Solid State NMR Spectroscopy

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This solid-state NMR report summarises the subject and results of 247 articles and original papers published in 2019. In addition to the published reviews, the two major sections in this report consider various methodological developments and a broad range of applications. The presented classification of papers into different sections and subsections is intended to ease the overview of the results obtained in 2019, as well as to evaluate the directions in which solid-state NMR is likely to develop in the near future.

1 Introduction

This contribution outlines recent advances and applications achieved in the area of solid-state NMR based on the literature published between 1 January 2019 and 31 December 2019.

In the following Section 2 of the report, review articles on both general and specific aspects of solid-state NMR techniques and their applications are considered. These reviews cover many diverse subject areas, such as developments of methods for quadrupolar nuclei, paramagnetic systems and dynamic nuclear polarisation (DNP), as well as structure and dynamics studies of proteins, nucleic acids, lipid membranes, nanomaterials and supramolecular systems.

Experimental and computational developments that are of methodological interest are arranged in Section 3, comprising: (3.1) proton NMR; (3.2) decoupling experiments; (3.3) DNP; (3.4) distance measurements; (3.5) multidimensional techniques; (3.6) computational developments; (3.7) NMR crystallography and (3.8) other experimental advances, including instrumental developments.

Various examples of solid-state NMR applications are collected in the final Section 4. This section is divided into subsections depending on the type of the material studied: (4.1) organic solids; (4.2) pharmaceutical and biomedical applications; (4.3) proteins; (4.4) nucleic acids; (4.5) polymers; (4.6) plant-derived materials; (4.7) metal organic frameworks; (4.8) organometallic and coordination compounds; (4.9) carbonaceous materials and soils; (4.10) glasses and ceramics; (4.11) micro- and mesoporous solids; (4.12) surface science and catalysis; (4.13) cements; (4.14) inorganic and other related solids; (4.15) electrolytes and battery materials; (4.16) minerals and (4.17) perovskites.

Overall, 247 references are included in this report. Compared to five years ago, some important qualitative changes can be noticed. In particular, there have been considerable increase in the number of publications making both advanced and routine use of (i) DNP-enhanced NMR experiments; (ii) distance measurements; (iii) ^{1}H-detected experiments and (iv) computational predictions of NMR parameters using density-functional theory (DFT). These and other methodological advances have also allowed to expand solid-state NMR to systems previously considered too complex such as large proteins and nucleic acids, as well as their structure and function inside human and plant cells or within intact live bacteria.

2 Reviews

2.1 Methodological and theoretical aspects

It is well known that increasing the magnetic field strength can radically improve the sensitivity and the spectral resolution of quadrupolar nuclei (with spin I greater than ½) via the reduction of the second-order quadrupole broadening. This and other aspects of the solid-state NMR of quadrupolar nuclei were discussed by Gan in his brief overview of spectral acquisition techniques, with the emphasis on the importance of inter-nuclei distance measurements, high magnetic fields, various 2D separation and correlation methods. The complications and consequences of spin dynamics under r.f. irradiation for quadrupolar nuclei and level-crossing with the satellite transition frequencies under magic-angle spinning (MAS) conditions were discussed. As noted in this review, the efficiency of many experiments for quadrupole nuclei with spin I greater than ½ scales down by a factor of I + ½ compared to the case with I = ½ since only two central transition spin states out of the 2S + 1 levels contribute to the spin correlation and polarisation transfer.[1]

Motivated by the development of new techniques for sensitivity and resolution improvements, recent advancements in solid-state NMR are expected to open a variety of fundamental and technological opportunities in materials science. In particular, the benefits of NMR for refined multidimensional correlations are becoming considerably more significant in recent years, as the fundamental limitations imposed by Boltzmann distribution are defeated by DNP and laser-enhanced hyperpolarisation techniques. As shown by Chmelka, despite these advancements, the information available from the analysis of the solid-state NMR data is still restricted and its combination with modern diffraction, microscopy, computational and materials synthesis methods is expected to considerably enhance the depth of the structural detail extractable from the NMR data. It is also expected that the understanding of materials structure achieved in this manner will promote discovery of new materials with novel and optimised properties.[2]

Another review of the methodological importance is that by Pell *et al.*, in which they consider advances in paramagnetic solution and solid-state NMR. Both the theory of paramagnetic NMR and the way it is currently employed were presented. The authors have attempted to unify different languages used by the NMR, EPR, computational chemistry and magnetism communities to provide an across-the-board coherent theoretical description. More specifically, the theory of the paramagnetic shift and shift anisotropy, both in the traditional and modern formalisms, was presented, and subsequently extended to periodic solid materials. As emphasised by the authors, and additional factor in the solid state is the impact of bulk magnetic susceptibility effects on the NMR spectrum. NMR techniques applied to the studies of paramagnetic systems in various research areas were also reviewed. The particular examples considered comprised solid battery electrode materials, metalloproteins, systems containing lanthanide ions and multi-component materials doped with paramagnetic species to measure the component domain sizes.[3]

A detailed review of ^{17}O NMR studies of organic and biological molecules in aqueous solution and in the solid state has been presented by Wu. In the first part, a general theoretical description of the nuclear quadrupole relaxation process was described. General features of quadrupole-central-transition (QCT) NMR were then discussed, which is a particularly powerful method for studying biomolecules in the slow motional regime. The second part of the review covered solid-state ^{17}O NMR studies of organic and biological molecules. The literature published since 2008 was included in this review article.[4]

Selected highlights of the recent literature on solid-state NMR of some of the relatively less-studied nuclei have been provided by Bryce. The roles of ultrahigh magnetic fields, r.f. pulse sequences, DNP, nuclear quadrupole resonance and isotopic enrichment were considered.[5]

Rankin *et al.* have reviewed recent developments of solid-state MAS DNP NMR spectroscopy at relatively high magnetic field strengths. MAS DNP can improve the sensitivity of NMR experiments by one to three orders of magnitude at static magnetic field $B_0 \geq 5$ T, thus allowing high-resolution spectra to be acquired. A historical perspective of DNP NMR of materials was presented, followed by the description of DNP transfers under MAS and the transport of polarisation by spin diffusion. Sample preparation, DNP hardware, the influence of key experimental parameters, such as microwave power, magnetic field, temperature and MAS frequency, as well as applications of MAS DNP NMR were also discussed.[6]

On a related subject, Konig *et al.* have reviewed the use of DNP-enhanced solid-state NMR for protein studies. Applications to well-folded amyloid fibrils formed by short peptides as well as full-length proteins were considered. Some recent DNP MAS NMR studies of disordered proteins and protein regions were also reviewed.[7]

2.2 Structural biology

Marchanka and Carlomagno have reviewed advances in solid-state NMR spectroscopy of RNA. The methodology developed by the authors was aimed at determining the structure of RNA. The particular subjects considered were methods for resonance assignments, collection of RNA-specific distance restraints, as well as detection of protein-RNA interfaces.[8]

Silva *et al.* have presented an overview of solid-state NMR studies of biomolecules with paramagnetic metal centres.[9]

Various solid-state NMR approaches employed for studies of protein structure and protein-lipid interactions have been reviewed by Aisenbrey *et al.* Several protocols were presented for reconstituting membrane proteins into oriented membranes, monitoring membrane alignment by ^{31}P NMR, studies by ^{15}N NMR and measurements of lipid order parameters using ^{2}H NMR.[10]

The review by Molugu and Brown considered cholesterol effects on the properties of lipid membranes. The solid-state NMR approach has allowed the average membrane structure, fluctuations and elastic deformation on cholesterol interaction to be quantified. Lineshape measurements were shown to provide equilibrium structural properties, while relaxation times allowed the molecular dynamics to be characterised. The dependence of ^{2}H NMR spin-lattice relaxation rates on segmental order parameters for lipid membranes was shown to be indicative of emergent viscoelastic properties.[11]

Recent developments in the solid-state NMR detection and identification of conformational states in cysteine-ethylation of tissue-extracted membrane proteins have been reviewed by Weber *et al*.[12]

Mandala and Hong have reviewed recent applications of solid-state NMR techniques based on ^{1}H detection under fast MAS and DNP.[13]

An overview of 20 years of progress in structural and dynamic studies of amyloids by solid-state NMR has been presented by Jaroniec. It was concluded that the ongoing research in this area is likely to contribute to the improved understanding of amyloid structure, polymorphism, interactions, assembly mechanisms and biological function and toxicity.[14]

Protein sample preparation techniques, including cell-free expression methods, for solid-state NMR investigations have been reviewed by Lacabanne *et al*.[15]

Finally, in the review titled "Paramagnetic solid-state NMR of proteins", the trends and progress of paramagnetic solid-state NMR of proteins over the past decade have been summarised, including potential applications of paramagnetic effects for sensitivity enhancement, structure determination and topological analysis for microcrystalline proteins, protein aggregates and membrane proteins.[16]

2.3 Materials science

Analysis of alumina structure using 3D correlation of solid-state NMR parameters has been reviewed by Chandran *et al.* Structural differences in aluminium (oxy)hydroxides arise from the variability of Al coordination numbers and degree of dehydroxylation. Identification of these phases using X-ray diffraction (XRD) has proven to be very difficult, while quadrupolar interactions of ^{27}Al nuclei are highly sensitive to site symmetry, thus allowing different phases to be fingerprinted and identified. Previously reported ^{27}Al NMR data allowed them to develop a new 3D correlative analysis. Providing a gold standard from crystalline samples, this approach demonstrated that any kind of crystalline or amorphous alumina can be assessed beyond the current limitations of characterisation. Methodological guidance was provided by the authors to assist consistent implementation of this analysis.[17]

Advances in NMR and DNP of nanocrystals have been reviewed by Gutmann *et al*. Materials considered included crystalline nanocellulose or microcrystalline cellulose, metal oxides, such as V-Mo-W oxides, catalytically active nanocrystalline metal nanoparticles, coated with protectants or embedded in polymers and lead-free perovskite materials. These materials were discussed in terms of their application and physico-chemical characterisation by solid-state NMR techniques combined with DFT calculations. Applications of ^{1}H, ^{2}H, ^{13}C, ^{15}N and ^{23}Na solid-state static or MAS NMR techniques for the characterisation of these materials, their surfaces and processes on their surfaces were discussed. The combination of these techniques with DNP for the identification of low-concentrated carbon- and nitrogen-containing surface species in natural abundance was also reviewed.[18]

