

topics in chemical instrumentation

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The Fourier Transform in Chemistry

Part 1. Nuclear Magnetic Resonance: Introduction

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Previous articles in this feature have described the fundamental concepts of the Fourier transform (FT) (1-3) and its application to infrared spectroscopy (IR) (4-6). Although the FT method has been applied to a number of instrumental techniques most chemists would probably list nuclear magnetic resonance spectroscopy along with IR spectroscopy as the principal beneficiaries of FT methodology.

There have been some notable similarities in the historical development of FT-IR and FT-NMR. The interferometer, which is the central component of an FT-IR spectrometer, was invented almost a century ago. Its widespread application to infrared measurements is now possible because of the availability of microcomputers and fast Fourier transform (FFT) programs, which are necessary to make the interferogram intelligible to the user. In addition to the desirable energy-throughput characteristics of the interferometer, the principal advantage of FT-IR is the short time required to obtain a large number of interferograms. Averaging these interferograms improves the signal/noise ratio, thus achieving the *multiplex advantage* (5). The greatly increased sensitivity of the FT-interferometric method has allowed the infrared spectroscopist to use a wide range of accessories, which, although available for many years, could not be used effectively with dispersive instruments.

The pulse method of observing nuclear magnetic resonance has been known since 1950, but, like interferometric IR, pulse NMR was not a common tool of chemists until Fourier transform methods became readily available. As with FT-IR, one of the major benefits of the use of FT in NMR has been the increased sensitivity made possible by the multiplex advantage, along with the higher magnetic fields that have become available in the last 20 years. The NMR spectroscopist can now routinely study insensitive nuclei, such as ^{13}C and ^{15}N , whose natural-abundance signals are too weak to be easily observed with swept fields. This increased capability has by itself led to the application of NMR to many interesting and complex chemical systems. However, the benefits of the FT method have been enhanced even more by the introduction of techniques using sequences of RF pulses of various amplitude and phase. Sequence methods bearing acronyms such as APT, DEPT, COSY, and NOESY now provide the chemist with the ability to determine the

number of hydrogens bonded to each carbon in a molecule, to unravel complex coupling patterns, and even to elucidate connections between bonded and nonbonded atoms. These pulse sequences represent an entirely new set of experiments that could not have been developed without the availability of the Fourier transform technique.

It is the goal of this series of papers to provide the reader with an understanding and appreciation of these new tools of nuclear magnetic resonance spectroscopy. The first two papers describe fundamental concepts of the pulse method and some of the special considerations for its use. The succeeding papers will present some of the simpler pulse sequence methods and will provide some practical examples of their appli-

cation to problems in structure determination.

Fundamental Concepts of Magnetization

It is expected that the reader will have some familiarity with the interpretation of a simple proton NMR spectrum. Nevertheless, to be able to explain the pulse NMR process, the fundamental concepts of the behavior of nuclei in a magnetic field should be reviewed first. The reader who is interested in a more in-depth treatment is referred to books by Farrar and Becker (7) and Slichter (8) or to a standard text (9, 10) on NMR.

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A nucleus with nonzero spin, I , behaves as a small bar magnet, with a magnetic moment, μ , given by:

$$\mu = \frac{\gamma h [I(I+1)]^{1/2}}{2\pi} \quad (1)$$

where h is Planck's constant and γ is the *magnetogyric ratio*, an inherent property of the nuclide. The observed value of the magnetic moment is the projection of μ on the z axis, μ_z . According to the results of quantum mechanics,

$$\mu_z = m_I \gamma h / 2\pi \quad (2)$$

where m_I is the magnetic quantum number. The allowed values of m_I are $I, (I-1), \dots, 0, \dots, (-I+1), -I$, giving rise to $2I+1$ possible states for the nucleus. In the absence of a magnetic field the energy of the nucleus is independent of m_I , but the degeneracy is removed when an external field is applied. In a field of magnitude B_0 , whose direction defines the z axis, the energies are given by

$$E = -\mu_z B_0 = -m_I \gamma h B_0 / 2\pi \quad (3)$$

In this series of papers discussion will be limited to spin $1/2$ nuclei, which give rise to only two states corresponding to $m_I = +1/2$ and $-1/2$, also often called the α and β spin states. The energy spacing between the two states is, therefore,

$$\Delta E = \gamma h B_0 / 2\pi \quad (4)$$

which corresponds in frequency to

$$f_0 = \gamma B_0 / 2\pi \text{ (Hz)} \quad (5)$$

If the magnetogyric ratio is positive (e.g., ^1H and ^{13}C), then the $+1/2$ state lies lower in energy, but the opposite is true for nuclei with negative γ 's (e.g., ^{29}Si and ^{15}N). The magnetogyric ratios of some important spin one-half nuclei are given in the table.

