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Solid State NMR Spectroscopy

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Review Contents

Solid-state NMR spectroscopy (SSNMR), a powerful tool providing atomic-level structural information, has been continuously applied to almost all fields of natural science, from chemistry to biochemistry, materials science, geology, and physics. The recent applications of SSNMR in areas such as biosolids, heterogeneous catalysis, and nanotechnology have shown the promise of obtaining detailed information in these nonclassical systems. The wide range of SSNMR is indicated by the large number of publications (approximately 2600) reporting solid-state NMR spectroscopic results between 2008 and early 2010. Aside from reports of experiments touching a wide variety of specific questions, there have been reviews of the spectroscopy in general (*1*−*3*), on its use in polymeric and supramolecular systems (*4*−*6*), on its use in organic and inorganic multicomponent materials (*7*), and on its use in biomolecular systems (*8*−*10*). It is important to remember that ongoing review series such as the *Specialist Periodical Reports* and *Progress in Nuclear Magnetic Resonance Spectroscopy* often have reports that focus on solid-state NMR spectroscopy.

The development of SSNMR methodology has been a very active and exciting part of the field. The stream of technical developments results in the new methods for chemists and biochemists to address problems in a variety of areas. SSNMR has been especially useful in exploring the structures and dynamics of biosolids like membrane proteins and lipid bilayers. Such applications, in turn, promote the technical developments that uniquely apply to such systems. SSNMR has long been used in characterization of solid materials, surfaces, and catalysis systems, systems that are generally on the nanoscale. The application of SSNMR to pharmaceutically important solids is also a relatively new area of study. It is already providing insight into the relationship between solid drug polymorphic structure and the drug's efficacy.

First-principles calculation of NMR parameters has a long history in aiding assignment of solution-state spectra. In recent work, a similar synergy between calculation and SSNMR measurements has become apparent in the investigation of solid consisting of small organic solids, as well as in materials containing large biomolecules. The application of computational methods to the interpretation of SSNMR spectra of heavy atoms is another evolving trend. These tools can be traced to the ever-increased accessibility of powerful computers and the developments in quantum computational techniques.

The majority of nuclei in the periodic table contain an isotope that is NMR-active, and of those, most will have a quadrupolar nucleus. Thus, more and more studies that specifically address the nature of quadrupolar nuclei have been seen in the literature. The techniques for obtaining spectra of these nuclei are often technically challenging, but the unique information available from spectra of quadrupolar nuclei has spurred the developments in this area.

METHODOLOGY AND TECHNICAL DEVELOPMENTS

One concern in using solid-state NMR for analysis is quantification of species, specifically in cross-polarization/magic-angle-spinning (CP/MAS) experiments. Recently, nuclear spin relaxation compensation has been demonstrated to aid in quantification (*11*). In a related study, it has been shown that corrections for spin−echo and phase distortion can improve quantitation (*12*). An important study has demonstrated that quantification of a pharmaceutical formulation can be carried out with the CP/MAS technique (*13*). Similarly, quantitation of an amyloid-like fibril-forming model peptide has been demonstrated (*14*). Quantification requires clear identification of NMR lines for the various components. A technique has been reported that allows the separation of overlapped ^{13}C signals in a CP/MAS experiment based on differences in ^{1}H T_1 (*15*).

Addressing a major problem in the application of NMR to certain lossy samples, such as biological samples, has been the focus of several developments in probe design. In one study, the issue is addressed by the design and use of a cross-coil double-resonance solid-state NMR probe (*16*). In the second, the insertion of a strip shield (*17*) was found to enhance probe performance. To address certain problems related to performing SSNMR at ever-increasing fields, a low-E MAS probe has been reported that minimizes some aspects of problems arising from working at the higher frequencies (*18*). In analogy to solution-state NMR, where cryogenically cooled probes have enhanced detection, a design for a cryogenically cooled CP/MAS probe has been proposed (*19*, *20*). Such probes should improve signal-to-noise, a major limitation for SSNMR. Application of a multiple-receiver configuration for studies

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of RNA has demonstrated that this technique has some advantages in solid-state NMR (*21*).

