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ZERO FIELD NMR

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ZERO FIELD NMR

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Introduction

The development of 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 ten times this frequency. Accompanying this trend is an inescapable and unfortunate increase in the cost of NMR instrumentation. This is illustrated in Figure 1 adapted from the recent "Pimentel Report", Opportunites in Chemistry.[1] There are several reasons for the desire 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 these depend linearly on the magnetic field, higher fields mean substantially higher sensitivity. Secondly if the NMR linewidths 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 mad rush for high magnetic fields, it is sometimes overlooked that a magnetic field can inflict 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 can in principle 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 obliterated yielding a broad, often featureless "powder pattern" from which little information can be obtained. An example of the proton NMR spectrum of 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, a polycrystalline sample yields a considerably less useful powder pattern. The solution to this problem is to perform the NMR 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 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] Field cycling[5] 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 in the time period in which the spin interactions are measured.

A schematic representation of the simplest field cycle and 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 in B_o 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 transforming the time domain signal will produce a zero field frequency domain spectrum with high resolution and full B_o sensitivity. An example is shown in Figure 4. This is the zero field NMR powder spectrum of a polycrystalline sample of the same four proton spin system whose high field NMR spectrum appears in Figure 2. Comparison of the experimental spectrum 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 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 data on 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 tunnelling.[9]

Effects of Motion

In addition to measuring the static dipolar couplings of rigid molecules, zero field NMR can be used to probe the effects of motion in disordered samples.[10] Small amplitude motions, for example the librational

motions of molecules, will average the normally axially symmetric dipolar interaction to a non-axially 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 broad high field powder lineshapes. 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.[11] 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.[12] 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. they are invariant to permutation and behave like a homonuclear I-I dipolar coupled spin pair. A sudden transition to zero field will initiate evolution for all spin species since no selection can be made, as in high field NMR, on the basis of irradiation frequency. Examples of such heteronuclear zero field NMR spectra have been

published.[12] The magnetization for different spin species (e.g. ^{13}C, ^{1}H) can be manipulated independently with radiofrequency pulses in high field to produce unique initial populations of the I and S spin states in zero field. In this way, certain zero field transitions may then be enhanced or removed, changing the appearance of zero field spectra from different functional groups (e.g. CH, CH_2, CH_3). Heteronuclear J-couplings in liquids have also been observed in zero field.[12] Since the scalar coupling in liquids is already isotropic, there is no advantage in going to zero field. However these experiments illustrate the role of field homogeneity in zero field NMR (the very narrow natural linewidth 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 if the frequency is large.[2] The applicability of these methods is limited at low frequencies (<100 kHz), such as those corresponding to deuterium (^{2}H), and also requires the use of radiofrequency irradiation in zero field.[5e,h] Fourier transform time domain NQR[6,13] avoids many of these problems.

High field NMR of quadrupolar nuclei is plagued, 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.[14] 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 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 lineshapes can be resolved as the deuterium signal is distributed widely over a wide bandwidth thus decreasing the signal-to-noise ratio. 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.[15] In this case, five inequivalent sites are determined. The high resolution of the zero field experiment enables 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. Many nuclei with low quadrupolar frequencies are directly accessible by zero field NQR studies, and among those studied in this laboratory in addition to deuterium are 7-Lithium[13], 14-Nitrogen[16] and 27-Aluminum.[17]

Two Dimensional Zero Field NMR

The connectivities between zero field NMR and NQR lines (which relate to connectivities between molecular sites) can be determined by extending the experiment to two time dimensions in zero field.[18] 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.[19] A zero field version of this experiment is shown as the field cycle in Figure 8a which has a pulsed field mixing period bewtween 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 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 diethylterephthalate.[18] This shows 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 identify sites by their quadrupole couplings and determine distances by their dipolar couplings in a two dimensional spectrum.

Zero Field Pulses

All of 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 in 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 and large quadrupolar coupling constants, this requires that a field of a few 100 to a few 1000 Gauss be applied for a period of a few tens of milliseconds which may be difficult experimentally.[4b] The other disadvantage is the lack of selectivity in the sudden transition which excites evolution of different isotopes 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.[16,20] 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 is adiabatic demagnetization in the laboratory frame[21] and results in an equilibrium zero field spin state. Sample A in figure 9, subjected to this adiabatic demagnetization has no magnetization but 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; pulses are applied at the resonance frequency which is zero in zero field. The sample is then adiabatically remagnetized back to high field for normal solid state NMR detection. The distinction between isotopes (e.g. ^{13}C or ^{2}H vs. ^{1}H) is achieved by making the pulses selective (e.g. by using composite pulses which are 2π rotations for all isotopes except the one of interest[22]). Isotope selectivity in zero field is analogous to spatial selectivity using inhomogeneous B_1 in high field.[23,24] A simple example is to apply a 360° pulse to the protons and a $(\gamma_Q/\gamma_H)\cdot 360$ pulse to a quadrupolar spin Q so the proton spins remain unchanged 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 large for exciting the low γ nucleus as they need only be applied for times on the order of microseconds.

Indirect Detection

Another advantage of the pulsed field cycle described in the last section is that it provides for level crossings between the protons and quadrupolar spins, such as deuterium and hydrogen, as in traditional field cycling NQR.[16] This allows the zero field evolution of the quadrupole spins to be detected by their effect on proton spins, yielding higher sensitivity polarization and detection. Indirect detection has long been used in frequency domain NQR experiments[5e,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 14-Nitrogen 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, which have magnetic field dependent orientational behavior are interesting systems to study by zero field methods, since their NMR spectra can be obtained without the perturbation of the magnetic field.[25] For example, one may question 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 nematic sample, does the macroscopic orientation relax and does the molecular order parameter change? This can be studied by observing the behavior of an aligned solute molecule dissolved in the liquid crystal. Through the intensities, frequencies and behavior of the signal under dc pulses, the ordering of the sample can be ascertained 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.[25] Such experiments have been performed in a number of nematic and smectic liquid crystals[26] and should be useful in the study of lyotropic systems.

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 effects such as low amplitude librations. When direct detection of zero field transitions with SQUID detectors 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 exciting and amusing developments.

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Figure Captions

Figure 1: Relationship between cost and frequency of commercial NMR spectrometers over the last 25 years. Adapted from "Opportunities in Chemistry", reference 1.

