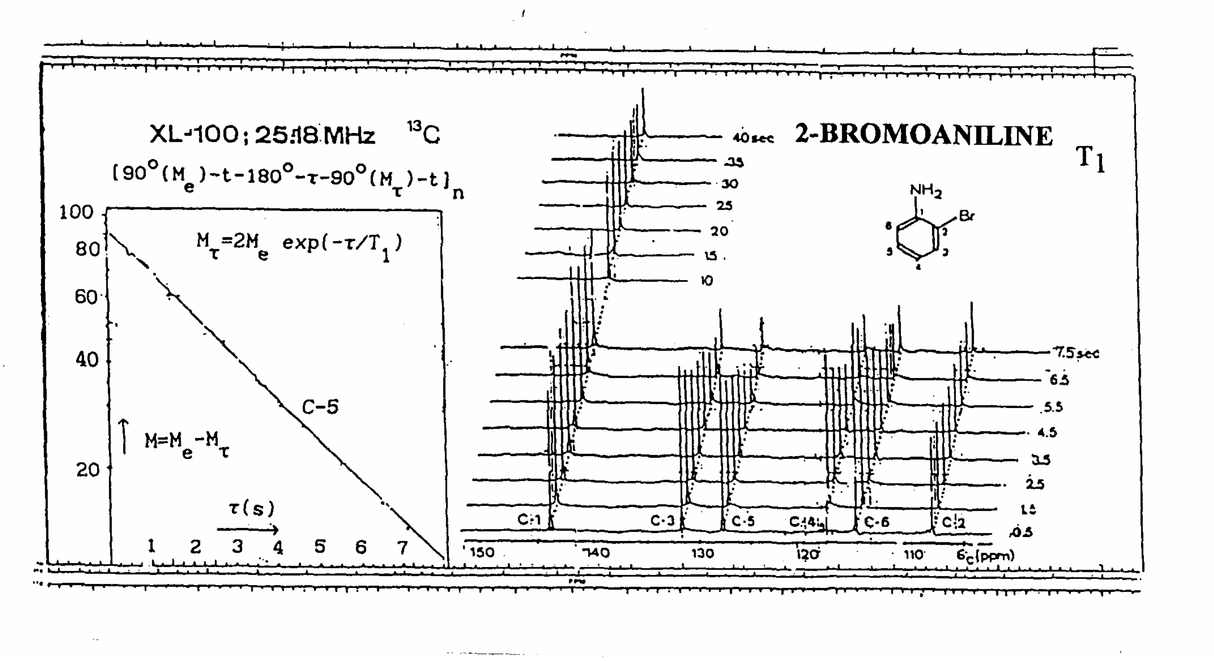


Fig. 3.77

2. *The measurement of the spin-spin relaxation*

Here we deal only with the *spin-echo technique* in detail. Its sequence is *90^o - t - 180^o - τ (echo) - t_d*. The spins are turned 90^o in direction y (Fig. 3.78.a). During the time τ spread in the plane xy since their precession frequencies are greater or smaller than the nominal one (Fig. 3.78b). A 180^o pulse turns the spins in the xy plane. During this second τ time the spins come closer each to one another (Fig. 3.78c). After t_d>5T_2 the starting state will be restored. Changing τ the FID will be measured. The signals change with exp(-2τ/T_2^*).

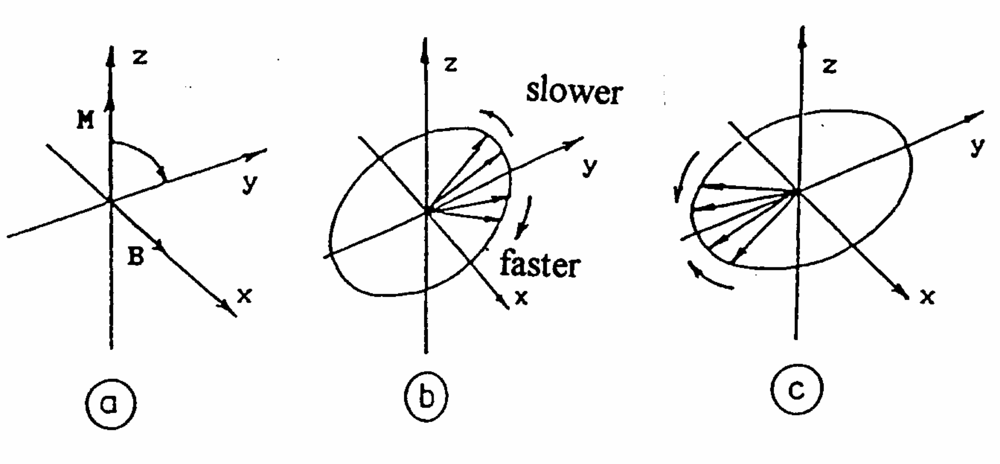


Fig. 3.78

3.10.8 Two-dimensional NMR spectroscopy

The principle of the two dimensional (2D) NMR technique is the change of two different times during the measurement. Therefore two different Fourier transformations are possible and two frequency domains are yielded.