Magnetogyric Ratios of Some Common Spin-1/2 Nuclei and Larmor Frequencies in a Fixed Magnetic Field of 7.0461 tesla

Nucleus	Magnetogyric Ratio, γ ($10^7 \text{ rad T}^{-1} \text{s}^{-1}$)	Larmor Frequency, f_0 (MHz) for $B_0 = 7.0461 \text{ T}$
^1H	26.7519	300.000
^{13}C	6.7283	75.435
^{15}N	-2.712	30.410
^{19}F	25.181	282.282
^{29}Si	-5.3188	59.601
^{31}P	10.841	121.442

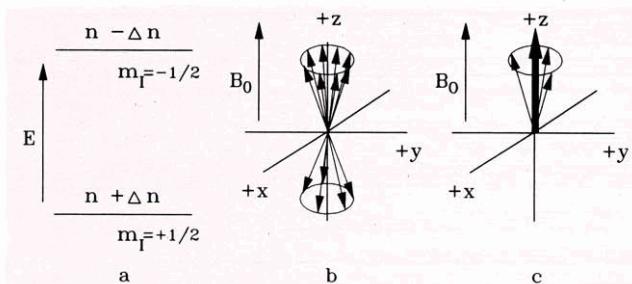


Figure 2. (a) Energy level diagram for $2n$ total nuclei (positive γ), showing the excess population in the lower energy state. (b) Schematic representation showing a greater number of spins aligned with the magnetic field (lower energy state). (c) Excess spin population aligned with the field resulting in a net magnetization in the $+z$ direction. The actual excess is much smaller than shown (about 50 ppm in a 7-T field rather than the 3 of 13 shown).

In an external magnetic field, the magnetic moment μ lies at an angle $\theta = \cos^{-1}(\mu_z / |\mu|)$ with respect to the field, as shown in Figure 1. According to classical mechanics, which is still useful for the visualization of many NMR concepts, the interaction of the spinning nucleus with the field causes the mag-

netic moment to precess about the axis of the applied magnetic field. Here the vector is precessing about the positive field axis, which is the lower energy state if γ is positive.

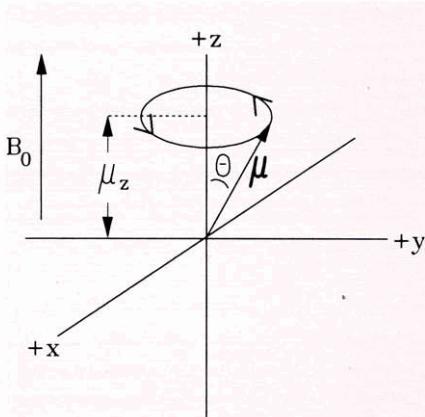


Figure 1. According to classical mechanics, an individual magnetic moment precesses about the axis of the applied magnetic field. Here the vector is precessing about the positive field axis, which is the lower energy state if γ is positive.

netic moment to precess about the magnetic field B_0 . The frequency of this motion is called the *Larmor frequency*, and is given by exactly the same expression as the quantum mechanical result (eq 5). The two energy states correspond to precession of μ about the axis aligned with (lower energy state if γ is positive) or opposed to the applied field.

The value of ΔE given by eq 4 is much less than kT at room temperature. A sample containing a collection of spin $1/2$ nuclei at equilibrium in the B_0 field will have a small excess population in the lower energy state,

The RF Magnetic Field

In an NMR experiment an oscillating magnetic field, B_1 , is applied perpendicularly to the static field B_0 . This is achieved by passage of a radiofrequency current through a coil whose axis is usually assigned as the x direction (Fig. 3a). The oscillating field along the x axis is equivalent to the vector sum of two magnetic vectors of equal amplitude, counter-rotating in the xy plane (Fig. 3b). If B_1 is oscillating exactly at the Larmor frequency of the nuclei being observed, then one of the component vectors of B_1 rotates precisely in step with the precessing nuclei; the vector that rotates in the opposite sense does not interact.