Mazur *et al.* have published a brief overview of the papers published over the last twenty years on solid-state ^{13}C NMR spectra of fullerenes, nanotubes, nanodiamonds and carbon nanostructures, such as milled graphite and its oxide, graphene, graphene oxide, carbon nanotubes, fullerenes and their derivatives. The main focus of this mini-review was on the characteristic values of experimental isotropic ^{13}C NMR chemical shifts and their interpretation in terms of local chemical environments of carbon nuclei.[19]

Recently published papers on solid-state NMR of hybrid halide perovskites have been reviewed by Franssen and Kentgens. The flexibility of NMR for studying the materials under different conditions (e.g. under illumination) was highlighted.[20]

2.4 Other applications

The review titled "The magic angle view to food: magic-angle spinning (MAS) NMR spectroscopy in food science" by Jensen and Bertram discusses how NMR spectroscopy has been used in food science and nutritional studies for many years for detailed studies and characterisation of solid and semi-solid food.[21]

Rossi *et al.* have provided an overview of the recent literature on supramolecular systems, paying particular attention to the study of weak interactions such as hydrogen and halogen bonds through solid-state NMR investigations.[22]

3 Experimental and Computational Developments

3.1 Proton NMR experiments

The residual broadening observed in ^{1}H spectra of rigid organic solids at natural abundance at MAS frequency of 111 kHz is typically a few hundred hertz. Paruzzo *et al.* have shown that refocusable and non-refocusable interactions contribute roughly equally to this residual broadening at high-fields (21.14 T) and that the removal of the non-refocusable part will produce significant increase in spectral resolution. They presented an experiment for the indirect acquisition of constant-time experiments at ultra-fast MAS (CT-MAS) which verifies this hypothesis. The combination of this experiment with the two-dimensional one pulse (TOP) transformation was shown to reduce the experimental time to a fraction of the original cost while retaining the narrowing effects. Results obtained with TOP-CT-MAS at 111 kHz MAS on a sample of β-AspAla yielded up to 30% higher resolution spectra than the equivalent one-pulse experiment, in less than 10 min.[23]

Penzel *et al.* have reported ^{1}H linewidth and T_1, $T_{1\rho}$ and T_2' relaxation data of the model protein ubiquitin acquired at MAS frequencies up to 126 kHz. They found a predominantly linear improvement in linewidths and coherence decay times of protons with increasing spinning frequency in the range from 93 to 126 kHz. Further attempt was undertaken to gain insight into the different contributions to the linewidth at fast MAS. For microcrystalline fully-protonated ubiquitin, inhomogeneous contributions were only a minor part of the ^{1}H linewidth and coherent effects were still dominant at 126 kHz MAS. In addition, site-specific ^{1}H relaxation rate constants during a spinlock at 126 kHz MAS were presented, as well as MAS-dependent bulk $T_{1\rho}(^{1}H^{N})$.[24]

Asami and Reif have demonstrated the advantages of accessing methyl groups in proteins via ^{1}H-detected solid-state MAS NMR using a random protonation method.[25]

Makrinich and Goldbourt have employed ^{1}H detection and phase-modulated pulse saturation to measure spin-lattice relaxation times of "invisible" quadrupolar nuclei with very large quadrupolar couplings. For ^{14}N, efficient cross-polarisation was achieved with a long-duration preparation pulse. It is shown that this experiment enables the characterisation of a large variety of materials containing halogens and metals.[26]

Solid-state fast field cycling ^{1}H NMR relaxation time measurements were employed by Conte *et al.* to study properties and changes in volatile compounds.[27]

3.2 Decoupling experiments

As pointed out by Paruzzo and Emsley, the development of homonuclear dipolar decoupling sequences to obtain high-resolution ^{1}H NMR spectra from solids has recently celebrated its 50th birthday. Over the years, a series of different decoupling schemes have been developed, starting with the pioneering Lee-Goldburg and WAHUHA sequences up to the most recent generation of experimentally optimised phase-modulated schemes, such as eDUMBO-1$_{22}$ and LG4. These schemes are known to yield over an order of magnitude reduction in ^{1}H NMR linewidths in solids. Paruzzo and Emsley have compared experimental results obtained using eight different decoupling schemes (LG, WHH-4, MREV-8, BR-24, FSLG/PMLG, DUMBO-1, eDUMBO-1_{22} and LG4) on three different microcrystalline powdered samples (alanine, glycine and β-AspAla) and at three different MAS frequencies (3, 12.5 and 22 kHz). They have also described the experimental protocol used to optimise these schemes with the aim to provide simple guidelines for the optimisation of CRAMPS experiments.[28]

Kouvatas *et al.* have undertaken a detailed study of the decoupling efficiency of the multiple-pulse (MP) scheme, its parameterisation and the choice of instrumental set up. The MP decoupling scheme is known to remove the broadening of spin-½ spectra produced by the heteronuclear scalar interaction with a half-integer quadrupolar nucleus, without reintroducing heteronuclear dipolar interactions. Through a numerical approach, the influence of the main intrinsic material parameters (heteronuclear dipolar and *J* coupling, the quadrupolar interaction) and instrumental parameters (spinning rate, pulse field strength) on efficiency and resolution enhancement of the scalar decoupling scheme was investigated. A guideline was then proposed to obtain the best resolution enhancement via the rationalisation of the instrumental and parameter set up. Various spin systems were tested (^{31}P-^{51}V in $VOPO_4$, ^{31}P-^{93}Nb in $NbOPO_4$, ^{119}Sn-^{17}O in $Y_2Sn_2O_7$), together with simulation results.[29]

A unified heteronuclear decoupling approach in solid-state NMR at fast MAS frequency and low r.f. amplitude was presented by Sharma *et al.* It was shown that the unified decoupling approach becomes increasingly effective in identifying the deleterious dipole-dipole and, in particular, *J* recoupling conditions which become critical for the low-amplitude r.f. regime. Numerical simulations and analytic theory were used to understand the effects of various nuclear spin interactions on the decoupling performance.[30]

The first application of homonuclear Lee-Goldburg (LG) decoupling on high density molecular hydrogen was reported by Meier *et al.*[31] At ideal LG conditions, the broad ^{1}H resonance of molecular ortho-hydrogen was narrowed 1600-fold, resulting in linewidths of 3.1 ppm.[31]

3.3 Dynamic nuclear polarisation

The types of materials which can be studied by solid-state NMR spectroscopy has been significantly expanded in recent years. However, many technologically relevant materials used in energy conversion and storage systems are electrically conductive. Such materials present a challenge for DNP NMR studies due to microwave absorption and sample heating. Svirinovsky-Arbeli *et al.* have examined several commercial carbon allotropes, commonly employed as electrodes or conductive additives and considered their effect on the extent of solvent polarisation achieved in DNP from nitroxide biradicals. They addressed the effect of sample conductivity by studying a series of carbons with increasing electrical conductivity. The results showed that while the DNP performance significantly drops in samples containing the highly conductive carbons, sufficient signal enhancement can still be achieved with some compromise on conductivity.[32]

Sugishita *et al.* have reported a new method for quantifying the local ^{1}H hyperpolarisation amplitude, which is applicable to un-oriented/powdered solid samples under MAS NMR conditions. The method is based on the ability to observe the high-order spin-correlated term ($2I_zS_z$) intrinsic to a hyperpolarised *I*-*S* two-spin state, separately from the lowest-order Zeeman term (S_z) in quasi-equilibrium magnetisation. It is expected to be useful for the characterisation of mesoscopic molecular assemblies of medical/biological importance.[33]

Observations of an NMR MASER (microwave amplification by stimulated emission of radiation) of hyperpolarised ^{1}H nuclei by DNP at 1.2 K at 6.7 T have been described. NMR signals lasting for several tens of seconds were observed on an ensemble of dipolar-coupled nuclear spins. Magnetisation dynamics were analysed in terms of the combined Bloch-Maxwell and Provotorov equations.[34]

The structural characterisation of organic and biological samples at natural abundance was reported by Smith *et al.* using DNP-enabled solid-state NMR techniques, including the extraction of long-range distance constraints using dipolar recoupling pulse sequences without the deleterious effects of dipolar truncation.[35]

The through-space transfer of magnetisation from protons to quadrupolar nuclei together with DNP was employed by Giovine *et al.* to enhance the NMR sensitivity of quadrupolar nuclei. They compared two approaches to achieve such transfer: PRESTO (Phase-shifted Recoupling Effects a Smooth Transfer of Order), which has been shown to be superior to CPMAS for quadrupolar nuclei, and D-RINEPT (Dipolar-mediated Refocused Insensitive Nuclei Enhanced by Polarisation Transfer) using symmetry-based $SR4_1^2$ recoupling, which has already been employed to transfer the magnetisation in the reverse process from half-integer quadrupolar spin to protons. These techniques were analysed using (i) average Hamiltonian theory, (ii) numerical simulations of spin dynamics and (iii) experimental $^1H\rightarrow^{27}Al$ and $^1H\rightarrow^{27}Al$ transfers in as-synthesized $AlPO_4$-14 and ^{17}O-labelled fumed silica respectively. The analysis revealed that PRESTO yields the highest transfer efficiency at low magnetic fields and MAS frequencies, whereas, owing to its higher robustness to r.f. field inhomogeneity and chemical shifts, D-RINEPT is more sensitive at high fields and MAS frequencies, notably for protons exhibiting large offset or CSA, such as those involved in hydrogen bonds.[36]

Vioglio *et al.* have employed DNP NMR approach for studying the time evolution of crystallisation processes, in which the crystallising system is quenched rapidly to low temperature at specific time points during crystallisation. The use of low temperatures allowed DNP to be used for enhancing the signal intensity in the solid-state NMR measurements, which is advantageous for detection and structural characterisation of transient forms that are present in small quantities.[37]

As reported by Good *et al.*, a biradical-tagged phospholipid can be used as a novel polarising agent for solid-state MAS DNP NMR of membrane proteins.[38]

