OFFICE OF NAVAL RESEARCH

Contract N00014-91-J-1475

Technical Report No. 4

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

by

J. F. Haw

In Press

Analytical Chemistry

Department of Chemistry
Texas A&M University
College Station, TX 77843

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A review of Nuclear Magnetic Resonance Spectroscopy in the period 4/90 - 12/91 with 684 references.
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Nuclear Magnetic Resonance Spectroscopy

INTRODUCTION AND SCOPE

NMR continues to grow and find new applications. A maturing understanding of spin physics has allowed the development of sophisticated techniques for assigning resonances, determining internuclear distances, and averaging or exploiting orientation-dependent interactions. The recent and continuing revolution in biotechnology would not be possible without the increasingly elegant NMR methods that are used routinely to characterize the structure and dynamics of proteins and nucleic acids and their interactions with other biomolecules. NMR imaging has revolutionized diagnostic medicine and is beginning to have an impact on nondestructive materials testing. Spatially localized spectroscopy is revealing the chemistry of the life process noninvasively.

The few remaining obstacles to high-resolution NMR spectroscopy of solids are falling rapidly. Multidimensional solid-state NMR experiments are revealing the structures of catalysts. High-temperature catalytic reactions are being simulated in NMR probes so that reaction mechanisms may be elucidated. NMR studies of high-Tc superconductors have been underway in a number of laboratories since shortly after the discovery of the prototypical materials. NMR spectroscopy has proven itself to be exceptionally adaptable to new problem areas. A good example of this was recently provided by Yannoni who accurately measured the bond distances in Ca months before the first crystal structure of a fullerene derivative was determined.

NMR spectroscopy continues to be invaluable as a routine technique for the study of structure and dynamics of organic and inorganic compounds. A significant fraction of the articles in the chemical literature mentions data obtained by NMR spectroscopy; if only in passing; and most chemists readily appreciate why Richard Ernst was awarded the Nobel Prize in chemistry for his contributions to NMR spectroscopy.

Books

A number of books on NMR spectroscopy have either been published or caught the eye of other reviewers in the past 20 months. In many cases, it was easier to find a book review in the Journal of the American Chemical Society, Journal of Magnetic Resonance, or some other publication than to get access to the book itself. Making a virtue of necessity, I have cited both the books and their respective reviews. There were quite a few additions to numbered series (A1-A10). Marshall published a new book on the Fourier transform (A11). Slichter published a third edition of Principles of Magnetic Resonance.
CONCEPTS IN MAGNETIC RESONANCE

A positive development in the NMR literature was the creation of the journal "Concepts in Magnetic Resonance" which is subtitled "An Education Quarterly". Each issue publishes three or four tutorials on various aspects of NMR spectroscopy. The level is variable, but is generally well suited to a second-year student specializing in NMR spectroscopy.

Some of the articles which caught my eye included treatments of density matrices (B1, B2), instrumentation (B3-B6), CRAMPS (B7), shaped pulses (B8), imaging (B9), and chemical shift anisotropy (B10).

INSTRUMENTATION

The best way to learn of new instrumental developments in NMR spectroscopy is to attend the annual Experimental NMR Conference (ENC) and to read the journals Magnetic Resonance Chemistry and Magnets and Measurement. These are the primary sources of information on the latest instrumental developments.

Two improvements in sample tubes for high-pressure solution NMR spectroscopy have been described (C1, C2).

One of the most important recent advances in solid-state NMR spectroscopy was the development of double rotation (DOR) and dynamic-angle spinning (DAS) for high-resolution studies of noninteger quadrupole nuclei. These techniques are extremely demanding on the design of the spinning system. Pines and co-workers have described designs of DOR (C3) and DAS (C4) probes and their applications to selected problems (see sections on solids). Another spinning system suitable for DAS studies has also been described (C5). Yan-ni and co-workers described the design of a magic-angle spinning (MAS) probe that works at temperatures down to 5 K and used it to study carbocations at near-liquid-helium temperatures (C6, C7). Stebbins has reviewed high-temperature solid-state NMR spectroscopy (C8). Temperatures over 1000 K have been achieved with a laser heating system (C9), and more conventional high-temperature probe designs have also been reported (C10, C11). Inductive heating has also been demonstrated as a method for achieving very high temperatures (C12). An apparatus for achieving temperature jumps in a short time has also been reported (C13).

