VIII. NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Molecules are extremely small entities; thus, their direct detection and direct investigation is still almost impossible. For the detection and detailed investigation of molecules of interest for us we need outstanding "chemical spies", who are willing to do their work all the time, able to report us about all possible suspicious (and less suspicious) activities of molecules, and do their work for almost free (chemists are usually not billionaires). The chemical spy (*a*) should report us about the structure, the movements, and the (chemical) reactions of molecules without any interference with these activities (so that the espionage would remain a secret); and (*b*) should be able to make his/her duty under widely differing circumstances and for all molecules in all phases.

An outstanding candidate for the job of a chemical spy is the nucleus (think of the related spectroscopic techniques), as nuclei are always part of all molecules in all phases. Furthermore, for the job they could use the magnetic moments they have anyhow, so they can work for us for next to nothing.

Nuclear magnetic moments are extremely sensitive to their environment and still interact with them only to a very minor extent. As most chemical elements have at least one isotope which has magnetic moment, most all molecules can be studied via their nuclear magnetic moments.

When a nucleus with a magnetic moment is placed in an external magnetic field, it assumes one of the few possible orientations which have different energies. For example, the nucleus of the H atom (the proton) can "choose" only between two possible orientations. We may loosely (and incorrectly) say that the magnetic moment of the proton may point toward the direction of the external field or in the opposite direction. The energy difference of the two orientations is ΔE. The splitting depends on the strength of the interaction between the nucleus and the magnetic field, more precisely it depends on the magnitude of the magnetic moment of the nucleus and the strength of the external field.

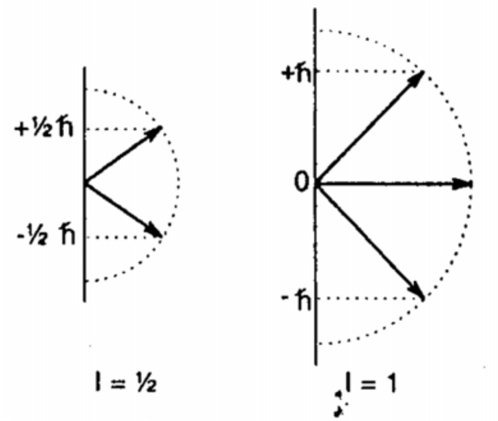


Fig. 1.3 Space quantization of spin-$\frac{1}{2}$ and spin-1 nuclei. The spin angular momentum has magnitude $[I(I+1)]^{1/2}\hbar$ and z component $m\hbar$, where m is given by eqn 1.4.

A) **A brief history of magnetic resonance (NMR and ESR) techniques**

Pauli (1924): a hypothesis to explain some of the details of hyperfine structure found in optical atomic spectra: in addition to acting as electrostatic point charges, some atomic nuclei possess magnetic moments.

Purcell, Torrey, Pound (1945); Bloch, Hansen, Packard (1945): first detection of nuclear resonance effects in bulk matter, after Rabi *et al*. (1938) observed NMR transitions in molecular beams.

Zavoisky (1945): first observation of electron spin resonance (ESR)

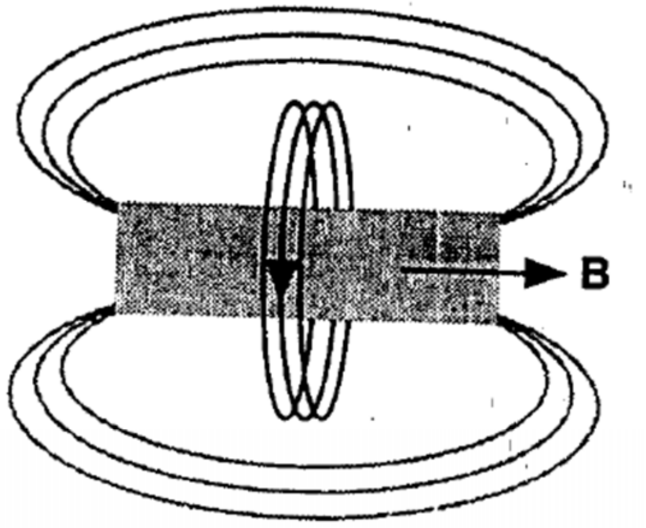
Arnold, Dharwatti, Packard (1951): observed the ^{1}H NMR spectrum of liquid CH_3CH_2OH, a spectrum of three lines (they resolved lines due to identical nuclei in chemically different environments and thus started the success story of high-resolution NMR).

Bloch, Purcell (1952): share the Nobel Prize in physics.

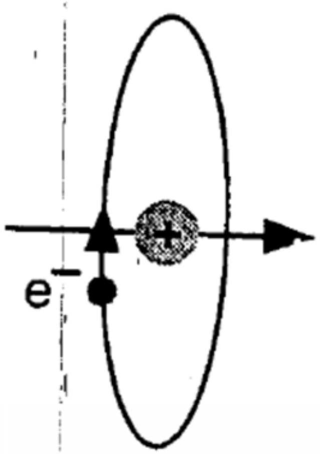
Richard R. Ernst (1991): Nobel Prize in chemistry for his contributions to the development of high-resolution NMR.

Kurt Wütrich (1992): Nobel Prize in chemistry for developing NMR for studying macromolecules of biochemical interest

Paul C. Lauterbur, Sir Peter Mansfield (2003): Nobel Prize in medicine (MRI)



Magnetic effect of current in a coil.



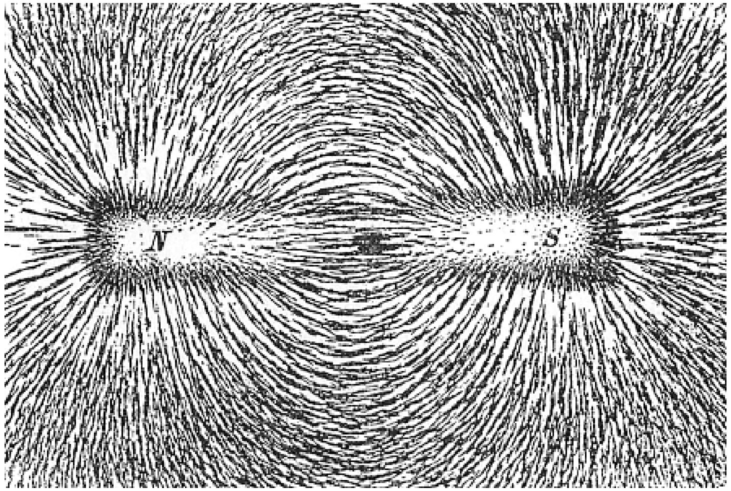
Magnetic effect of circulating electron in a paramagnetic atom.

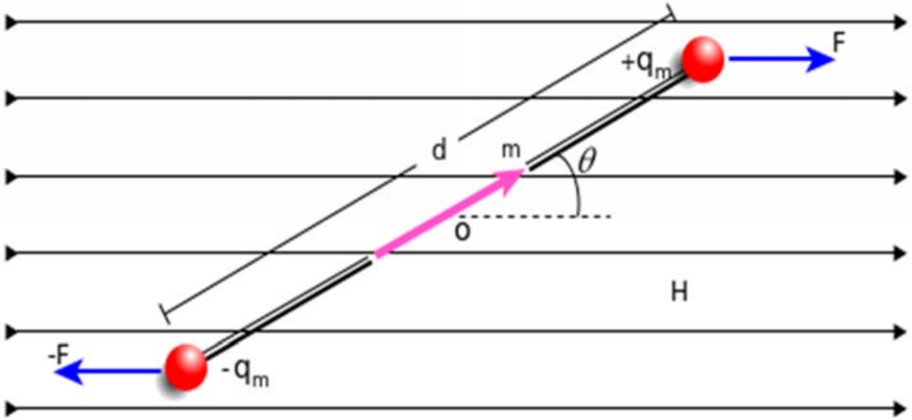
B) Magnetizability – classical treatment

1. Introduction

All moving charges (in our case protons and electrons) produce magnetic fields. It is generally true that magnetic effects are caused by moving charges, and they can be observed by moving charges.

Magnetic fields are characterized by magnetic field lines. If a permanent magnet is placed in a magnetic field in an angle with the field lines, it experiences a torque. If the magnetic flux density (**B**, vide infra) has the strength of 1 tesla (see the definition of the unit later), the magnitude of the torque is the **m** magnetic moment of the magnet.





The magnetic flux density of Earth changes from place to place and its magnitude is about 50 μtesla. This **B** causes compasses to point toward the north. (Superconducting) magnets employed during NMR measurements are much stronger, their magnetic flux density is on the order of 0.3 – 18 tesla.

The magnetic moment per unit volume, $\mathbf{M} = \mathbf{m} / V$, is the magnetization (magnetic polarization), [**M**] = A m^{-1}. For isotropic substances the magnitude of **M** (magnetization) is connected with the **H** magnetic field vector via the equation $\mathbf{M} = \chi \mathbf{H}$, the dimensionless proportionality constant χ is the magnetic susceptibility (thus, [**H**] = A m^{-1}). The susceptibility is negative for a diamagnetic material and positive for a paramagnetic material. The susceptibility of any substance can be written as the sum of a paramagnetic contribution χ_p and a (negative) diamagnetic contribution χ_d.

The relation between **B** and **H** is $\mathbf{B} = \mu \mathbf{H}$, where the proportionality constant μ is called the (relative) magnetic permeability. The magnetic permeability of vacuum is 1, that of air is 1.000 000 3, of diamagnetic and paramagnetic materials slightly less and more than 1, respectively, while that of ferromagnetic materials may exceed 1000.

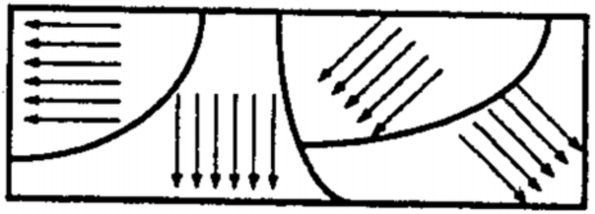
2. Magnetism of materials

The magnetic susceptibility χ is independent of the **H** magnetic field vector.