It has been reported that not only the MAS rotor material but also the distribution of the membrane samples within the NMR rotor have a pronounced effect on the DNP enhancement. These observations were rationalised with the cooling efficiency and the internal properties of the sample, monitored via their T_1 relaxation, microwave on versus off signal intensities and the DNP effect. The data suggested that the speed of cooling has a pronounced effect on the membrane properties and concomitantly the distribution of biradicals within the sample.[39]

A new methyl-based toolkit for exploring proteins has been presented by Mao *et*[PH1] *al.*, which combines DNP with the heteronuclear Overhauser effect, carbon-carbon-spin diffusion and isotope-labelling schemes. It was shown that methyl groups can serve as dynamic sensors for probing local molecular packing within proteins. They can also be used as "NMR torches" to selectively enlighten their molecular environment, e.g., to selectively enhance the polarisation of nuclei within residues of ligand-binding pockets. The use of ^{13}C-^{13}C spin diffusion enabled probing carbon-carbon distances within the subnanometer range. The new method was applied to a large membrane protein, the light-driven proton pump green proteorhodopsin, offering insight into the functional mechanism of the early step of its photocycle.[40]

A tailored solid-state NMR approach has been developed that allow protein structure inside human cells to be studied under DNP conditions. The authors demonstrated the method using ubiquitin, which is involved in cellular functioning. The results were shown to pave the way for structural studies of larger proteins or protein complexes inside human cells.[41]

A photochemically induced DNP (photo-CIDNP) ^{15}N MAS NMR analysis of a bacterial photosynthetic reaction centre of *Rhodobacter sphaeroides* (wild-type) has been reported by Paul *et al*.[42]

Kirui *et al.* have described a new protocol for preparing uniformly ^{13}C,^{15}N-labelled fungal materials for solid-state NMR and DNP experiments. The new protocol is potentially applicable to a range of carbohydrate-rich materials, including the natural cell walls of plants, fungi, algae and bacteria, as well as synthesised or designed carbohydrate polymers and their complexes with other molecules.[43]

MAS DNP applications are usually based on the use of nitroxide biradicals as polarising agents. In materials science, however, the use of nitroxides often limits the signal enhancement to the surface and subsurface layers. There is therefore a need for hyperpolarisation approaches which provide sensitivity in the bulk of micron-sized particles, e.g. via the use of paramagnetic metal ions. Wolf *et al.* have demonstrated the remarkable efficacy of Mn(II) dopants, used as endogenous polarisation agents for MAS DNP, in enabling the detection of ^{17}O at a natural abundance of only 0.038%. Distinct oxygen sites were identified in the bulk of micron-sized crystals, including the battery anode materials $Li_4Ti_5O_{12}$ and $Li_2ZnTi_3O_8$, as well as $NaCaPO_4$ and $MgAl_2O_4$, all doped with Mn(II) ions.[44]

3.4 Dipolar couplings and distance measurements

As pointed out by Jain *et al.*, rotational-echo double resonance (REDOR) and dipolar-coupling chemical shift correlation (DIPSHIFT) are commonly used experiments to probe heteronuclear dipole-dipole couplings between isolated pairs of spin-½ nuclei. It has been shown that REDOR and DIPSHIFT are in fact alternate implementations of the same experiment. In particular, dipolar dephasing curves in REDOR were obtained by increasing the recoupling duration while keeping the position of the pulses constant. DIPSHIFT, on the other hand, was shown to be a constant-time version of REDOR.[45]

A new approach has been described for determining accurate ^{19}F-^{19}F distances in multispin systems, using finite pulse r.f. driven recoupling at high MAS frequencies of 40–60 kHz. Crystalline "molecular ruler" solids, difluorobenzoic acids and 7-fluoro-L-tryptophan, were used whose intra- and intermolecular ^{19}F-^{19}F distances are known. The optimal experimental conditions for accurate distance determinations were described, including the choice of phase cycle, the relative advantages of selective inversion 1D versus 2D correlation experiments and the appropriate numerical simulation protocols.[46]

Measurements of strong one-bond dipolar couplings have been reported using REDOR in solid-state MAS NMR. The authors have demonstrated the results on isolated ^{13}C-^{15}N and ^{1}H-^{13}C spin pairs at 20 and 62.5 kHz MAS respectively.[47]

Gopinath *et al*. have achieved substantial savings in experimental time using a new subclass of Polarisation Optimized Experiments (POEs) that concatenate TEDOR and SPECIFIC-CP transfers into a single pulse sequence. They designed new 2D and 3D experiments for distance measurements, heteronuclear shift correlations and resonance assignments using one experiment. These were tested on N-Acetyl-Val-Leu dipeptide, microcrystalline U-^{13}C,^{15}N ubiquitin and single- and multispan membrane proteins reconstituted in lipid membranes.[48]

The standard procedures to adjust the rotor angle are usually not highly accurate, resulting in a slight mis-adjustment of the rotor from the magic angle on the order of a few millidegrees. This small mis-setting has no significant impact on the spectral resolution, but is sufficient to reintroduce anisotropic interactions. Xue *et al.* have used the latter to accurately measure site-specific ^{1}H-^{15}N dipolar couplings in a heavily deuterated protein. The method has been shown to be applicable at arbitrarily high MAS frequencies, since neither rotor synchronisation nor particularly high r.f. field strengths are required. The off-MAS method allowed the quantification of order parameters for very dynamic residues.[49]

An integrative approach for exact distance measurements for structure and dynamics in solid proteins by fast MAS NMR has been described by Grohe *et al.*[50]

To obtain multiple long-range distance restraints rapidly and with high sensitivity for protein structure determination, Shcherbakov have demonstrated a new ^{1}H-detected fast MAS NMR technique that yields many long distances in a 2D resolved fashion. Distances between ^{1}H and ^{19}F were measured up to ~15 Å, with an accuracy of better than 10%. Exogenous fluorines were sparsely introduced into the aromatic residues of the protein, which was perdeuterated and back-exchanged to give amide protons. This ^{1}H-^{19}F distance experiment, termed HSQC-REDOR, was demonstrated on the singly fluorinated protein, GB1. Combining the ^{1}H-^{19}F distance restraints with ^{13}C-^{19}F distances and chemical shifts, a GB1 structure was calculated with a backbone RMS (root mean square) deviation of 1.73 Å from the high-resolution structure.[51]

3.5 Multidimensional techniques

A longitudinal relaxation optimisation scheme to enhance the signal sensitivity of solid-state HSQC NMR experiments has been reported by Han *et al.* Under the proposed scheme, the ^{1}H spins of ^{1}H-X (^{15}N or ^{13}C) were selected for signal acquisition, whereas other ^{1}H spins were flipped back to the axis of the static magnetic field. Three biological systems were used to evaluate this approach, including a seven-transmembrane protein, an RNA and a whole-cell sample. For all samples, the proposed scheme led to a 1.3-2.5-fold gain in sensitivity.[52]

Pandey *et al.* have employed proton-detected 3D ^{1}H anisotropic/^{14}N/^{1}H isotropic chemical shift correlation NMR under fast MAS to measure the chemical shift anisotropies (CSAs) of protons bonded to nitrogen atoms, which are of significant interest due to their common role as H-bonding partners in many chemical, pharmaceutical and biological systems. Although very fast (~100 kHz) MAS experiments have enabled the measurement of ^{1}H CSAs directly from solids, overlapping NH proton resonances are common due to the narrow chemical shift (CS) distributions, and necessitate the introduction of an additional frequency dimension to the regular 2D ^{1}H CSA/^{1}H CS correlation method to achieve sufficient resolution. The results by Pandey *et al.* demonstrated that the proposed 3D NMR experiment is capable of resolving the ^{1}H resonances of amide NH groups through the ^{14}N isotropic shift frequency dimension, and enabling the accurate measurement of site-specific ^{1}H CSAs from powder samples under fast MAS conditions. In addition to the 3D ^{1}H CSA/^{14}N/^{1}H CS experiment, an approach employing ^{14}N-edited 2D ^{1}H CSA/^{1}H CS experiment was also demonstrated as an additional means to address spectral overlap of NH resonances with aliphatic and other resonances in solids.[53]

Quantitative analysis of ^{14}N quadrupolar coupling using solid-state ^{1}H-detected ^{14}N NMR was reported by Jarvis *et al.* The authors exploited the sensitivity of ^{1}H-detection to characterise ^{14}N sites using a moderate r.f. field to generate coherence between the ^{1}H and ^{14}N at moderate and fast MAS frequencies. Efficient numerical simulations allowed the resulting ^{14}N lineshapes to be quantitatively analysed to determine both the size and asymmetry of the quadrupolar interaction.[54]

Excitation schemes for the indirect detection of ^{14}N via solid-state HMQC NMR experiments have also been evaluated. This HMQC method exploits the transfer of coherence between single- (SQ) or double-quantum (DQ) ^{14}N coherences and SQ coherences of a suitable spin-1/2 ‘spy’ nucleus, e.g. ^{1}H. The efficiencies of four ^{14}N excitation schemes (DANTE, XiX, Hard Pulse (HP) and Selective Long Pulse (SLP)) were compared using numerical simulations of *J*-HMQC spectra and either SQ-SQ or DQ-SQ ^{1}H-{^{14}N} D-HMQC experiments on L-histidine·HCl and *N*-acetyl-L-valine at 18.8 T and 62.5 kHz MAS. The results demonstrated that both DANTE and SLP have a more efficient ^{14}N excitation profile than XiX and HP. Further results showed that SLP is ideally suited for widespread, non-specialist use in solid-state NMR analyses of nitrogen-containing materials.[55]

A ^{1}H-detected 3D ^{15}N CS/^{15}N CSA/^{1}H CS correlation experiment has been described which employs a γ-encoded CSA recoupling scheme. The 3D experiment was applied to glycyl-L-alanine, resulting in site-resolved ^{15}N lineshapes from which CSA parameters were retrieved by SIMPSON fittings. It was shown that this 3D method is robust with respect to offset mismatches, and weakly dependent on r.f. inhomogeneity within mis-sets of ±10% from the theoretical value.[56]