Figure 4 again shows the magnetic moments of the Boltzmann excess population of spins. In order for a signal to be detected, there must be a component of the magnetization in the horizontal plane. At equilibrium there is no observed signal, because the vectors are uniformly distributed in a cone centered on the z axis. When the frequency of B_1 exactly matches the Larmor frequen-

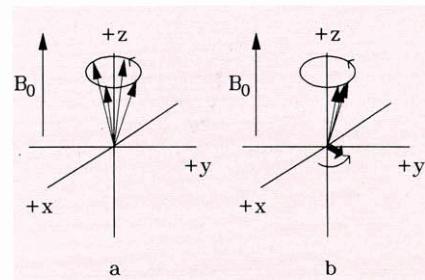


Figure 4. Magnetic moments of the Boltzmann excess spin population. (a) At equilibrium the vectors are uniformly distributed about the direction of the B_0 field. (b) The nuclei bunch together and move in phase when the applied B_1 field matches the Larmor frequency.

cy, some of the nuclei are induced to flip their spins, causing a net absorption of energy from the B_1 field. At the same time the nuclear magnetic moments are forced to move toward one side of the cone and to precess as a group following the in-step component of the B_1 vector. The resulting xy

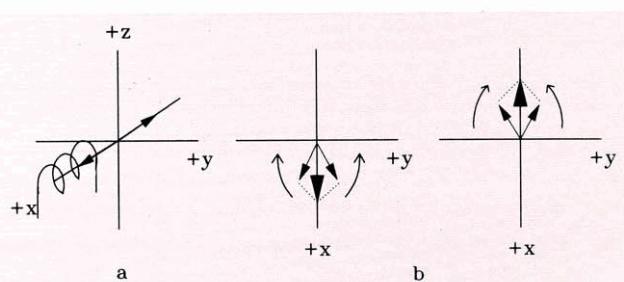


Figure 3. (a) Passage of RF current through a coil oriented along the x axis produces an oscillating B_1 field, which (b) can be expressed as the vector sum of two counter-rotating vectors of equal length.

component can be detected by a receiver coil in the horizontal plane.

The transition of nuclei between the lower and upper energy levels is analogous to absorption of UV/visible photons of the correct energy by a molecular chromophore, except that the modes of emission of energy differ. In NMR the situation is complicated because of the very small Boltzmann excess of spins in the lower energy state. A B_1 magnetic field oscillating at the Larmor frequency induces both upward and downward spin transitions of a nucleus with equal probability. As long as there is a greater number of nuclei in the lower energy state, the rate of energy absorption exceeds the rate of emission, and a signal is observed. However, unless there is some means for the nuclei to return to the lower energy state, continued B_1 irradiation will cause the spin populations to become equal. In this state of *saturation* there is no net absorption of energy and no signal. In contrast to many other systems (e.g., electronically excited states), spontaneous emission occurs to a negligible extent. Energy can be effectively transferred from a nuclear spin to its environment only by interaction with a local magnetic field that is oscillating at the Larmor frequency f_0 . To understand the origins of this field it is necessary to take a closer look at the microscopic environment of the nucleus.

Nuclear Relaxation

A nucleus does not exist in isolation, but as part of a molecule, which, if it is in a nonviscous liquid, is perpetually tumbling at random. This motion may be represented mathematically by a plot versus time of a geometric property of the molecule. The parameter of particular importance to NMR relaxation is the angle of an internuclear vector with the \mathbf{B}_0 axis. Like any other physical process, the time dependence of molecular motion is related by the Fourier transform to a distribution of motional frequencies. The time domain behavior is often described in terms of the *correlation time*, τ_c , which may be considered as the average time over which a molecule maintains a certain geometric arrangement. For molecular tumbling τ_c corresponds approximately to the average time for a molecule or functional group to turn through one radian and is of the order of 10^{-12} – 10^{-10} s for a small molecule in a nonviscous liquid. Fourier analysis shows that motional frequencies span the range from zero to over $1/\tau_c$ rad/s. For a 10^{-11} -s correlation time this corresponds to a frequency range of zero to more than 10^{11} Hz, which means that there will be a frequency component of molecular motion at the Larmor frequency of any nucleus in any foreseeable magnetic field. It is this molecular motion that, in combination with local magnetic fields, allows the nuclei to exchange energy with their surroundings (historically referred to as "the lattice") and return toward the equilibrium population. This process of *spin-lattice* (or longitudinal) *relaxation* is nominally first-order. The rate constant is the reciprocal of T_1 , the *spin-lattice relaxation time*, which is the parameter commonly used to specify the efficiency of the process.

In diamagnetic systems the principal source of the required local magnetic field is the direct through-space interaction of two

nuclear magnetic dipoles. Figure 5 shows such an interaction between a ^{13}C nucleus and a proton that is near, but not necessarily bonded to, the carbon. The magnetic field strength that is induced at the carbon nucleus by the proton magnetic moment depends on the angle, ψ , between the magnetic moment vector and the internuclear vector. The direction of the former is defined by the fixed magnetic field (cf. Fig. 1), but, as the molecule tumbles, the internuclear vector reorients with respect to \mathbf{B}_0 , and ψ changes. The average value of the induced field is zero, so it has no effect on chemical shifts. However, the rapidly fluctuating magnetic fields do provide an important means of re-

and on the inverse of the correlation time. In liquids dipolar relaxation produces typical proton or carbon T_1 values of about 10^{-2} to 10^2 s; a small molecule in a nonviscous medium will have a short correlation time and a long T_1 , but the T_1 values of a viscous polymer sample will be very short.