Figure 2: Proton 180 MHz NMR spectrum of polycrystalline 1,2,3,4 tetrachloronaphthalene-bis(hexachlorocyclopentadiene) adduct, a relatively isolated four proton system. The broad powder pattern (~20 kHz) shows no resolved features from which one may derive information about the molecular structure.

Figure 3: 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 preserved by maintaining 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 obviously at lower right.

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.

Figure 6: (a) Deuterium high field NMR spectrum of polycrystalline perdeuterated diethylterephthalate. Only the singularities of the methylene and aromatic sites are distinguishable at ~±55 and ~±70 kHz as the signal intensity is distributed over such a broad frequency range. From the overlapping powder lineshapes, three separate quadrupolar sites are seen. (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, methyl sites and the ν_o lines in order of decreasing

frequency. Quadrupolar coupling constants and small asymmetry parameters are determined for five inequivalent sites in the molecule.

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_o lines, methyl and ring sites. The methyl sites show a slight asymmetry as indicated by the shape of the methyl signal and the corresponding low frequency signal. Four lines are observed for the ring sites as the solid state structure causes the positions near and far from the methyl groups to be inequivalent. A triplet of lines may be assigned to each of two sites labeled A and B.

Figure 8: Two dimensional zero field cycle and spectrum of selectively CD_2 deuterated diethylterephthate. 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 mixes magnetization 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.

Figure 9: Pulsed field cycling with adiabatic demagnetization and remagnetization. (a) Demagnetized sample (A) is different from one which has resided in zero field an extended period (B). Both have no magnetization, but the demagnetized sample will spontaneously and

immediately polarize when returned to a field, while the other requires a time on the order of the spin lattice relaxation time, T_1, to polarize. This is 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 large fields for brief periods of time, selective use of the magnitude, direction, and duration of the pulses and level crossings in heteronuclear spin systems.

Figure 10: Indirectly detected 14-nitrogen zero field NQR spectrum of polycrystalline ammonium sulfate. Six lines corresponding to two inequivalent quadrupolar sites (labelled 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[14] at zero field allowing observation of the lower frequency lines.

Figure 11: Ordering in nematic 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.

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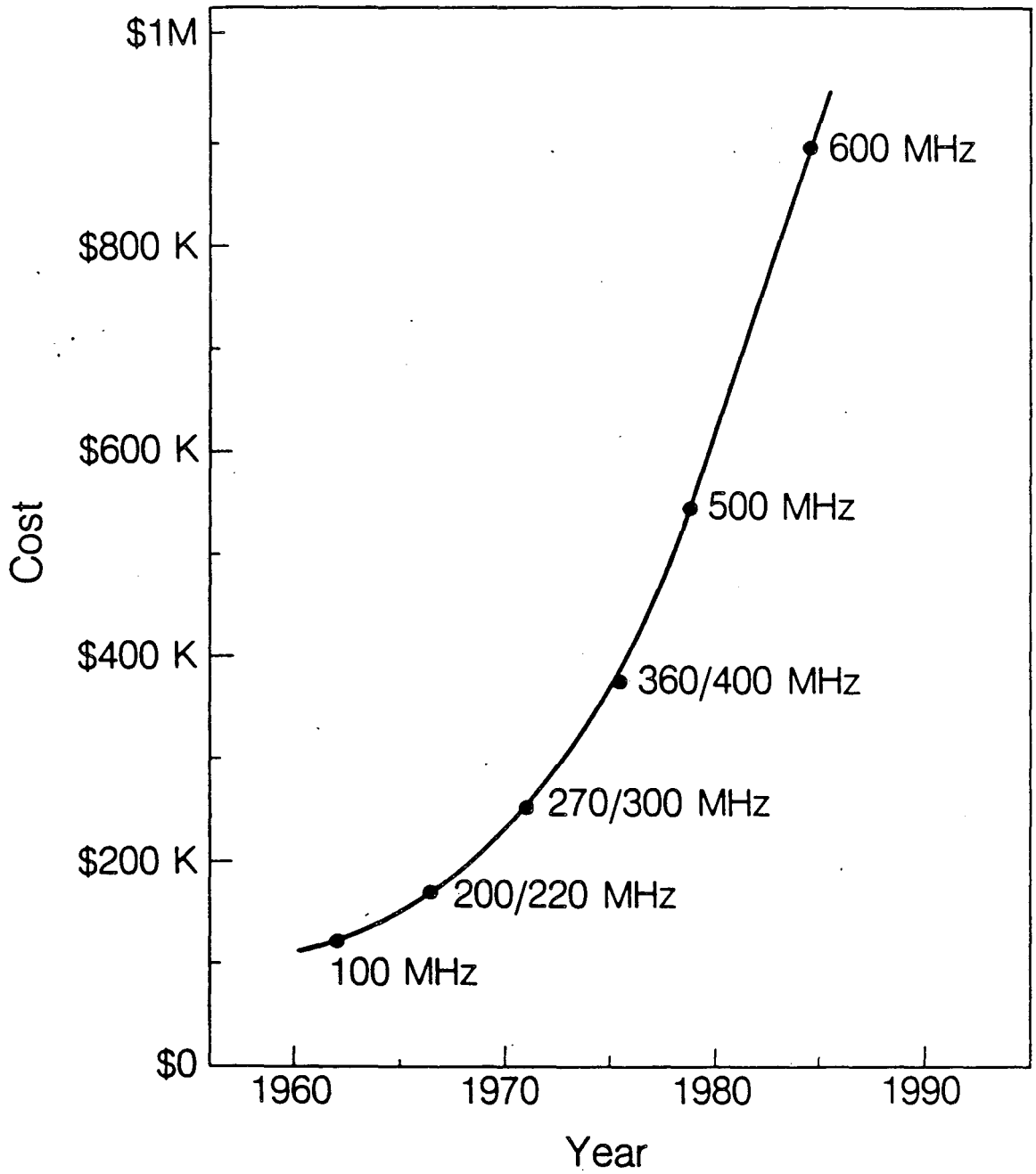