Modified versions of through-bond heteronuclear correlation (HETCOR) experiments have been presented to take advantage of the light-induced hyperpolarisation that occurs on ^{13}C nuclei due to the solid-state photo-CIDNP effect. Such ^{13}C-^{1}H photo-CIDNP MAS *J*-HM(S)QC experiments were applied to acquire the 2D ^{13}C-^{1}H correlation spectra of selectively ^{13}C-labelled photochemically active cofactors in the frozen quinone-blocked photosynthetic reaction centre of the purple bacterium *Rhodobacter sphaeroides* (wild-type). The resulting spectra contained no correlation peaks arising from the protein backbone, which greatly simplified the assignment of aliphatic region.[57]

Homonuclear 2D NMR is known to be essential for the characterization of small and large molecules, such as organic compounds, metabolites and biomacromolecules. However, for complex samples homonuclear 2D spectra display poor resolution, making spectral assignment very cumbersome. A new method has been proposed that exploits the differential T_2* relaxation times of individual resonances and resolves the homonuclear correlation 2D NMR peaks into pseudo3D spectra, where time is the third dimension. The method was applied to membrane proteins embedded in lipid bilayers.[58]

Hoffmann *et al.* have described band-selective homonuclear CP-based 3D solid-state NMR experiments for protein resonance assignments. They have demonstrated how a set of six 3D experiments can be used for unambiguous assignment of the protein backbone as well as certain sidechain resonances.[59]

A novel ultra-high dimensional approach has been reported, where 5D peak lists are reconstructed from several 2D projections for protein samples of different molecular sizes and aggregation states, which show limited dispersion of chemical shifts or inhomogeneous broadenings. The resulting datasets were shown to be particularly suitable for automated analysis, and yielded rapid and unbiased assignments of backbone resonances.[60]

Differences in the molecular mobilities of the individual components in heterogeneous mixtures were exploited by Zhang *et al.* to enhance the sensitivity in solid-state 2D HETCOR NMR spectra. Pulse sequences were described that enable the sequential acquisition of ^{1}H-^{13}C HETCOR NMR spectra for both rigid and mobile components in a single experiment by taking full advantage of the abundant proton magnetisation. As demonstrated, these pulse sequences can be used for dynamics-based spectral editing and resonance assignment.[61]

3.6 Theoretical and computational developments

As shown by Malar *et al.*, ^{1}H-detected solid-state fast MAS NMR is currently redefining the NMR applications, in particular in structural biology.[62] Understanding the contributions to the spectral linewidth is therefore of paramount importance. When disregarding the sample-dependent inhomogeneous contributions, the NMR proton linewidth is defined by homogeneous broadening, which has incoherent and coherent contributions. Quantitating these contributions in multi-spin systems remains an open issue. The coherent contribution is mainly caused by the dipolar interaction under MAS and is determined by the molecular structure and the ^{1}H chemical shifts. Simulations based on numerically exact direct integration of the Liouville-von Neumann equation can give valuable information about the lineshape, but are limited to small systems (<12 spins). An alternative simulation method for the coherent contributions was presented based on the partially analytic calculation of the second moments of large spin systems. The method was validated on a simple system by predicting the ^{19}F MAS NMR linewidth in CaF_2. Simulation results were also compared with experimental data for ubiquitin.[62]

Mananga has applied and compared the Floquet-Magnus and Fer expansion schemes employed in theoretical treatment of NMR experiments. These expansion schemes were used for the calculation of effective Hamiltonians and propagators and an important iterative approach for the Floquet-Magnus expansion was presented. To understand the differences between two approaches, explicit calculations were performed for the multiple-pulse spin-locking experiment.[63]

Kusaka *et al.* have developed a noise reduction method for solid-state NMR using multivariate analysis. Principal component analysis was first applied to CPMAS and ^{13}C spin-lattice relaxation measurements. The CP contact time and the delay time in spin-lattice relaxation measurements were continuously changed to obtain a series of spectra, which were then used for noise reduction using principal component analysis. The noise reduction method successfully produced spectra with improved signal-to-noise ratios. It has been shown that this noise reduction method shortens the measurement time and allows for detection of components with minute signals.[64]

The complete ^{31}P NMR chemical shift tensors for 22 inorganic phosphates obtained from ab initio computations have been shown to correspond closely to experimentally obtained parameters. Further improvement was found when structures determined by diffraction were geometry optimised. The authors have shown that the cases where correspondence is significantly improved upon geometry optimisation point to the crystal structures requiring correction.[65]

Chernyshov *et al.* have studied the effect of the local structure on the ^{31}P NMR chemical shift tensor (CST) experimentally and via computations using the DFT Gauge Independent Atomic Orbital (GIAO) approach. It was shown that a significant contribution originates from a small number of non-covalent interactions between the phosphorus-containing group under question and the atoms of adjacent molecules. A robust and computationally effective approach designed to attribute a given experimental ^{31}P CST to a certain local morphology was also proposed.[66]

Saouli *et al*. have investigated the influence of structural parameters on computations of the ^{93}Nb quadrupolar interaction and chemical shift parameters in various niobates using first-principles approaches.[67]

A protocol for the computation of NMR shifts of paramagnetic spin-coupled solids has been described and applied to the olivine-type lithium-ion battery cathode materials $LiMPO_4$ (M = Mn, Fe, Co, Ni) and the related binary phosphates MPO_4 (M = Fe, Co). The protocol included Fermi-contact, pseudocontact and orbital contributions to the chemical shifts. It combined periodic DFT computations with multi-reference post-Hartree-Fock methods. ^{7}Li and ^{31}P shift tensors for all materials were predicted as guidelines for further experimental studies.[68]

The ^{1}H CSA is known to be sensitive to the local environment of protons in crystalline systems. Plane-wave (PW) DFT calculations have been carried out using two functionals to precisely characterise the ^{1}H NMR CSTs of the solid forms of maleic, malonic and citric acids and L-histidine hydrochloride monohydrate. The level of agreement between the PW DFT and experimental CSA data was assessed.[69]

The Hubbard correction value U_{eff} used in DFT+U calculation of paramagnetic solid-state NMR shifts was optimised by Liu *et al*.[70]

Computational predictions of NMR parameters can be of help in the interpretation and assignment of NMR spectra of solids. However, the statistical representation of possible chemical environments for a solid solution is challenging. Moran *et al.* have illustrated the use of a symmetry-adapted configurational ensemble in the simulation of NMR spectra, in combination with solid-state NMR experiments. They have shown that for the interpretation of the complex and overlapped lineshapes that are typically observed, it is important to go beyond a single-configuration representation or a simple enumeration of local environments. The ensemble method led to excellent agreement between simulated and experimental spectra for $Y_2(Sn,Ti)_2O_7$ pyrochlore ceramics, where the overlap of signals from different local environments prevents a simple decomposition of the experimental spectral lineshapes.[71]

To analyse the X-ray and ^{13}C CPMAS NMR results for 2,6-dimethylphenyl and phenyl 2,3,4,6-tetra-*O*-acetyl β-glucosides and phenyl α-mannoside, the GAAGS (Genetic Algorithm-Assisted Grid Search) method was used to determine the low-energy conformers of α-mannosides and β-glucosides. The orientation of the aryl pendant group was calculated using molecular mechanics and DFT methods.[72]

As described by Emani *et al*., the analysis of solid-state NMR data for the elucidation of molecular dynamics (MD) involves modelling the restriction to overall tumbling by neighbours, as well as the concentrations of water and buffer. Atomistic MD trajectories of peptide aggregates with varying degrees of hydration were analysed by Emani *et al*. to mimic an amorphous solid-state environment and predict NMR relaxation rates. The methodology was demonstrated on a previously characterised amphiphilic 14-residue lysine-leucine repeat peptide.[73]

3.7 NMR Crystallography

Solid-state NMR measurements coupled with DFT calculations have been used to demonstrate how hydrogen positions can be refined in a crystalline system by Cui *et al*. In particular, the precision afforded by REDOR NMR to interrogate ^{13}C-^{1}H distances was exploited along with DFT determinations of the ^{13}C tensor of carbonates (CO_3^{2-}). Nearby ^{1}H nuclei perturb the axial symmetry of the carbonate sites in the hydrated carbonate mineral hydromagnesite. A match between the calculated structure and solid-state NMR was found by testing multiple semi-local and dispersion-corrected DFT functionals and applying them to optimise atom positions, starting from X-ray determined atomic coordinates. This was validated by comparing calculated and experimental $^{13}C\{^{1}H\}$ REDOR and ^{13}C CSA tensor values. The results showed that the combination of solid-state NMR, XRD and DFT can improve structure refinement for hydrated materials.[74]

Calculations based on the DFT method were used to elucidate the solid-state NMR spectra of Li_2MnO_3. While XRD allowed accurate quantification of planar defects, the use of solid-state NMR revealed limited vacancy concentrations that were undetected by XRD, as NMR is highly sensitive to the atomic local environments. The combination of these methods proved effective in overcoming the challenges of describing limited concentrations of disorder in transition metal oxides, providing information about structural variables that are essential to their application.[75]

A combination of high-field solid-state MAS NMR spectroscopy, XRD and first-principles calculations was used to elucidate the crystalline structure of $CsSc_3F_{10}$ by Rakhmatullin *et al*. The remarkable feature of $CsSc_3F_{10}$ is an unusually high cesium coordination number of 18. ^{45}Sc-^{19}F D-HMQC experiments were employed to investigate the connectivity of scandium with fluorine atoms. NMR parameters were determined using DFT calculations and compared with the experimental data.[76]

3.8 Other experimental developments

The feasibility of static ^{2}H NMR rotating frame relaxation measurements for characterisation of slow timescale motions in powder systems has been demonstrated by Vugmeyster and Ostrovsky. Using the model compound dimethyl sulfone-d_6, they showed that these measurements yield conformational exchange rates and activation energy values in agreement with the results from other techniques. Furthermore, it was shown that the full Liouvillian approach as opposed to the Redfield approximation was necessary to analyse the experimental data.[77]