Accurate measurement of sample temperatures in NMR spectroscopy can be a vexing problem. Refinements in ratio pyrometry have been reported that seem applicable to very high temperatures (C14, C15). Chemical shift thermometry for MAS NMR spectroscopy and its application to measuring temperature gradients have received attention (C16-C18).

Low-temperature probe designs for dilution refrigerator (C19) and matrix isolation experiments were also described (C20).

A spinning speed controller for MAS experiments was described (C21) and several other texts were published and reviewed (A13-A17). Two books discussed biological applications (A18, A19). Others dealt with imaging (A20), polymer microstructure (A21), and ^3P (A22). Farrar published a second edition of his text "Introduction to Pulse NMR Spectroscopy" (A23) and the first volume of this treatment on density matrices (A24).

DATA PROCESSING, CALCULATIONS, AND SIMULATIONS

The data processing demands of modern NMR experiments continue to grow as a result of multidimensional spectroscopy, computationally-intensive alternatives to Fourier transformation, distance-geometry calculations from NOE data, etc.

This has been reflected in two trends in data processing hardware. Spectrometer vendors are starting to move away from in-house data systems to generic interfaces that connect to commercial high-performance workstations. Secondly, data processing is increasingly performed off-line. Indeed, several

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fairly sophisticated NMR data processing packages are available that run on PCs and McIntosh computers. As NMR spectroscopists begin to make use of recent advances in computational chemistry, techniques such as molecular mechanics and ab initio calculations will be integrated with experimental results. This section reviews recent developments in data processing and other computer-intensive reports including spectral simulation, interpretation, and chemical shift calculations.

NMR data processing was reviewed in detail by Hoffman and Levy (D1). Several parts of an introductory review on the Fourier transform have appeared in Journal of Chemical Education (D2–D4). Improvements in multidimensional FT data processing have also been discussed (D5, D6). Both linear prediction and maximum entropy methods have been explored as alternatives to Fourier transformation, and these methods have been reviewed (D7). Many workers regard the improvements in resolution and sensitivity provided by maximum entropy to be purely cosmetic. Jones and Hore have critiqued this method (D8, D9). Several improvements in linear prediction methods have been reported (D10, D11). Even standard nonlinear least squares has been considered as an alternative to Fourier transformation (D12). If the FT is used (as it still is in almost all cases), the resulting spectrum requires phase correction; and new algorithms for doing this automatically have been reported (D13, D14).

Computer methods are being used for structural elucidation (D15) including the application of neural networks (D16) and graph theory (D17, D18). Chemical shifts have been analyzed or predicted using structure–property relationships or other methods (D19–D30). First-principles calculation of chemical shifts have been carried out using ab initio or other molecular orbital methods (D31–D38).

Several unrelated computer-intensive studies that also deserve citation include the following. A statistical method for correcting for finite spinning speeds in magic-angle-spinning spectra was reported (D39). A procedure for interactive product-operator calculations was described (D40). Ernst has discussed computer-optimized TOSCY experiments (D41). Finally, a method to evaluate the octane number of gasoline from $^1H$ spectra was reported (D42).

Relaxation is at least an incidental issue in many of the papers cited in other sections of this review. Several stand-out papers dealing mainly with relaxation are cited here. Anet and co-workers have shown that there can be an antisymmetric component of the shielding tensor that can, under special circumstances, result in the surprising observation of $T_2 > T_1$ (E1). Interesting relaxation effects in solids were reported (E2–E5). Farrr has been exploring differential line broadening and other relaxation phenomena in solution (E6–E8), and related ideas have been applied to macromolecules (E9) and membrane structure (E10).