Doing experiments under extreme conditions has been a challenge that has frequently been taken up by NMR spectroscopists. Increasing spinning speed in MAS experiments has continued to be an effort of probe designers. For example, there have been reports of stable magic angle spinning (MAS) at 65 kHz and higher (*22*). Another area of interest in solid-state NMR is working at temperatures well away from ambient conditions. A report has recently demonstrated that MAS experiments can be done at sample temperatures as low as 25 K (*23*). Of course, measuring temperature in the sample under MAS has always been difficult. Recently, the use of the temperature-dependent chemical shift of ^{79}Br in KBr for determining temperature under MAS conditions opens up the rather wide range from 20 to 320 K to exploration with MAS NMR (*24*).

Among the potentially useful developments in solid-state NMR spectroscopy is the indirect detection of otherwise difficult-to-observe nuclei. In the early days of solid-state NMR, several groups used indirect detection, but since the 1970s most rare spins have been detected directly. The modern indirect methods are possible because of the accessibility of high MAS rates and newly developed, sophisticated homo- and heteronuclear decoupling schemes. ^{1}H detection of ^{1}H−^{13}C correlations near the ^{14}N nuclei has been demonstrated (*25*). A 3D version of this experiment has also been reported (*26*). A recent review (*27*) surveys the indirect detection of ^{14}N in biological systems. The ^{1}H resonance has been used to detect quadrupolar nuclei indirectly, such as in the detection of the correlation of ^{1}H resonances with ^{23}Na (*28*). Indirect detection of scalar couplings under ultrahigh MAS has been demonstrated (*29*−*31*). To overcome large solvent signals that might appear in the ^{1}H detection of biosolid samples, a method of solvent suppression in solid-state NMR has been proposed (*32*).

A method using correlation between the chemical-shift anisotropy (CSA) pattern and sidebands for accurate measurement of shift parameters has been reported (*33*). ^{1}H CSA measurements of hydrogen-bonded functional group using fast MAS have also been presented (*34*). The chemical-shift tensor's orientation relative to bonding and molecular axes, important in determining the internuclear distance and dihedral angles in many systems, was measured under slow MAS conditions (*35*).

Recycle delays are critical factors in NMR experiments, often determining the rate of build-up of signal. A recent study has shown that the longitudinal relaxation of ^{13}C becomes much more effective (and hence the recycle delay can be shortened) by the use of band-selective pulses that rely on spin diffusion (*36*−*38*). In an alternative experimental design, pulse field gradient pulses were utilized in several solid-state MAS multidimensinoal experiments, allowing multiple experiments to be carried out in a single scan, thus saving time (*39*).

Another area of methodology important in solid-state NMR is the development of new schemes to enhance homonuclear decoupling (*40*−*42*) and heteronuclear decoupling (*43*). On a similar topic, dipolar recoupling continues to see some developments to improve the technique (*44*).

PHARMACEUTICAL CHEMISTRY

Solid-state NMR spectroscopy is a powerful tool widely applied to nearly all aspects of pharmaceutical chemistry: characterization of the active pharmaceutical ingredient (API), the drug products, and excipients in solid dispersions, as well as exploration of interactions between API and excipients in solid dispersions and between API and membrane proteins. A recent general review covers many of these topics (*45*). More specifically, five crystal forms of the asthma-therapy drug, terbutaline sulfate, have been characterized using ^{15}N and ^{13}C CP/MAS NMR (*46*). The high-speed MAS ^{1}H NMR and ^{1}H−^{13}C correlation spectra clearly indicated, for example, hydrogen bonding in the drug as formulated (*46*). The sensitivity of solid-state NMR to structural parameters provided the ability to specify polymorphism in three vitamin D compounds (*47*). The structural features of the L-enantiomer of *N*-benzoylphenylalanine were also analyzed with CP/MAS ^{13}C and ^{15}N NMR (*48*). In a study of troglitazone solid dispersions, the subtle differences in structure due to differences in recrystallization method were shown to be detectable by ^{13}C CP/MAS but not by powder X-ray diffraction (*49*).