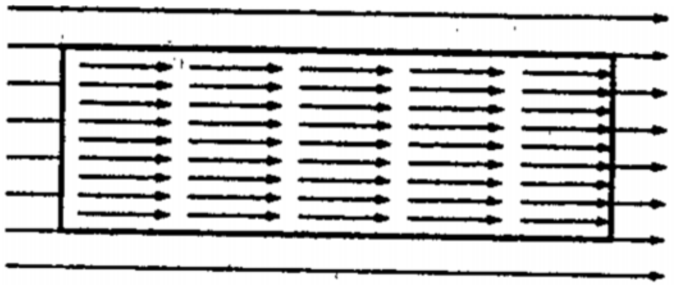
Diamagnetism results from the induction of microscopic currents in a sample by the external magnetic field. The magnetic dipoles produced in this way are aligned in a direction opposite to that of the external field. The diamagnetic effect is produced in all substances. The magnetic susceptibility χ of diamagnetic materials is a negative number of the order of 10^{-6}; thus, the μ magnetic permeability just slightly deviates from 1.

Paramagnetism results from the orientation of permanent magnetic dipoles in a substance. These permanent dipoles are due to the spin of unpaired electrons or to the angular momentum of electrons in orbitals of atoms or molecules. Electrons in orbitals with $l = 1$, 2, 3, … have angular momentum and therefore produce a magnetic dipole moment. Nuclei with magnetic moments produce a paramagnetic effect, but this effect is only about a millionth as large as paramagnetism due to orbital moments of unpaired electrons. The χ magnetic susceptibility of paramagnetic materials is a positive number of the order of $10^{-5} - 10^{-6}$, which decreases with the increase of the temperature. The magnetization **M** points toward the **H** magnetic field vector.

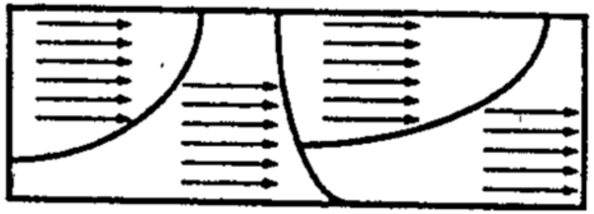
Paramagnetic – no applied field



Ferromagnetic – unmagnetised



Paramagnetic with field applied



Ferromagnetic – magnetised

Ferromagnetic materials include iron, cobalt, and nickel, as well as their alloys formed with each other or with other elements (*e.g.*, Mn, Al, Cr, Si). There are ferromagnetic alloys in which none of the components are ferromagnetic. In ferromagnetic materials the magnetization is orders of magnitude larger than in other materials, but neither **M** nor **B** is proportional to **H**, the relation between them is more complicated. Upon increasing **H**, **M** increases only up to a limit. Ferromagnetic materials loose their ferromagnetism above a certain temperature, called the Curie-point (*e.g.*, Fe: 769 °C, Co: 1075 °C, Ni: 360 °C). Above this temperature ferromagnetic materials become paramagnetic. Ferromagnetism is displayed only by solids. Ferromagnetism is a solid state property, it’s not a property of individual atoms or molecules.

In antiferromagnetic materials the magnetic moments of the atoms or molecules align in a regular pattern, another case of ordered magnetism, with neighboring spins pointing in opposite directions. This material property is also exhibited only at sufficiently low temperature.

C) Basics of NMR

1. Nuclear magnetic moments

Magnetic nuclei possess an intrinsic angular momentum, which we call nuclear spin (classical interpretation: the nucleus rotates about its intrinsic axis). Magnitude: $\sqrt{I(I+1)}\hbar$, where *I* is the so-called nuclear spin quantum number, which can take integer and half-integer values. Protons, neutrons (and electrons, as well) have half-integer spins (I = ½). Nuclei with $I \neq 0$ possess magnetic moments.

I	Nucleus
0	^{12}C, ^{16}O
1/2	^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P
1	^{2}H, ^{14}N
3/2	^{11}B, ^{23}Na, ^{35}Cl, ^{37}Cl
5/2	^{17}O, ^{27}Al
3	^{10}B

NB: we are mostly interested in I = ½ nuclei (biochemical NMR: ^{1}H, ^{13}C, ^{15}N, ^{19}F, and ^{31}P. Of course, the spin-5/2 ^{17}O nucleus is also of interest.

no. of protons	no. of neutrons	l
even	even	0
odd	odd	1 or 2 or 3 or …
even	odd	1/2 or 3/2 or 5/2 or …
odd	even	1/2 or 3/2 or 5/2 or …

NB1: There are several exceptions from the “rules” stated.

NB2: Explanation of the rule: protons and neutrons possess not only spins but also orbital angular momenta. These angular momenta couple to each other vectorially, just like we learned before (*e.g.*, *j*–*j* coupling for atoms). This total momentum is what we call nuclear spin. Nuclei have a shell structure, to some extent resembling electron shells. In NMR we deal only with the ground states of nuclei (considerable simplification of the picture).

2. Magnetizability of nuclei

I: total nuclear spin angular momentum → $\sqrt{I(I+1)}\hbar$
I: spin quantum number
I_z: *z* component of nuclear spin → $m_I\hbar$

In complete analogy with the case of the electron spin (Dirac's relativistic treatment), the $\boldsymbol{\mu}$ nuclear magnetic momentum is linearly related to the nuclear spin angular momentum:

$$\boldsymbol{\mu} = \gamma_\mathrm{N}\,\mathbf{I} = \frac{g_\mathrm{N} e}{2m_\mathrm{p}}\mathbf{I},$$

where γ_N is the so-called gyromagnetic (sometimes also called magnetogyric) ratio, g_N is the nuclear *g*-factor, and m_p is the mass of the proton.

Definition of the basic unit of the nuclear dipole moment, the nuclear magneton:

$$\mu_\mathrm{N} = \frac{e\hbar}{2m_\mathrm{p}} \equiv \frac{1}{1836}\mu_\mathrm{B},$$

where μ_B is the Bohr-magneton known from electronic structure theory.

	spin-I	g_N	$\gamma/10^7\ \mathrm{T^{-1}s^{-1}}$	ν/MHz	natural abundance/%
neutron	½	–3.826			
^{1}H	½	5.585	26.75	$\boxed{400.0}$	99.985
^{2}H	1	0.857	4.11	61.4	0.015
^{13}C	½	1.405	6.73	100.6	1.108
^{14}N	1	0.404	1.93	28.9	99.63
^{15}N	½	–0.566	–2.71	40.5	0.37
^{17}O	$\frac{5}{2}$	–0.757	–3.63	54.3	0.037
^{19}F	½	5.257	25.18	376.5	100.00
^{29}Si	½		–5.32	79.6	4.70
^{31}P	½		10.84	162.1	100.00

Magnetic moments of nuclei are not simply the sum of the magnetic moments of protons and neutrons.

Since magnetic fields are produced by moving electric charges (currents), it is possible to connect the strength of the field of any magnet, including a single magnetic dipole, with basic mechanical and electrical units. The magnetic flux density **B** determines the magnetic force on a moving charged particle. The SI unit is tesla: $1\ \mathrm{T} = 1\ \mathrm{N\ A^{-1}\ m^{-1}} = 1\ \mathrm{kg\ s^{-2}\ A^{-1}}$.

The above ν “NMR frequency” values are for a field of 9.4 T.

3. Effect of external magnetic field

In the absence of an external magnetic field, the $2I + 1$ possible orientations of a spin-I nucleus all have the same energy (degeneracy). Switching on the magnetic field “removes” this degeneracy, if a $\boldsymbol{\mu}$ magnetic moment interacts with the magnetic flux density **B** than the interaction energy is

$$E = -\boldsymbol{\mu} \cdot \mathbf{B}.$$

In a strong magnetic field the z quantization axis is not arbitrary, it coincides with the direction of the field (components of the magnetic moment: constant z component, many arbitrarily oriented components in the xy plane precessing about the quantization axis with a so-called Larmor frequency):

$$E = -\mu_z B.$$

We know that $\mu_z = \gamma_{\mathrm{N}} I_z$ and $I_z = m_I \hbar$, thus

$$E = -m_I \hbar \gamma_{\mathrm{N}} B.$$

In summary, the energy depends linearly on the strength of the external magnetic field and the gyromagnetic ratio (a constant for a given nucleus). Distance of the $2I + 1$ equidistant energy level components is $\hbar \gamma_{\mathrm{N}} B$ (linear dependence on m_I).

Transitions among the energy levels can be induced by applying electromagnetic radiation with frequency equal to the energy level spacing → nuclear magnetic resonance (NMR) spectroscopy. Since these transitions take place between magnetic states, they are induced by the oscillating magnetic field of the radiation rather than the oscillating electric field, and are called magnetic dipole transitions.

The selection rule governing NMR spectroscopy is simply $\Delta m_I = \pm 1$. Thus, transitions can occur only between neighboring energy levels (by now we got used to this selection rule).

Based on $\Delta E = h\nu = \hbar\gamma_{\mathrm{N}} B$,

$$\nu = \frac{\gamma_{\mathrm{N}} B}{2\pi} ,$$

and this is what we call Larmor-frequency (important: for each non-interacting nucleus there is thus one well-defined Larmor frequency, which depends on the gyromagnetic ratio (γ_{N}) of the nucleus and the strength of the applied magnetic field).

We learned that in spectroscopy the probability of emission and absorption is equal. In NMR spectroscopy both absorption and emission may occur. Since spontaneous emission is extremely small and can be neglected for NMR, the processes of absorption and stimulated emission are the only ones that are relevant. At thermal equilibrium, according to the Boltzmann equation

$$\left(\frac{N_{\text{upper}}}{N_{\text{lower}}}\right)_{\text{eq}} = e^{-\Delta E/kT} = e^{-g_N \mu_N B/kT} \cong 1 - \frac{g_N \mu_N B}{kT}.$$

Then, the excess population in the lower state is

$$\frac{N_{\text{lower}} - N_{\text{upper}}}{N_{\text{lower}} + N_{\text{upper}}} = \frac{g_N \mu_N B}{2kT}$$

Thus, the intensity of the magnetic resonance signals increases if B increases or T is lowered. The population difference, based on the above equation, is 3.2×10^{-5} ($\Delta E = 2.65 \times 10^{-25}$ J and $kT = 4.14 \times 10^{-21}$ J), very small.

