

**ANNUAL REPORTS ON
NMR SPECTROSCOPY**

Volume 24

ANNUAL REPORTS ON

NMR SPECTROSCOPY

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ANNUAL REPORTS ON NMR SPECTROSCOPY

Edited by

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VOLUME 24



ACADEMIC PRESS

Harcourt Brace Jovanovich, Publishers

London • San Diego • New York
Boston • Sydney • Tokyo • Toronto

ACADEMIC PRESS LIMITED
24-28 Oval Road,
LONDON NW1 7DX

U.S. Edition Published by

ACADEMIC PRESS INC.
San Diego, CA 92101

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**A catalogue record for this book is available from the
British Library**

ISBN 0-12-505324-X
ISSN 0066-4103

Phototypesetting by Alden Multimedia Ltd, Northampton
Printed in Great Britain at the University Press, Cambridge

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Preface

The protean nature of the applications of NMR is regularly reflected in this series of reports and Volume 24 is no exception. It is an ineluctable fact that all areas of science appear to benefit upon submission to the blandishments of NMR. The examples provided here encompass solid state NMR, solid state NMR imaging, NMR studies of interfaces, NMR investigations of cells and organisms, mercury-199 NMR and some applications of NMR in the area of coal science.

It is a pleasure for me to be able to convey my sincere thanks to all of the authors for their dedication in the preparation of their reports. The continuing success of this series depends upon the cooperation of both the contributors and the production staff which is much appreciated.

University of Surrey
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G.A. WEBB

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N.J. CLAYDEN

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Developments in Solid State NMR

N.J. CLAYDEN

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1. INTRODUCTION

Solid state NMR continues to be a fertile area for research with developments in many aspects of the technique, including improved instrumentation, pulse sequences and data analysis. Much of the diversity in the experiments stems from the desire to measure or remove different nuclear spin interactions. This forms an important theme in solid state NMR. Although more emphasis is being placed on correlating nuclear spin interactions, in particular the chemical shift and dipolar coupling, it is still true to say that the main aim is to eliminate the contribution of interfering interactions in order to observe the one of interest. Even when the purpose of the experiment is to correlate the nuclear spin interactions, the unique development of one interaction in a time period has been important and hence the increased use of two-dimensional experiments. Unlike solution state NMR, though, two-dimensional experiments are not so widely used in the solid state, principally because of the low sensitivity in many of the experiments. Given this background it is logical to consider the developments as they apply in the three main nuclear spin interactions, namely the chemical shift, dipolar coupling and quadrupolar coupling. An area of potential, NMR imaging of solids, is taken separately, as are developments aimed at improving the sensitivity. In such a complex area as solid state NMR undoubtedly there will be experiments which do not adequately fit the classification adopted; however, I hope these will be kept to the minimum.

Rapid growth in the availability of commercial solid state NMR spectrometers has meant that the application of the technique to problems in chemistry, physics, biochemistry and material science have blossomed. It is therefore difficult to do justice to the review of all aspects. Consequently, I intend to restrict this review to developments in the techniques of solid state NMR and will not deal with applications, except in so far as they impinge on the technical merits. However, it would not be right to introduce the new experiments without placing them in context and to point out their strengths and weaknesses. For those interested in the applications reviews and books are available in various areas as follows: glasses and minerals,^{1,2} studies of supported metal particles both with and without adsorbed molecules,³ polymers,⁴⁻¹¹ principles of multiple-quantum NMR,¹² NMR in one and two dimensions,¹³ coherence in NMR,¹⁴ high-temperature superconductors,¹⁵ imaging of materials,¹⁶ general solid state NMR,¹⁷⁻¹⁹ solid state NMR in inorganic chemistry,^{20,21} recent developments in solid state NMR techniques,²² two-dimensional methods in polymers,²³ biochemistry,²⁴⁻²⁶ ceramics,²⁷ zeolites²⁸ and NMR microscopy.²⁹ An excellent account of some recent developments in nuclear magnetic resonance including the solid state is provided by two volumes commemorating J.S. Waugh's 60th birthday.^{30,31}

Topics covered include: high-temperature superconductors, ^2H NMR of inclusion compounds, ^1H MAS NMR imaging and heteronuclear couplings by REDOR.