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Figure 1
Zero Field NMR
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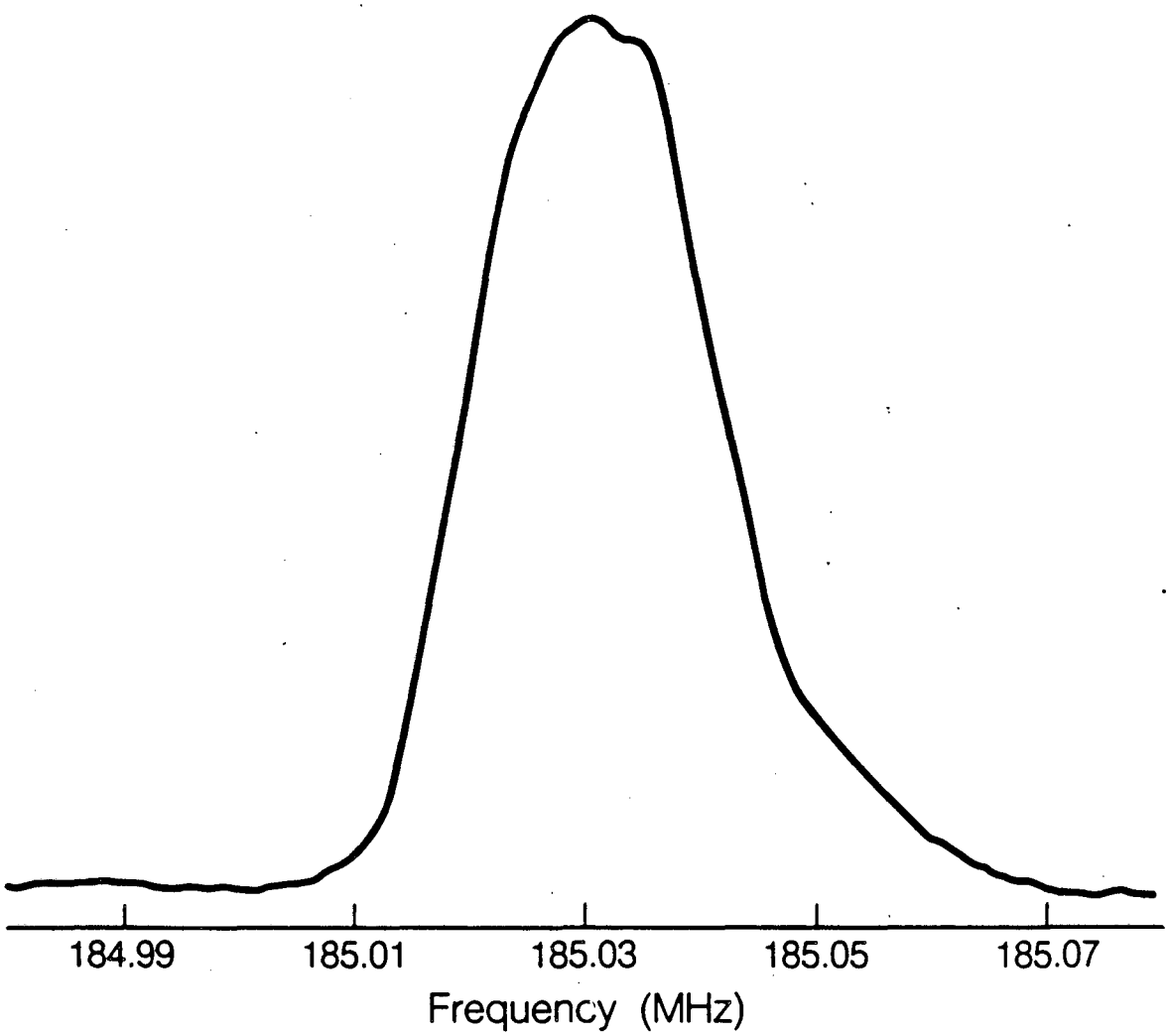

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Figure 2
Zero Field NMR
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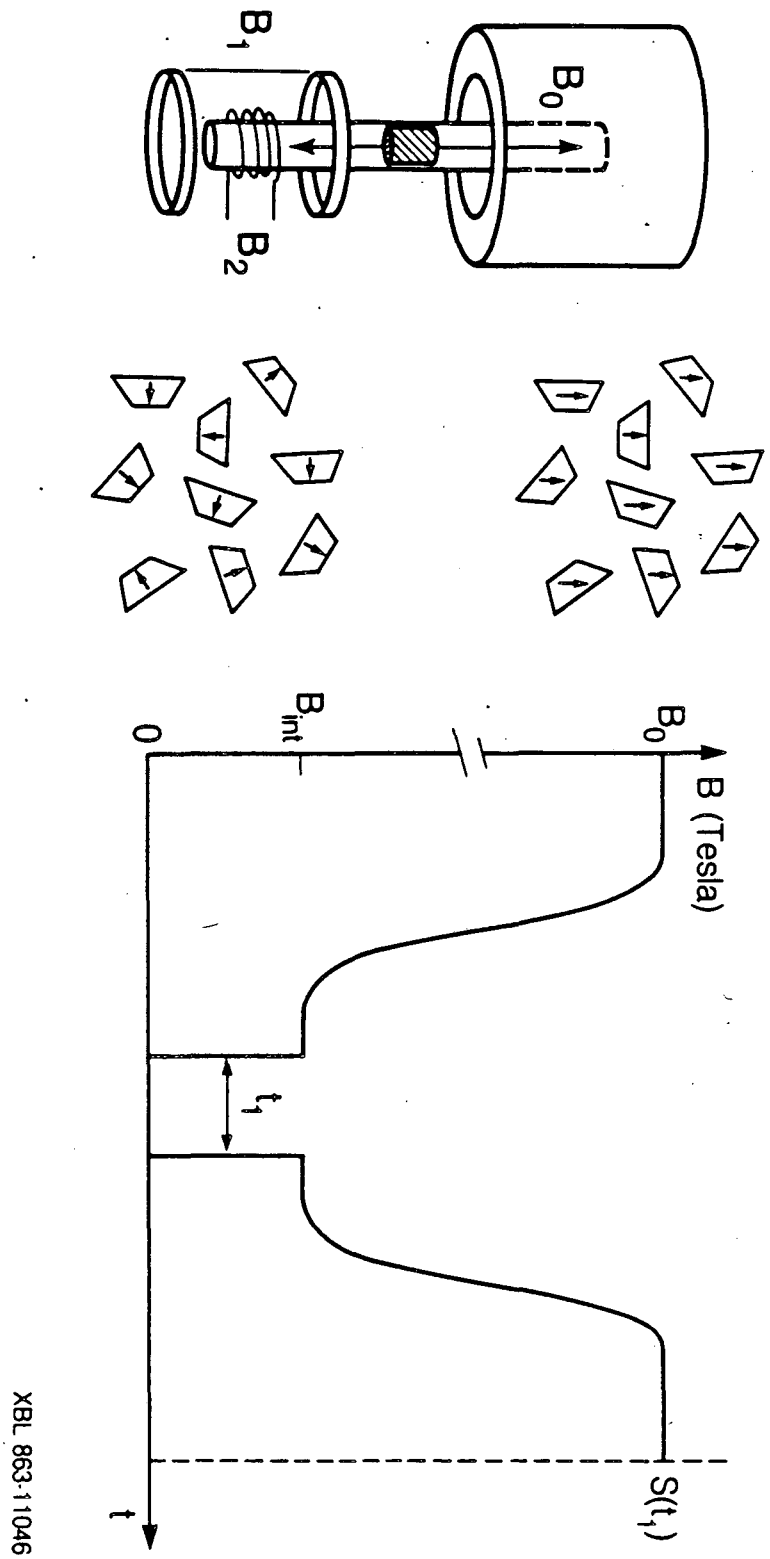