4. Spin relaxation

Consider a molecule with only spin-1/2 nuclei. In the absence of an external field, $N_\alpha = N_\beta$ (equilibrium). Apply a uniform external magnetic field B_0 in the z direction. The instant after the field is turned on, we have equal populations; however, in the presence of B_0, the α spins have a lower energy ($\hat{H}\left|M_I\right\rangle = -g_N \mu_N B_0 M_I \left|M_I\right\rangle$) than the β spins (α and β stand for the M_I = +1/2 and –1/2 nuclear spin wavefunctions), resulting in a non-equilibrium population distribution.

The important question is how could the system achieve the new population $N_\alpha > N_\beta$?

One distinct possibility is that it is achieved via spontaneous emission, $A_{mn} \propto \nu_{mn}^3$. At optical frequencies ($\approx 10^{14}$ Hz), spontaneous emission leads to lifetimes of $\approx 10^{-8}$ s. NMR energy differences are small, and ν_{mn} is $\approx 10^8$ Hz for a typical B_0. Thus, it'd take thousands of years for the β spin population to be depleted to near its equilibrium value. We need another explanation.

The second feasible possibility is that interactions between the nuclear spins and their surroundings allow for a nonradiative energy transfer to occur between the spins and their surroundings. Spin-lattice relaxation: any relaxation process involving nonradiative energy transfer between spins and surroundings (the "lattice" is the crystal). We are mainly interested in spin-lattice relaxation in liquids.

$W_{\alpha\beta}$; $W_{\beta\alpha}$: spin-lattice relaxation transition probabilities per second for upward and downward transitions, respectively

$N_{\alpha,\mathrm{eq}}$; $N_{\beta,\mathrm{eq}}$: equilibrium populations

At equilibrium: $N_{\alpha,\mathrm{eq}}W_{\alpha\beta} = N_{\beta,\mathrm{eq}}W_{\beta\alpha}$.

Because NMR energy-level differences are small, $N_{\beta,\mathrm{eq}}$ is only slightly less than $N_{\alpha,\mathrm{eq}}$, and the two W's are nearly equal. From the definition of W's:

$$\frac{dN_\beta}{dt} = -N_\beta W_{\beta\alpha} + N_\alpha W_{\alpha\beta} \ .$$

Let $N := N_\alpha + N_\beta$ (total number of spins) and $n := N_\alpha - N_\beta$ (population difference). Obviously, $N_\alpha = \tfrac{1}{2}(N+n)$ and $N_\beta = \tfrac{1}{2}(N-n)$, thus $dN_\beta \big/ dt = -\tfrac{1}{2}dn/dt$.

So,

$$dn/dt = -n(W_{\alpha\beta} + W_{\beta\alpha}) + N(W_{\beta\alpha} - W_{\alpha\beta}).$$

At equilibrium, $dn/dt = 0$; thus,

$$n_{\mathrm{eq}} = \frac{N(W_{\beta\alpha} - W_{\alpha\beta})}{W_{\alpha\beta} + W_{\beta\alpha}}.$$

Then,

$$dn/dt = -(n - n_{\mathrm{eq}})(W_{\alpha\beta} + W_{\beta\alpha}).$$

After integration, and setting $n(t = 0) = n_0$:

$$n - n_{\mathrm{eq}} = (n_0 - n_{\mathrm{eq}})\exp[-(W_{\alpha\beta} + W_{\beta\alpha})t].$$

After a time T_1, where $T_1 := (W_{\alpha\beta} + W_{\beta\alpha})^{-1} \approx (2W_{\alpha\beta})^{-1} \approx (2W_{\beta\alpha})^{-1}$, the population difference deviation from its final equilibrium value, $n - n_{\mathrm{eq}}$, has fallen to $1/e$ of its initial deviation. The time T_1 is called the spin-lattice relaxation time (longitudinal relaxation time). According to experience,$T_1 \in (10^{-2}, 10^{2}$ s). The quantity $1/W_{\alpha\beta}$ is the average lifetime, τ_α, of state α, and then $\tau_\beta = 1/W_{\beta\alpha}$.

Hallmarks of NMR spectroscopy

- can be applied in all phases, but most typically it is applied in liquids (biochemistry, MRI = Magnetic Resonance Imaging);
- in solids provides information about the distance between nuclei with magnetic moments and about their orientations in the crystal;
- liquid crystal NMR is a competitive method to determine complete structure of molecules (+ MW, GED), best technique is a combination of all three augmented with quantum chemistry;
- can be applied to elements of almost the whole periodic table (analytic applications, elemental analysis);
- high sensitivity in liquid phase, large molecules can be studied (most common application), including larger peptides and smaller proteins;
- large amount of structural information;

- NMR spectroscopy has become a tool as useful, if not more useful, to the organic chemist as IR spectroscopy (the number of proton peaks, their relative intensities, and their chemical shifts aid greatly structural determinations);
- sensitivity of detecting a given nucleus depends on three important factors: the gyromagnetic ratio γ (cubic dependence); nuclear spin quantum number I (quadratic dependence); and the strength of the applied external magnetic field, B (3/2 power). Obviously, natural abundance is also a determining factor. Receptivity (relative abundance multiplied with sensitivity) with respect to ^{13}C (given external field): ^{1}H = 5670, ^{15}N = 0.022, ^{19}F = 4370 and ^{31}P = 377.

A few characteristic NMR spectra

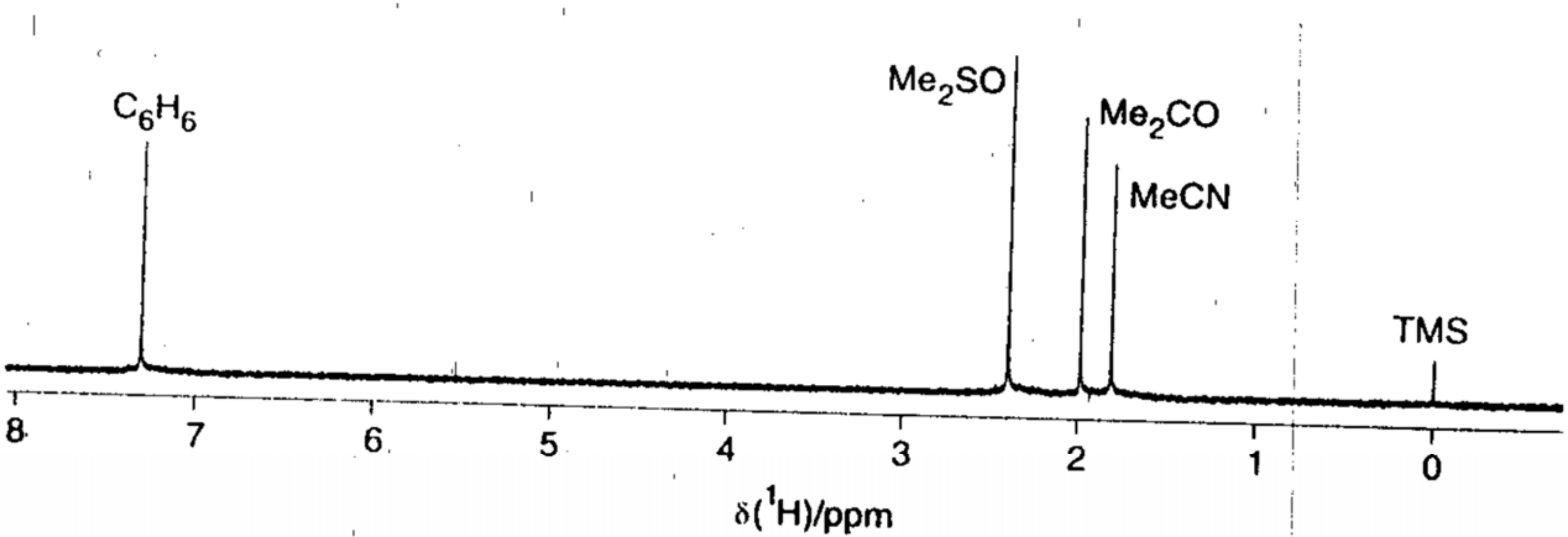


Fig. 2.5 400 MHz ^{1}H NMR spectrum of a mixture of benzene, dimethylsulphoxide, acetone, acetonitrile and tetramethylsilane.

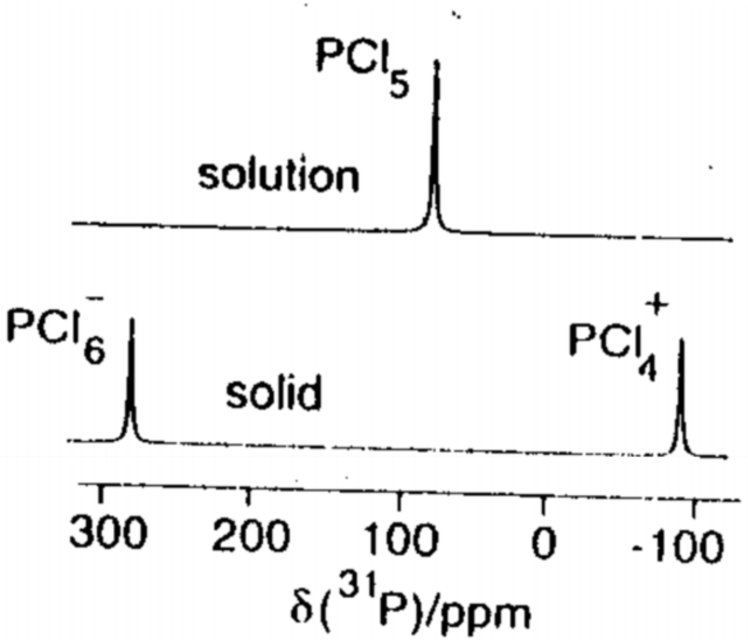


Fig. 2.6 ^{31}P NMR spectra of phosphorus pentachloride in the solid state and in solution in CS_2.