2. SENSITIVITY

Arguably the single most important impediment to the wider application of solid state NMR is the low sensitivity of the technique. This arises from the small magnitude of the energy separation between the nuclear spin states in a magnetic field, giving only a small difference in populations. For a typical field of 5 T at room temperature the population ratio for ^1H is only 1.00001. The overall sensitivity of the NMR experiment can be tackled in two ways: first, by increasing the nuclear spin polarization and second, by improving the efficiency of the detection. Improvements in magnet technology are increasing the static fields, B_0 , available such that persistent high-resolution magnets of 14.1 T are now common, thereby giving a greater nuclear spin polarization. However, increasing B_0 is not a realistic way to improve the sensitivity markedly because the step changes in the field strength which are required are not foreseeable.

At the other end of the experiment one could look for a more sensitive detection device than an rf coil operating by Faraday's law. One such device is the SQUID³² which has been employed to detect low frequencies.³³⁻³⁵ With the higher frequencies more typically seen in NMR experiments, though, the advantage of the SQUID is no longer seen. Indirect detection schemes based on the optical detection of magnetic resonance (ODMR)³⁶⁻³⁸ also offer an increase in sensitivity because of the higher frequencies of the optical radiation. This is reflected in applications such as hole-electron recombinations in semiconductors.³⁹ Nevertheless, these applications are limited and optical detection methods cannot be considered a general method for sensitivity enhancement.

In essence, NMR would be more sensitive if only the polarization of the nuclei could be increased. Within the realm of conventional NMR this means low temperatures and polarization transfer methods. Polarization is most commonly transferred from electrons to the nucleus of interest or from protons to a less abundant nucleus. Highly polarized nuclei can be prepared by methods developed for producing atomic beams,^{40,41} involving multipole magnets and adiabatic rf transitions for nuclei such as ^{23}Na and ^7Li , while for the inert gases, spin transfer from an optically pumped species can be used to prepare polarizations of up to a few per cent.⁴² Because these have not been widely applied, the full capabilities are as yet unknown. In the case of ^{131}Xe the T_1 of the nuclear magnetization is sufficiently long to allow experi-

ments involving polarization and then removal to a high field magnet. This offers the possibility of studying surfaces and porous materials such as zeolites,⁴³ along the lines of previously reported experiments using normal polarization levels.^{44,45}

2.1. Low-temperature NMR

Both in principle and in practice very low temperatures < 1 K can bring about drastic improvements in the signal intensity. To achieve the most significant benefit requires temperatures as low as 10–30 mK, when the signal is 10^4 greater than at room temperature. Now we are dealing with robust signals of the order of a volt. The price to be paid for this is an enormous increase in the nuclear spin–lattice relaxation time and the experimental problems of working at low temperature. Particular attention has been paid to the mechanisms of nuclear spin relaxation and the nature of linewidths in insulators below 1 K,⁴⁶ since long relaxation times are expected because of the reduction in lattice vibrations which are important in the coupling of the nuclear spin to the lattice. If lattice vibrations were the only source of relaxation low-temperature NMR would be a curiosity; however, it has been observed that ^3He can mediate nuclear spin–lattice relaxation at surfaces.^{47–50} Moreover, coupled relaxation of surface spins is a phenomenon which occurs in all solids immersed in ^3He ; it is characterized by a temperature-independent T_1 . Have we reached a Holy Grail for NMR: high sensitivity associated with surface selectivity? In one sense, yes, when the solid has a high surface area but no if the intent is to study single crystal faces. At the millikelvin temperatures used in these experiments it can be difficult to establish the true temperature and one direct method is to use the temperature dependence of the lineshape which is evident at low temperatures.⁵¹ For example, the Pake doublet in $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ becomes markedly skewed at temperatures below 50 mK (Fig. 1).