1. *J, δ spectroscopy*

The measurement consists of three sections. During the preparation the nuclear spins are turned around x into y with a 90° pulse. During the evolution the spin system changes under the effect of different factors: spin-spin relaxation, inhomogenity of the external magnetic field, Larmor precession, spin-spin coupling. The first two factors influence the line width (Eqs. 3.115 and 3.116).

This method is a 2D spin-echo technique. Its sequence is similar to the original spin-echo one: $90^o_x - t_1/2 - 180^o_x - t_1/2 - t_2$. The spins are rotated always around x (Figs. 3.79a and b).

A simple AB spin system is characterized by the resonance frequencies ν_A and ν_B and their coupling constant J. The lines of the doublet of nuclear spin A are denoted in Fig. 3.79 by A1 and A2, respectively. In Fig. 3.79b the relative positions of the lines are shown at times a, b, c and d (see Fig. 3.79a). The vectors A1 and A2 move clockwise around the z axis according to the length of time t_1 (their angle is φ). Their angle of precession is labeled by Φ on Fig. 3.79b. It was supposed $\nu(A1) > \nu(A2)$ (this fact is labeled by + and -). At time d the two vectors have symmetric positions to y. Their phase differences are their angle to y. Fig. 3.79c. shows the change in phase of the vectors as function of the time t_1. It is clear from the figure: the frequency of the phase modulation is the coupling constant J. After the Fourier transformation of this t_1 function one gets the frequency function (F_1, here the frequencies are denoted usually by F).

Besides the 1D function $\delta(F_1)$ we receive also the $J(F_2)$ function. The result is a 2D data matrix. Fig. 3.80a presents 5 NMR lines and the data matrix. The data points belonging to the same F_2 frequency are positioned along a 45° straight line. After a transformation these lines are positioned vertically (Fig. 3.80b). So we have the chemical shifts without the couplings. Fig. 3.80c shows the possible 2D presentations: the panorama diagram (this is used more frequently) and the contour diagram. Fig. 3.80d is an example: The 1D spectrum and the two 2D presentations are shown.

This J,δ spectroscopy is a very good tool for the separation of the lines originated from the chemical shifts and the spin-spin couplings.

