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Zero-Field NMR

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Introduction

The development of nuclear magnetic resonance (NMR) as an analytical method in chemistry has been dominated by a trend towards ever increasing magnetic fields. Whereas the 60-MHz spectrometer was an exciting instrument in the previous decade, experiments are now done at 10 times this frequency. Accompanying this trend is an inevitable and unfortunate increase in the cost of NMR instrumentation. This is illustrated in Figure 1, adapted from the recent "Pimentel Report", *Opportunities in Chemistry*.[1] There are several reasons for the inclination to perform NMR measurements at the highest possible field. Firstly, the sensitivity of NMR detection depends on both the magnitude of the magnetization and the frequency at which it precesses. Since both of these depend linearly on the magnetic field, higher fields mean substantially higher sensitivity. Secondly if the NMR line widths increase less than linearly with magnetic field, then the spectral resolution is improved as the frequency differences increase. Thirdly, the appearance and interpretation of the spectra is simplified as the scalar couplings in liquids become more nearly first order.

In this frantic rush for high magnetic fields, it is occasionally overlooked that a magnetic field can impose at least one element of damage on an NMR experiment. Suppose we wish to work with samples other than isotropic liquids, for example disordered systems such as polycrystalline solids, amorphous materials or partially ordered polymers or biological compounds. The spin–spin couplings in such materials are able, in principle, to provide information about structure and dynamics. However, due to the anisotropy of the magnetic dipolar interactions which give rise to these couplings, molecules having different orientations with respect to the magnetic field will experience different spin–spin couplings and thus yield different NMR spectra. The spectrum of a powder is a superposition of spectra from all the different orientations. Most fine structure is thereby obliterated, yielding a broad, often featureless "powder pattern" from which little information can be obtained. An example of the proton NMR spectrum from a polycrystalline organic solid, containing four hydrogens per molecule, is shown in Figure 2. The situation is similar to that encountered in crystallography. Although oriented crystals provide sharp X-ray or neutron-diffraction patterns from which structural information can be extracted, polycrystalline samples yield considerably less useful powder patterns.

One solution to this problem is to perform the NMR experiment using principles well-known in other forms of magnetic resonance, for example nuclear quadrupole resonance (NQR)[2] or optically detected magnetic resonance,[3] namely to work in zero field. In this review we describe some simple recent adaptations of field cycling techniques designed to allow the observation of just such Fourier transform NMR spectra in zero field.

Zero-Field NMR

In the absence of a magnetic field defining an axis in space, all orientations are equivalent, and orientationally disordered materials should provide sharp crystal-like spectra. The only problem is to overcome the low sensitivity inherent in the low frequencies of

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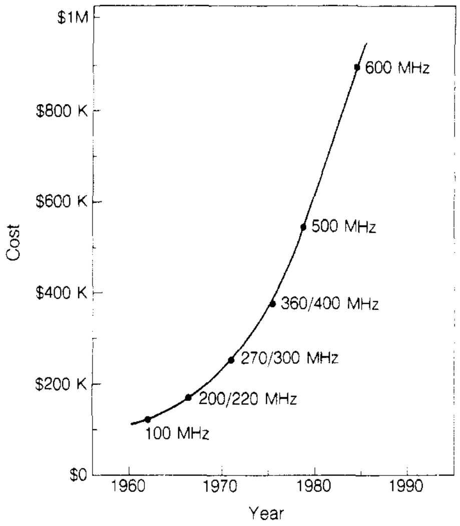

Figure 1. Rough picture of the relationship between cost and frequency of commercial NMR spectrometers over the last 25 years, adapted from ref 1.

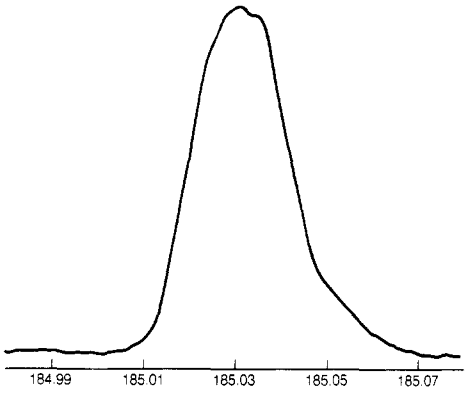

Figure 2. Proton 180-MHz NMR spectrum of polycrystalline 1,2,3,4-tetrachloronaphthalene–bis(hexachlorocyclopentadiene) adduct, a relatively isolated four-proton system displaying a broad powder pattern (~20 kHz) with essentially no resolved features. The structure for this molecule is shown in Figure 4.

zero-field NMR. To take advantage of the high resolution of zero field and the high sensitivity of high field, we employ adaptations of well-known field-cycling methods.[4,5] Field cycling involves the use of a high-field magnet for the sensitivity pertinent to the polarization and detection periods of the experiment, with the field removed during the time period in which the spin interactions are measured.