In a study of stannic oxide it has been observed that the ^{115}Sn chemical shift powder patterns were inhomogeneously broadened, which was attributed to coupling between the ^{115}Sn and paramagnetic ions. At the low temperatures used relaxation of the electron spins is also greatly inhibited. It is unclear to what extent the inhomogeneous broadening is going to restrict the applicability of ultra low-temperature NMR. Distortions can also arise in the lineshape because the Fourier transform spectrum no longer represents the steady state absorption and dispersion spectrum.⁵² This is encountered as a dependence of the lineshape on the flip angle.

Low-temperature NMR will be complicated for materials showing chemical shift inequivalence and abundant spin dipolar coupling, because all

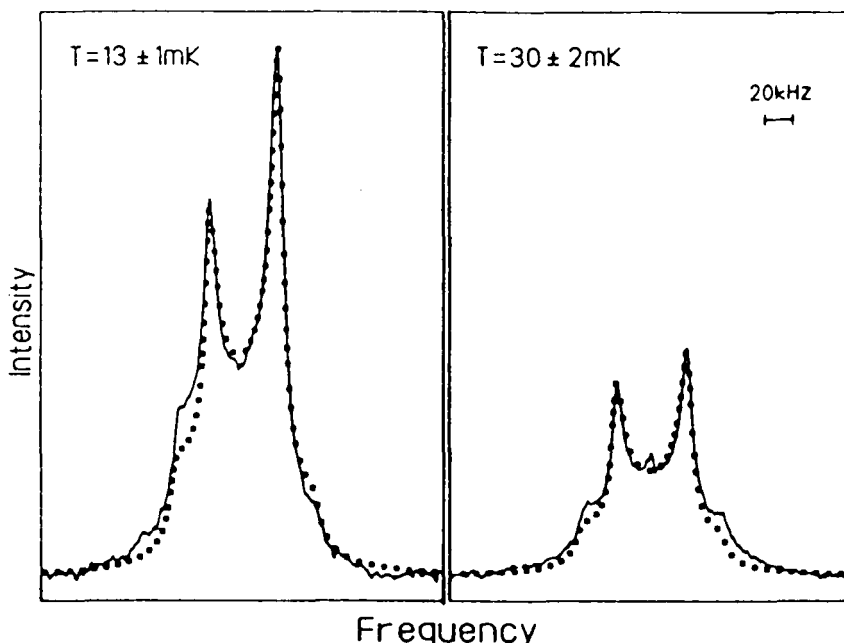


Fig. 1. Proton resonance spectra of slightly hydrated CaSO_4 powder immersed in liquid ^3He at 13 and 30 mK. The solid lines are the experimental spectra. The squares represent the best-fit theoretical spectra. (Reproduced with permission from Kulns *et al.*⁵¹)

work must be carried out on static samples and to date no multiple-pulse sequences, apart from Carr–Purcell echo trains, have been used. When a single environment is expected chemical shift powder patterns can be readily understood, as was the case for ^{13}C O adsorbed on SnO_2 at 0.01–1 K. The ^{13}C T_1 of 540 s was not outrageously long, values of the same order are seen in the crystalline phase of polyethylene.⁵³

2.2. Polarization transfer

2.2.1. Cross-polarization

The transfer of magnetization from an abundant spin, normally protons, to a rare spin, such as ^{13}C , has been of major importance in allowing the development of solid state NMR.⁵⁴ Without this increase in sensitivity the range of experiments would be greatly restricted. Cross-polarization has been achieved in three ways, shown schematically in Fig. 2; first, using adiabatic demagnetization in the rotating frame (ADRF) where dipolar order is