Figure 3
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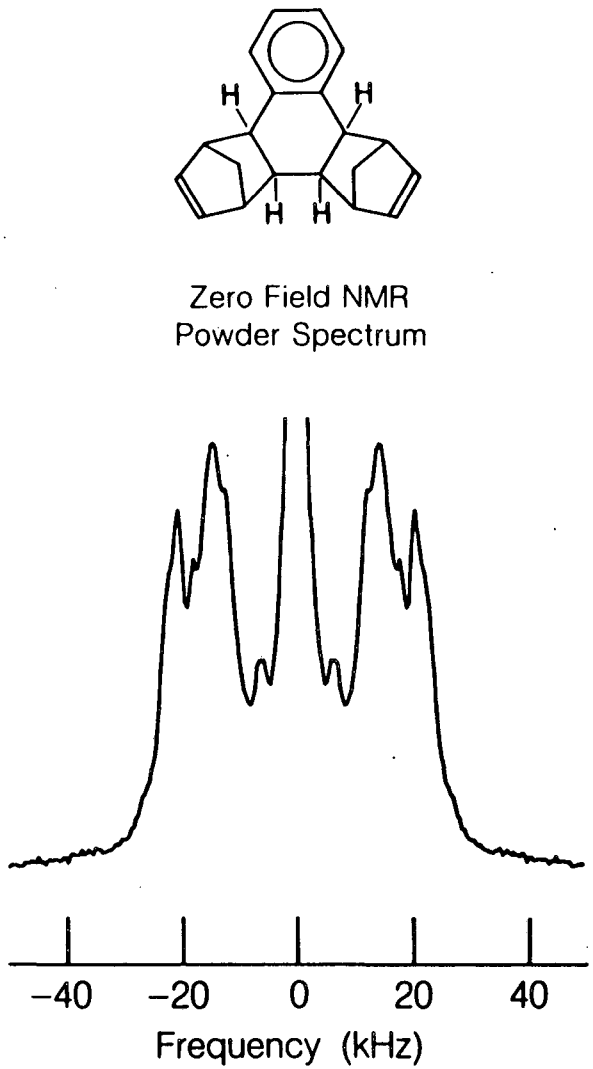