Approximately 50% of solid pharmaceutical products are in the form of hydrochloride salts. Solid-state ^{35}Cl NMR spectroscopy has been used to study HCl in local anesthetic pharmaceuticals (*50*). The results distinguish polymorphic structures. The ^{35}Cl nucleus is an excellent probe of the environment, reporting not just on chemical shift but also on the local electric field gradient parameters.

SSNMR methods have been applied to the study of drug loading and release mechanisms (*51*, *52*). The interaction of the lipophilic drug, trifluoperazine (TFP), with dimyristoyl phosphatidylcholine (DMPC) was monitored using the ^{13}C CP/MAS NMR method at natural abundance. The results provided insight into the drug's mode of action and its absorption, distribution, and metabolism profile (*53*).

The structures of pharmaceutically significant steroids continued to be investigated using ^{13}C CP/MAS and high-speed MAS ^{1}H methods (*54*, *55*). SSNMR techniques, such as ^{1}H detected 2D solid-state ^{13}C−^{1}H and ^{15}N−^{1}H methods, were used to study the structures of biopharmaceutical samples such as aprotinin and insulin in various forms (*32*).

COMPUTATIONAL METHODS

The combination of first-principles computation with the solid-state NMR experiment is becoming a mainstay in solid-state analysis. In this protocol, experimental ^{13}C chemical shift anisotropies (CSA) are compared to the predicted CSA based on either X-ray crystal structures or on structures with optimized geometries. Density functional theory (DFT) methods seem to be extensively used to give insight into the subtle structural details of molecules, along with NMR measurements. Examples of this type of study include investigations of pharmaceutically important flavanoids (*56*, *57*) and of bilirubin (*58*). The weak hydrogen bonding in uracil and 4-cyano-4′-ethynylbiphenyl has been studied with the combination of experimental measurements and calculations of ^{1}H, ^{13}C, and ^{15}N chemical shifts (*59*). The DFT methods can be extended to account for the effects of temperature (*60*) and motion (*61*).

The hydrogen-bond-mediated *J*-couplings $^{2h}J_{NN}$ across intra- or intermolecular N−H···N hydrogen bonds in two 6-aminofulvene-1-aldimine derivatives, which had been previously measured, were verified by DFT calculations (*62*).

Calculations of chemical shielding may not only be applied to light nuclei such as ^{13}C, ^{15}N, and ^{1}H but also to heavier nuclei such as ^{29}Si (*63*), ^{33}S (*64*), ^{43}Ca (*65*), ^{51}V (*66*), ^{95}Mo (*67*), and ^{207}Pb (*68*). For many of these nuclei, it has been found necessary to include relativistic spin−orbital effects to achieve qualitative agreement between calculations and experiments (*68*).

QUADRUPOLAR AND HEAVY NUCLEI

Quadrupolar nuclei ($I > {}^1/_2$) have the additional, generally dominating influence of the coupling of the nucleus to the electric field gradient at the site of the nucleus. As a result, in the solid state, this interaction is frequently the parameter of interest in many studies. Its effect on the spectrum depends on the magnitude of the electric field gradient and on the nuclear quadrupolar coupling constant. Measurement of the effects on the spectrum is, then, a means to determine the electric field gradient. Detection is often difficult because of the very broad resonance lines. With the ever-expanding use of ultrahigh magnetic fields, more quadrupolar nuclei are becoming accessible to study with NMR spectroscopy, as the examples below demonstrate.