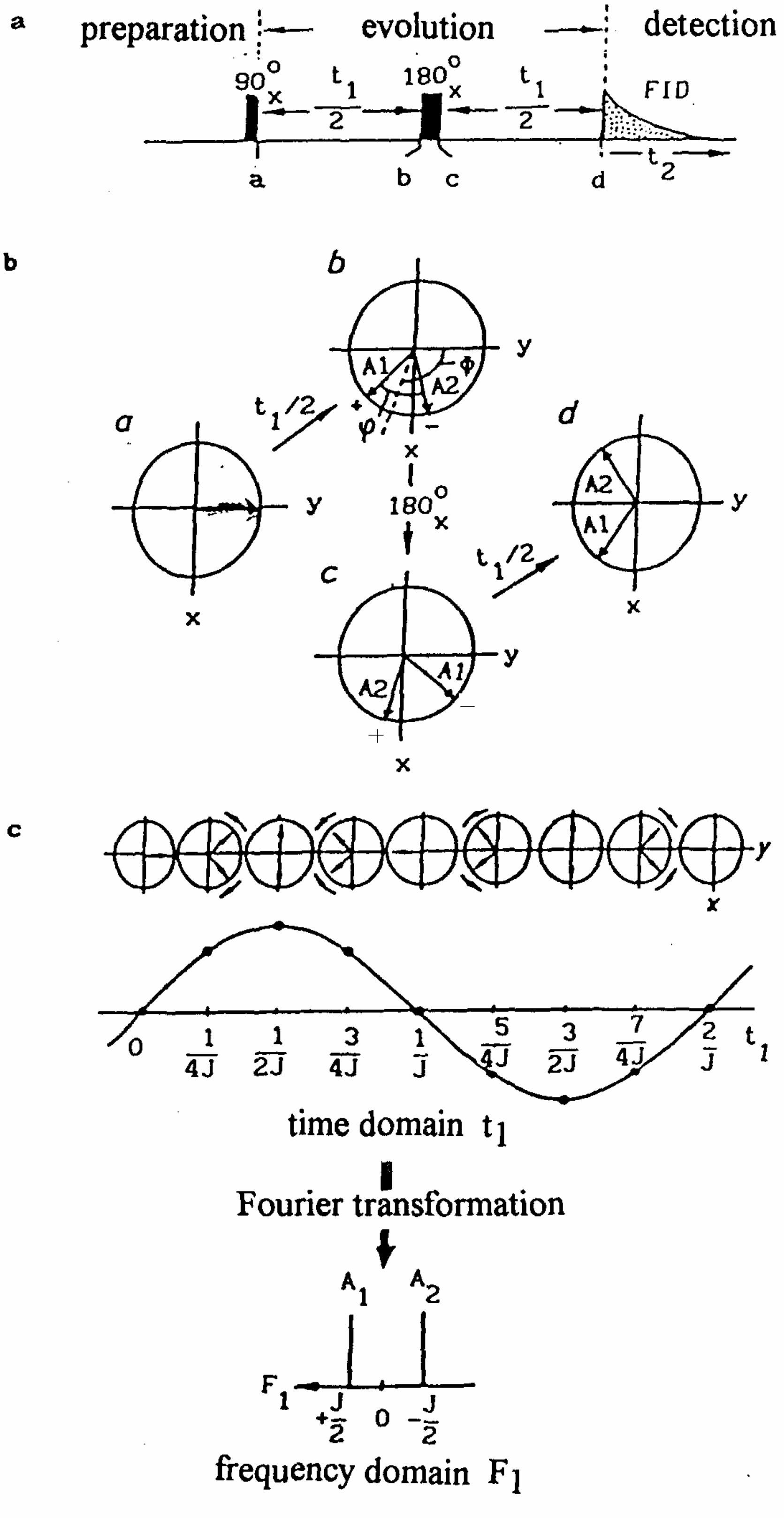

a
preparation
evolution
detection
90^o_x
$\frac{t_1}{2}$
180^o_x
$\frac{t_1}{2}$
FID
t_2
a
b
c
d
b
b
y
A1
A2
Φ
φ
+
-
x
$t_1/2$
a
y
x
180^o_x
d
A2
A1
y
x
c
y
A1
A2
+
-
x
$t_1/2$
c
y
x
0
$\frac{1}{4J}$
$\frac{1}{2J}$
$\frac{3}{4J}$
$\frac{1}{J}$
$\frac{5}{4J}$
$\frac{3}{2J}$
$\frac{7}{4J}$
$\frac{2}{J}$
t_1
time domain t_1
Fourier transformation
A_1
A_2
F_1
$+\frac{J}{2}$
0
$-\frac{J}{2}$
frequency domain F_1