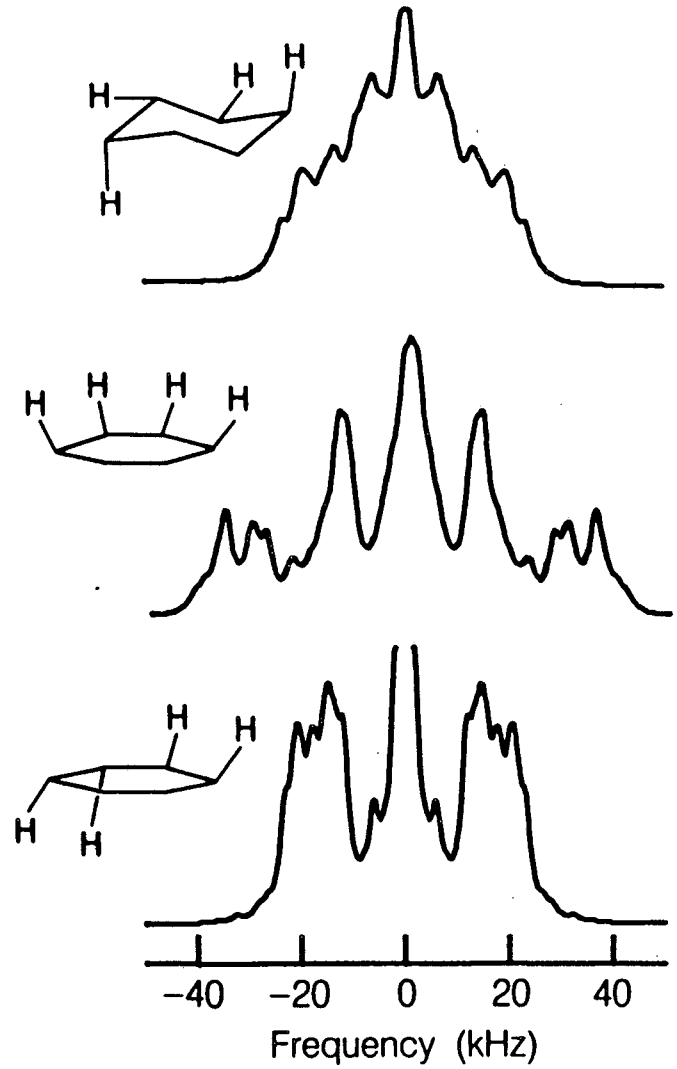

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Figure 4
Zero Field NMR
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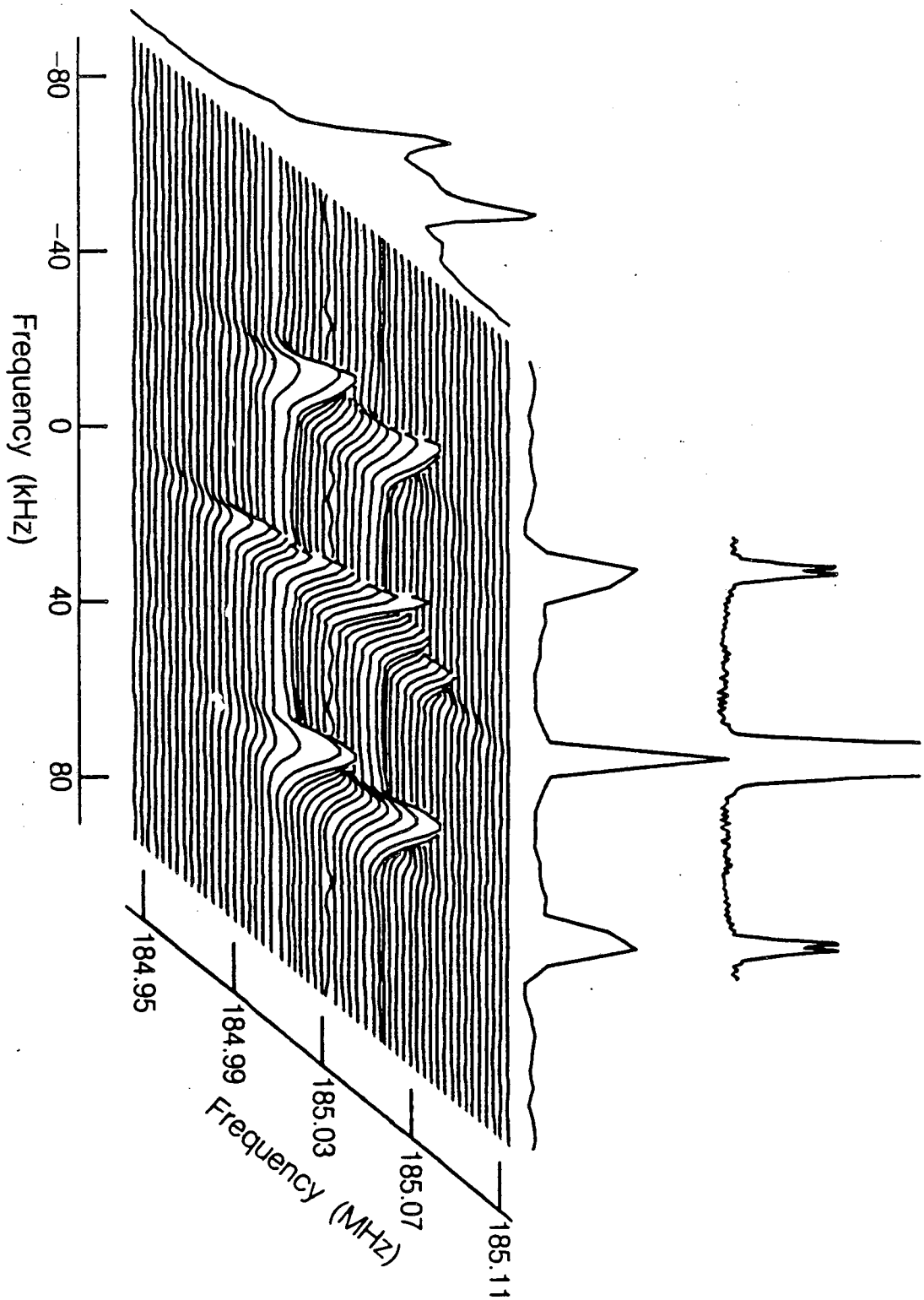

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Figure 5
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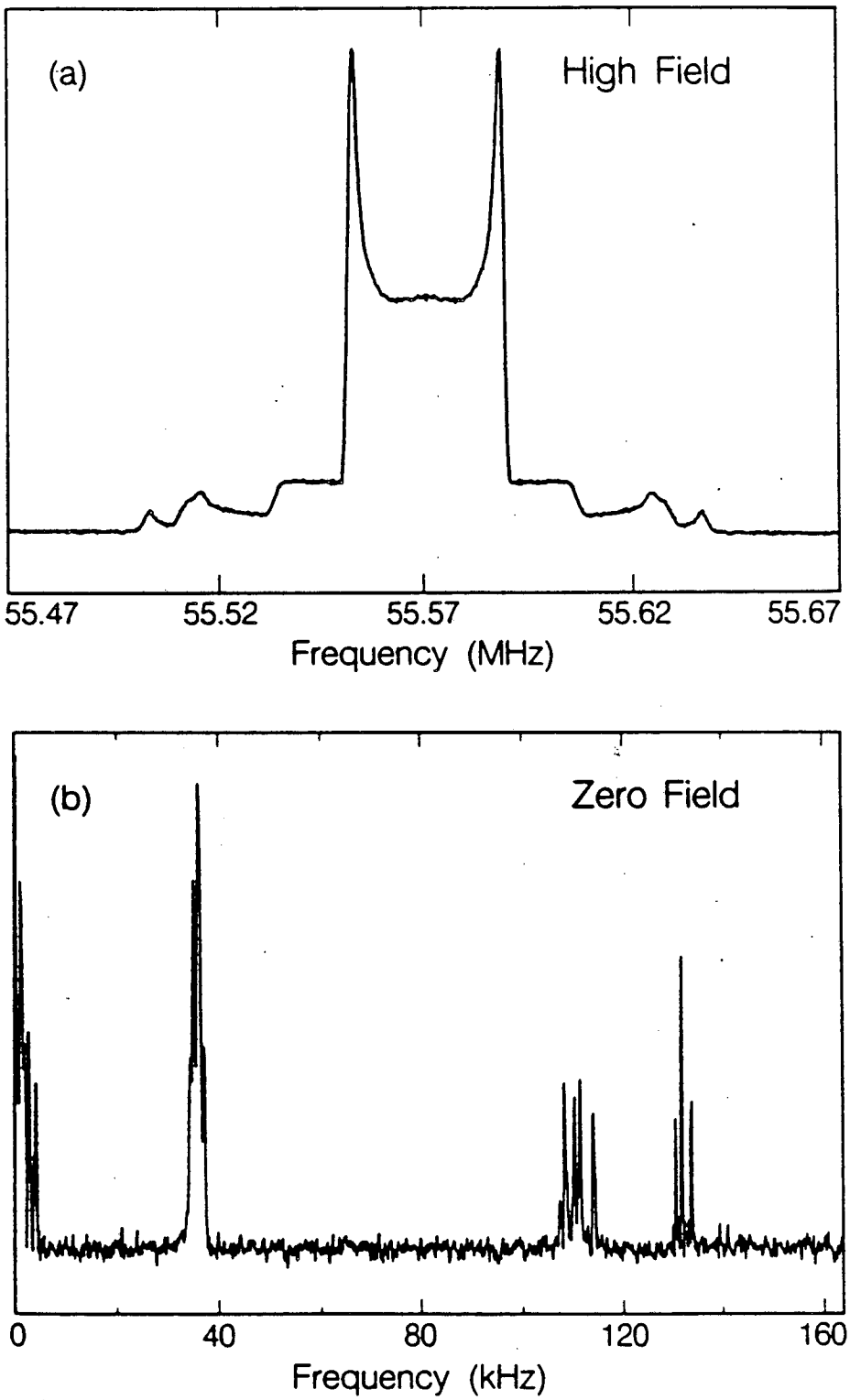