^{7}Li MAS NMR was used to investigate the surface layers on $LiNi_{1/2}Mn_{1/2}O_2$ cathode material for Li-ion batteries (*69*). The formation of a Li^+ inner-sphere complex on the surface of lepidocrocite was confirmed by ^{7}Li MAS NMR (*70*). Because of the high symmetry of the choline headgroup in phosphotidylcholine, the ^{14}N quadrupole coupling is significantly reduced, which allows the use ^{14}N solid-state NMR spectroscopy to study the aligned phospholipid bilayers and oligomerization of membrane associated peptides (*71*). A complete review of ^{17}O NMR spectroscopy, including experimental methods and their applications, has appeared (*72*). The ^{17}O MAS spectra of alanine tripeptides (obtained at ultrahigh field) showed that differences between parallel and antiparallel β-sheet structures can be discerned with NMR (*73*). In another study with the same nucleus, the ^{17}O MAS spectra are shown to be sensitive to the local molecular structure of the β-polymorph of glycine (*74*). Several groups have demonstrated the feasibility of obtaining ^{17}O quadrupole constants and CSA tensor elements experimentally and predicting them with DFT calculations (*75*−*77*). Because of its remarkable sensitivity, small CSA contributions, and well-defined quadrupole constant and asymmetry parameter, $Na_2MgEDTA{\cdot}4H_2O$ was proposed as a reference compound for static and MAS ^{25}Mg NMR (*78*). The disordered binding of Mg^{2+} to the DNA-repair protein, apurinic/apyrimidic endonuclease 1, was discovered and characterized using low-temperature ^{25}Mg NMR (*79*). With the use of the wideband-uniform-rate-smooth-truncation (WURST) sequence, population transfer from the satellite transitions to the central transition made it possible to measure the ^{33}S spectrum of the natural-abundance complex, $(CH_3NH_3)_2WS_4$, to obtain the parameters of all three overlapped resonances (*80*). The availability of ultrahigh magnetic fields allows one to dramatically improve the resolution of ^{35}Cl resonances, as is shown by recently reported spectra of organic hydrochloride salts at 18.8 T (*81*) and halide ionic liquids at 21.1 T (*82*). One of the more difficult nuclei to analyze has been ^{43}Ca. Solid-state ^{43}Ca NMR spectra of six natural-abundance crystalline calcium phosphates have been obtained (*83*). The predicted isotropic chemical shifts determined with DFT calculations were found to agree well with experimental results, and the comparison of experimental and calculated results shows a clear dependence of the isotropic chemical shift on the bond distance, Ca−O, in these materials. ^{45}Sc NMR spectra of the silicide Sc_2RuSi_2, acquired at 9.4 and 11.9 T, reveal two distinct scandium sites that are predicted by DFT calculations (*84*). Potential applications of solid-state ^{51}V NMR to vanadia systems with paramagnetic centers in catalytic systems have been reviewed (*85*). Studies of solid-state ^{51}V NMR and DFT calculations were applied to eight-coordinate nonoxo vanadium hydroxyimino propioate acetate complexes in oxidized amavadin (*86*) and three *cis*-dioxovanadium(V) complexes (*87*). Quantum mechanic studies predict that the active-site geometries of vanadium bromoperoxidase (VBPO) and vanadium chloroperoxidase (VCPO) should be very similar. The experimental solid-state ^{51}V NMR chemical shifts in these two materials, however, are different, indicating how ^{51}V can be a very sensitive probe for exploring the active-site in these enzyme systems (*88*). Solid-state ^{67}Zn NMR spectroscopy was used to characterize H_2O-bound mononuclear tetrahedral Zn^{2+} (*89*). The NMR results provide insight into the mechanisms of action for Zn metalloproteins. The solid-state ^{53}Cr NMR spectra of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) salts have been obtained by a stepped-frequency quadrupolar Carr−Purcell Meiboom−Gill (QCPMG) method at high applied magnetic field strengths of 11.75 and 18.8 T (*90*). The ultrahigh-field ^{59}Co solid-state NMR spectrum was obtained for $Co(C_8H_{13})(C_4H_6)$, demonstrating the potential use of the quadrupolar information for studying processes such as the formation of 1,2-polybutadiene (*91*). The structural differences of amorphous and crystalline germanium oxides were measured with ultrahigh-field ^{73}Ge NMR, with comparison to DFT calculations on potential structures (*92*). In a similar example, solid-state ^{89}Y NMR and DFT calculations were used to probe the nature of the Y coordination environment in $Y_2Ti_{2-x}Sn_xO_7$ (*93*). Solid-state ^{91}Zr NMR, typically done at ultrahigh fields, was used in the investigation of the metal environments in zirconium halides (*94*) and in zirconium phosphates (*95*). Solid-state ^{95}Mo NMR spectroscopy has been applied to determine the local structure of the Mo species in xMo/HZSM-5 zeolite catalysts (*96*) and in a series of molybdate salts at ultrahigh fields (*97*). In the zeolite, the NMR results were interpreted in terms of the structure of the active Mo center for the methane dehydroaromatization (MDA) reaction; in the latter study, the NMR results were interpreted in terms of the distortion of the MoO_4^{2-} anion from T_d symmetry. A review of ^{103}Rh NMR spectroscopy, showing some of the first reported solid-state ^{103}Rh NMR spectra, was recently published (*98*). Again, at ultrahigh magnetic fields, solid-state ^{115}In NMR spectra of four different coordination