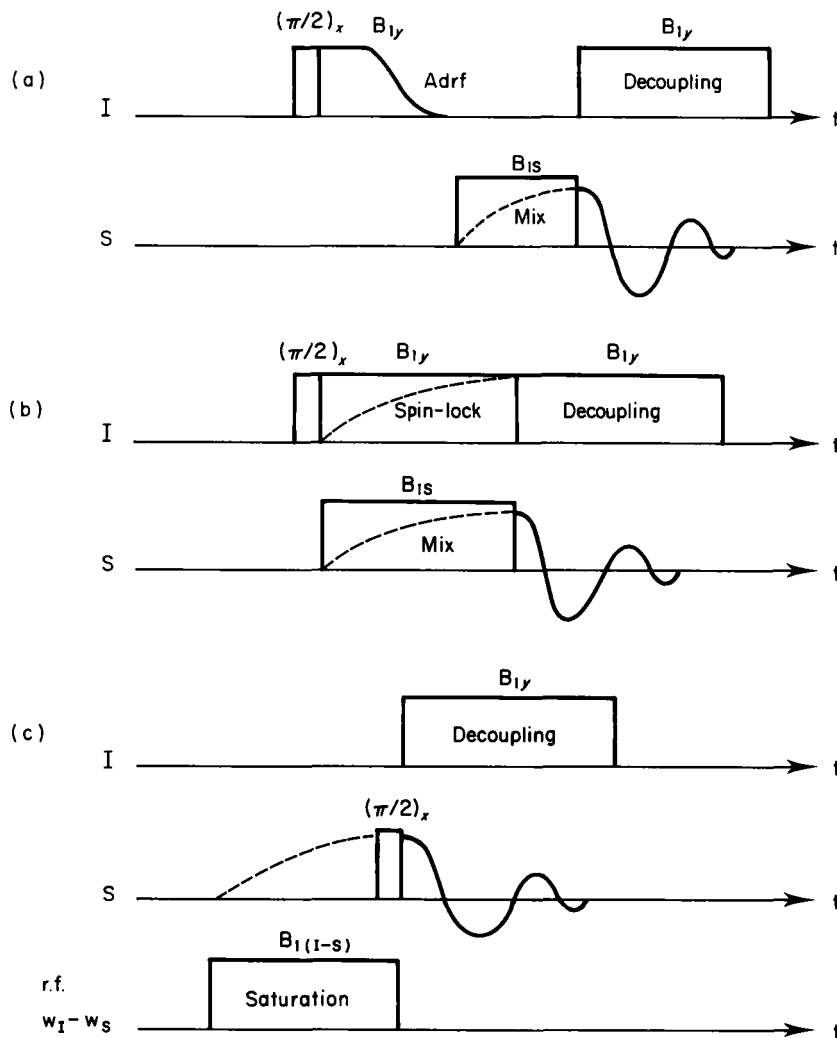


Fig. 2. Sequences for cross-polarization from an abundant spin, I, to a rare spin, S. (a) ADRF, adiabatic demagnetization in the rotating frame, (b) spin-lock and (c) nuclear solid effect.

created from the proton magnetization followed by its transfer into the rare spin;⁵⁵ second, by spin-locking in the rotating frame and transferring the magnetization by applying matched rf fields to both the spin systems meeting the so-called Hartmann-Hahn condition;⁵⁶ and third, by a solid effect involving the saturation of forbidden transitions.^{57,58} ADRF relies on the

existence of dipolar order and thus is not compatible with magic-angle spinning, which greatly reduces the relaxation time of dipolar order, and the solid effect requires a triply tuned probe. Hence the overwhelming importance of the spin-lock cross-polarization method.

A modified spin thermodynamic treatment of spin-lock cross-polarization which considered the broadening of the abundant spin energy through quantized states has led to the proposal of a new cross-polarization pulse sequence which is much less sensitive to mismatching.⁵⁹ This sequence involved the synchronous reversal of the phase on both the spin-locking rf fields. Important elements of the theoretical description were the existence of a number of spin reservoirs which were in quasi-equilibrium at different spin temperatures and the role of dipolar coupling in attaining equilibrium between these reservoirs.