Carnahan *et al.* have demonstrated that fast MAS and proton detection with the D-RINEPT pulse sequence can be generally applied to enhance the sensitivity and resolution of solid-state ^{17}O NMR experiments. Complete 2D $^{17}O\rightarrow^{1}H$ D-RINEPT correlation NMR spectra were typically obtained in less than 10 h from less than 10 mg of material, with low to moderate ^{17}O enrichment (less than 20%). Two-dimensional ^{1}H-^{17}O correlation solid-state NMR spectra allowed overlapping oxygen sites to be resolved based on proton chemical shifts or by varying the mixing time used for ^{1}H-^{17}O magnetisation transfer.[78]

Recent progress in probe technology has extended the range of available MAS frequencies up to >100 kHz, enabling the detection of resolved resonances from sidechain protons, which are important reporters of structure. Xue *et al.* have characterised the interplay between MAS frequency in the newly available range of 70-110 kHz MAS probes and proton content on the spectral quality obtainable on a 1

GHz spectrometer for methyl resonances. Variable degrees of proton densities were tested on microcrystalline samples of the α-spectrin SH3 domain with selectively protonated methyl isotopomers (CH_3, CH_2D, CHD_2) in a perdeuterated matrix. The experimental results were supported by simulations which allowed the prediction of the sensitivity outside this experimental frequency window.[79]

Duong *et al.* have demonstrated the possibility to use UDEFT (Uniform Driven Equilibrium Fourier Transform) technique to improve the sensitivity and the quantification of ^{29}Si MAS NMR. They derived an analytical expression of the signal-to-noise ratios of UDEFT and single-pulse (SP) experiments subsuming the contributions of transient and steady-state regimes. The sensitivity of SP, UDEFT and CPMG techniques were compared using mesoporous silica. Furthermore, experiments on a flame-retardant material proved that UDEFT technique provided a better quantification of ^{29}Si sites with higher sensitivity than the SP method.[80]

4 Applications

4.1 Organic solids

^{1}H NMR experiments were performed on the insensitive high-explosive 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) at high-speed MAS rates of up to 60 kHz by Mason *et al*. Well-resolved spectra were produced which were useful for the study of the chemical and structural properties of LLM-105. Long ^{1}H T_1 values were observed for the main amine peaks. Advanced NMR measurements and simulations revealed unique spectral properties due to the strong network of intramolecular and intermolecular hydrogen bonding, and provided insights into the structure of LLM-105.[81]

A simple 1D MAS NMR method has been presented that provides selective NMR spectra of COH moieties in uniformly ^{13}C-enriched organic materials. This method, termed hydroxyl-proton selection (HOPS), eliminates the magnetisation of protons directly bonded to carbons by recoupling the ^{1}H-^{13}C dipolar interaction for ~70 μs, which also serves as a filter to suppress ^{1}H magnetisation of CH_3 groups. After cross-polarisation, the signals of C-OH and COOH carbons were observed selectively, allowing to distinguish alcohols from ethers.[82]

Experimental solid-state ^{13}C MAS NMR and DFT gauge-including projector augmented wave (GIPAW) calculations have been used to probe disorder and local mobility in diethylcarbamazine citrate. This compound has been used as the first option drug for the treatment of filariasis, a disease endemic in tropical countries caused by adult worms of *Wuchereria bancrofti* transmitted by mosquitoes. 2D ^{13}C-^{1}H dipolar-coupling-mediated correlation spectra were used to explore the intermolecular interaction between diethylcarbamazine and citrate molecules. The dynamic behaviour was also investigated by varying the temperature and correlating the experimental MAS NMR results with DFT GIPAW calculations.[83]

Solid-state ^{13}C NMR has been used in conjunction with selectively ^{13}C-labelled mono- and disaccharides to measure ^{13}C-^{13}C spin-couplings (J_{CC}) in crystalline samples. This experimental approach allowed direct correlation of J_{CC} values with specific molecular conformations since molecular conformation is essentially static in crystalline samples and can be determined by XRD. J_{CC} values measured in the solid state in known molecular conformations can then be compared to corresponding J_{CC} values calculated in the same conformations using DFT methods. Representative $^{1}J_{CC}$, $^{2}J_{CCC}$ and $^{3}J_{COCC}$ values were studied as either intra-residue couplings in the aldohexopyranosyl rings of monosaccharides or inter-residue (trans-glycoside) couplings in disaccharides. The results demonstrated that accurate J_{CC} values can be measured in crystalline saccharides that have been suitably labelled with ^{13}C, and the DFT-calculated J_{CC} values compare favourably with those determined by solid-state ^{13}C NMR.[84]

The principal values of the ^{13}C chemical shift tensor for the β and δ polymorphs of π-[TTF...TCNE] (TTF = tetrathiafulvalene; TCNE = tetracyanoethylene) have been analysed to understand the abnormally long intra-dimer bonding.[85]

The reactivity of adamantylamine toward aliphatic carboxylic acids, sulfone derivatives and aromatic amino acids was screened using simple mechanochemical methods. Seven new molecular salt structures were reported exhibiting improved physicochemical properties. To carefully characterise these compounds, multiple techniques were combined, including solid-state ^{13}C and ^{15}N NMR.[86]

The structures of rhenium(I) complexes with 3-hydroxyflavone and benzhydroxamic acid as *O,O*'-bidentate ligands have been studied using ^{13}C CPMAS NMR spectroscopy by Schutte-Smith *et al*.[87]

A solid-state ^{17}O NMR study of crystalline carboxylic acids has been reported by Wu *et al*. It was found that, while these compounds form discrete hydrogen-bonded dimers in the crystal lattice, their solid-state ^{17}O MAS NMR spectra display different features and temperature dependencies. Experimentally observed ^{17}O NMR spectral changes were attributed to thermal averaging between the two tautomers that are produced as a result of concerted double-hydrogen hopping dynamics within each dimer. Based on computations, it was concluded that the periodic plane-wave DFT calculations can produce reliable ^{17}O NMR parameters (chemical shift and quadrupolar coupling tensors) for both tautomers. The same periodic DFT calculations also produced reasonable energy values for the studied dimers.[88]

The correlation between the strength of the magnetic field and the spectral width of solid-state ^{33}S NMR spectra in an organosulfur compound with the quadrupolar coupling constant of ~40 MHz has been presented by Yamada *et al*.[89]

4.2 Pharmaceutical and biomedical applications

Solid-state ^{1}H MAS NMR has been shown to be applicable for the determination and quantification of the active pharmaceutical ingredient (API) in the final drug product, especially at low drug load formulations. Diagnostic solid-state ^{1}H NMR spectra of APIs within tablets were obtained by using combinations of frequency-selective saturation and excitation pulses and 2D experiments. Selective saturation pulses efficiently suppressed the broad signals from the most commonly encountered excipients, such as lactose and cellulose, allowing observation of the high-frequency API ^{1}H NMR signals. Solid-state ^{1}H NMR provided a 1−3 orders of magnitude reduction in experiment time compared to standard solid-state ^{13}C NMR experiments, enabling diagnostic spectra of dilute APIs within tablets to be obtained within minutes.[90]

The use of time domain (TD) NMR for the characterisation of crystalline APIs containing solid dosage forms has been demonstrated by Okada *et al*. Carbamazepine and indomethacin were used as examples of poorly water-soluble APIs. It was found that the T_1 relaxation time measured by TD-NMR is a useful parameter for distinguishing between crystalline and amorphous states. Physical mixtures of APIs with polyvinylpyrrolidone and their solid dispersion were also examined. The results indicated that TD-NMR allows the evaluation of not only the crystalline form of APIs but also the miscibility of APIs and polymers.[91]

The application of the TD-NMR relaxation measurements was further extended to indomethacin containing solid dispersions.[92]

The structure and dynamics of itraconazole have been investigated by solid-state ^{13}C 2D PASS MAS NMR and spin-lattice relaxation time measurement to obtain insight into its antifungal, antiviral and anticancer activities. It was found that the motional correlation time of carbon nuclei residing at the sidechain region is 2–3 orders of magnitude less than that of those in the 1,2,4-triazole ring.[93]

Lu *et al.* have developed two new 3D solid-state NMR methods, including ^{1}H-^{19}F-^{1}H and ^{19}F-^{19}F-^{1}H correlation experiments, and successfully applied them to characterise a fluorinated drug molecule, aprepitant, and its commercial nanoparticulate formulation EMEND. These ^{1}H-detection methods utilise the significantly enhanced sensitivity and resolution of ^{1}H and ^{19}F afforded by 60 kHz ultrafast MAS and enable the analysis of milligram quantities of samples. The 3D techniques simultaneously provided homonuclear ^{1}H-^{1}H and ^{19}F-^{19}F and heteronuclear ^{1}H-^{19}F correlations of the crystalline aprepitant without interference from other pharmaceutical components in the drug product. Moreover, the results demonstrated that ^{19}F is a highly sensitive spin for probing molecular details of fluorinated drug substances in solid formulations due to the absence of signal interference from pharmaceutical excipients, as well as for characterising structural properties of a broad range of fluorine-containing materials.[94]

The results of ^{13}C and ^{15}N CPMAS NMR studies of indirubin have been reported by Alkorta *et al.*[95]

A robust protocol for unambiguous assignment of ^{13}C and ^{1}H chemical shifts of crystalline and amorphous APIs has been tested on the γ polymorph of indomethacin. Specifically, 1D ^{13}C-edited experiments, 2D ^{13}C-detected homo- and hetero-nuclear correlations and 2D ^{1}H-detected techniques under ultrafast MAS provided enhanced resolution to identify overlapping ^{13}C signals and assign the ^{1}H chemical shifts.[96]

The temperature dependence of the relative stability of piracetam polymorphs has been studied using solid-state NMR techniques combined with DFT calculations. Piracetam is drug widely used in the treatment of age-associated mental decline and disorders of the nervous system, such as Alzheimer's disease and dementia, and exists in three polymorphic forms (P1, P2 and P3).[97]

Glycopolymeric vesicles designed to target tumour cells loaded with two drugs, ellipticine and curcumin, were characterised using solid-state NMR and CASTEP calculations to shed light on the nature of the drug, the polymer and their interactions. Intermolecular interactions between the polymeric vesicles and the drugs, ellipticine as well as curcumin, were detected using 2D ^{1}H MAS NMR, indicating that the drugs are localised in the hydrophobic layer of the vesicles.[98]