complexes, indium acetylacetonate, tris(tropolonato) indium, indium triiodide, bis(tris(4-methoxyphenyl)phosphine oxide), and indium trichloride tris(2,4,6-trimethoxyphenyl)phosphine, were acquired (*99*). These experiments offer the possibility of ^{115}In NMR as a means for characterization of solids materials that contain indium. The first detailed ^{209}Bi NMR spectroscopic investigation of bismuth-containing materials has been carried out using a frequency-stepping method (*100*). Frequency-stepping is essential due to the extremely broad resonance lines. The local Ba environment in β-barium borate has been probed with static ^{135}Ba and ^{137}Ba solid-state NMR spectroscopy at an ultrahigh magnetic field (*101*). The ^{135}Ba and ^{137}Ba spectra are completely dominated by second-order quadrupolar interactions.

BIOSOLIDS

Three general reviews about biomolecular solid-state NMR have appeared (*9*, *102*, *103*). Reviews on more specific subjects such as the characterization of the structure and dynamics of paramagnetic proteins (*104*), deuteron NMR studies of the G-protein receptor (*105*), NMR structure determinations of antimicrobial peptides (*106*, *107*) and amyloid proteins (*108*), and a review of measurement and interpretation of chemical shift anisotropy related to protein dynamics (*109*) have also been published recently.

A challenging problem in biomolecular solid-state NMR is to prepare high-quality crystalline and enriched samples that can be used for analysis. Techniques of isotropic labeling of proteins to yield sufficient material for NMR structure determination have been described (*110*, *111*). A labeling strategy applied to aligned proteins has been discussed (*112*, *113*).

Chemical-shift assignment is the first step in solid-state biomolecular NMR studies. ^{13}C and ^{15}N chemical shift assignments for a number of proteins have been reported (*114*−*116*). With more attention focused on biomolecular systems of high molecular weight, the strategy for chemical shift assignment becomes more complex and requires a careful consideration of the methods used (*117*).

Labeling often helps to simplify spectra of these complex molecules. A ^{19}F solid-state NMR study of a selectively ^{19}F-labeled protein has been reported (*118*). A strategy of selectively ^{13}C- and ^{15}N-labeling thioredoxin allowed the authors to simplify correlation spectra, structure analysis, and dynamics studies (*119*, *120*).