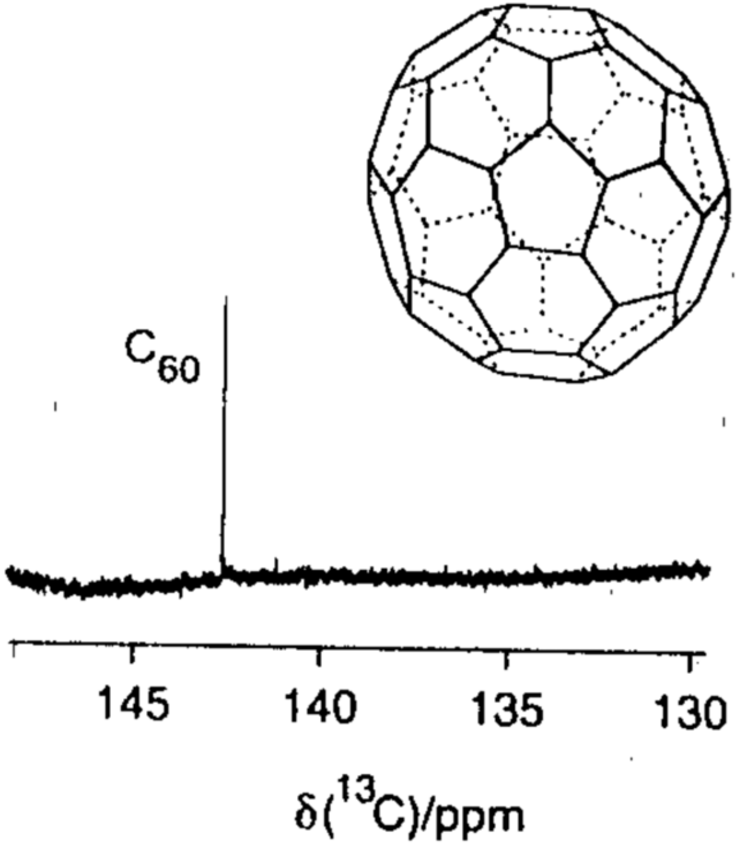


Fig. 2.9 ^{13}C NMR spectrum of buckminsterfullerene, C_{60}.

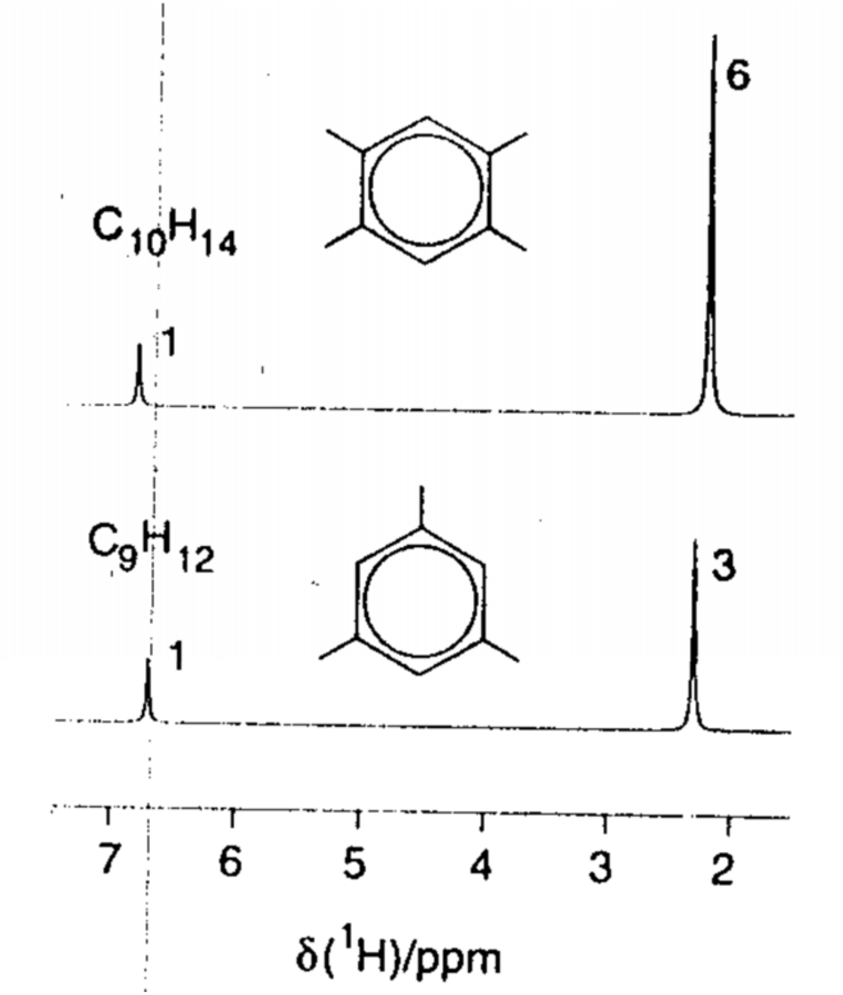


Fig. 2.8 ^{1}H spectra of compounds with molecular formulae C_9H_{12} and $C_{10}H_{14}$. The relative intensities of the peaks, obtained by integration, are as shown.

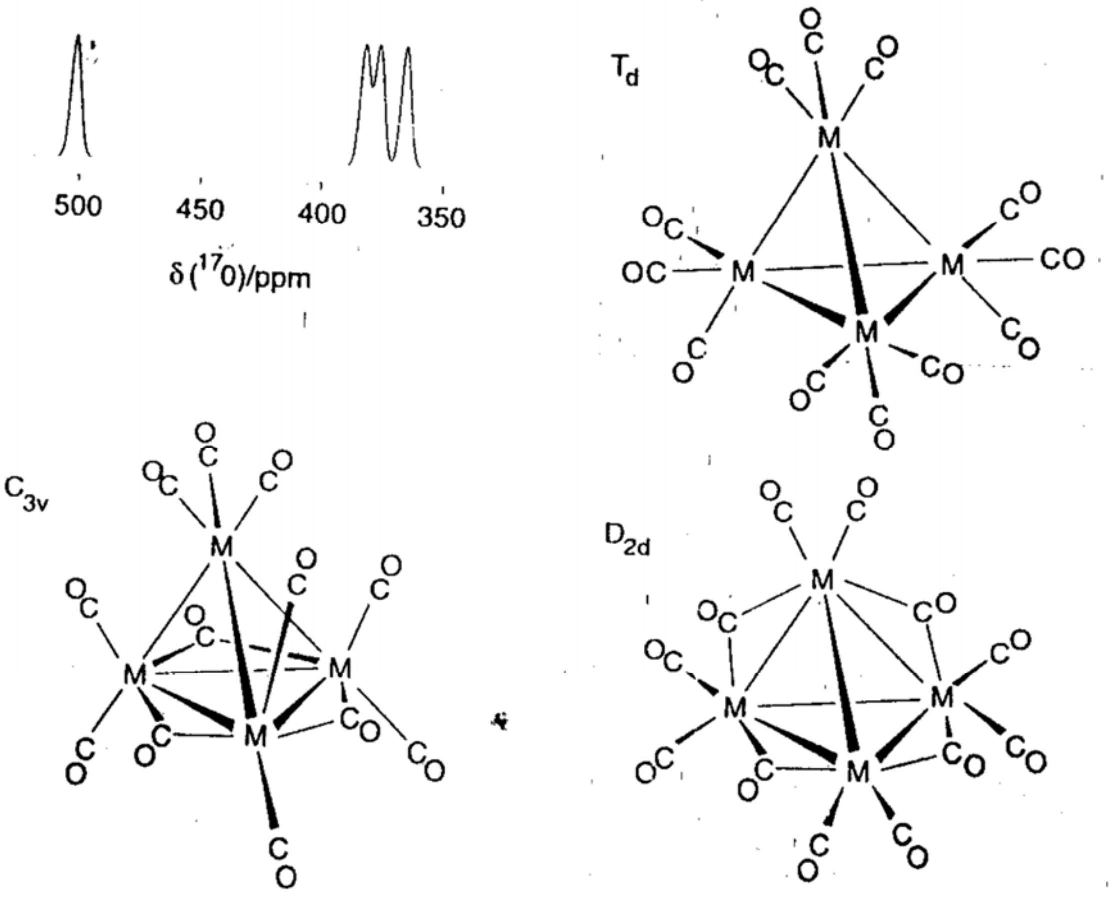


Fig. 2.7 The ^{17}O NMR spectrum of $Co_4(CO)_{12}$ in chloroform at −25°C is consistent with the C_{3v} structure shown, but not the T_d or D_{2d} forms.

A brief quantum mechanical treatment

NMR transitions are between energy levels that correspond to different orientations of the nuclear magnetic dipole moment in an applied magnetic field **B**. The classical energy of interaction between an isolated nuclear magnetic moment **μ** and **B** is

$$E = -\boldsymbol{\mu}\cdot\mathbf{B} = -g_{\mathrm{N}}\mu_{\mathrm{N}}\hbar^{-1}\mathbf{I}\cdot\mathbf{B} = -g_{\mathrm{N}}\mu_{\mathrm{N}}\hbar^{-1}BI_z,$$

where we chose the z axis to coincide with the direction of the uniform applied field, and I_z is the z component of **I**.

The quantum mechanical operator for interaction between a nuclear magnetic moment and a magnetic field:

$$\hat{H} = -g_{\mathrm{N}}\mu_{\mathrm{N}}\hbar^{-1}B\hat{I}_z = -\gamma_{\mathrm{N}}B\hat{I}_z,$$

where $\gamma_{\mathrm{N}} := \dfrac{g_{\mathrm{N}}\mu_{\mathrm{N}}}{\hbar}$ is the gyromagnetic ratio.

The eigenfunctions and eigenvalues of $\hat{H}$ follow from the (by now) well-known equations of angular momentum algebra:

$$\hat{I}_z \left| M_I \right\rangle = m_I \hbar \left| M_I \right\rangle;$$
$$\hat{H} \left| M_I \right\rangle = -g_{\mathrm{N}} \mu_{\mathrm{N}} B m_I \left| M_I \right\rangle, \text{ where } m_I = I, I-1, \ldots, -I .$$

The energy levels are:

- evenly spaced;
- diverge as the applied magnetic field increases;
- for positive g_{N}, the negative m_I values lie highest.