Figure 6
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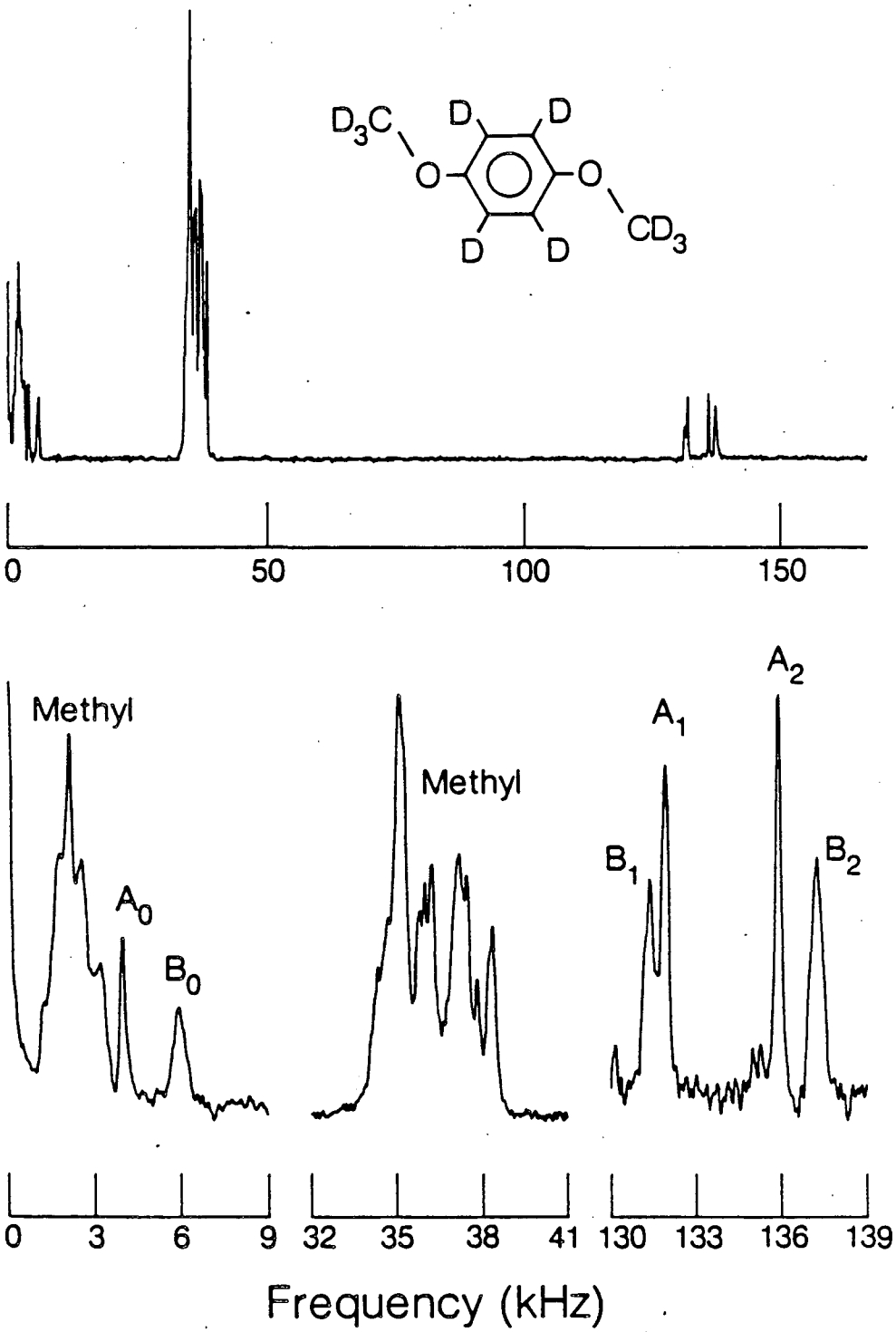