Solid-state ^{43}Ca and ^{13}C NMR studies of the ethylene glycol solvate of atorvastatin calcium have been reported. The ^{13}C and ^{43}Ca chemical shift and ^{43}Ca quadrupolar coupling tensor parameters were determined. The results were interpreted in terms of the reported XRD crystal structure of the solvate and were compared with the NMR parameters of atorvastatin calcium trihydrate, the active pharmaceutical ingredient in Lipitor. Hartree-Fock and DFT calculations of the NMR parameters based on a cluster model derived from the optimised XRD crystal structure of the ethylene glycol solvate of atorvastatin calcium were shown to be in reasonable agreement with the experimental ^{43}Ca and ^{13}C NMR parameters.[99]

As described by Hirsh *et al.*, variable-hydrate APIs are known to form thermodynamically and kinetically stabilised solid phases over a continuous range of hydration levels. Some of these forms can be problematic in the production of solid dosage forms (e.g., tablets and capsules), where manufacturing processes can induce changes in the hydration level of the API, resulting in transformations to undesirable solid phases. Using solid-state ^{35}Cl NMR, Hirsh *et al.* have studied the local and long-range structural effects of water under different storage and processing conditions. Solid-state ^{35}Cl NMR spectra were shown to be sensitive to the presence of water and revealed distinct Cl^- environments in the hydrated and dehydrated forms of the API. They were also used for probing the local environments of Cl^- ions in tablets processed using either wet or dry granulation.[100]

Lau *et al.* have demonstrated that NMR measurements of ^{19}F chemical shift anisotropy and ^{1}H-^{19}F dipolar couplings provide unprecedented information on the molecular orientations of two fluorine-containing statin drugs within the heterogeneous environment of reconstituted high-density lipoprotein nanoparticles, a drug delivery system under clinical investigation.[101]

Various statins and their interactions with phospholipid membranes were also studied by Galiullina *et al*. Using ^{1}H NOESY MAS NMR, it was shown that atorvastatin, cerivastatin, fluvastatin, rosuvastatin and some percentage of pravastatin intercalate the lipid-water interface of membranes to different degrees. Based on cross-relaxation rates, the different average distribution of the individual statins in the bilayer was determined quantitatively.[102]

Molecular interactions between the active pharmaceutical ingredient and a polymer have potentially a substantial impact on the physical stability of amorphous solid dispersions. To gain insight into the nature of the molecular contacts and mechanistic roles in various physicochemical and thermodynamic events, a spectroscopic characterisation of posaconazole (POSA) formulations, a triazole antifungal drug, has been undertaken. Solid-state NMR techniques including spectral editing, heteronuclear ^{1}H-^{13}C, ^{19}F-^{13}C, ^{15}N-^{13}C and ^{19}F-^{1}H polarisation transfer and spin correlation and ultrafast MAS were applied. Active groups in triazole and difluorophenyl rings showed interactions with two polymers, hypromellose acetate succinate and hypromellose phthalate, including intermolecular O–H…O=C and O–H…F–C hydrogen bonding and π–π aromatic packing.[103]

Porcino *et al.* have shown how solid-state NMR can be used to understand the interactions between nano-sized metal-organic framework (MOF) interfaces and both the surface-covering groups and the drug loaded inside the micropores. Aluminium-based MOFs loaded with phosphorus-containing species were studied.[104]

Using solid-state NMR spectroscopy and complementary tools, a loading-dependent structural model of polymeric micelles encapsulating curcumin has been proposed. Changes in the chemical shifts and cross-peaks in 2D NMR experiments provided evidence for the involvement of the hydrophobic polymer block in the curcumin coordination at low loadings, while an increase in the interaction with the hydrophilic polymer blocks was observed at higher loadings.[105]

Using a suite of advanced MAS NMR techniques and powder XRD experiments, a comprehensive structural analysis of bone-inductive biomedical implants and pyrophosphate-bearing calcium phosphate cements, has been presented by Yu *et al.* 2D MAS NMR experiments showed close contacts between the amorphous pyrophosphates and the monetite phase. Heteronuclear ^{1}H-^{31}P and homonuclear ^{31}P-^{31}P correlation NMR experiments enabled minor cement constituents, that could not be ascertained by the Rietveld method, to be detected, identified and quantified.[106]

Contact lenses are worn by over 140 million people each year and significant research is being carried out to identify hydrogel components. ^{13}C CPMAS NMR was employed to compare the carbon composition of soft contact lenses. ^{13}C NMR spectra of individual polymer components enabled the determination of the approximate molecular carbon contributions of major lens components.[107]

The hydroxyl content of bone apatite mineral has been measured using solid-state ^{1}H NMR with a multiple-pulse dipolar filter under MAS. This new method succeeded in resolving the main hydroxyl peak at ~0 ppm from whole bone, making it amenable to rigorous quantitative analysis. The proposed methodology, involving line fitting, the measurement of the apatite concentration in the studied material and adequate calibration, proved to be suitable for monitoring bone mineral hydroxylation in different species and over the lifetime of the animal.[108]

4.3 Proteins

4.3.1 Methodology

Gallo *et al.* have presented a suite of two-receiver solid-state NMR experiments for backbone and sidechain resonance assignment of proteins. The experiments rely on either dipolar or scalar coupling for polarisation transfer and were devised to acquire a ^{1}H-detected 3D experiment and a nested ^{13}C-detected 2D experiment from a shared excitation pulse. Two-dimensional rows were signal averaged during 3D planes to compensate for the lower sensitivity of the ^{13}C detection. It was shown that the 3D dual receiver experiments do not suffer from any appreciable signal loss compared to their single receiver versions and need no extra optimisation. At the same time, the acquired data is higher in information content at no extra time cost.[109]

Extensive deuteration is used to simplify NMR spectra by diluting and minimising the effects of the abundant ^{1}H nuclei, and perdeuteration has been widely applied in solution NMR and solid-state MAS NMR of proteins. Oriented sample solid-state NMR of proteins, however, is at a much earlier stage in this regard. Long *et al.* have mapped out the effects of perdeuteration on solid-state NMR spectra of aligned samples by closely examining differences in results obtained on fully protiated and perdeuterated samples, where all of the carbon sites have either ^{1}H or ^{2}H bonded to them respectively. Linewidths in the ^{15}N chemical shift, ^{1}H chemical shift and ^{1}H-^{15}N dipolar coupling frequency dimensions were compared for peptide single crystals as well as membrane proteins. Linewidth differences were not found between fully protiated and perdeuterated samples. However, in the absence of effective ^{1}H-^{1}H homonuclear decoupling, the linewidths in the ^{1}H-^{15}N heteronuclear dipolar coupling frequency dimension were greatly narrowed in the perdeuterated samples. As shown by the authors, in oriented sample solid-state NMR, the effects of perdeuteration can be exploited in experiments where ^{1}H-^{1}H homonuclear decoupling cannot be applied.[110]

Recent developments in solid-state NMR spectroscopy have also enabled structural biology with small amounts of non-deuterated proteins, largely alleviating the typical demands of sample production. Using a 29 kDa carbonic anhydrase:acetazolamide complex, Vasa *et al.* have shown that different aspects of solid-state NMR assessment of a complex spin system can be accessed using a non-deuterated sample in combination with adequate spectroscopic tools. The demonstrated access to protein structure, protein dynamics, as well as biochemical parameters in amino acid sidechains, such as histidine protonation states, is likely to be transferable to proteins that are not expressible in *E. coli*.[111]

Perez *et al.* have presented a strategy that combines sparse paramagnetic solid-state NMR restraints with atomistic simulations. Their approach explicitly accounts for uncertainty in the interpretation of experimental data through the use of a semi-quantitative mapping between the data and the restraint energy. The new approach was applied to solid-state NMR data for the model protein GB1 labelled with Cu^{2+}-EDTA at six different sites. The authors were able to determine the structure to 0.9Å accuracy within a single day of computation on a GPU cluster.[112]

4.3.2 Dynamics studies

Studying protein dynamics on microsecond-to-millisecond (μs-ms) time scales can provide important information about protein function. In MAS NMR, μs dynamics can be probed by $R_{1\rho}$ rotating-frame relaxation dispersion experiments in different regimes of r.f. field strengths: at low r.f. field strength, isotropic chemical shift fluctuation leads to "Bloch-McConnell-type" relaxation dispersion, while on approaching rotary resonance conditions bond angle fluctuations manifest as increased $R_{1\rho}$ rate constants ("Near-Rotary-Resonance Relaxation Dispersion"). Marion *et al.* have explored the joint analysis of both regimes to gain comprehensive insight into motion in terms of geometric amplitudes, chemical shift changes, populations and exchange kinetics. They used numerical simulations to illustrate these effects and applied the methodology to the study of a previously described conformational exchange process in ubiquitin.[113]

Protein-water interactions are known to affect protein structure and dynamics. As such, the function of many proteins can be directly related to the presence and exchange of water molecules. While the structural water sites can be characterised by XRD, the dynamics within functional water-protein network architectures remains mainly unknown. Singh *et al.* have employed solid-state NMR relaxation dispersion measurements with a focus on the active-site residues in the enzyme human carbonic anhydrase II (hCAII) that constitute the evolutionarily conserved water pocket. Together with the NMR chemical shifts, signal broadening and results of MD simulations and DFT shift calculations, the relaxation data suggested the presence of a fast μs-timescale dynamics in the pocket throughout the protein-water network. It was proposed that the reorganisation of the water pocket:enzyme architecture may be important for enzymatic activity of this and other proteins.[114]

Dynamic processes in biological solids can be monitored via the quantification of dipolar couplings. Under MAS, order parameters are normally obtained by recoupling of anisotropic interactions involving the application of r.f. pulses. Xue *et al.* have shown that amide backbone order parameters can be estimated accurately in a spin-echo experiment in the case where the rotor spinning angle is slightly mis-calibrated. They have applied this method to determine methyl order parameters in a deuterated sample of the SH3 domain of chicken α-spectrin in which the methyl containing sidechains valine and leucine were selectively protonated.[115]