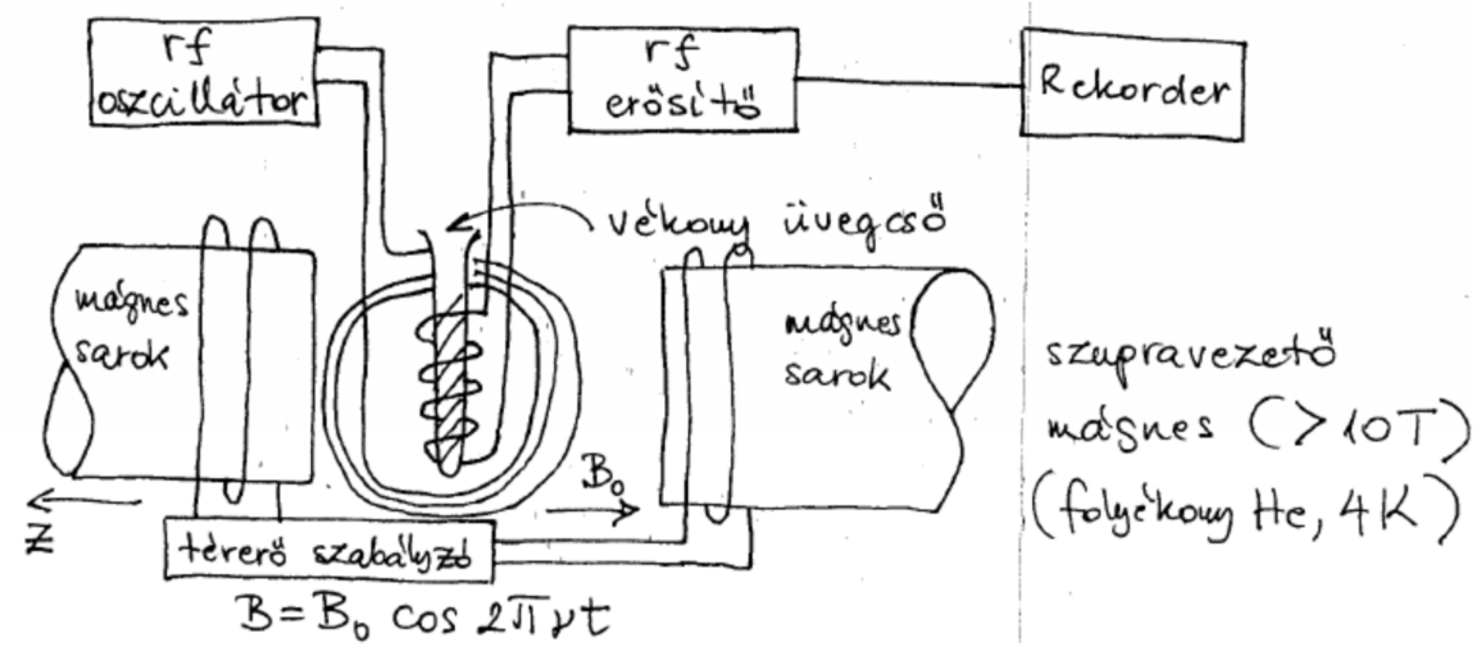
Furthermore, since $\hat{H}$ is Hermitian, $\left\langle M'_I \middle| M''_I \right\rangle = \delta_{m'_I m''_I}$

To obtain the NMR selection rules is a rather involved process (through the use of time-dependent perturbation theory). Final result: $\Delta m_I = \pm 1$. This selection rule gives for the frequency of an NMR transition:

$$\nu = g_N \mu_N B / h = \frac{\gamma_{\mathrm{N}} B}{2\pi} .$$

Thus, although there are 2 I + 1 nuclear spin energy levels, they are equally spaced, and the selection rule allows only transitions between adjacent levels; hence we get a single NMR absorption frequency.

Measurement



Two possible schemes to observe an NMR transition:

(1) Apply a constant field B and vary the frequency ν of the EM to which the sample is exposed until $\nu = \gamma B / 2\pi$ is satisfied.

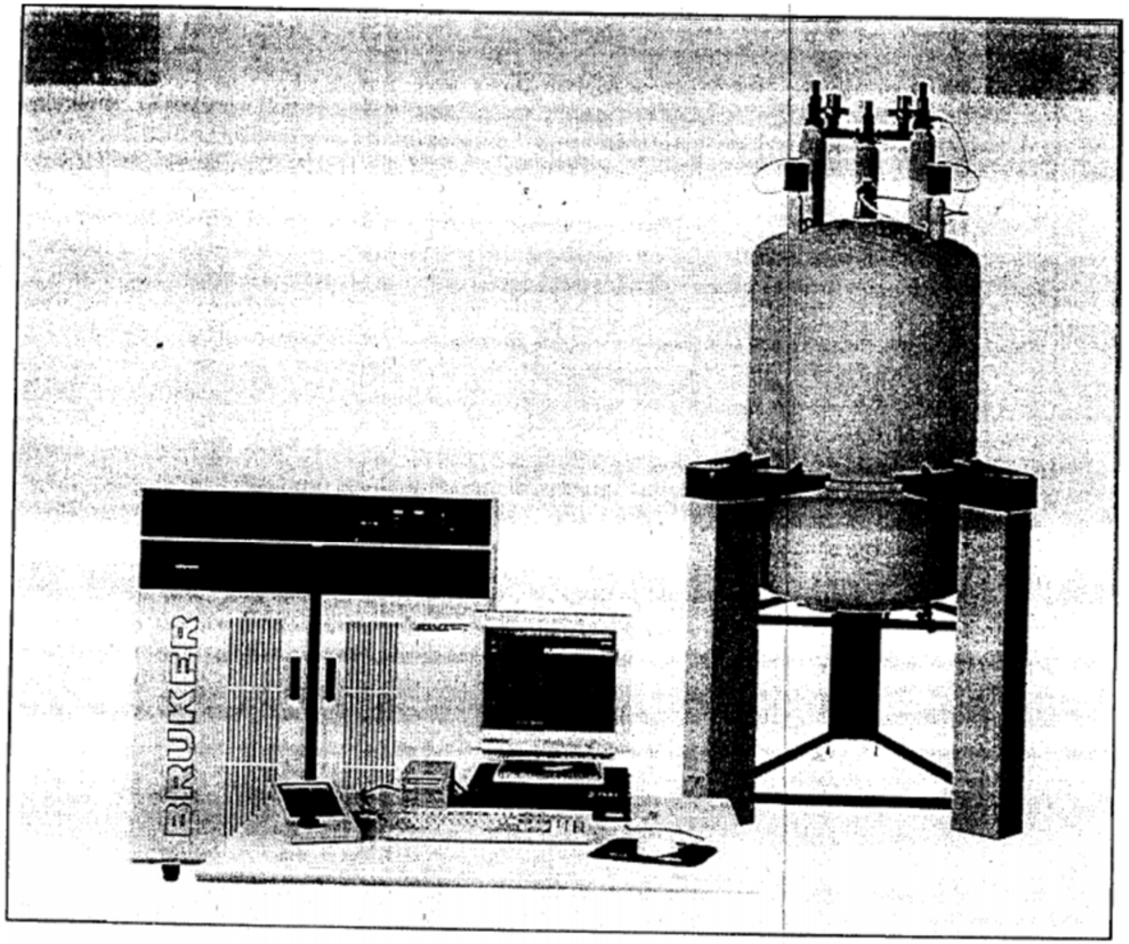
(2) Expose the sample to a fixed-frequency EM signal and slowly vary the applied magnetic field. The rf-frequency is held stable (*e.g.*, 60–800 MHz for protons, 60 MHz corresponds to B = 1.4 T).

The use of high magnetic fields has advantages:

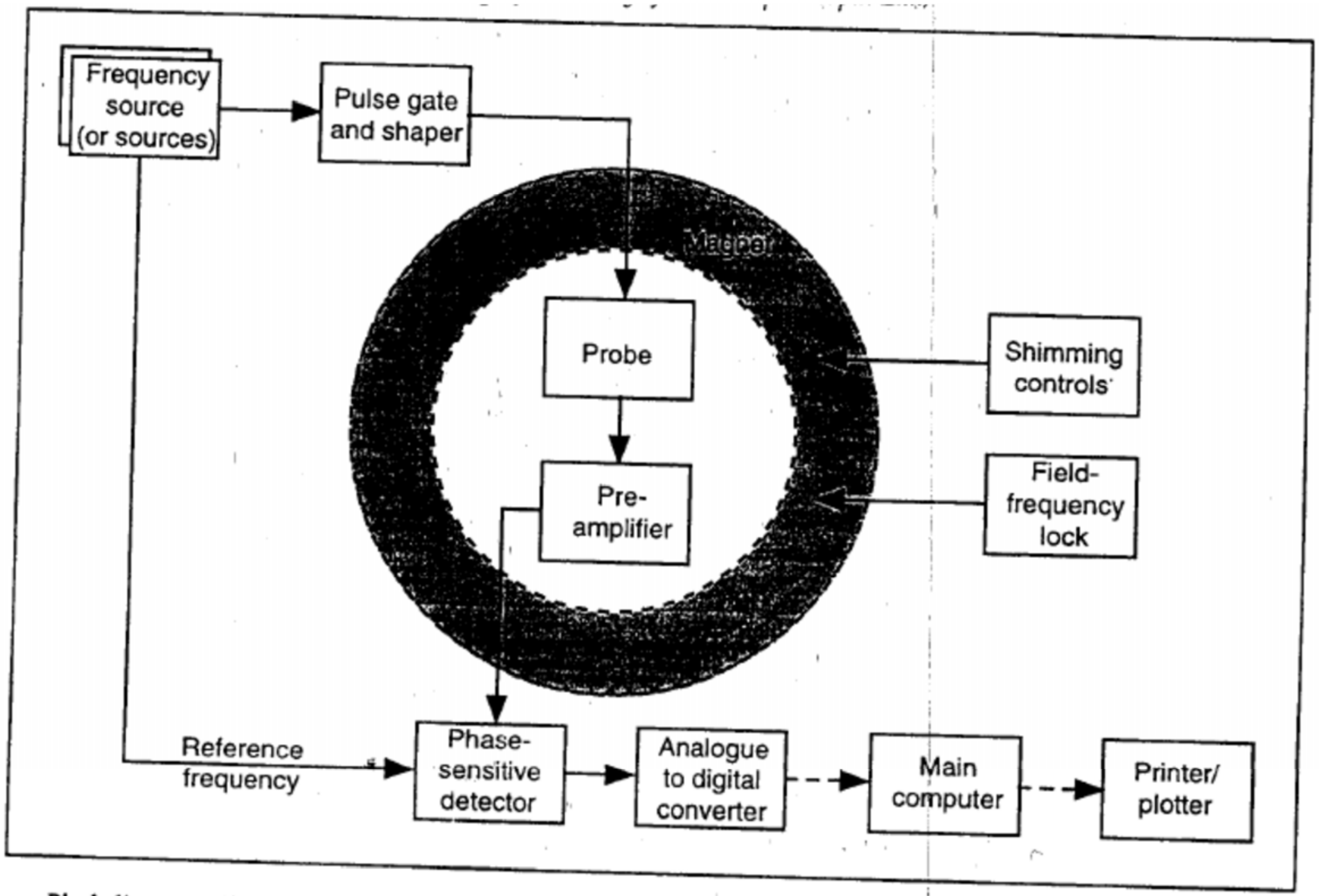
(1) the field increases the population difference between the two spin states → stronger net absorption;

(2) a high field might simplify the appearance of certain spectra;

(3) improves resolution.