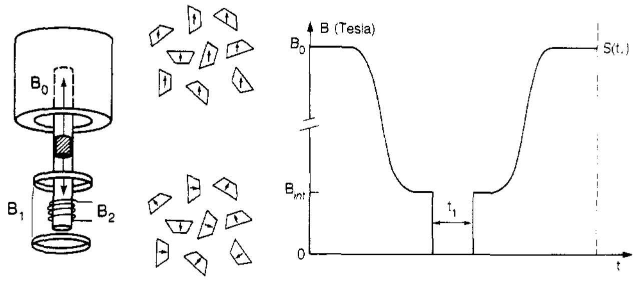

Figure 3. A simple zero-field NMR cycle. The applied field is decreased adiabatically by mechanically shuttling the sample out of the bore of a superconducting magnet. The magnetization (shown schematically by the polarization of the nuclear moments in the crystallites in the direction of the field) is preserved in this process and is further maintained by holding the sample in an intermediate field, B_1, which is larger than the local internal fields. A second coil produces a pulsed field B_2 which rapidly cancels all other fields and initiates evolution of the spin system in zero field. The local interactions now determine the axis system in zero field and are identical for all crystallites. Reapplication of the intermediate field terminates the zero-field evolution, and the sample is returned to high field where the magnitude of the signal is measured. The period t_1 is incremented in successive field cycles to produce a time domain signal which, when Fourier transformed, produces the zero-field NMR spectrum. By measuring the full signal in high field it is also possible to obtain a two-dimensional NMR spectrum with one zero-field and one high-field frequency dimension.

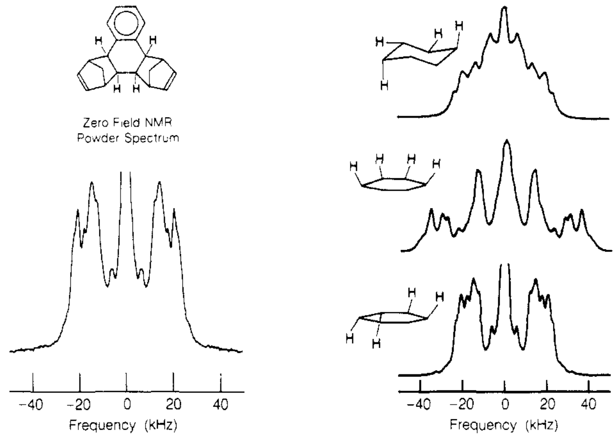

Figure 4. Zero-field NMR spectrum (at left) of the same four-proton solid system shown at high field in Figure 2. The observed peaks are a result of resolved dipolar couplings between the proton spins. The appearance of the zero-field spectrum is sensitive to changes in the relative positions of the nuclei as shown at right in three examples of simulated zero-field NMR spectra. The best fit to the experimental spectrum and the corresponding arrangement of protons is the one at lower right.

A schematic representation of a simple field cycle and the corresponding apparatus is illustrated in Figure 3. Removal of the sample to an intermediate field followed by a sudden transition to zero field causes the magnetization produced initially in B_0 to oscillate at frequencies characteristic of the local magnetic dipolar or electric quadrupolar interactions. Reapplication of the field allows detection in high field as a function of the time in zero field. Fourier transformation of the time domain signal will produce a zero-field frequency domain spectrum with high resolution and full B_0 sensitivity. An example is shown in Figure 4. This is the zero-field NMR powder spectrum of the same four-proton spin system whose high-field NMR spectrum appears in Figure 2. Comparison of the experimental spectrum in Figure 4 with computer simulations of zero-field spectra for different possible hydrogen positions (three are shown) allows a determination of the geometry of the central cyclohexane ring in this molecule.[6] This version of the zero field experiment has