Fig. 3.79

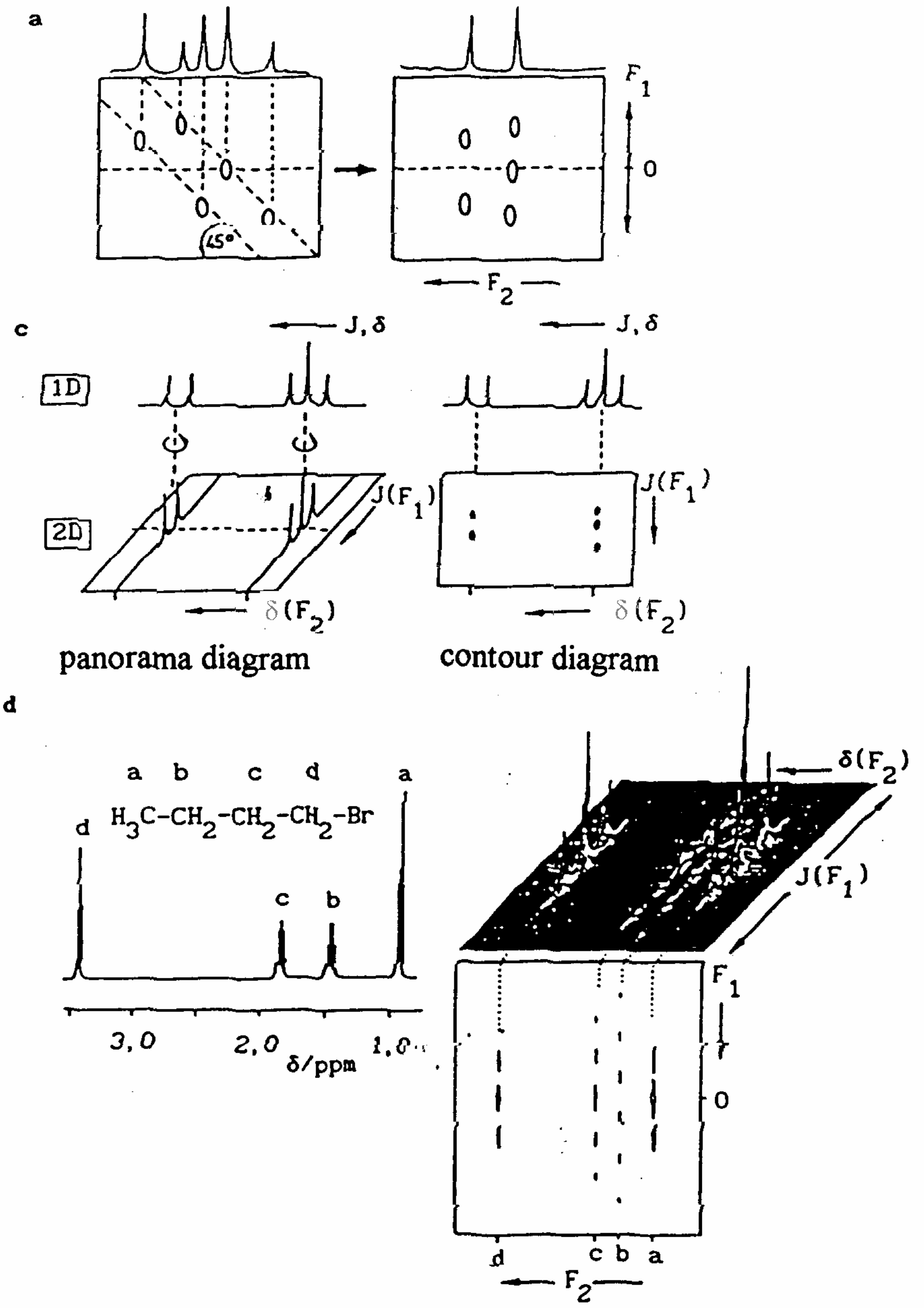
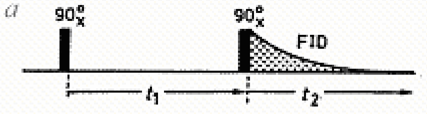


Fig. 3.80

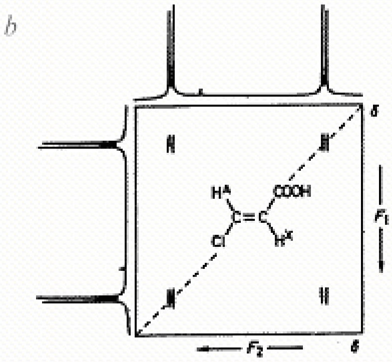
2. *Correlation spectroscopy (COSY).*

This is a very important method of the discovering the nuclei that are coupled to one another. The COSY sequence is $90^o_x - t_1 - 90^o_x - t_2$ (Fig. 3.81a). The t_1 time is changed and the FID signal is detected during t_2 for all t_1. The result of the two Fourier transformations is a δ,δ spectrum. The contour diagram contains spots that point to the correlation of the nuclei. The diagonal signals are "autocorrelation" signals, the off-diagonal signals are important (Fig. 3.81b).

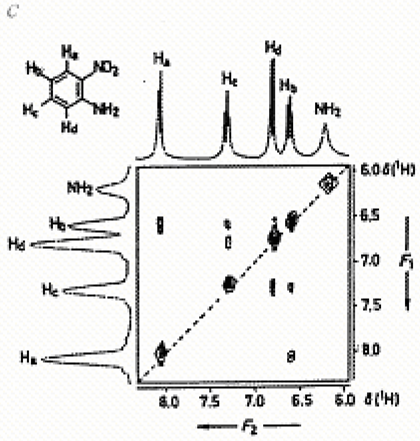
COSY SPECTROSCOPY



pulse sequence of the COSY spectrum



COSY spectrum of the AX system



COSY spectrum of o-nitroaniline

Fig. 3.81