Another source of fluctuating magnetic fields, and consequent reduction in T_1 , is the presence of paramagnetic entities. An unpaired electronic spin, because of its large magnetic moment, is a much more effective relaxer than a nuclear spin. For this reason, oxygen must be carefully excluded in experiments sensitive to T_1 effects. On the other hand, the addition of small amounts of paramagnetic compounds can reduce the inconveniently long T_1 's of isolated carbons. Chromium(III) acetylacetone, $\text{Cr}(\text{acac})_3$, is commonly used for this purpose. There are also several other relaxation processes that may compete with the dipolar mechanism (7), but they are usually of less practical importance for spin-1/2 nuclei.

The xy magnetization that gives rise to the NMR signal decays as T_1 effects cause the nuclei to lose their excess energy and return to their equilibrium orientations about the z axis. There is also another class of relaxation processes that causes the loss of detectable magnetization (i.e., the grouping of the magnetic moment vectors that is depicted in Fig. 4b) without transfer of energy to the surroundings. It is convenient to define an overall time constant for the loss of detectable magnetization, called T_2 , which is of great practical significance because it determines the *spectral resolution*.

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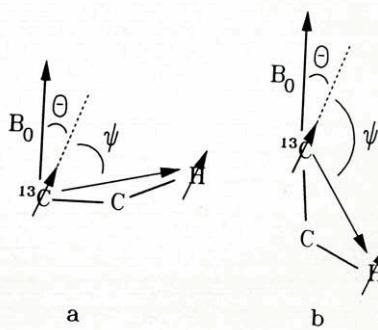


Figure 5. Representation of the dipolar interaction showing two orientations of the internuclear vector with respect to the fixed magnetic field. The angle θ is defined by the direction of \mathbf{B}_0 , but ψ changes as the molecule tumbles.

laxation called the *dipolar mechanism*. The magnitude of the associated T_1 depends on the sixth power of the internuclear distance

Spectral resolution is defined in terms of the observed NMR line width ($\Delta f_{1/2}$, full width at half maximum intensity), which is equal to $1/(\pi T_2^*)$. T_2^* is called the effective spin–spin, or effective transverse, relaxation time. The word “effective” is included because usually the major contributor to the linewidth is lack of homogeneity of the B_0 magnetic field. True spin–spin relaxation (T_2) arises from the same effects that determine T_1 , except that T_2 relaxation can be promoted by low-frequency motions as well as those in the range of f_0 . Other processes that do not affect T_1 , such as spin exchange by nearby nuclei and chemical exchange effects, can cause T_2 to be less than T_1 , but the reverse can never occur. For liquids the two are usually equal. If T_1 is very short, then the resulting small value of T_2^* will produce line broadening.

The RF Pulse

Until the mid-1970's most commercial NMR's were continuous-wave (CW) instru-

ments. In the CW operational mode the nuclei are successively brought into resonance by slowly varying either the radio frequency or the B_0 magnetic field. The expression comes from the *continuous* application of the RF while the resonance is being observed. In *pulse methods* the nuclei in the entire frequency region are excited by a single burst of RF power (a pulse), and the resulting signal is measured *after* the RF is turned off. Except for extremely simple systems, Fourier transformation is required to convert the resulting signal into a usable form, and therefore pulse NMR is often called FT-NMR.

Fourier analysis is also essential to understanding the effect of the pulse itself. A pulse of monochromatic RF with a rectangular envelope can be described in the frequency domain as a band of frequencies centered at the RF frequency. Figure 6 shows the frequency-domain signal for two different pulse lengths. The center value, which is the monochromatic frequency produced by the pulse generator, is often called the *spectrometer frequency*, f_s . The Heisenberg principle states that there is a minimum uncertainty in the simultaneous specification