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Figure 7
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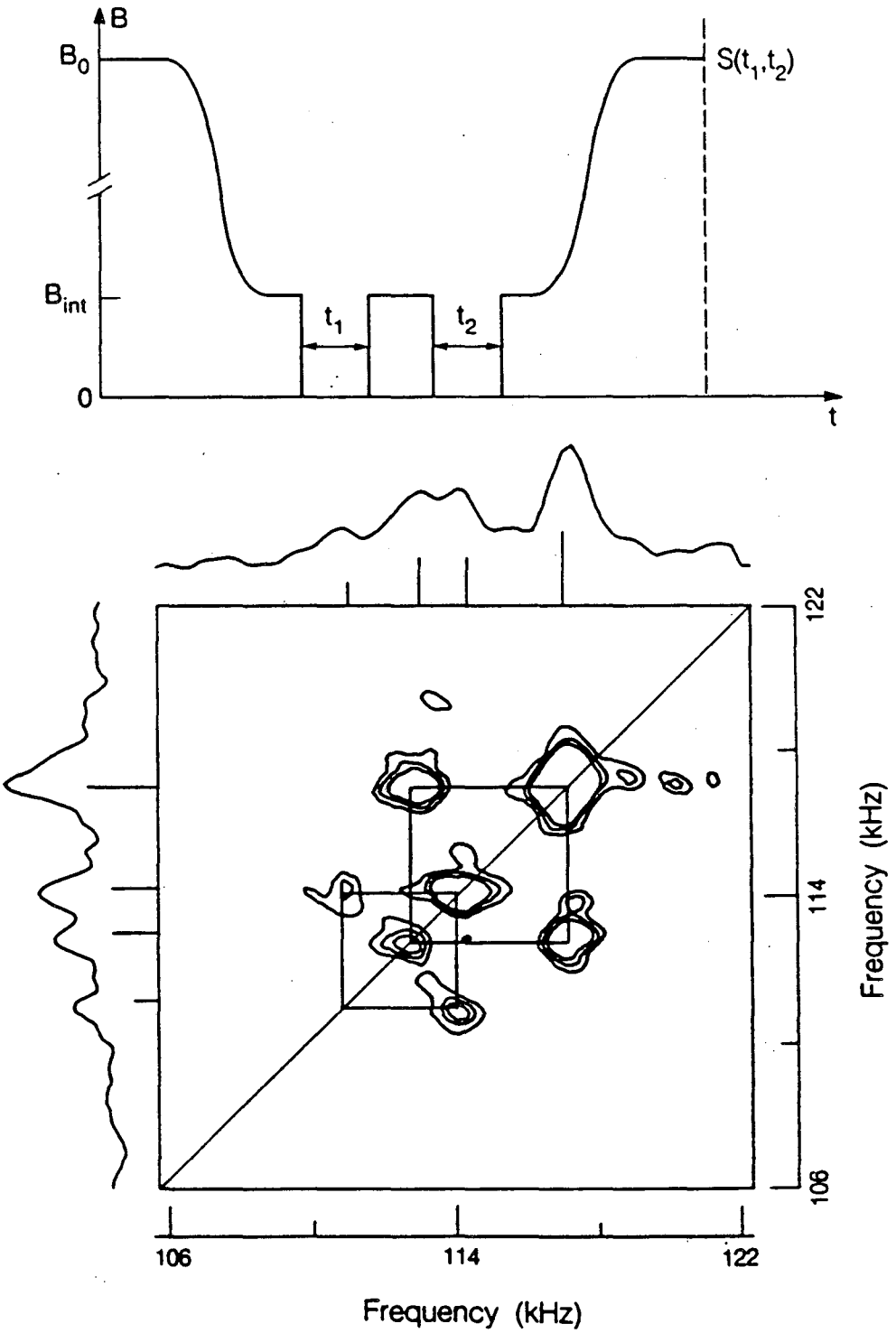

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Figure 8
Zero Field NMR
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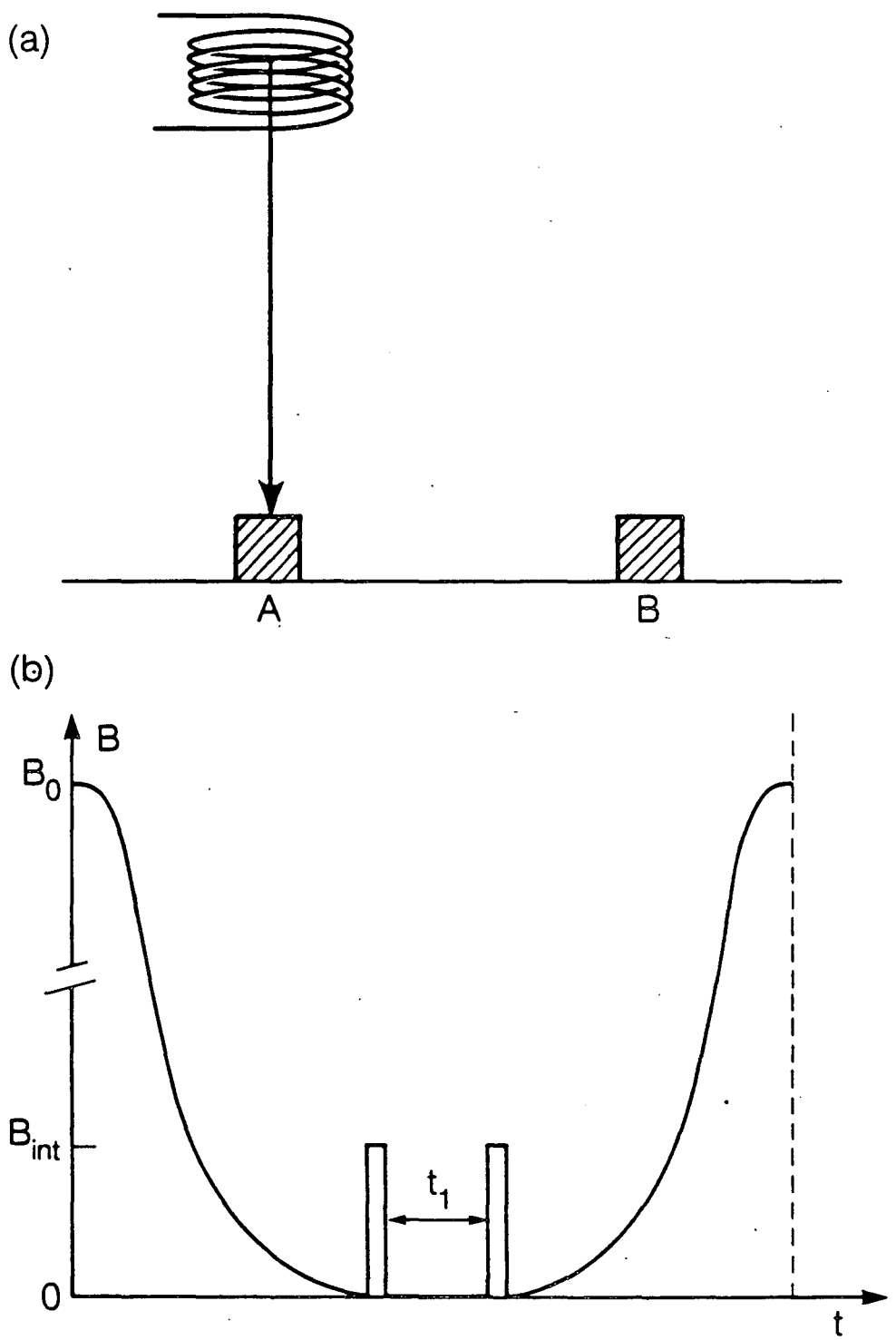

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Figure 9
Zero Field NMR
Thayer and Pines