Several unrelated relaxation studies also caught my eye. Relaxation rate matrix analysis was discussed for interproton distance determination (E11), $T_2$ processes in porous rocks were studied (E12), $T_1$ was used to probe surface viscosity (E13), and field-cycling relaxation spectroscopy was used to study protein backbone fluctuations (E14). Other contributions relating to relaxation theory included a treatment of relaxation under continuous rf fields (E15) and solutions of the Bloch equations in the linear response approximation (E16).

Magnetic resonance pulse sequences were once composed nearly exclusively of rectangular pulses. Advances in rf electronics and theoretical methods for obtaining shaped pulses tailored for specific purposes have led to a continuum of designer pulse sequences. Shaped pulses can be designed using a variety of methods including average Hamiltonian theory and iterative numerical simulations. Gezelter and Freeman have recently reported the use of neural networks simulated on a serial computer for the design of shaped pulses (F1). The early results are very encouraging. Shaped pulses are commonly used for selective excitation (F2, F3).

Molecular hydrogen exists in two isomers with a total spin of 1 (ortho hydrogen) or 0 (para hydrogen). In 1987 Weitkamp proposed and later demonstrated that very large enhancements in $^1H$ signal intensities could be obtained by synthetically incorporating hydrogen enriched in the para...
MULTIDIMENSIONAL NMR SPECTROSCOPY

Multidimensional NMR spectroscopy used to be a fancy way of saying 2-D NMR spectroscopy. In the last several years it has come to include 3- and 4-D NMR spectroscopy. Just as a 2-D experiment involves an evolution period and a detection period, a 3-D experiment involves two evolution periods prior to detection. The three time periods correspond (after Fourier transformation) to the three frequency axes. The development of higher-dimensional experiments is largely motivated by the application of NMR spectroscopy to increasingly more complicated problems in biological chemistry involving molecules of ever higher molecular weight. The improved resolution afforded by multidimensional filtering has allowed NMR structures to be determined for proteins of 150 residues or greater. Applications to protein structure determination have been covered in two recent reviews (G1, G2). The use of 2-D NMR spectroscopy to study chemical exchange kinetics has also been reviewed (G3). There were a number of reports of applying 3-D (G4-G11) and 4-D (G12-G18) NMR spectroscopy to proteins as well as applications of multidimensional NMR spectroscopy to nucleic acids (G16-G19). 2-D NMR spectroscopy was applied to paramagnetic molecules (G20) and at high pressure to study phospholipid vesicles (G21). An improved method for 2-D data collection was also proposed (G22).

BIOMOLECULES IN SOLUTION

There was a large number of applications of NMR to proteins, nucleic acids, and other biomolecules in solution. In a review article such as this, one cannot hope to do justice to this large and diverse field. I have attempted to cite representative work to highlight trends rather than provide a comprehensive listing of citations.

SYNTHETIC POLYMERS IN SOLUTION

This field has reached a high level of maturity. $^{13}$C NMR analysis of polymers was recently reviewed (I1). $^{31}$P analysis has been applied to Naion (I2). The chemistry of polyphosphazenes and related materials has been studied (I3-I5). Many studies have dealt with microstructures (I6-I10) or conformation (I11, I12). 2-D NMR spectroscopy was used to probe polymer-polymer interactions (I13). A $^{13}$C study of a soluble polyacetylene was reported (I14).

INORGANIC COMPOUNDS IN SOLUTION

One of the more interesting applications of NMR spectroscopy in recent years was the proposal by Hamilton and Crabtree that $^{13}$C $T_2$ measurements could be used to distinguish between classical and nonclassical transition-metal hydrides. Halpern and co-workers recently published a de-
Some recent developments in NMR analysis of solids have been reviewed by Chmelka and Fines (K1). One of the more interesting new experiments has been Tyko’s development of zero-field NMR spectroscopy in high field (K2, K3). Several approaches for the study of dynamics by multidimensional spectroscopy or line shape analysis have been reported (K4–K7). An anomalous effect of MAS speed on chemical shifts of cuprous halides has been interpreted as due to the Lorentz force (K8). Thankfully, this effect is restricted to ionic conductors.