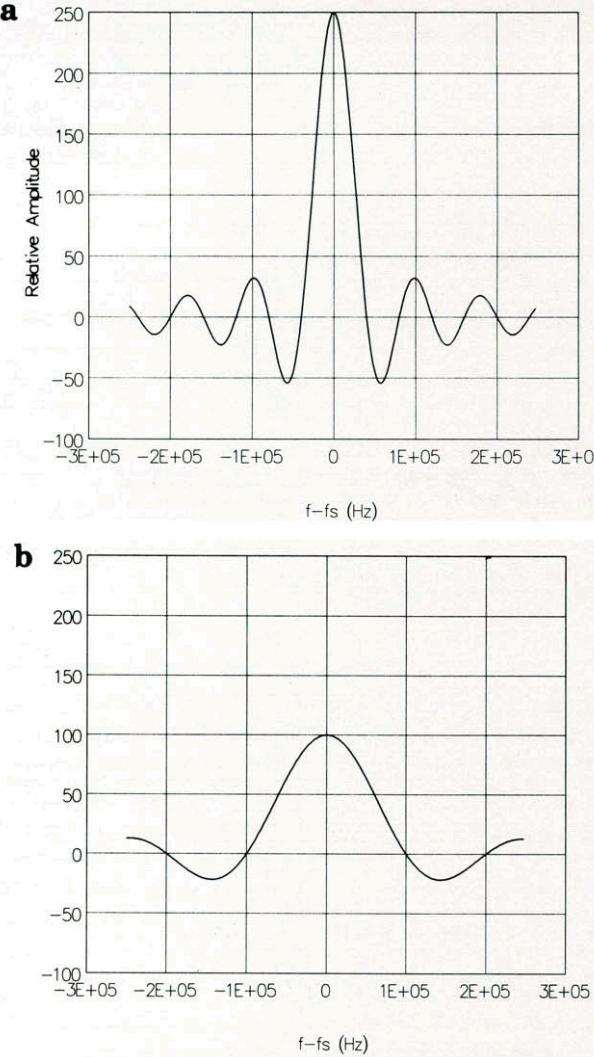


Figure 6. The Fourier transform of a rectangular RF pulse t_p in duration with frequency f_s and amplitude A is the sinc function,

$$\frac{At_p}{2} \frac{\sin[\pi t_p(f - f_s)]}{\pi t_p(f - f_s)}$$

(a) $t_p = 25\mu s$; (b) $t_p = 10\mu s$. The value of A is 2×10^7 for each plot.

of both the energy (and hence the frequency) of a system and the duration of the measurement. As Figure 6 shows, this means that, as the pulse length decreases, the width of the frequency band must increase. For a typical pulse length of 10 μ s, the flat central portion of the frequency band, where the amplitude is within 1% of the peak value, is about 16000 Hz wide. For a 7.05-T field ($f_s = 300$ MHz for protons, 75 MHz for ^{13}C) this region easily spans the range of chemical shifts of the commonly observed nuclei (15 ppm or 4500 Hz for protons, 200 ppm or 15000 Hz for ^{13}C). However, as Figure 6 also shows, because the irradiation is spread over a wider frequency band, a shorter pulse results in a lower power at the center frequency. An RF generator for pulse NMR should be capable of delivering a short, high-power pulse with a precisely defined envelope, and the probe should be designed for efficient conversion of RF power into the B_1 field.

Before discussing how the nuclei respond in a pulse experiment, it is useful to reconsider the behavior of the spins in the fixed magnetic field, \mathbf{B}_0 . Figure 7a again shows schematically the excess population of spins aligned with \mathbf{B}_0 (+z direction) and precessing about it at the Larmor frequency, f_0 . Figure 7b shows an alternate representation of the situation, in which the axes are allowed to rotate at the Larmor frequency. The spins now appear to be fixed in orientation with respect to the x' and y' axes. In either case the resultant of the population excess is the magnetization vector, \mathbf{M} , which at equilibrium points along the +z axis.

Now consider the application of an RF field whose frequency, f_s , is the same as the

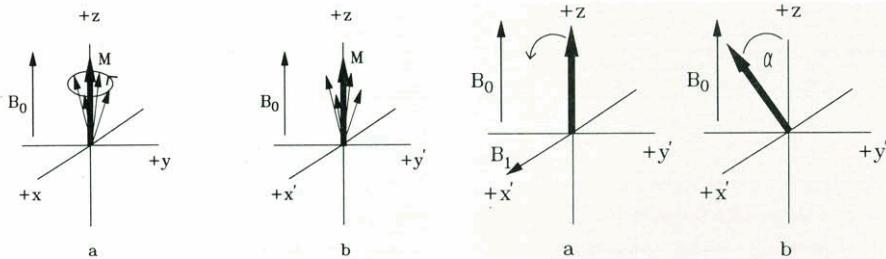


Figure 7. Alternate coordinate axes for a nuclear spin system in a \mathbf{B}_0 magnetic field oriented along the z axis. (a) When the x and y axes are fixed, the nuclear moments precess about the z axis at the Larmor frequency. (b) When the coordinate system rotates about the z axis at the Larmor frequency, the moments appear to be stationary. In either case the resultant is a bulk magnetization vector pointing in the z direction.