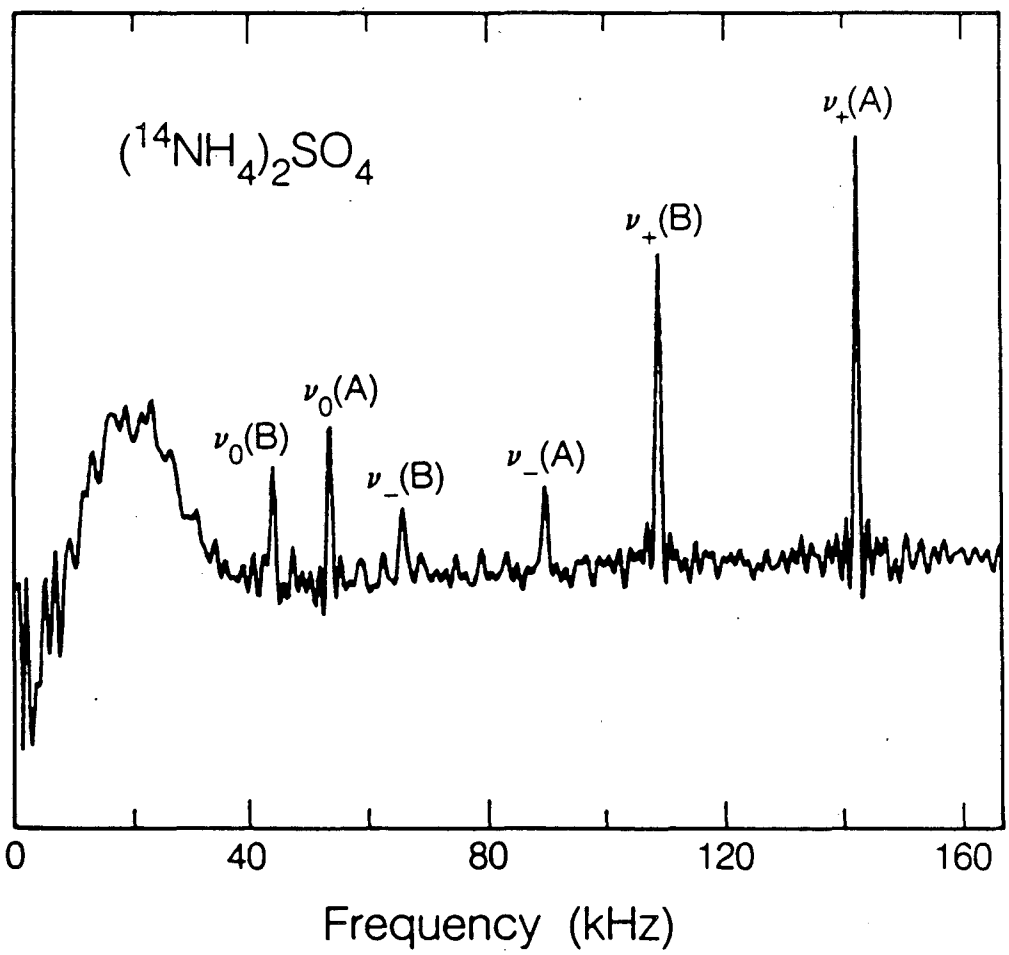

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Figure 10
Zero Field NMR
Thayer and Pines

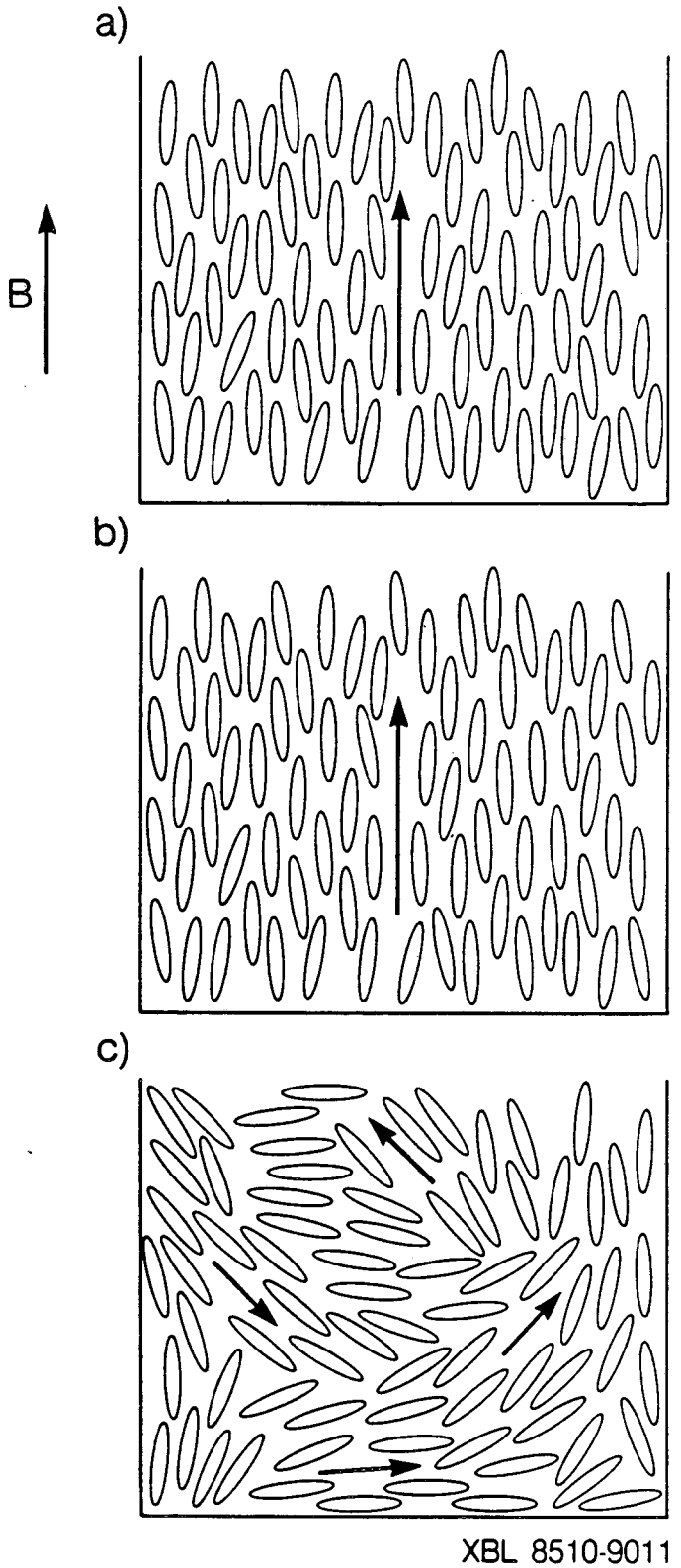

Figure 11
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