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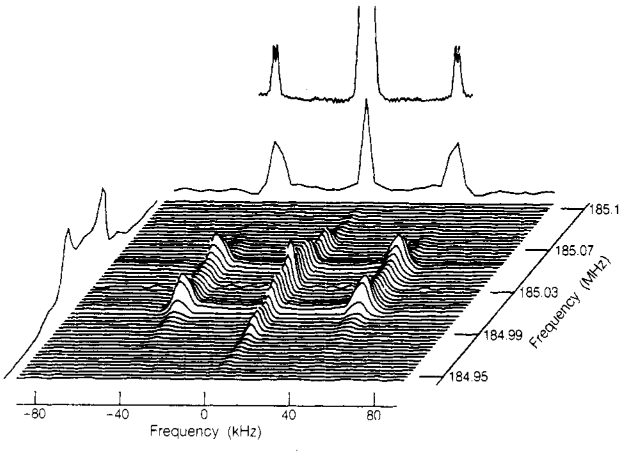

Figure 5. Two-dimensional proton NMR spectrum (one high-field dimension and one zero-field dimension) of water molecules in polycrystalline barium chlorate monohydrate. The spectrum above is the zero-field NMR spectrum of a sample diluted to 10% protons and 90% deuterium to remove dipolar couplings between water molecules which broaden the lines. Here the motionally induced asymmetry (due to small amplitude twisting, waving, and rocking modes) in the dipolar interaction is manifested as a splitting in the zero-field lines.

been used for a number of experiments, including the determination of the four hydrogen positions in the unit cell of polycrystalline $Os_3(CO)_{10}H_2$ yielding results in excellent agreement with neutron diffraction in crystals.[7] If instead of reducing the field to zero as in Figure 3, it is reduced to a low field B_w, then the low-field NMR spectrum can be obtained in a similar fashion.[8] Such spectra are useful in studying quantum mechanical tunneling.[9]

Effects of Motion

Beyond investigation of the static dipolar couplings in rigid molecules, zero-field NMR can be used to probe the effects of motion in disordered samples.[10,11] Small amplitude motions, for example, the librational motions of molecules, will average the normally axially symmetric dipolar interaction to a nonaxially symmetric form. These small perturbations in the nuclear-spin interactions produce correspondingly small signal amplitude or frequency changes which may be difficult to observe in high-field powder line shapes. On the other hand the motionally induced asymmetry should be manifested as a splitting in the narrow zero-field NMR spectral lines. As an example, in barium chlorate monohydrate, internuclear couplings broaden the zero-field resonance lines of the protons in the water molecules to widths of a few kilohertz as shown in Figure 5. This spectrum was obtained by a two-dimensional high-field–zero-field NMR experiment[6] as explained in the caption. Through dilution of the spin system with deuterium to ~10% protons, a splitting in the zero-field NMR spectrum is observed. It is, in fact, possible to measure the amplitudes of the librational modes of the water molecules in this way.[12] This will probably be a useful way to study motions of isotopically labeled large molecules.

Heteronuclear Zero-Field NMR

Zero-field NMR is not limited to homonuclear spin systems. Heteronuclear dipolar couplings can also be observed and display characteristic features in the zero-field spectrum.[13] A peculiar feature of heteronuclear systems, in contrast to high-field NMR, is that since Zeeman couplings and chemical shifts vanish, an $S = {}^{13}C$ and $I = {}^{1}H$ spin are indistinguishable in zero field; i.e., their mutual coupling is invariant to permutation and they behave in a manner similar to a homonuclear *I–I* dipolar-coupled spin pair.[14] A sudden transition to zero field will initiate evolution for all spin species since no selection can be made, as it can in high-field NMR, on the basis of irradiation frequency. Examples of such heteronuclear zero-field NMR spectra have been published.[13] The magnetization for different spin species (e.g., ^{13}C, ^{1}H) can be manipulated independently with radiofrequency pulses in high field to produce specified initial populations of the *I* and *S* spin states in zero field. In this way, the intensities of particular zero-field transitions may be enhanced or made to vanish, rendering readily distinguishable the appearance of zero-field spectra deriving from different functional groups (e.g., CH, CH_2, CH_3).

Heteronuclear *J*-couplings have also been observed in zero field for isotropic liquids.[13a] Since the scalar coupling in liquids is not anisotropic, there is no apparent advantage in going to zero field. However these experiments illustrate the role of residual inhomogeneous fields in zero-field NMR (the very narrow natural line width and small size of the spin–spin interactions requires the use of homogeneous zero fields) and may be useful in two-dimensional liquid NMR.