rotation frequency of the frame. The applied RF is still composed of two counter-rotating vectors (cf. Fig. 3), but now the component vector that rotates in the same direction as the frame appears to be stationary. As far as the nuclei are concerned, the other component may be ignored because its frequency (twice f_s) is totally outside the range of chemical shifts. In the rotating frame the stationary vector behaves as a nonoscillating magnetic field, \mathbf{B}_1 , perpendicular to \mathbf{B}_0 . Assuming for the time being that f_s corresponds exactly to the Larmor frequency, the nuclei tend to precess about the \mathbf{B}_1 field (Fig. 8). Because the RF is applied for a very short time period, the effect is only a partial revolution of the net magnetization vector, which is said to be "tipped"

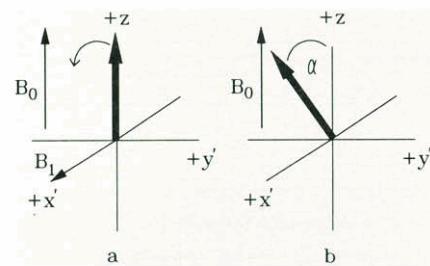


Figure 8. The effect of an RF pulse. (a) Viewed in the rotating frame, the nuclei tend to precess about the \mathbf{B}_1 magnetic field. (b) After the \mathbf{B}_1 field has been removed, the magnetization vector makes an angle α with the z axis.

toward the $-y'$ axis (assuming that the \mathbf{B}_1 field points in the $+x'$ direction when viewed from the origin).¹ The tip angle, α , is given (in radians) by

$$\alpha = \gamma B_1 t_p \quad (6)$$

The RF pulse is usually designated by the value of α that it produces and the axis to which it is applied. The term $(\pi/2)_x$ or 90°_x refers to a pulse directed along the $+x'$ axis. (The prime is usually omitted from the subscript.) At the end of a 90°_x pulse the magnetization vector points along the $-y'$ axis. The length of a typical 90° pulse is about 10^{-5} s. For protons this requires a B_1 field of about 6×10^{-4} T, compared to B_1 fields of the order of 10^{-8} T for CW work. B_0 fields are much larger and range from 1.4 to 14 T,

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corresponding to proton frequencies of 60–600 MHz.

Because the pulse produces a wide band of frequencies of almost equal amplitude, the nuclei throughout the entire chemical shift range are all effectively tipped by the same angle.² As far as the excitation pulse is concerned, each chemically shifted nucleus may be considered to belong to a frame rotating at the corresponding Larmor frequency. However, to understand what happens after excitation it is necessary to assign the frame to a single frequency, which is chosen to be the spectrometer frequency, f_s , the value at the center of the frequency band.

The Free Induction Decay

Figure 9 shows the behavior of the magnetization following excitation by a 90°_x pulse. The B_0 field is still present, and the nuclei continue to precess about it. Focusing for the moment on the nuclei whose Larmor frequency corresponds exactly to the frequency of the rotating frame, this means that, in the absence of relaxation effects, the magnetization vector would remain directed along the $-y'$ axis (Fig. 9a). However, T_1 and T_2^* processes both act to reduce the $-y'$ component of the magnetization. B_0 inhomogeneities, the principal source of T_2^* effects, cause groups of nuclei in different parts of the sample to experience slightly different local B_0 fields. Figure 9b shows only two of the many such microscopic sections of the sample (called *isochromats* because the field is the same within the section). One group is shown precessing slightly ahead of the frame, and the other group is lagging behind. The net effect is a decrease in the $-y'$ component of the magnetization. At the same time T_1 relaxation processes cause a gradual return of the magnetization towards the z axis (Fig. 9c), further decreasing the component along $-y'$. Because field inhomogeneities usually cause T_2^* to be less than T_1 , an intermediate situation often occurs as in Figure 9d, where the $-y'$ component of the magnetization decays to zero before the spin population can achieve the Boltzmann distribution. At some later time (after at least 5 times T_1) the magnetization has again returned to its equilibrium value (Fig. 9e).

Returning now to the laboratory frame, the $-y'$ component corresponds to a magnetization vector rotating in the xy plane. Just as in the CW mode of operation, a receiver coil (usually the same coil used to excite the nuclei) is situated in the xy plane, where it senses the rotating magnetization. As the $-y'$ component decreases, the oscillating voltage from the coil decays, and it reaches zero when the condition of the spins corresponds to the situation depicted in Figure 9d. The record of the receiver voltage in the time domain is called the *free induction decay* (FID), because the nuclei are allowed to precess "freely" in the absence of the B_1 field. The FID is the Fourier partner of the NMR frequency spectrum.