Still on the theme of mismatched Hartmann-Hahn conditions, another model has been proposed to explain cross-polarization in the rotating frame involving a comparison of the rare spin rf field and the density of ^1H states.⁶⁰ The model of the density of states arising from the quantization of the dipolar energy provides a clear explanation of why only a small fraction of rare spins are polarized under mismatched conditions. In both treatments the inefficiency of cross-polarization under mismatched conditions is considered to be thermodynamic and not kinetic. When a rare spin is poorly polarized under mismatched Hartmann-Hahn conditions multiple contacts can be used to successively polarize it.⁶¹

A simple example of two spin reservoirs, and one which is discussed in the paper of Levitt *et al.*, is important in a later paper dealing with a two-stage feature in cross-polarization.⁶² Here, the authors use a depolarization sequence to show a rapid initial stage brought about by directly bonded H followed by a slower second stage when the $^{13}\text{CH}_n$ subsystems come to what they call quasi-equilibrium with the ^1H reservoir. The two reservoirs are then the isolated I-S spin pair and the remaining ^1H spins. It was noted that a turning point is seen in the variation in the intensity with depolarization time which occurs at an intensity equal to $1/(n + 1)$ of the initial value for a CH_n spin system. This was suggested as a reliable method for distinguishing between CH and CH_2 resonances in a ^{13}C NMR spectrum.

A simple modification to the basic spin-lock cross-polarization pulse sequence involving a depolarization step has been proposed,⁶³⁻⁶⁶ which can be used to distinguish between different phases in a material as well as providing an alternative to the dipolar dephasing experiment.⁶⁷ In this experiment the phase of the abundant spin rf field is shifted by 180° for a short period, typically up to $150\ \mu\text{s}$, at the end of a normal cross-polarization. During this period depolarization takes place with a time constant T_{CH} , allowing particular resonances or phases to be selected in the final spectrum. Thus for a

semicrystalline polymer the more mobile amorphous phase, which has a longer T_{CH} , can be selectively observed by nulling the crystalline component using the appropriate delay.⁶⁸ Similarly, it is possible to choose a depolarization period which will null each of the carbon resonances in a spectrum such as that of polypropene (see Fig. 3). A simple extension of the cross-depolarization method involving an additional repolarization can be used to null simultaneously methine and methylene carbons.⁶⁹ As a method for differentiating between methine and methylene carbons it suffers from the drawback that the time constants T_{CH} will vary from sample to sample and the ranges for the two types of groups overlap. Cross-polarization is normally used from the abundant spin to the rare spin to enhance the sensitivity but it is possible to carry out the polarization transfer in the reverse direction as a method of spectral assignment.^{70,71}

Although cross-polarization is an invaluable technique, care must be taken when trying to quantify the intensities in the resulting NMR spectrum. This is true even for homogeneous samples, but especially so for heterogeneous ones. For any sample the cross-polarization dynamics of a rare spin, such as ^{13}C , are defined by two time constants, T_{CH} and $T_{1\rho}$,⁷² with T_{CH} depending on the dipolar coupling between the rare and abundant spin. When the sample is homogeneous there will be a common $T_{1\rho}$ leaving only the questions, how long should the contact time be to ensure that for all carbons it is $5 * T_{CH}$, and is this attainable?⁷³

Quantifying the intensities in a heterogeneous material is, in contrast, complex. At one extreme there may be a component which is so mobile that the dipolar couplings are effectively averaged to zero, making cross-polarization totally useless. Little can be done in these circumstances except to try a lower temperature to freeze the mobile component or use single-pulse excitation. Less marked differences in T_2^* can also lead to distortions because of decay of the magnetization during the preparation pulse,⁷⁴ only in this case it is the rigid phase which will be underestimated. This effect will be most marked when a long ^1H preparation pulse is used. If the components have similar T_2^* but differ in $T_{1\rho}$ it is possible to quantify the results providing the cross-polarization dynamics are known.⁷⁵ To some extent the problems of differing $T_{1\rho}$ can be overcome by using a multiple cross-polarization method which seeks to maximize the contact time to fulfil the $5 * T_{CH}$ condition but minimize the $T_{1\rho}$ decay during the process.^{76,77} At best this increases the effectiveness of the cross-polarization by a bond length or so and is not a real answer to the problems of determining quantitative results.