State-of-the-art: a 600-MHz high-resolution NMR spectrometer which uses digital technology for most stages of signal generation and detection. The cabinet at left contains major electronic control and data storage components: centre is the UNIX workstation through which the system is operated, and at right is the superconducting magnet. (See Section 3.3.) *(Photograph courtesy of Bruker Spectrospin Ltd.)*



Block diagram of basic spectrometer components.

Consequences of a radiofrequency pulse

If we apply a single, short but intense pulse in the radiofrequency (rf) region of the electromagnetic spectrum at the Larmor frequency, a large number of transitions will occur. Since most of the transitions will be absorption, the difference in the Boltzmann-populations will decrease. As a result the magnetizability in the z direction (M_z) will also decrease.

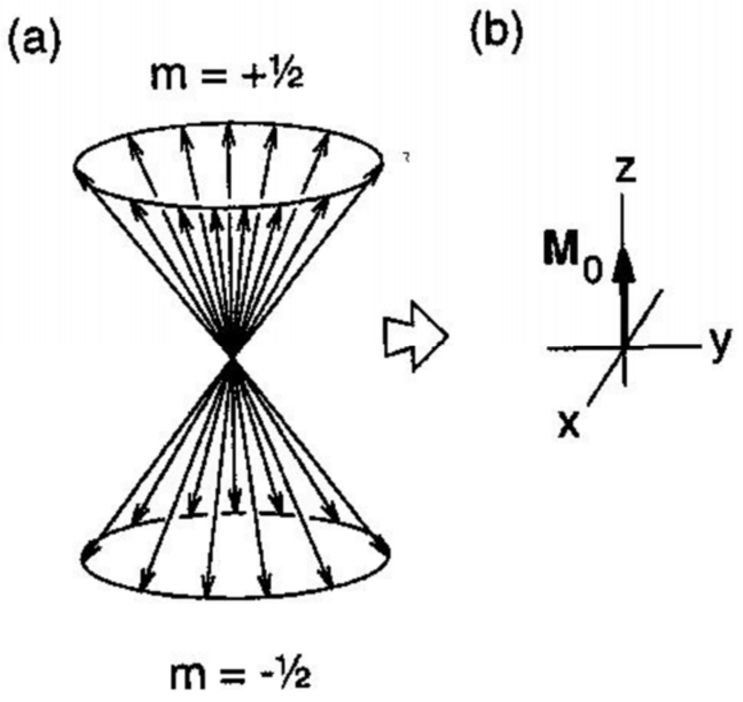


Fig. 6.3 Vector model of a collection of spin-$\frac{1}{2}$ nuclei at thermal equilibrium in a magnetic field along the z axis. (a) The magnetic moments of the individual spins: there is a slight excess of nuclei in the $m = +\frac{1}{2}$ state, which is lower in energy than the $m = -\frac{1}{2}$ state (for nuclides with positive gyromagnetic ratio). At equilibrium, the phases of the individual magnetic moments in the xy plane are random. (b) The net magnetic moment of a large number of spins.

Though made up from the individual quantum mechanical nuclear magnetic moments, the total magnetization of the sample conveniently obeys the rules of classical mechanics. Thus, we can (almost) forget about QM when discussing simple NMR experiments.

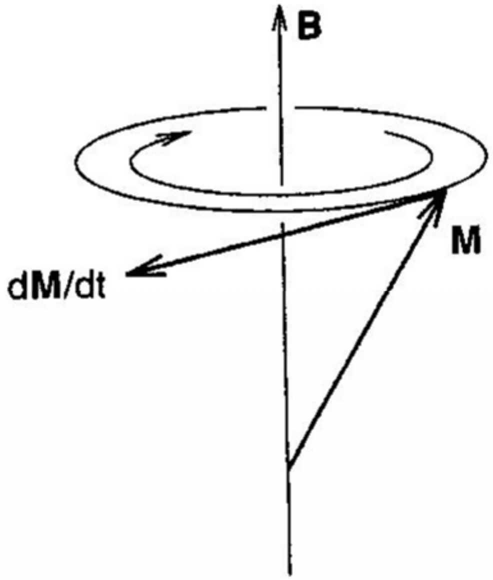


Fig. 6.4 The motion of a magnetization ***M*** in a magnetic field ***B***. The rate of change of ***M*** (d***M***/d*t*) is perpendicular to both ***M*** and ***B***, such that ***M*** precesses around ***B*** at an angular frequency $\omega = \gamma B$. The magnitude of the magnetization, and the projection of ***M*** onto ***B***, remain unchanged.

The angular frequency (unit: radians per second) corresponds to the previously mentioned Larmor-frequency. This behavior is analogous to the motion of the axis of a gyroscope or spinning top in a gravitational field.

In an NMR experiment, **B** has two components: the strong, static field $\mathbf{B}_0$ along the z axis (chemical shifts are not yet introduced) and a weak radiofrequency field $\mathbf{B}_1(t)$ which rotates in the xy plane at a frequency ω_{rf}. The total field, the vector sum of $\mathbf{B}_0$ and $\mathbf{B}_1(t)$, is thus tilted slightly away from the z axis, and rotates around it at frequency ω_{rf}. Easy concept to avoid time dependence of the rf field: rotating frame.

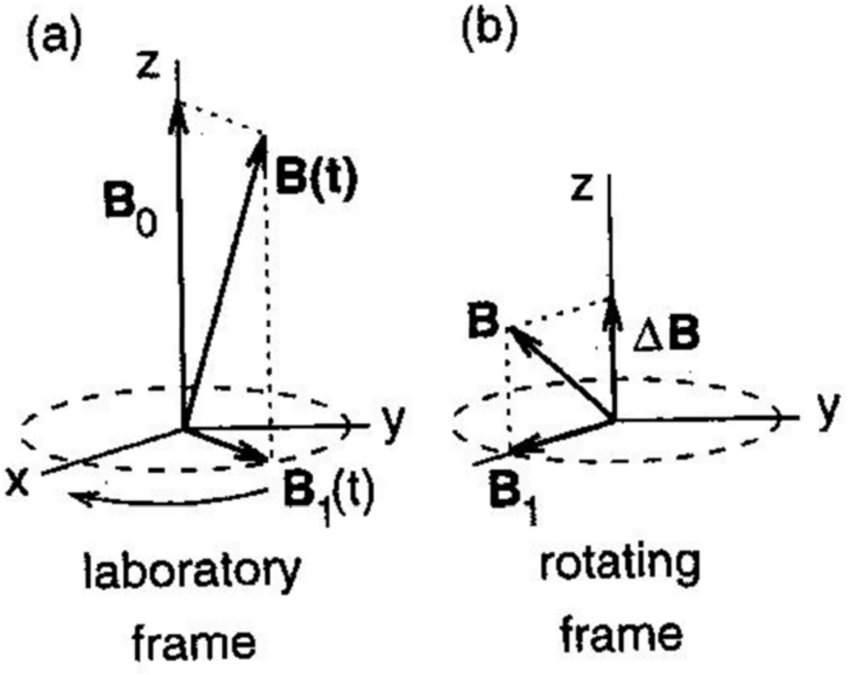


Fig. 6.5 The magnetic fields present in an NMR experiment. (a) In the 'laboratory frame', the net field $\boldsymbol{B}(t)$ is the vector sum of $\boldsymbol{B}_0$, the strong static field along the z axis, and $\boldsymbol{B}_1(t)$, the electromagnetic field rotating around $\boldsymbol{B}_0$ at frequency ω_{rf}. (b) In a coordinate system rotating in step with $\boldsymbol{B}_1(t)$ (the 'rotating frame'), the time-independent effective field $\boldsymbol{B}$ is composed of the offset field $\Delta\boldsymbol{B}$, and the radiofrequency field $\boldsymbol{B}_1$.

In the laboratory frame (*i.e.*, the “real world”) and in the absence of $\mathbf{B}_1$, $\mathbf{M}$ should precess around $\mathbf{B}_0$ at frequency $\omega_0 = \gamma B_0$. If ω_0 were identical to the radiofrequency ω_{rf}, then $\mathbf{M}$, like $\mathbf{B}_1$, would appear stationary in the rotating frame; in general, the frequency with which $\mathbf{M}$ appears to precess around the z axis, is reduced from ω_0 to the offset frequency $\Omega = \omega_0 - \omega_{\mathrm{rf}}$. Thus, an effective, offset field ΔB along the z axis in the rotating frame can be defined as follows: $\Delta B = \Omega/\gamma = (\omega_0 - \omega_{\mathrm{rf}})/\gamma = B_0 - \omega_{\mathrm{rf}}/\gamma$. Although B_0 is necessarily always much greater than B_1, the residual field ΔB can be comparable to B_1 if the transmitter frequency is close to resonance ($\omega_0 \approx \omega_{\mathrm{rf}}$).

The concept of a rotating frame is exceedingly convenient not only because it removes the unpleasant need to think about time-dependent fields, but also because NMR spectrometers detect offset frequencies rather than the actual resonance frequencies.

The simplest NMR experiment involves applying a single, short, intense burst of monochromatic rf radiation to a sample, previously at thermal equilibrium. The transmitter frequency ω_{rf} is set close to the resonance frequency of the spins, ω_0, so that the offset field ΔB is small compared to the strength of the radiofrequency field, $B_1 >> \Delta B$. Under these conditions the field experienced by the spins in the rotating frame is simply $\mathbf{B}_1$.