The FID's and transformed spectra for some simple proton systems are shown in Figure 10. Figure 10a corresponds to a system containing only one type of proton (H_2O) observed with the spectrometer fre-

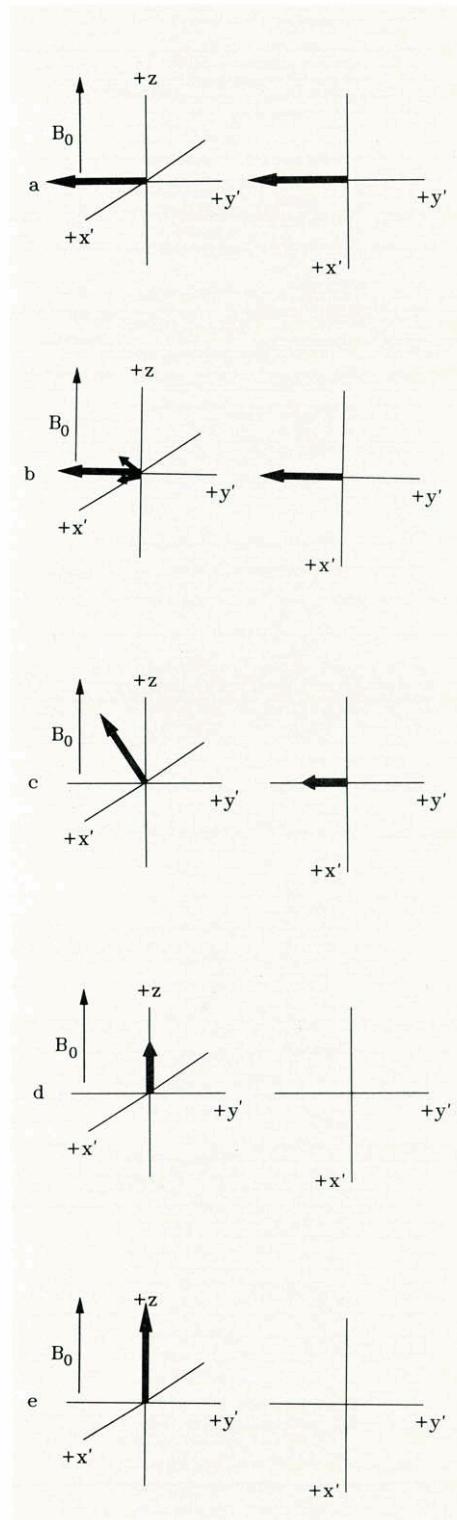


Figure 9. Behavior of nuclei after a 90°_x pulse. The frame is rotating at the spectrometer frequency, f_s , which is assumed to be equal to the Larmor frequency. (a) Immediately after the pulse the tipped magnetization vector is fixed in the rotating frame. (b) T_2^* effects (mainly B_0 inhomogeneity) cause locally divergent Larmor frequencies. Only two divergent isochromats are shown here. (c) At the same time T_1 relaxation is taking the magnetization back toward the z axis. (d) T_2^* effects have resulted in complete loss of magnetization in the $x'y'$ plane, but the nuclei have not returned to equilibrium. (e) Complete restoration of equilibrium z axis magnetization.