In some cases, using sophisticated pulse sequences allows one to assign resonances, in particular by comparison of the results of different NMR experiments. The ^{13}C−^{13}C double-quantum solid-state NMR method was used to investigate molecular dynamics of solid ubiquitin (*121*). A modified centerband-only detection-of-exchange (CODEX) NMR experiment on ^{15}N and ^{1}H was used to study slow motions of the SH3 domain of chicken β-spectrin (*122*). A similarity in side-chain dynamics of the SH3 domain of β-spectrin between solution and solid state was observed from NMR relaxation measurements (*123*). The backbone motion of a microcrystalline protein has been investigated via the measurement of ^{15}N T_1 relaxation times at two different magnetic fields (*124*). The authors separated out the ^{1}H−^{15}N dipole and ^{15}N CSA cross relaxation rates. The analysis of ^{13}C chemical shifts allowed other investigators to identify the unfolded and native helical secondary structure of the protein HP35 created by rapid freeze-quenching from a thermally unfolded state (*125*). Solid-state NMR spectroscopy has continued to play an important role in structural studies of antimicrobial peptides (*126*, *127*), amyloids (*128*−*131*), and influenza virus proteins (*132*−*134*).

CATALYSIS AND SURFACES

Recent reviews on applications of solid-state NMR spectroscopy in catalysis and surface are listed in the following. High-resolution solid-state NMR spectroscopy was applied to understand the nature of active sites on well-defined heterogeneous catalysts prepared by surface organometallic chemistry (*135*). Many aspects of immobilized catalyst systems, in which one or two metal complexes are bound to oxide supports via bifunctional phosphine linkers, was summarized (*136*). The solid-state ^{51}V NMR chemical shifts for paramagnetic solids as heterogeneous catalysts have been compiled (*85*). The basicity of zeolite catalysts has been shown to be characterized by solid-state NMR spectroscopy with the use of various probe molecules (*137*). In situ ^{13}C MAS NMR investigation of the reactivity of surface alkoxy species in acidic zeolite catalysts has been summarized (*138*). Applications of in situ flow MAS NMR spectroscopy in heterogeneous catalysis have also been reviewed (*139*).

Most of the research in this area has, still, been focusing on structural characterization of heterogeneous catalysts and surfaces, for example, Sigma-2 and ZSM-12 zeolites (*140*), dealuminated H−Y zeolites (*141*), low-silica X zeolites (*142*), microporous aluminophosphate AlPO4-40 (*143*) and silicoaluminophosphate SAPO-34 (*144*), mesoporous Al-MCM-48 materials (*145*), functionalized mesoporous SBA-1 silicas (*146*), alkylidene-based organometallic complexes immobilized on amorphous silica surfaces (*147*), surfactant-templated layered silicates (*148*), rutheniumdoped mesoporous silica (*149*), silicate glasses (*150*), layered niobates (*151*), 12-tungstophosphoric acid ($AlPW_{12}O_{40}$) (*152*), and heteropoly acids supported on silicalite-1 zeolite (*153*). Solid-state NMR investigations have also monitored the formation or crystallization processes of some heterogeneous catalysts, for example, $AlPO_4$-5 molecular sieve (*154*), zeolite ZSM-5 (*155*), sodium aluminosilicate glasses (*156*), and biogenic calcite (*157*).

Probe molecules were applied for NMR characterization of the Brønsted and Lewis acidity of heterogeneous catalysts, for example, trimethylphosphine (TMP) at Keggin-type 12-tungstophosphoric heteropoly acid (HPW) (*158*), trimethylphosphine oxide (TMPO) at H-β zeolite (*159*), and TMPO at H-mordenite zeolite (*160*). Many other aspects of structural change, adsorption/desorption behavior, and surface interaction within the host−guest complex have also been studied by SSNMR (*161*−*167*).

Some research has been conducted to observe the intermediate species on working catalysts and to elucidate the reaction mechanisms in heterogeneous catalysis. Observation of the propagating alkylidene as well as stable metallacyclobutane intermediates on a well-defined heterogeneous alkene-metathesis catalyst was achieved (*168*). Mechanistic issues about Beckmann rearrangement on zeolite catalysts were studied by ^{15}N and ^{13}C solid-state NMR spectroscopy (*169*, *170*). The mechanism of ethylbenzene disproportionation on zeolite catalysts was examined by solid-state ^{13}C MAS NMR spectroscopy (*171*). In situ ^{1}H solid-state NMR techniques have

been used to simultaneously detect the reactivity of both catalyst and alkane reactant protons (*172*). Activation and conversion of light alkanes including methane on bifunctional zeolite catalysts have been investigated (*173*−*176*), as has been the reactivity of surface methoxy species on heteropolyacids revealed by solid-state NMR spectroscopy (*177*, *178*). A new approach to in situ continuous-flow laser-hyperpolarized ^{129}Xe MAS NMR together with ^{13}C MAS NMR has been applied to study the adsorption and reaction kinetics in a nanospace (*179*).