Zero-Field NQR

Frequency domain methods have long been used to observe quadrupolar nuclei ($I \geq 1$), where direct detection of a quadrupolar resonance is possible when the frequency is large.[2] The applicability of these methods is limited at low frequencies ($\lesssim$100 kHz), such as those corresponding to deuterium (^{2}H), and also requires the use of radiofrequency irradiation in zero field.[4e,h] Fourier transform time domain NQR[6,15] avoids many of these problems.

High-field NMR of quadrupolar nuclei is burdened, even more so than dipolar coupled systems, by the problems of a broad spectral range due to orientational disorder and the magnitude of quadrupolar coupling constants.[16] One of the most desirable quadrupolar nuclei to study is deuterium because it can often be easily substituted for the proton, and is accessible at high fields due to small quadrupolar coupling constants. Subtle changes related to the asymmetry of the electric field gradient or the presence of two very similar sites

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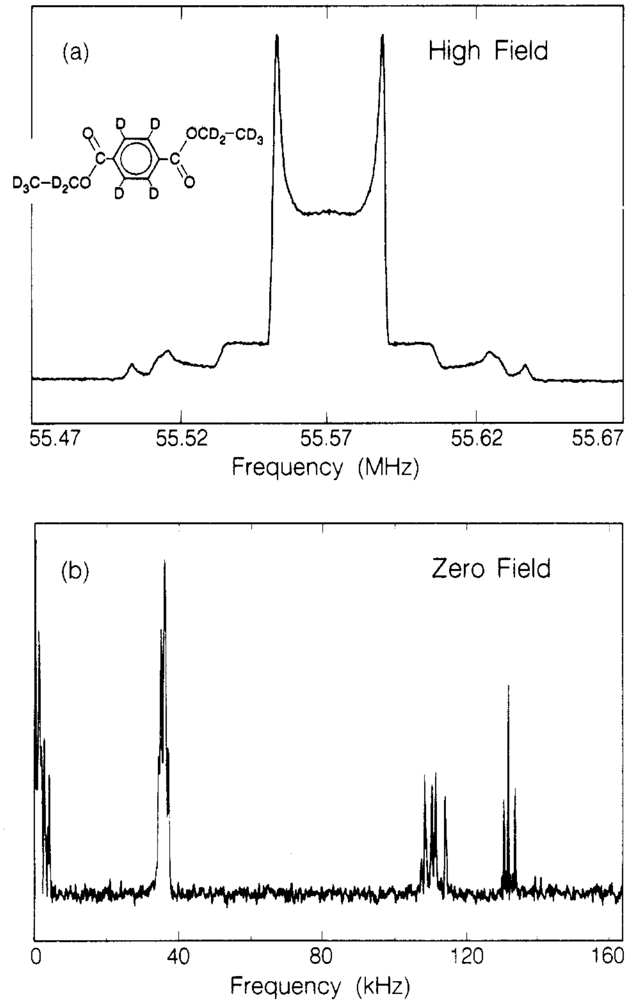

Figure 6. (a) Deuterium high-field NMR spectrum of polycrystalline perdeuterated diethylterephthalate. From the overlapping powder line shapes, three separate quadrupolar sites can be discerned. (b) Zero-field deuterium NQR spectrum of the same sample. Four distinct frequency regions with resolved peaks are evident and correspond to the aromatic, methylene, and methyl sites and the ν_0 lines in order of decreasing frequency. Quadrupolar coupling constants and small asymmetry parameters are established for five inequivalent sites in the molecules.

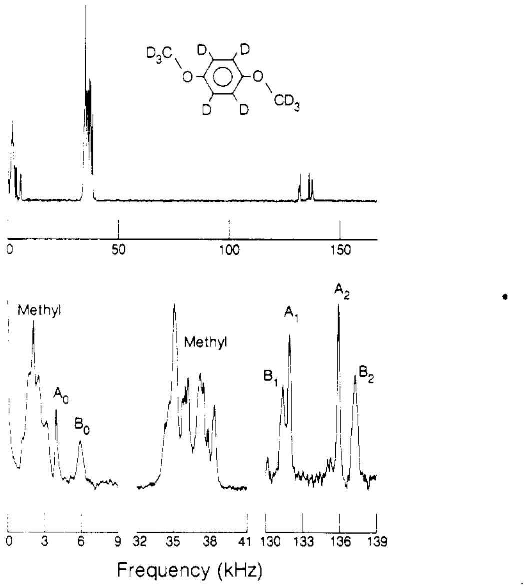

Figure 7. Zero-field deuterium NQR spectrum of polycrystalline perdeuterated 1,4-dimethoxybenzene. At top is the Fourier transform frequency spectrum. Below it are expanded views of the three distinct regions of the spectrum. In order of increasing frequency, these are the ν_0 lines and methyl and ring sites. The methyl sites exhibit a slight asymmetry as indicated by the shape of the methyl signal and the corresponding low-frequency signal. Four lines are observed for the aromatic ring sites, a consequence of inequivalence by the proximity of the methoxy groups in the solid-state conformation.