**Proton and Fluorine Spectroscopy.** The spectroscopy of abundant spins in solids (usually \(^1\)H or \(^19\)F) is often dominated by strong homonuclear dipolar couplings. Progress continues to be made in coherent averaging by multiple pulse sequences and/or high speed MAS. Some of the most important applications of \(^1\)H NMR analysis to solids are in the area of catalysis. Protons are typically chemically dilute on oxide surfaces, and MAS at modest speeds usually suffices for high resolution. Thus, \(^1\)H studies of solid catalysts are reviewed in the Adsorption Phenomena and Catalysis section.

**Distance Measurements.** There has been a renaissance in the use of dipolar couplings to determine internuclear distances. These couplings are inversely related to the third power of the separation. Although nonspinning techniques continue to be useful (K19), there have been several breakthroughs that have allowed information about dipolar couplings to be preserved in high-resolution spectra obtained with modest speeds usually suffices for high resolution. Thus, \(^1\)H studies of solid catalysts are reviewed in the Adsorption Phenomena and Catalysis section.

**SOLIDS IN GENERAL**

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PAR105
SEN03 1 Chemical Shift Anisotropy. There is a lot of interest in further developing methods for recovering CSA data from high
SEN08 6 resolution MAS spectra. A variety of strategies for doing this
SEN11 9 were proposed or refined during the period of the review
SEN19 17 (K49–K50). Chemical shift tensors were measured using
SEN17 8 single-crystal methods (K51) and in the presence of dipolar
SEN17 15 couplings (K52). Refinements in the TOSS experiments for
SEN17 16 sideband suppression were also reported (K53–K55).

PAR106
SEN03 1 Coupling and Decoupling. Scalar coupling is usually less
SEN06 7 important in solid-state vs solution-state NMR as a result of
SEN09 14 the lower resolution, and in the case of scalar coupling to 1H,
SEN12 14 the need to remove dipolar couplings. J couplings can be
SEN15 4 important in 31P MAS spectra and for many inorganic compo-
SEN15 8 unds. In the case of highly mobile systems such as weakly-
SEN17 9 adsorbed molecules on catalysts, plastic crystals, inclusion
SEN19 16 complexes, or elastomers, the NMR properties may be in-
SEN19 22 intermediate between solid-like and solution-like, and even J
SEN19 26 couplings to 1H may be observed. Several articles focused on
SEN19 30 J coupling during the period of the review (K56–K60). Im-
SEN19 34 proved strategies for 1H dipolar decoupling in 13C MAS NMR
SEN19 37 were also proposed (K63–K65).

PAR111
SEN03 1 Quadrupoles. The development of DOR and DAS was
SEN09 12 described above. Several applications of DOR are cited in the
SEN10 10 section on Adsorption Phenomena and Catalysis. Pines has
SEN15 16 described pure adsorption phase DAS (K66). Most experi-
SEN15 18 ments on quadrupoles used MAS or variable-angle spinning
SEN18 17 (VAS) (K87–K89). Several developments in 2H spectroscopy
SEN21 18 were reported (K76–K79). The effects of dipolar coupling to
SEN21 25 I = 1 nuclei on the spectrum of spin-1/2 nuclei were discussed
SEN24 20 (K80–K82). NQR with a dc SQUID was developed (K83).

PAR114
SEN02 1 ADSORPTION PHENOMENA AND CATALYSIS
SEN03 1

SEN08 2 The application of NMR methods to the study of catalysts
SEN12 5 and adsorbed species continues to grow. At first glance, NMR
SEN15 10 spectroscopy might seem inappropriate to the study of surfaces
SEN19 23 due to its low inherent sensitivity relative to traditional forms
SEN22 26 of surface spectroscopy. Indeed, NMR studies of two-di-
SEN25 28 mensional surfaces have been few in number, and there has
SEN25 30 been little effort to connect NMR studies to the single-crys-
SEN27 32 tal-face world of UHV surface science. The virtue of NMR
SEN29 34 spectroscopy is that it is frequently applicable to the actual
SEN31 37 working catalyst with remarkable sensitivity. Amorphous
SEN34 40 oxide and zeolite catalysts typically have surface areas mea-
SEN37 43 sured in tens or hundreds of square meters per gram. Since
SEN40 46 radio waves readily penetrate through such catalysts, the
SEN43 49 NMR experiment integrates over a considerable surface area.
SEN46 52 NMR spectroscopy is now being used in situ in mode to
SEN49 55 investigate the reaction mechanisms of various catalytic
SEN52 58 processes.