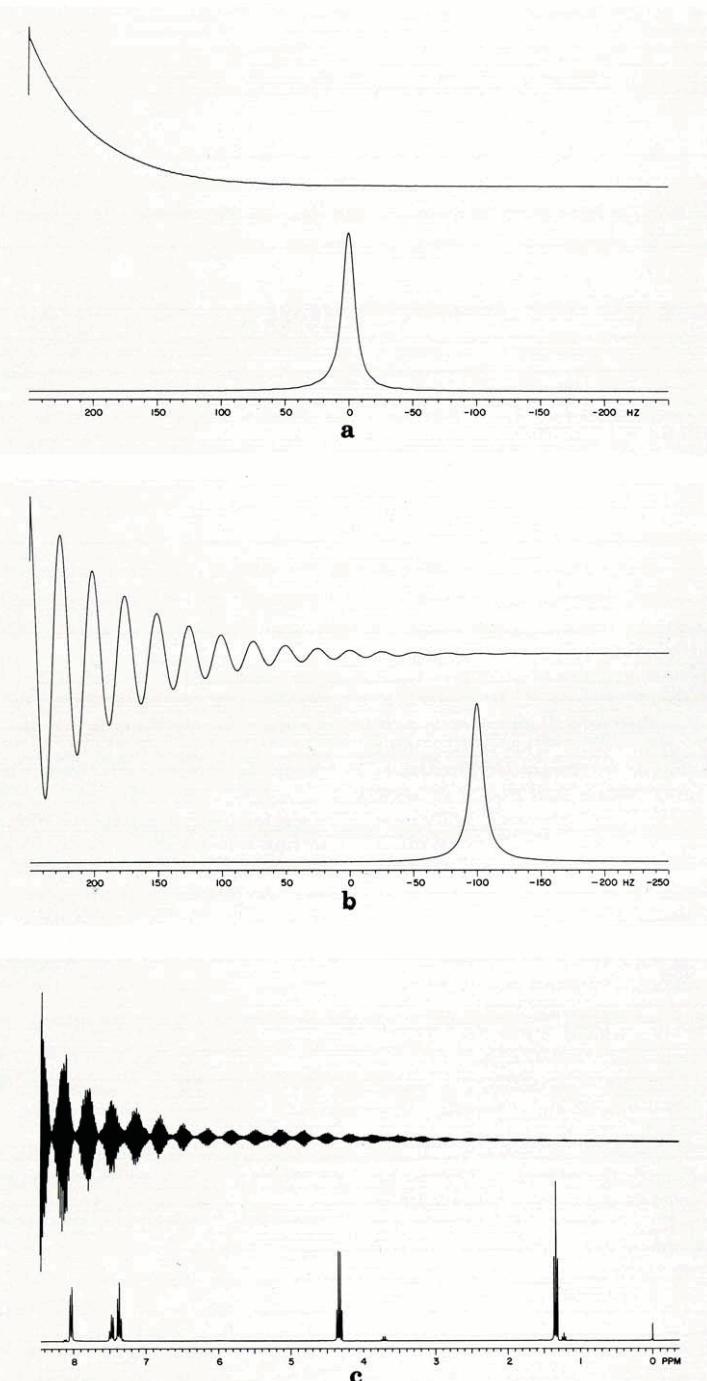


Figure 10. FID's and transformed frequency spectra. (a) Single-proton system (H_2O containing approx. 50 ppm Mn^{2+} to broaden the line for better presentation) with Larmor frequency equal to f_s . (b) Single-proton system with Larmor frequency slightly less than f_s . (c) Compound (ethyl benzoate at 300 MHz) with protons in several environments.

frequency, f_s , exactly equal to the Larmor frequency, f_0 . In the data acquisition process f_s is subtracted electronically from the observed signal prior to digitization. The subtraction has the effect of placing the detector in the rotating frame, so that in this situation the output is nonoscillatory. The FID shows a simple exponential decay with time constant equal to T_2^* . In Figure 10b the

same single proton sample is observed, but this time the spectrometer frequency is slightly greater than f_0 . In the frame rotating at f_s , the magnetization vector is not stationary. The vector's rotation frequency corresponds to the difference between f_0 and the spectrometer frequency, so the FID consists of sinusoidal oscillations of constant frequency whose envelope is a decreas-

ing exponential with time constant T_2^* . The corresponding frequency spectrum shows that the Larmor frequency is slightly shifted from the spectrometer frequency. In a sample (ethyl benzoate) that contains several protons with different chemical shifts and splitting effects, the various rotation frequencies produce a complicated interference pattern (Fig. 10c) that would be totally unintelligible without the aid of the Fourier transform.

The oscillatory character of the FID, especially the one shown in Figure 10b, may remind the CW NMR user of the "ringing" seen on the tails of rapidly swept peaks. The behavior of the nuclei is indeed similar in both situations. In the CW mode the magnetic vectors are caused to rotate as a group when f_s or B_0 , whichever is swept, meets the resonance condition. After resonance is past the nuclei continue to precess "freely", as in the pulse experiment. The difference between the nuclear precession frequency and the frequency of the applied RF is observed as the ringing pattern. The amplitude of the oscillations decays with the same T_2 time constant discussed above. The ringing tail and the FID of a single resonance do not appear exactly the same, however. The oscillations of the FID have a constant frequency, whereas the frequency of the ringing tail oscillations is proportional to the steadily increasing difference between the Larmor and spectrometer frequencies. A ringing tail as displayed on a chart recorder shows a decreasing period with increasing time, and it usually appears shorter than a corresponding FID because of the limited frequency response of the recorder and its associated circuitry.

This paper has covered the basics of the interaction of spin- $\frac{1}{2}$ nuclei with static and RF magnetic fields. Practical applications of pulse FT-NMR will be discussed in subsequent articles in this series.

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¹ The direction of the precession of nuclei about the \mathbf{B}_0 magnetic field and of the tipping of the net magnetization vector by the RF field (precession about \mathbf{B}_1) is consistent with current convention (13). The final results are unaffected if both directions are reversed, as in some texts.

² The actual trajectory of a nuclear spin vector when excited by a pulse that is not exactly at the Larmor frequency is quite complicated, but fortunately the perturbations caused by off-resonance excitation cancel out almost entirely in practice (11, pp 69-72; 12, pp 50-60; 13, pp 99-111).