may not be resolved in powder patterns. As an example, the 55.6-MHz deuterium NMR spectrum of perdeuterated polycrystalline diethylterephthalate is shown in Figure 6a. Only the most prominent singularities of the methyl, methylene, and aromatic line shapes can be resolved since the deuterium signal is distributed over a wide bandwidth. In contrast, the zero-field deuterium spectrum in Figure 6b, has four distinct groups of peaks with sharply resolved fine structure. From such a spectrum the resonances from different sites in the molecule can be assigned.[17] In this case, five inequivalent sites are established. The high resolution of the zero-field experiment permits the determination of very similar quadrupolar coupling constants and small asymmetry parameters. Figure 7 shows a further example in perdeuterated dimethoxybenzene. The two doublets around 135 kHz are a consequence of the inequivalence of deuteron sites in the aromatic ring. This is due to the solid-state conformation of the molecule. The doublet (B) with the larger asymmetry parameter arises from the aromatic deuterium positions near the methoxy groups. Many nuclei with low quadrupolar frequencies are directly accessible by zero-field NQR studies; among those studied in this laboratory in addition to deuterium are lithium-7,[15] nitrogen-14,[18] and aluminum-27.[19]

Two-Dimensional Zero-Field NMR

The connectivities between zero-field NMR and NQR lines (which are related to connectivities between molecular sites) can be determined by extending the experiment to two time dimensions in zero field.[20] The basic scheme of two-dimensional NMR is to obtain the signal as a function of two independently incremented time variables, t_1 and t_2, and then Fourier transform with respect to both, resulting in a two dimensional frequency spectrum[21] A zero-field version of this experiment is shown as the field cycle in Figure 8a which has a pulsed-field mixing period between t_1 and t_2. Magnetization which oscillates at two possible frequencies of the system in the two time periods, for example the ν_+ and ν_- quadrupolar frequencies of a given site, will produce an off-diagonal or "cross-peak" between these two frequencies if the mixing sequence connects (transfers coherence between) the transitions. An experimental illustration of the connectivities in a spin $I = 1$ system appears in Figure 8b which shows the two-dimensional zero-field spectrum of the methylene region of a sample of selectively deuterated diethyl-

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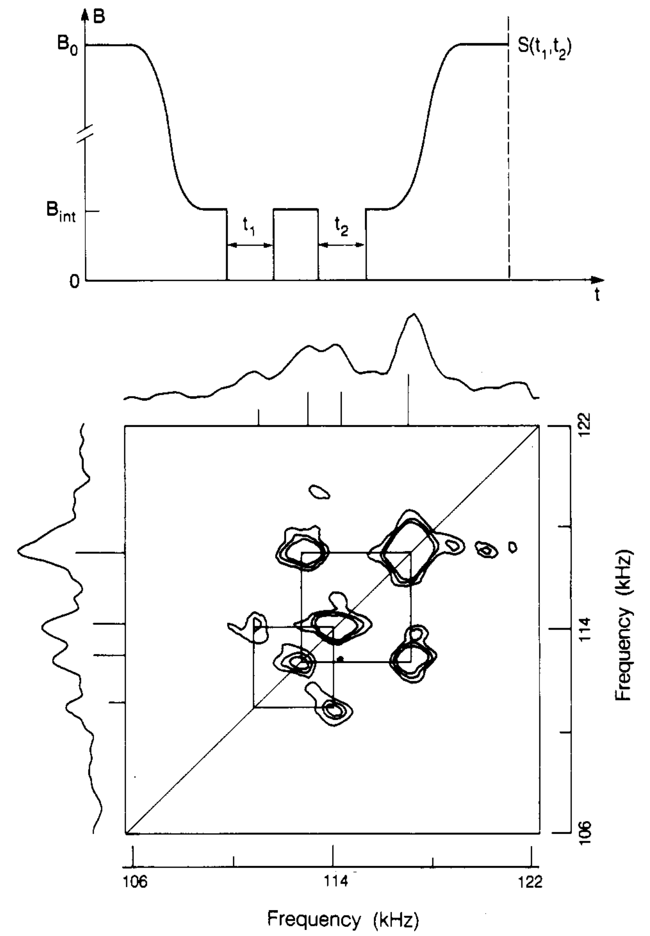