PAR117
SEN03 1 NMR analysis has also made remarkable contributions to
SEN09 14 the understanding of framework structures of zeolites and
SEN12 18 aluminum phosphate molecular sieves. Although most such
SEN15 21 studies involve MAS, DOR was quickly applied to sharpen
SEN18 22 the resonances of quadrupolar nuclei in catalysts.

PAR120
SEN03 1 This section also reviews NMR studies of surface-bound
SEN06 1 alkylsilanes as well as clathrates and inclusion complexes.

PAR123
SEN03 1 Reviews. Slichter and co-workers have reviewed NMR
SEN09 14 techniques for the study of supported transition-metal cata-
SEN12 17 lysts (L1). Frye and co-workers reviewed the use of NMR
SEN15 19 spectroscopy to determine zeolite lattice structure (L2).
SEN17 28 Klinowski reviewed molecular sieve catalysts (L3, L4). 1H
SEN19 30 MAS studies were reviewed by Mastikhin and co-workers (L5).

PAR126
SEN03 1 1H Studies. Magic-angle spinning alone generally suffices
SEN07 14 for reasonable resolution in studies of catalysts, and the re-
SEN10 22 sidual line width may simply reflect heterogeneity (L6). Other
SEN12 25 1H studies dealt with acid sites and acidity (L7–L11), silanol
SEN15 28 groups (L12), and adsorbates (L13, L14). In a similar vein,
SEN18 31 29F MAS NMR spectroscopy has also been applied to catalysts
SEN21 34 (L15).

PAR129
SEN03 1 Zeolite Frameworks. The application of standard 29Si
SEN08 7 and/or 27Al MAS NMR spectroscopy to the study of frame-
SEN11 10 works is a routine characterization method (L16–L24). The
SEN14 13 combination of NMR spectroscopy and X-ray powder dif-
SEN17 15 fraction can be fruitful (L25–L27). Frye and co-workers have
SEN19 19 been determining bonding connectivities in zeolites by 2-D
SEN22 22 solid-state experiments (L28–L33). Gallium is sometimes
SEN25 28 substituted for aluminum in zeolite synthesis, and 71Ga MAS
SEN28 31 NMR spectroscopy has been explored in their study (L34,
SEN31 34 L35).

PAR132
SEN03 1 Organic Adsorbates. 13C MAS NMR spectroscopy has
SEN06 7 been used to characterize reaction products on catalysts.
sometimes after progressive off-line heating (L30-L41). Haw
and co-workers have studied catalytic reaction mechanisms
with an in situ variable-temperature approach. Processes
studied include reactions of unsaturated hydrocarbons
(142-144), cracking reactions (145), and methanol-to-gasoline
chemistry (146, 147). MAS NMR spectroscopy has also been
used to study templates (148-152) and the effects of adsor-
bates on 29Si spectra of zeolites (153). Several studies ad-
dressed coke formation on catalysts (154-158).