Common experimental approaches for characterising structural conversion processes, such as protein folding and self-assembly, do not report on all aspects of the evolution from an initial state to the final state. Jeon *et al.* have presented an approach based on rapid mixing, freeze-trapping and low-temperature solid-state NMR with DNP signal enhancement. Experiments on the folding and tetramerisation of the 26-residue peptide melittin following a rapid pH jump showed that multiple aspects of molecular structure can be followed with millisecond time resolution. It is expected that time-resolved solid-state NMR will find many applications in biomolecular structural conversion processes, including early stages of amyloid formation, viral capsid formation and protein-protein recognition.[116]

Structure and dynamics of natural and regenerated chicken feather β-keratin were investigated by ^{13}C CPMAS, ^{13}C and ^{1}H spin-lattice relaxation times and ^{13}C 2D PASS MAS NMR measurements. The motional correlation time at each carbon site of both natural and regenerated chicken feather β-keratin and CSAs were determined. The change in molecular dynamics of structural protein after pre-treatment was monitored by 2D PASS MAS NMR and ^{13}C relaxation measurements. This type of comprehensive study is expected to provide information about the interrelation between the structure and dynamics of proteins.[117]

4.3.3 Amyloid proteins

Deuterium solid-state NMR techniques under static conditions were employed to discern details of the μs–ms timescale motions in the flexible N-terminal subdomain of $A\beta_{1-40}$ amyloid fibrils. In particular, rotating frame ($R_{1\rho}$) and newly developed time-domain quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) relaxation measurements were used at the selectively deuterated sidechains. The two experiments were shown to be complementary in terms of probing somewhat different timescales of motions, governed by the tensor parameters and the sampling window of the magnetisation decay curves.[118]

Static solid-state ^{2}H NMR was also employed to probe the dynamics of selected sidechains of the N-terminal domain of $A\beta_{1-40}$ fibrils. Lineshape and relaxation data suggested a two-state model in which the domain's free state undergoes a diffusive motion that is quenched in the bound state. It was also found that the diffusive motion is quenched in the absence of solvation. The solvent acted as a plasticizer, reminiscent of its role in the onset of global dynamics in globular proteins. Using ^{2}H T_1 measurements, the conformational exchange rate constant between the free and bound states under physiological conditions was determined. Zinc-induced aggregation led to the enhancement of the dynamics, manifested by faster conformational exchange, faster diffusion and lower freezing-curve midpoints.[119]

Paramagnetic solid-state NMR spectroscopy was used to characterise protein-solvent interfaces in human Y145Stop prion protein amyloid fibrils.[120]

High-order assemblies of amelogenin, the major protein in enamel protein matrix, are believed to act as the template for enamel mineral formation. The leucine-rich amelogenin (LRAP) is a natural splice-variant of amelogenin. It has been shown that LRAP aggregates hierarchically into assemblies of various sizes in the presence of both calcium and phosphate ions. Solid-state NMR, combined with XRD and microscopic techniques, was applied to give a picture of LRAP self-assemblies by Ma *et al*. They confirmed that LRAP assemblies with different sizes all contained a consistent rigid segment with β-sheet secondary structure, and that the β-sheet segment would further assemble into amyloid-like structures.[121]

Solid-state NMR and STEM were employed by Hwang *et al.* to compare the 3D structures of mouse and human α-synuclein fibrils.[122]

4.3.4 Membrane proteins

Membrane protein folding, structure and function are known to strongly depend on a cell membrane environment, while detailed characterisation of folding within a lipid bilayer is challenging. Studies of reversible unfolding yield valuable information on the energetics of folding and on the hierarchy of interactions contributing to protein stability. A methodology has been proposed by Xiao *et al.* that combines H/D exchange and solid-state NMR to follow membrane protein unfolding in lipid membranes. Atomistic description of the unfolding pathway of a seven-helical photoreceptor was obtained. The pathway was visualised through solid-state NMR-detected snapshots of H/D exchange patterns as a function of temperature.[123]

Determining the environment surrounding a protein often allows its function to be better understood. By using ^{1}H-detected solid-state NMR, it has been shown that reduced spin diffusion within the protein under conditions of fast MAS, high magnetic field and sample deuteration allows the efficient measurement of site-specific exposure to mobile water and lipids. This site specificity was demonstrated on two membrane proteins.[124]

Many membrane proteins are known to sense and induce membrane curvature for function. However, information about how proteins modulate their structures to cause membrane curvature is scarce. Liao *et al.* have presented the results of their solid-state NMR studies of two virus membrane proteins: the influenza M2 proton channel, which has a drug-binding site in the transmembrane pore, and a parainfluenza virus fusion protein, which merges the cell membrane and the virus envelope during virus entry. The chemical shift values were analysed to follow conformational changes.[125]

The main function of the major histocompatibility complex class II (MHC II) membrane proteins is associated with a large number of autoimmune diseases, such as diabetes type I and chronic inflammatory diseases. It is assembled from DQ alpha 1 (DQA1) and DQ beta 1 (DQB1) transmembrane helical domains. The structure and topology of the DQA1 and DQB1 domains were studied by oriented ^{2}H and ^{15}N solid-state NMR. It was found that the DQB1 and to a lesser extent the DQA1 transmembrane helical domains exhibit a strong fatty acyl chain disordering effect on the inner segments of the ^{2}H-labelled palmitoyl chain of POPC bilayers.[126]

The membrane topology of the peptide 18A, a derivative of apolipoprotein A-I, was also investigated in detail using solid-state ^{15}N or ^{2}H NMR techniques. Apolipoprotein A-I is the dominant protein component of high-density lipoproteins with important functions in cholesterol metabolism.[127]

Eddy *et al.* have reported the results of their structural characterisation of the human membrane protein VDAC2 in lipid bilayers using MAS NMR techniques. VDAC2 has been implicated in cardio-protection and plays a critical role in a unique apoptotic pathway in tumour cells. Despite its medical importance, there have been few biophysical studies of VDAC2 in large part due to the difficulty of obtaining homogeneous preparations of the protein for spectroscopic characterisation. The excellent resolution in the MAS spectra achieved by Eddy *et al.* allowed several sequence-specific assignments of the signals for a large portion of the VDAC2 N-terminus and other residues in 2D and 3D heteronuclear correlation experiments.[128]

Cellular solid-state NMR spectroscopy was used to examine the β-barrel assembly machinery complex (BAM) in native membranes. To reduce spectral crowding, ^{1}H-detected experiments were employed together with amino-acid specific isotope-labelling in ^{13}C,^{13}C correlation experiments. The results provided insight into the overall fold and assembly of the BAM complex in native membranes.[129]

4.4 Nucleic acids

In recent years, solid-state NMR is emerging as one of the most informative techniques for structural and dynamics characterisation of RNAs, which play important role in cellular processes. Despite successful applications, further research is needed to broaden the scope of solid-state NMR studies of RNAs. One particular issue in this regard is sample preparation, as most solid-state NMR applications rely on availability of RNA crystals to ensure high-quality spectra. In their communication, Zhao *et al.* highlighted that sufficient hydration of non-crystallised RNA could provide spectra with similar quality to that of crystallised RNA. A simplified RNA preparation technique was proposed based on ethanol precipitation. The new approach was successfully applied for the preparation of two different RNAs varying in molecular size: a genomic RNA from the dimerization initiation site of HIV-1 and an adenine riboswitch. Solid-state ^{31}P NMR spectra were employed to compare the linewidths of spectra from samples prepared using different techniques.[130]

Protein–nucleic acid interactions play an important role not only in energy-providing reactions, but also in reading, extending or repairing genomes. In favourable cases, these can be characterised using diffraction techniques, though complementary methods are needed for studying non-crystalline complexes. Weigand *et al.* have demonstrated how solid-state NMR spectroscopy can detect and classify protein–nucleic interactions through site-specific ^{1}H- and ^{31}P-detected techniques. The sensitivity of ^{1}H chemical shift values to non-covalent interactions involved in these molecular recognition processes was used to probe directly the chemical bonding state. It was shown that these ^{1}H- and ^{31}P-detected NMR techniques can be used to characterise interactions in sediments of the 708 kDa dodecameric DnaB helicase in complex with ADP : AlF_4^- : DNA, despite the very large size of the complex.[131]

The ability of the modern solid-state NMR spectroscopy to investigate very large complexes is further demonstrated by Damman *et al.* Liquid-liquid phase separation is increasingly recognised as a process involved in cellular organisation. Thus far, a detailed structural characterisation of this intrinsically heterogeneous process has been challenging. Damman *et al.* combined solid-state and solution NMR to obtain insights into the assembly and maturation of cytoplasmic processing bodies that contain messenger RNA (mRNA), as well as enzymes involved in mRNA degradation. The results revealed that the enhancer of decapping 3 protein domains exhibit diverse levels of structural organisation and dynamics.[132]

Using in-cell NMR, the effect of toxins and antimicrobial peptides on intact cells can be studied. It has been shown that solid-state ^{31}P NMR can be used to quantitatively characterise the dynamic behaviour of DNA within intact live bacteria. Lipids were also identified, although ^{31}P dynamic filtering methods indicated a range of dynamic states for phospholipid headgroups. The authors demonstrated the usefulness of this methodology for monitoring the activity of the antibiotic ampicillin and the antimicrobial peptide maculatin 1.1 against Gram-negative bacteria.[133]

4.5 Polymeric materials

Solid-state ^{1}H NMR lineshape analysis and DQ ^{1}H NMR experiments have been used by Alam *et al.* to study the segmental and polymer chain dynamics as a function of temperature for a series of thermosetting epoxy resins produced using different diamine curing agents. Materials containing a ferrocene-based diamine curing agent were evaluated to address the role of ferrocene on the atomic-level polymer dynamics. DQ ^{1}H NMR experiments at temperatures above the glass transition point provided a measure of the relative crosslink and entanglement densities.[134]

Detailed chemical structures and kinetics of chemical reactions at the surface and core regions of ^{13}C-labelled atactic-poly(acrylonitrile) (aPAN) films heat-treated under air have been investigated by solid-state NMR and ESR. It was demonstrated that both ^{13}C MAS NMR spectral patterns and ^{1}H spin–lattice relaxation time (T_{1H}) values depend strongly on the film thickness. The thickness dependence of apparently single T_{1H} values was interpreted in terms of superposition of the short and long T_{1H} components at the surface and inner cores, respectively. Two-dimensional T_{1H}-filtered ^{13}C-^{13}C through-bond correlations were employed to selectively observe either well-stabilised aPAN structures at the surface or poorly stabilised ones at the inner core in the films.[135]