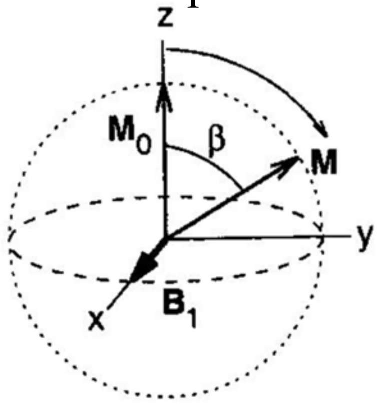
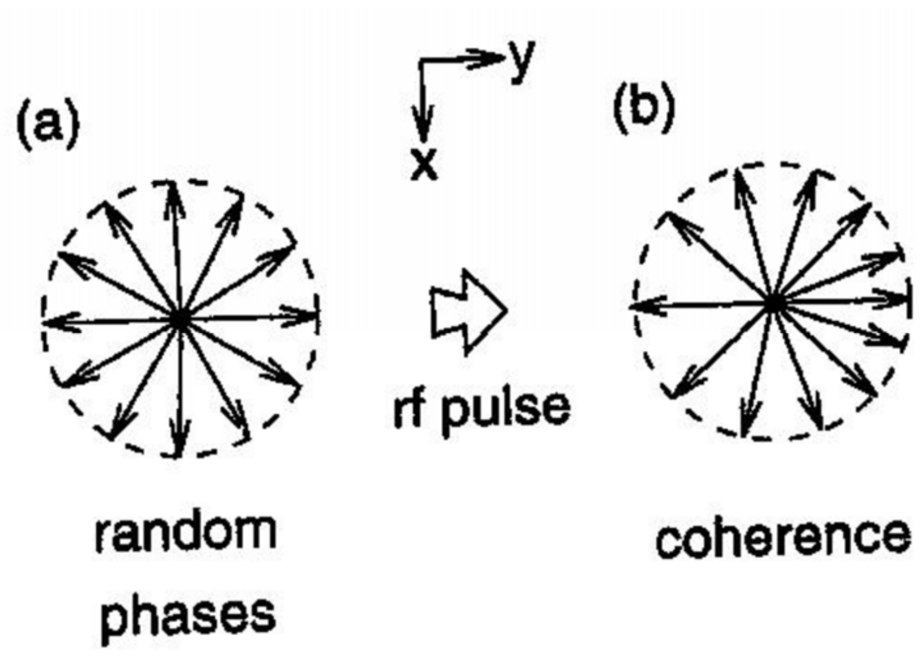
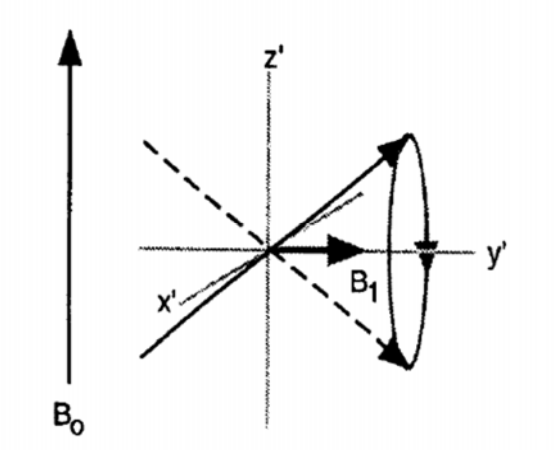
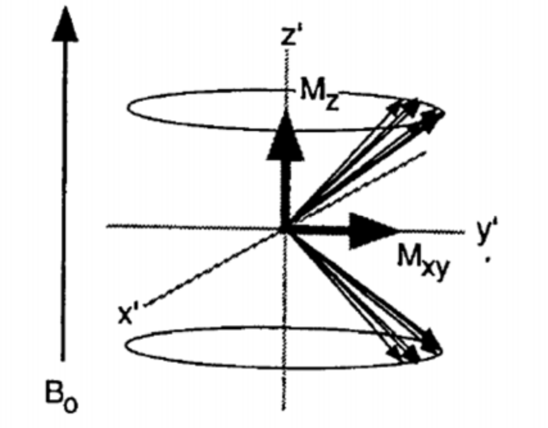


Fig. 6.6 The effect of a radiofrequency pulse on a collection of nuclear spins at equilibrium is to rotate the magnetization away from the *z* axis, around the direction of B_1, through an angle β (eqn 6.5).

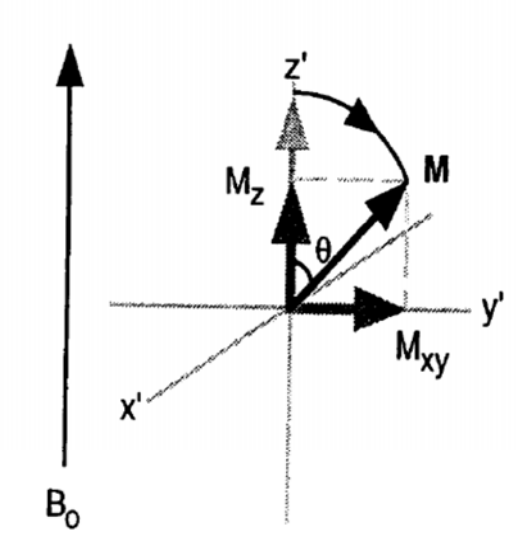




Application of a rotating magnetic field B_1 (stationary in the rotating frame) induces transitions between the two allowed states.



Magnetisation M_{xy} produced by phase coherence between spins after applied radiofrequency pulse.



Flip angle θ.

The angle through which the magnetization turns is called the flip angle, $\beta = \gamma B_1 t_p$, where t_p is the duration of the pulse in seconds and β is in radians. The most commonly used pulses have 90° or 180° flip angles (NB: a 180° pulse inverts the original population difference between two spin-1/2 states).

Starting from the equilibrium state with random phases, a pulse along the *x* axis in the rotating frame causes the spins to 'bunch together' to some extent, producing a net *y* magnetization in the sample. This phase correlation amongst the spins is known as phase coherence. That is, coherent EM radiation induces a coherence among the spins such that the orientations of the individual magnetic moments in the *xy* plane are no longer random, the net magnetization induced is M_{xy}.

The next step is to discover what happens to the magnetization *after* the pulse (*e.g.*, a 90° pulse).

There are two distinct relaxation processes. First, the recovery of the *z* magnetization to its equilibrium value: spin-lattice relaxation, with exponential time constant T_1 (spin-lattice relaxation, longitudinal relaxation time). Second, the decay to zero of the *xy* magnetization, with a time constant T_2 (spin-spin relaxation, transversal relaxation time).

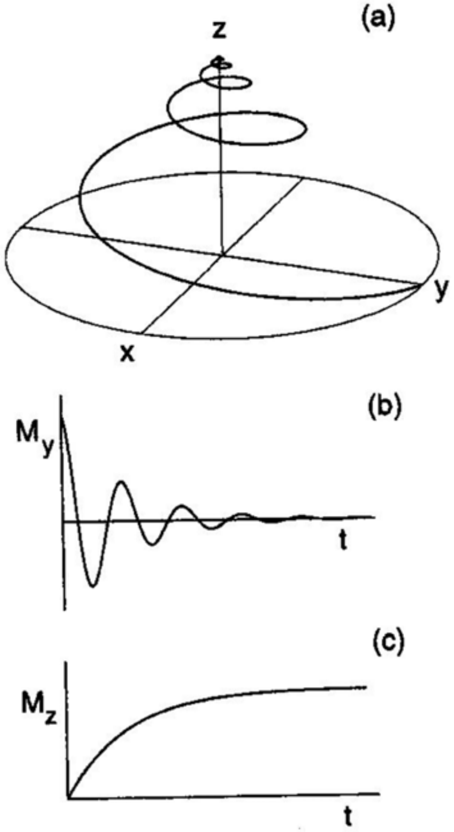
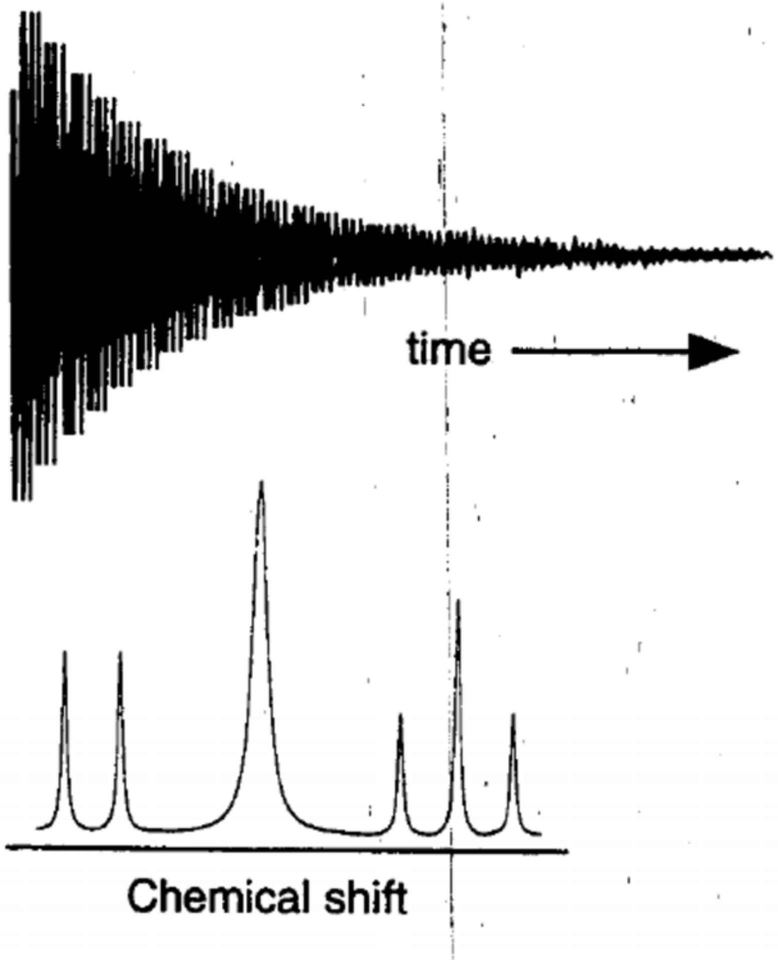
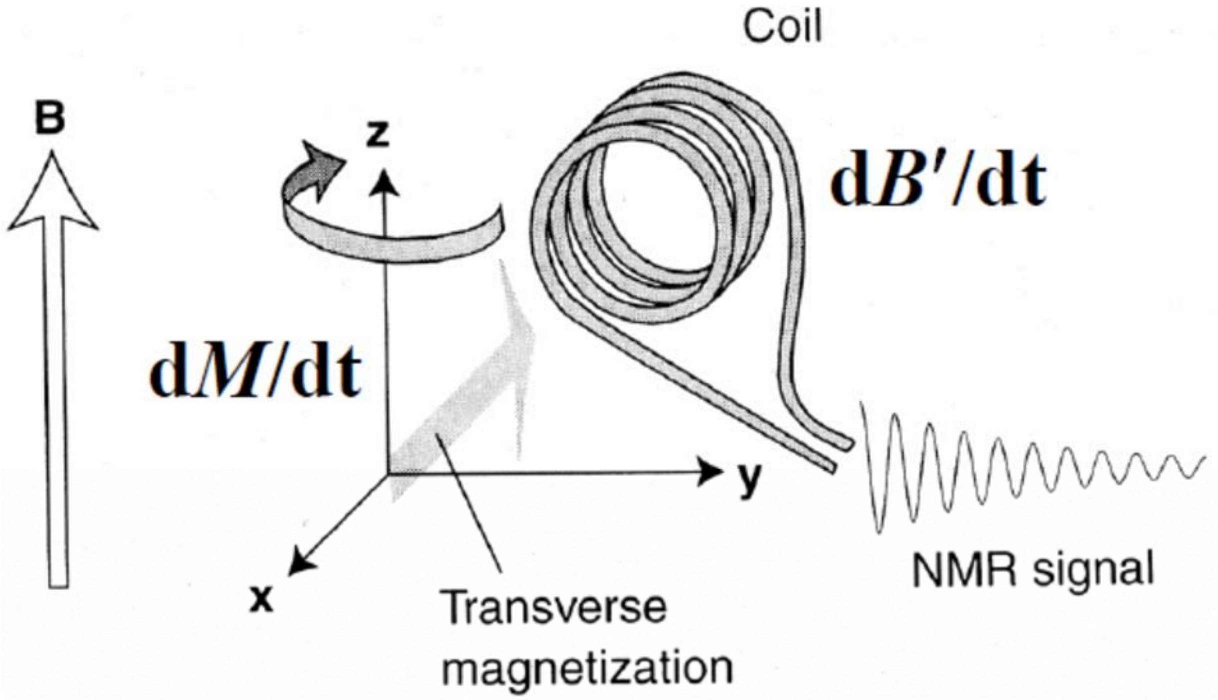