Figure 8. Two-dimensional zero-field cycle and spectrum of selectively CD_2 deuterated diethylterephthalate. (The compound is shown in Figure 6). The zero-field spectrum is obtained as a function of two independently incremented time periods, t_1 and t_2, which are separated by application of an intermediate pulsed field. This transfers coherence between the zero-field transitions. As seen in the experimental spectrum, off-diagonal peaks indicate connectivities between the zero-field quadrupolar transitions. In this case transitions can be assigned to inequivalent deuterium sites in the CD_2 groups.

terephthalate.[20] The spectrum of the fully deuterated molecule was shown in Figure 6. Figure 8b demonstrates that among the four lines in the CD_2 region of the spectrum, lines 1 and 3 belong to one deuteron and lines 2 and 4 to the other inequivalent deuteron. With this type of experiment one can expect to identify sites by their quadrupole couplings and determine distances by their dipolar couplings in a two-dimensional spectrum.

Zero-Field Pulses

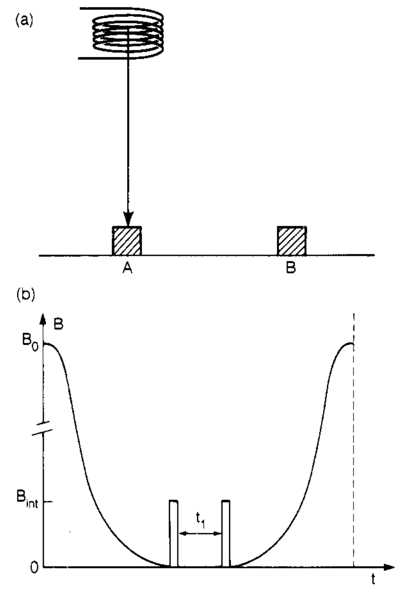

Figure 9. Pulsed-field cycling with adiabatic demagnetization and remagnetization. (a) Demagnetized sample (A) is different from one which has resided in zero field for an extended period (B). Neither exhibits any magnetization, but sample A will spontaneously and immediately polarize when returned to a field, while B requires a time on the order of the spin-lattice relaxation time, T_1, to polarize. This behavior makes possible the demagnetization field cycle employing dc pulsed magnetic fields shown schematically in (b). The sample is demagnetized to zero field where a state of zero-field spin order results. Brief dc pulses will initiate evolution in zero field for the time t_1. The evolution is terminated by a second pulse, and the sample is returned to high field for sampling of the magnetization. This field cycle provides flexibility in employing intense fields for brief periods of time, selective use of the magnitude, direction, and duration of the pulses, and level crossings in heteronuclear spin systems.

The experiments presented thus far have utilized a sudden switch off of the applied field to induce zero-field evolution as in Figure 3. Two principal disadvantages of this approach come to mind. The first is the requirement that the intermediate field used be larger then the local spin interactions so that the Zeeman interaction dominates. For nuclei with small magnetogyric ratios (γ) and large quadrupolar coupling constants, this requires that a field of a few hundred to a few thousand gauss be applied for a period of a few tens of milliseconds which may be awkward experimentally.[5b] The other disadvantage is the lack of selectivity in the sudden transition which excites evolution of different isotopes and spin species in zero field. The experiment can be made selective and more flexible by a simple modification of the field cycle which uses pulsed dc magnetic fields to excite different nuclear spins in zero field.[18,22] The field cycle of Figure 9 illustrates the use of dc pulses in the zero field period. First the sample is removed completely to zero field. This implements adiabatic demagnetization in the laboratory frame[23] and results in a zero-field spin state with no magnetization. Sample A in Figure 9, subjected to this adiabatic demagnetization will indeed exhibit no magnetization; however it is ordered, and thus different from an unmagnetized sample B which has been out of the magnet for an extended period of time. Application of a pulsed dc field to A will change the state of the system and cause evolution in zero field for a time t_1 which may then be terminated with a second dc pulse. This is entirely analogous to pulsed NMR in high field; here, the pulses are applied at the resonance frequency in zero field which is zero. The sample is then adiabatically remagnetized back to high field for normal NMR detection. The distinction between isotopes and spins (e.g., ^{13}C or ^{2}H vs. ^{1}H) is realized by making the pulses selective (e.g., by using composite pulses which are 2π rotations for all spins except the one of interest[24]). Isotope selectivity in zero field is analogous to spatial selectivity using inhomogeneous B_1