Two possible advantages of the nuclear solid effect are that it can be used when the $T_{1\rho}$ is short and it is not influenced by magic-angle spinning, as is the spin-lock cross-polarization. Like the spin-lock method the maximum enhancement is a factor of γ_I/γ_S . To generate the nuclear solid effect the

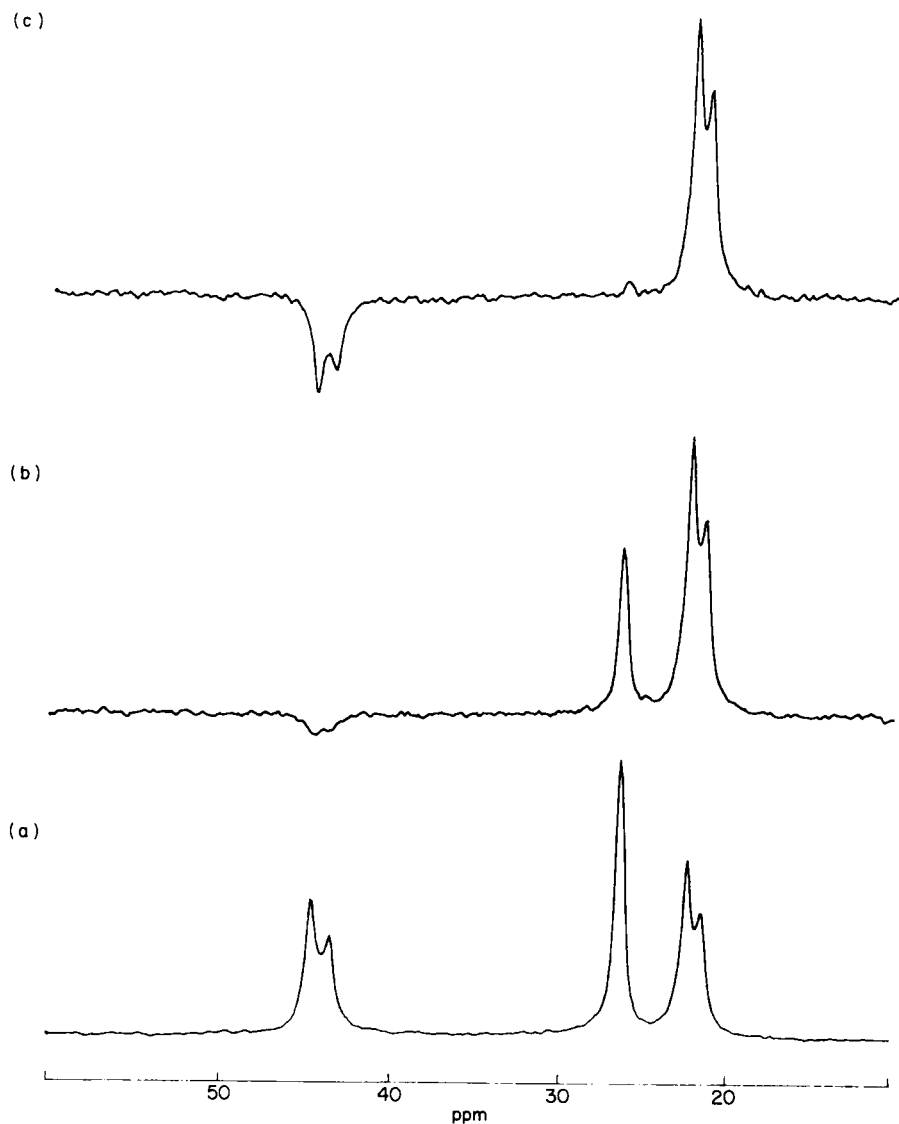


Fig. 3. Cross-depolarization of a highly crystalline polypropylene (a) showing the selective nulling of the (b) methine and (c) methylene carbon resonances.