Inorganic Adsorbates. Inorganic clusters and organo-
motivate other such investigations, low solubility, conforms-
to the study of clathrates (159-160). Another very promising
new approach those of analogous studies in solutions. One reason
is the lack of conformational averaging in typical
powder samples. Bryant has shown that the resolution ob-
tained in 13C CP/MAS spectra of lyophilized lysozyme can
be improved by partial hydration (161). Solid-state studies of
biomolecules are motivated by reasons similar to those that
motivate other such investigations, low solubility, conformational
change upon dissolution, etc. The resolution problem
is frequently dealt with by labeling, or sometimes double
labeling, the structural feature of interest. The development
of MAS experiments that preserve dipolar couplings has affor-
ded the opportunity for doing distance determinations that
cannot conveniently be done crystallographically for a lack
of suitable crystals. One such method is rotational resonance,
which is applicable for measuring internuclear distances from
homonuclear dipolar couplings. Griffin and co-workers have
used rotational resonance to identify the configuration of
retinal in bacteriorhodopsin (162). Another very promising
high-resolution technique for distance determinations is the
REDOR experiment. Schaefer and co-workers have been
promising
promoted
silica or noble metals. NMR spectroscopy has also
served as a probe for adsorbates. Inorganic clusters and organo-
molecular catalysts (163-166). A number of problems in
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of 13C CP/MAS spectra of lyophilized lysozyme can
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retinal in bacteriorhodopsin (162). Another very promising
high-resolution technique for distance determinations is the
REDOR experiment. Schaefer and co-workers have used this technique to detect cross-links
Solid-state NMR spectroscopy has been applied to
study dynamics in biomolecules including DNA duplexes,
proteins (M4, M5), a DNA intercalation complex (M6),
and model cell membranes (M10).

Principal components of chemical shift tensors in biomolecules
have been measured in an effort to obtain more structural
information than that attained by isotropic shifts alone (M11,
M12).

Other work in solid-state NMR spectroscopy of biomolecules
has been covered in reviews on DNA (M13) and proteins
(M14).

SOLID POLYMERS

Solid state NMR techniques such as MAS, wide-line 2H,
and relaxation studies are widely applied to characterize the
morphology and dynamics of polymers. The structure of the
polymer is typically known, but this can be the main issue
in studies of resins and cross-linking.

Studies of local motions in polymers have been reviewed
(N1). Harris has observed nuclear Overhauser enhancements
in polymer films (N2). Tonelli has studied polymer chains
confined to channels in clathrates (N3, N4). Speiss has ad-
vanced the use of 2-D NMR spectroscopy to study ultraslow
chain motion (N5).

Selected applications of NMR spectroscopy to solid poly-
mers are probably most usefully cited on the basis of material
of several categories. There were a number of studies
which related solid-state NMR and X-ray crystallographic
data (O1-O9). Studies of stereochemical nonrigidity in solid
inorganic compounds have become almost as common as
analogous studies in solutions (O10-O16). A number of studies
have been directed at measuring chemical shift tensors and/or
indirect spin-spin coupling tensors in inorganic compounds
(O17-O23). Variable-temperature studies have probed mag-
netic properties (O24, O25), and an improvement in the res-
solution of spectra of paramagnetic lanthanide complexes has
been reported (O26). Phosphorus multiple bonds have been
classified (O27, O28). NMR analysis continues to be
applied to the study of phase transitions of various sorts
(O29-O31).

Several other studies of interest did not fit into any easily
contrived categories. The 29Si MAS spectrum of SiAl is very
sensitive to Ag+ diffusion over a wide temperature range (O22).

A single-crystal 23Na study of the sodide Na+cryptand
[2.2.2]-Na+ has been reported (O33). 195Hg MAS NMR
spectroscopy has been used to probe coordination number in
Hg(II) complexes (O34), and 27Al MAS has characterized
AlCl3-THF complexes (O35).

INORGANIC MATERIALS

Some of the more creative applications of NMR spectro-
cy to inorganic materials included Eckert's studies of
non-oxide glasses and related materials (P1-P10), Stebbins'
and silicates at extremes of temperature and pressure
(P11-P13), and the application of DAS and DOR to 19O
analysis of solid silicates (P14). MAS NMR analysis was also
applied to silicates and aluminates (P15-P20). Other classes
of materials investigated included semiconductors (P21-P23),
cermics (P24-P28), and inorganic polymers (P29-P33). Claya
and other layered materials were also studied (P34-P40).