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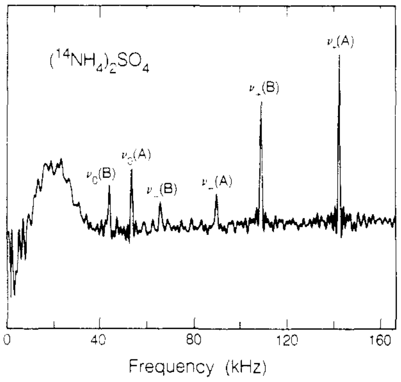

Figure 10. Indirectly detected nitrogen-14 zero-field NQR spectrum of polycrystalline ammonium sulfate. Six lines corresponding to two inequivalent quadrupolar sites in the unit cell (labeled A and B) are resolved. The proton signal still appears as a broad peak at low frequencies but has been reduced greatly through the use of selective dc pulses for excitation[18] at zero field, allowing observation of the lower frequency nitrogen-14 lines.

fields in high-field NMR.[24,25,26] The simplest example is the application of a 360° pulse to the protons and a $(\gamma_Q/\gamma_H)\cdot 360°$ pulse to a quadrupolar spin Q so that the proton spins remain unperturbed from their demagnetized state and only the quadrupolar spins evolve. Similarly, other nuclear species may be manipulated independently. These short pulses can be made quite intense for exciting the low γ nucleus, since they need only be applied for times on the order of microseconds.

Indirect Detection

A further advantage of the pulsed-field cycle described in the last section is that it allows level crossings between the protons and quadrupolar spins, such as deuterium and hydrogen, in a manner similar to traditional field cycling NQR.[18] This allows the zero-field evolution of the quadrupolar spins to be monitored by their effect on proton spins, yielding higher sensitivity polarization and detection. Indirect detection has long been used in frequency domain NQR experiments,[4e,h] but in its usual form allows the protons to absorb low-frequency zero-field irradiation directly, producing a low-frequency signal which obscures the NQR lines. Using the selective dc pulsed fields described above, the time domain experiment alleviates such problems. An example of a nitrogen-14 zero-field spectrum obtained by selective pulses in zero field and indirect detection with protons is shown for polycrystalline ammonium sulfate in Figure 10.

Other Systems

Materials, such as liquid crystals and polymers, which have magnetic field-dependent orientational behavior are appealing systems to study by zero field methods, since their NMR spectra can be obtained without the perturbation of the magnetic field.[27] For example, one may speculate whether the macroscopic or molecular ordering changes in the absence of an applied field. This is illustrated in Figure 11. When the magnetic field is removed from an aligned sample, does the macroscopic orientation relax and does the molecular order parameter change? This can be studied by observing the behavior of the liquid crystal molecules themselves or of aligned solute molecules dissolved in the liquid crystal. Through the intensities, frequencies, and behavior of the signal under dc pulses, the ordering of the sample can be investigated by the zero-field NMR spectra. The zero-field dipolar frequencies observed are a measure of the molecular ordering of the sample measured by NMR in the absence of a perturbing magnetic field. On the timescale of the zero-field experiment, a few 100 milliseconds in low or zero fields, no change in the nematic liquid crystal orientation was observed.[27] Such experiments have been performed in a number of nematic[28] and smectic[29] liquid crystals and should be useful in the future study of lyotropic systems and biological membranes.

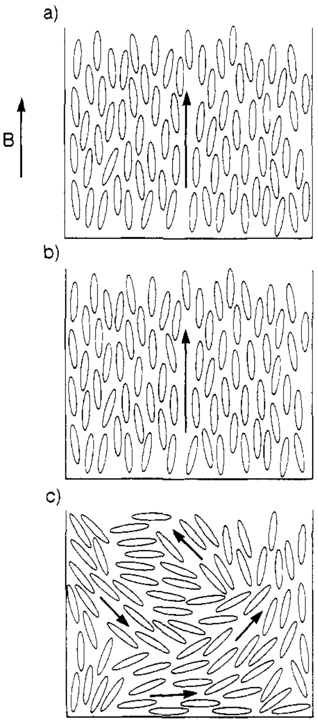

Figure 11. *Ordering in liquid crystal systems (a) in the presence* of a large applied magnetic field, (b) and (c) possible scenarios in the absence of an applied field. In (b) the sample remains aligned along the original field direction while in (c) the director is randomly oriented. The molecular ordering in such systems can be measured by zero-field NMR without the perturbing effects of high magnetic fields.