MATERIALS AND NANOMATERIALS

SSNMR has been applied to the polymeric materials since the early days of the technique. A few examples of recent applications are solid-state NMRs characterization of paramagnetic metal cyanide coordination polymers (*180*), of unmodified and isotopically labeled polythiophenes (*181*), and of microporous functionalized polymers (*182*).

Another area of study in which SSNMR has been widely applied is inorganic solids. Recent examples of the applicability of solid-state NMR spectroscopy to structural studies of inorganic solids include investigations of Ta oxyfluoride materials (*183*), binary transition-metal phosphides (*184*), silica-coated $BaSO_4$ submicronic particles (*185*), and $CaSiO_3$ polymorphs (*186*). SSNMR is also very useful for characterization of organometallic compounds and inorganic−organic hybrid materials. For example, ^{31}P NMR spectra of solid [tris(dimethylphenylphosphine)](2,5-norbornadiene)Rh(I) hexafluorophosphate were acquired at several magnetic field strengths (*187*). ^{2}H solid-state NMR spectra of transition metal complexes were measured over a wide temperature range (*188*). ^{1}H Lee−Goldburg (LG) CRAMPS methods have been demonstrated for studying these inorganic−organic hybrid materials (*189*). The rotational dynamics of organo-fuctionalized mesoporous silica were studied with solid-state ^{2}H NMR spectroscopy (*190*). ^{13}C CP/MAS NMR is also a facile method for characterization of periodic mesoporous organosilicas (PMOs) (*191*, *192*).

NMR has long been a method for probing the nature of liquid crystals, which although somewhat fluid, often give NMR spectra that indicate order and structure, like a solid. Recently, the measurement of heteronuclear dipolar coupling using two-dimensional separated local field (SLF-2D) NMR experiments has been shown to be a powerful technique for investigating structure and dynamics in liquid crystals (*193*). Liquid crystal materials containing fullerenes were also characterized by solid-state ^{13}C NMR under stationary and magic angle spinning sample conditions (*194*).

Finally, SSNMR methods have also been used to investigate so-called "new materials" such as nanomaterials, nanofibers, and films. The structures of synthetic nanodiamonds have been characterized by solid-state NMR spectroscopy (*195*, *196*). Titania nanotubes, before and after immobilization of phenols, were studied by ^{13}C solid-state NMR (*197*). C/F interactions in single-walled carbon nanotubes (SWCNTs) were studied by solid-state ^{19}F NMR spectroscopy (*198*). The structure of nanofibers of polyaniline (PANI) formed by oxidation of aniline with ammonium persulfate have been determined by solid-state ^{13}C and ^{15}N NMR experiments (*199*). The boundary films generated on metal and ceramic surfaces have been characterized using multinuclear solid-state NMR (*200*).

SUMMARY

Solid-state NMR continues to be used to solve a variety of problems in chemistry, materials science, and biology. With the ability to detect resonances of the majority of nuclei in the periodic table readily have come more and more applications to a wider array of problems. The availability of higher magnetic field, in particular, has made possible the study of nuclei which were, for all practical purposes, inaccessible. The development of a wide variety of techniques that parse the interactions affecting NMR spectra into manageable spectroscopic information has allowed the application of NMR to solids where it was once impossible to gain useful information. There is little doubt that, as magnetic fields get more intense, MAS becomes faster, selective decoupling becomes more complete, and control of the information content of NMR spectra becomes more routine, NMR will become even more pervasive in analysis.

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