High-resolution 27Al spectra of small particles of AF, were
FULLERENES

The discovery and isolation of C_{60} and a growing number of other fullerenes is probably the most interesting development in chemistry in recent memory, certainly since the discovery of high-T_c superconductors (see below). Early success in fullerene research was controlled to a large extent by access to materials, so it is not surprising that the first NMR papers on C_{60} came from groups at the IBM Almaden Research Center (Qi) and AT&T Bell Laboratories (Q2). Solid C_{60} undergoes rapid isotropic motion at room temperature that averages the 13C chemical shift anisotropy (Q1, Q3). This motion is quenched at 77 K, and it was possible to measure principal components of the 13C chemical shift tensor of 220, 156, and 40 ppm (Q1). These values compare favorably to a theoretical calculation (Q3). As mentioned in the Introduction and Scope, Yannoni and co-workers used the Carr-Purcell sequence to measure bond lengths in 13C-enriched C_{60} at 77 K (Q4). These values were 1.45 ± 0.015 and 1.40 ± 0.015 Å.

HIGH-T_c SUPERCONDUCTORS

NMR experiments are contributing to the understanding of magnetic properties of high transition temperature ceramic superconductors. Studies of the YBa$_2$Cu$_3$O$_y$ family were reviewed by Walstedt and Warren (R1). A number of superconductor materials have been investigated by $^{13}$Cu and/or $^{65}$Cu (R2-R7), $^{13}$C (R8-R11), $^{29}$Si (R12, R13), or $^{87}$Rb (R14-R16) spectroscopy. Relationships between theories of superconductivity and NMR experiments have also been explored (R17-R19).

GAS-PHASE NMR SPECTROSCOPY

NMR studies of gases are generally geared toward understanding the energetics of collisions. Gas-phase NMR studies published during the period covered by this review included studies related to conformational processes (S1, S2), nuclear shielding (S3-S5), and relaxation phenomena (S6-S8).

IMAGING, MICROSCOPY, AND DIFFUSION

NMR imaging has had a profound effect on clinical medicine, and it is having an effect on chemical problems involving spatial inhomogeneities. One of the most intriguing examples of this to catch my eye was the detection of chemical waves in the Mn$^{2+}$-catalyzed Belousov-Zhabotinsky reaction (T1). Clinical aspects of imaging and spatially-localized spectroscopy are outside the scope of this review, but the interested reader is referred to a good introductory article (T2). Some of the most common applications of NMR imaging in chemistry and engineering include diffusion of solvents in swollen polymers (T3-T5) and Cu and/or water in porous rock (T6-T8). In the limit of smaller sample sizes and high spatial resolution, NMR imaging is frequently referred to as NMR microscopy (T9-T11). Since microscopy can be performed in standard wide-bore (89-mm) magnets, it is likely to grow in popularity among chemists. Volume-localized spectroscopy is important for slice selection in vivo spectroscopy or other problems requiring selective excitation of a spatial region near the coil (T12-T14). This can be possible even for solids (T15-T17). Solid-state NMR imaging has been reviewed (T18), and several improvements or applications of the technique have been reported (T19-T26). In spite of the apparent difficulty of imaging a rotating solid, the advantages of line narrowing have motivated study (T27-T29). NQR imaging has also been reported (T30).

Field gradients are also used in NMR studies of diffusion, dating from the work of Stejskal and Tanner in the mid-60s. The availability of pulsed-field gradient coils has extended the range of this method. Several applications of diffusion methods were reported (T31-T36) and others were cited in the section on Adsorption Phenomena and Catalysis. The role of diffusion in imaging studies should not be neglected (T37, T38).
ACKNOWLEDGMENT

This work was supported by the Office of Naval Research (Grant No. N00014-88-K-0239) and by the National Science Foundation (Grant No. CHE-8918741). I thank Liz Porter for developing the software used for the bibliographic listings.

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SEN1516
SEN1519
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SEN1525
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SEN1534
SEN1537
SEN1540
SEN1543
SEN1546
SEN1549
SEN1552
SEN1555
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The number of words in this manuscript is 16934.

The manuscript type is R.

Running Heads

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Author Index Entries

Haw, J. F.

Text Page Size Estimate = 11.8 Pages

Graphic Page Size Estimate = 0.0 Pages

Total Page Size Estimate = 11.8 Pages

Note: Graphic Estimate Equals Zero