Concluding Remarks

The time domain zero-field NMR and NQR methods described in this account are in their infancy, but they have already demonstrated their applicability to a variety of chemical problems. The combination, through various forms of field cycling, of high resolution and high sensitivity produce narrow line spectra in polycrystalline solids or partially ordered materials. These "crystal-like" spectra may be obtained without the use of single crystals and provide structural and dynamical information either lost in the high-field powder spectra or unobtainable through frequency-domain NQR methods. The spectra are sensitive to subtle motional

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effects such as low-amplitude librations. When direct detection of zero-field transitions with SQUID detectors[30] becomes routine, two-dimensional NMR should be particularly valuable for structure determinations. Extensions to spin decoupling and other multiple-pulse experiments are also imminent and will certainly extend the applicability of zero-field NMR. A number of laboratories are now engaged in such studies, and we look forward to a period of amusing and possibly useful developments.

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Electron-Transfer Mechanisms in Electrophilic Aromatic Nitration

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Nitration via Electron Transfer—A Longstanding Hypothesis

In 1980 Schofield[1] finished the introductory chapter of his magnificent textbook on aromatic nitration by the following passage: "Speculation about the mechanisms of nitration, which might be said to have started with Euler's nitronium ion hypothesis, is thus far from complete, nor is it ever likely to be. There are certainly surprises to come."

One piece of speculation that has recurred often in the history of aromatic nitration is the one-electron-transfer (ET)[2] mechanism of nitration by NO_2^+. Already in 1933 Hückel[3] quoted the suggestion of a radical cation mediated mechanism by Meerwein, Pfeiffer, and Wizinger,[4] but the accompanying reaction formula did not display a radical cation, but instead the Wheland intermediate. It was left to Kenner[5] and Weiss[6] to express the ET mechanism in modern nomenclature in the middle of the 1940s (eq 1 and 2), although the

$$\mathrm{ArH} + \mathrm{NO_2}^+ \rightarrow \mathrm{ArH}^{\bullet+} + \mathrm{NO_2} \qquad (1)$$

$$\mathrm{ArH}^{\bullet+} + \mathrm{HSO_4}^- \rightarrow \mathrm{H_2SO_4} + \mathrm{Ar}^\bullet \xrightarrow{\mathrm{NO_2}} \mathrm{ArNO_2} \qquad (2)$$

proton abstraction step of eq 2 nowadays is considered a rather unlikely one. The ET mechanism was generalized by Weiss to be valid as well for other types of electrophilic aromatic substitution, such as halogenation and sulfonation. In general, the spirit of that period was happily tolerant of one-electron mechanisms or at least suggestions thereof; even the archetype of a two-electron-centered mechanism, that of the Diels–Alder reaction, was seriously expressed in an ET version by no less a person than R. B. Woodward![7]

Nagakura et al.[8] later developed these ideas theoretically and showed that in the gas phase the energy levels of the LUMO of typical charged electrophiles, like NO_2^+ (−11.0 eV), I^+ (−10.4 eV), and Br^+ (−11.8 eV), are lower than that of the HOMO of benzene (−9.24 eV); i.e., there is a strong driving force for ET from benzene to these cations. This was later confirmed in gas-phase studies,[9] ET being the predominant process for the reaction between benzene and substituted benzenes on the one hand and CH_3^+, NO_2^+, and NO^+ on the other. Further implications of the ET mechanism were explored by Pedersen et al.[10] They found correlations between log *k* for substitution and ionization potentials of substrates and between orientation of substitution and hyperfine coupling constants of the corresponding radical cations.

On the experimental side, a number of observations of radical cation formation in the reactions between aromatic or heteroaromatic compounds and NO_2^+ or $HNO_3/HClO_4$ were published.[11] Analogous results were obtained with NO^+ as the oxidant, and since the NO formed is easily removable, this method has turned out to be a good way of preparing radical cation salts.[12] It was also noted that side reactions during aromatic

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[2] Sometimes the acronym SET is used to denote single electron transfer, but this is not necessary in view of the basic postulate that electrons always are transferred one by one; see: Semenov, N. N. *Some Problems in Chemical Kinetics and Reactivity*; Princeton University Press: Princeton, NJ, 1968.

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