Fig. 6.9 Following a 90° pulse, the magnetization precesses around the *z* axis and at the same time returns to its equilibrium position along the *z* axis (a). The transverse components of ***M*** decay towards zero with characteristic time T_2, the spin–spin relaxation time (b). The *z* component grows back to M_0 with time constant T_1, the spin–lattice relaxation time (c).

The oscillating, decaying transverse magnetization is detected by the NMR spectrometer via the voltage induced in the receiver coil. This signal is known as the free induction decay signal (FID). The FID is the sum of the individual oscillating voltages from the various nuclei in the sample with characteristic offset frequencies, amplitude, and T_2. It contains all the information necessary to obtain an NMR spectrum.



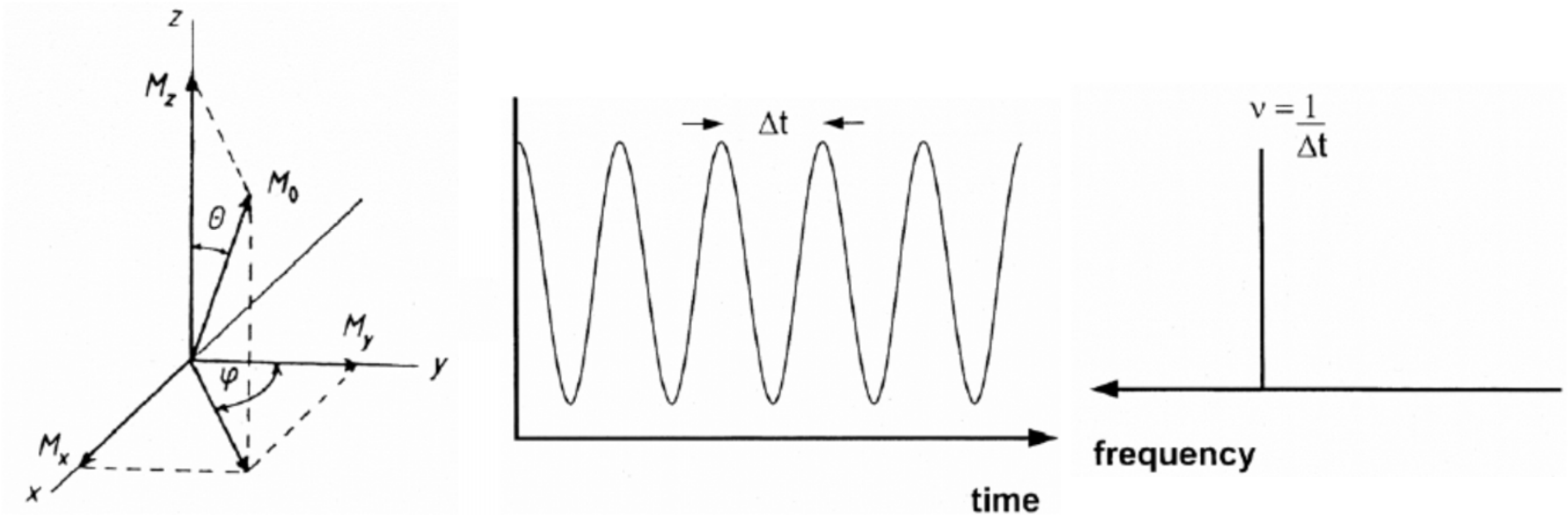
A "real" FID and part of its spectrum.

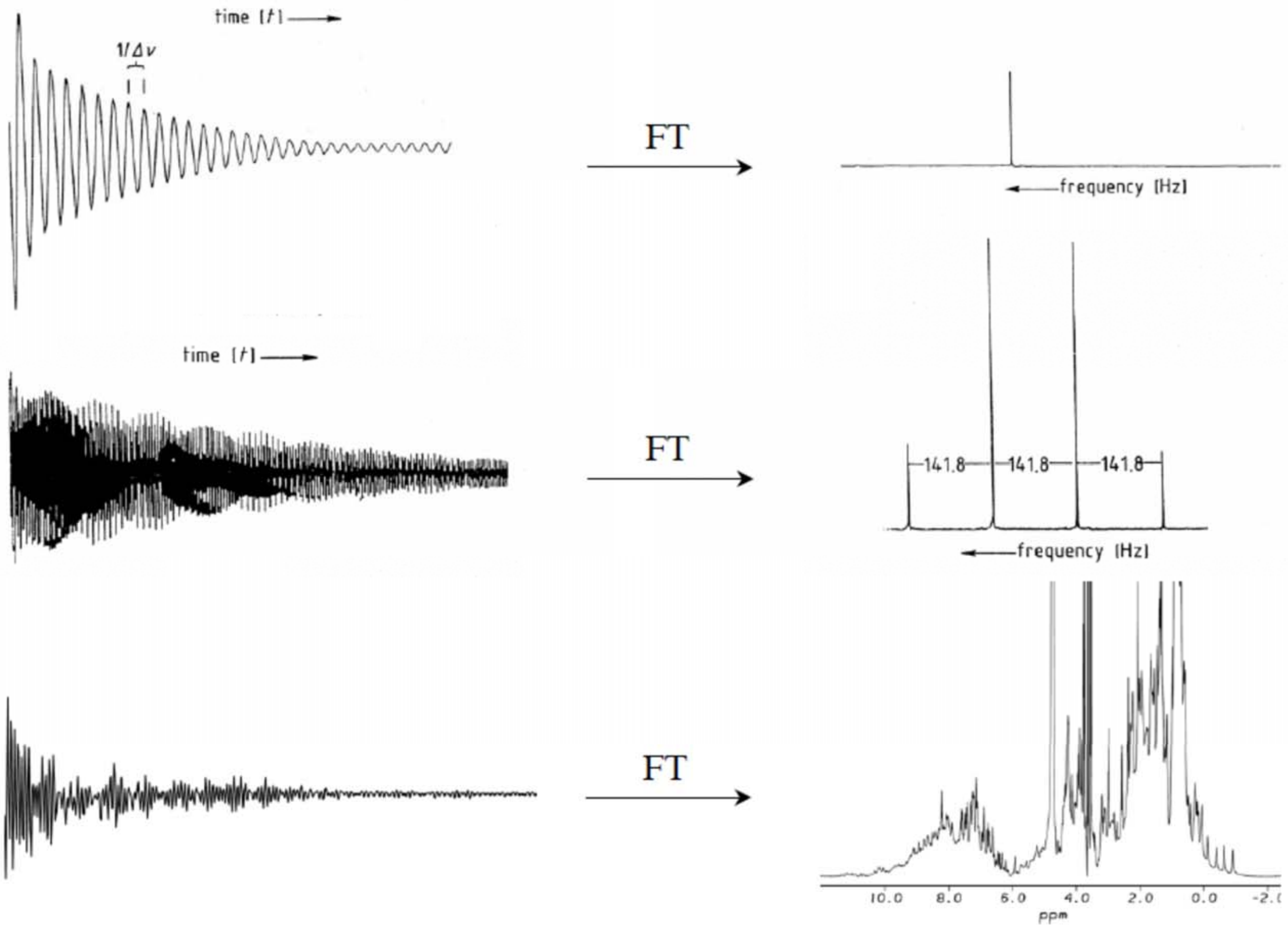


The voltage induced in the detector coil is proportional to the rate of the change of the magnetic flux in the coil, which in turn is proportional to the rate of change of the oscillating transverse magnetization (Faraday's Law of Induction).

The final step is to unravel all the oscillating components in the FID to obtain the NMR intensity $I(\omega)$ as a function of ω. This is done by means of a Fourier transform (FT).

Schematic overview of the processes responsible for NMR spectroscopy

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1/Δν
FT
← frequency [Hz]
time [t] →
FT
141.8
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10.0
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