The oxidative and non-oxidative degradation behaviour of a flexible polyurethane foam, synthesised from toluene diisocyanate and a polyether polyol, has been reported by Allan *et al*. Solid-state ^{13}C NMR indicated that ring fusion of the aromatic components within the foam occurs at temperatures above 300 °C, which leads to a nitrogen-containing carbonaceous char with a complex aromatic structure. It was proposed that the aromatic nitrogen-containing species, such as toluene diisocyanate and diaminotoluene, undergo secondary reactions and ring fusion under the confined conditions of the degradation, to yield a complex char structure.[136]

Variable-temperature solid-state NMR spectra and relaxation times have been measured by Nishida *et al.* to study polyethylene glycol (PEG) and its interaction with biomass constituents in coniferous wood (Japanese cypress). Signal intensity changes were observed in the ^{1}H and ^{13}C pulse transfer saturation (PST) MAS NMR spectra depending on the melting point of the impregnated PEG and the measurement temperature. PEG impregnation into cypress decreased the T_{1H} values at 80 °C for short to medium chain PEG in the liquid phase while it decreased T_{1H} values at ambient temperature for long chain PEG in the solid phase.[137]

The structure and thermosetting mechanism of silicon-containing polyarylacetylene resins containing Si-(R_1, R_2), where R_1 and R_2 represent methyl, phenyl or acetylenic groups, have been investigated using ^{13}C and ^{29}Si CPMAS techniques. It was found that biphenyl and naphthalene rings are formed via a Diels–Alder reaction between the Ph—C≡C and C≡C groups and that the terminal alkyne mainly transforms into ethylenic bonds.[138]

Solid-state ^{11}B NMR has been employed to investigate the boron coordination environments in silicone boronic acid polymers. From the analysis of the ^{11}B quadrupolar lineshape, the coordination number and coordination sphere symmetry of boron was determined. Elastomer formation was attributed to cross-linking between boronic acid sites through four-coordinated boron centres.[139]

The ^{1}H–^{29}Si multiple-contact (MC) CPMAS NMR experiment has been evaluated by Smet *et al.* using silicate-siloxane copolymers, known as polyoligosiloxysilicones (POSiSils). The method provided quantitative ^{29}Si NMR data in experimental times much reduced compared with single pulse acquisition. A related method, the ^{29}Si–^{29}Si DQ/SQ MC CPMAS NMR experiment, provided structural information about through-space proximities between all silicon atoms. The results obtained expand the applicability of NMR crystallography to inorganic polymers with different dimensionalities and heterogeneous relaxation characteristics.[140]

Silicone polymers were also studied by Dorn *et al.* They determined the microstructure of the silicon-based functional polymer poly(1,4Si_6) arising from the dehydrocoupling polymerisation of cyclosilane 1,4Si_6. Solid-state ^1H-^{29}Si refocused INEPT NMR experiments allowed the unambiguous determination of the number of attached protons to a silicon atom for each ^{29}Si NMR site in 1,4Si_6 and poly(1,4Si_6). ^{29}Si CPMAS spectra of poly(1,4Si_6) showed the development of SiH resonances upon polymerisation. From DFT calculations on trimer models, the preference of chair or twist-boat conformations were established. ^{29}Si chemical shift calculations of the lowest-energy structures showed that conformers and stereoisomers are expected to give rise to distinct ^{29}Si NMR peaks and likely explain the appearance of multiple sets of ^{29}Si NMR signals in experimental spectra.[141]

Solid-state DNP-enhanced NMR has been applied to study selenate-loaded selenium water remediation materials. A significant reduction in experiment time was achieved for ^{13}C measurements with DNP. For the selenium remediation materials, efficient acquisition of $\{^1H\}^{77}Se$ heteronuclear correlation spectra was achieved, providing information about the nature of the binding of the remediated selenate ions with the grafted sidechains.[142]

4.6 Plant-derived materials

4.6.1 Cellulose

Ghosh *et al.* employed solid-state NMR to study the internal structure and dynamics of commercial and natural cellulose. They measured ^{13}C CSA parameters and spin-lattice relaxation rates (R_1) for each carbon site. Two distinct peaks were observed for some of the carbon sites, which were attributed to the nuclei in amorphous and paracrystalline regions. Molecular correlation times were calculated using T_1 and CSA parameters. It was found that the molecular correlation time of the amorphous region is an order of magnitude less than that of the crystalline region.[143]

^{13}C CPMAS NMR has been applied for the quantification and structural characterisation of cellulose in cotton polyester blends. The results demonstrated that solid-state NMR can be used for a reliable determination of cellulose and polyester in both preconsumer and postconsumer waste textiles.[144]

As indicated by Kirui *et al.*, the insufficient resolution of conventional methods has limited the structural elucidation of cellulose and related materials, especially for those with relatively low crystallinities. They studied the molecular structure of unlabelled cotton cellulose by combining DNP-enhanced natural abundance solid-state ^{13}C–^{13}C correlation spectroscopy with statistical analysis of the observed and literature-reported chemical shifts. This study provided significant insights into cotton cellulose and presented a widely applicable strategy for analysing the complex structure of cellulose-rich materials without isotope-labelling.[145]

Existing NMR methods were revised to estimate the crystallinity of cellulose by Sparrman *et al*. They also introduced a complementary NMR method based on ^{13}C T_1 relaxation times. It was shown that the ^{13}C T_1 differs by an order of magnitude for amorphous and crystalline polymers, including cellulose. The authors used the signal boost of ^1H-^{13}C CP and the difference in ^{13}C T_1 as a filter to calculate the degree of crystallinity. The method was applied to five cellulosic samples and the obtained degree of crystallinity compared with values estimated from deconvoluted X-ray scattering patterns.[146]

The same group also determined the molecular orientation distribution in a Lyocell-regenerated cellulose fibre bundle using rotor synchronised (ROS) MAS NMR spectroscopy to measure CSA parameters. The chemical shift tensor was also calculated using DFT for the crystalline cellulose II structure.[147]

A new simple method based on solid-state ^{13}C CPMAS NMR has been described, which relies on the quantification of the intricate signals of the washed oxidised sample of cellulose using the sharp C1 signal of intact cellulose as an internal standard. This new NMR method was applied to microfibrillated cellulose. It is anticipated that this method could be applied to a wide range of substrates with a different morphology and crystallinity.[148]

Cellulose nanocrystal films with either disordered or chiral nematic structures of varying helical pitch have been investigated using solid-state ^{23}Na NMR. The results showed that the Na^+ cations are well hydrated in the cellulose nanocrystal films. Linewidth analysis indicated that the Na^+ cations move in confined spaces. Using ^{23}Na 2D nutation NMR, the Na^+ environments within the ordered and disordered films were distinguished. The approach described by the authors has been shown to be useful for characterising the extent of order in nanocellulose samples.[149]

4.6.2 Polysaccharides

To understand how acidic conditions affect the molecular structure and dynamics of wall polysaccharides, *Arabidopsis thaliana* primary cell walls have been characterised and compared at pH 6.8 and 4.0 using quantitative solid-state ^{13}C NMR spectra. ^{13}C INEPT spectra, which selectively detect highly dynamic polymers, indicated that some of the homogalacturonan (HG) and rhamnogalacturonan (RG) chains in the interfibrillar region become more dynamic in the acidic wall compared to the neutral cell wall, whereas other chains become more rigid. Dipolar couplings and 2D ^{13}C-^{13}C correlation spectra were also measured. Water-polysaccharide ^{1}H spin diffusion data showed that cellulose microfibrils are better hydrated at low pH.[150]

The structure and dynamics of the second most abundant biopolymer, α-chitin, have been studied by using ^{13}C CPMAS NMR spectral analysis, ^{13}C relaxation measurements at 8 chemically different carbon sites and CSA measurements by 2D PASS MAS NMR. A large value of the CSA was observed for the carbonyl group carbons, which was attributed to electrostatic effects, hydrogen bonding and molecular magnetic susceptibility. ^{13}C relaxation was mainly governed by the CSA, especially at high values of the external magnetic field (11.74 T). The correlation times at different carbon sites were also calculated using T_1 and CSA values.[151]

The interaction between wheat starch and *Mesona chinensis* polysaccharide (MCP) was found to change the molecular mobility of the water and carbohydrate populations in starch-MCP gels, when measured using ^{1}H and ^{13}C NMR relaxation methods. The C6 site of the starch glucan monomer was observed to have the largest mobility change in the presence of MCP. Two mobility populations of C6 were observed, possibly corresponding to the C6 in the linear chains of both amylose and amylopectin, and another to the C6 involved in the branching of amylopectin.[152]

Corn starch plasticised with urea and/or glycerol was also studied using ^{1}H and ^{13}C NMR. The information on the interactions between plasticizers and starch macromolecules as well as the arrangement of starch macromolecules depending on the storage time, were obtained from ^{1}H wideline, ^{1}H MAS and ^{13}C CPMAS NMR spectra. The ^{1}H chemical shifts for the groups of the plasticizer molecules enabled characterisation of the interactions between urea and glycerol in starch. The free water amount in starch samples was also estimated using ^{1}H MAS NMR.[153]

4.6.3 Lignin

Lignin is a complex aromatic biopolymer that strengthens and waterproofs plant secondary cell walls, enabling mechanical stability in trees. Removal of lignin is a key step in paper production and biomass conversion to biofuels. To understand the physical nature of lignin's interactions with wall polysaccharides, DNP-enhanced solid-state NMR studies of intact maize stems were undertaken, which revealed that lignin has abundant electrostatic interactions with the polar motifs of xylan.[154]

Hydrolysis lignin is formed as a by-product of cellulose production. The ability of hydrolysis lignin to retain water was studied using solid-state ^{1}H and ^{13}C NMR. The samples were humidified in desiccators containing different saturated salts solutions with different relative air humidity. It was found that the hydrolysis lignin is hydrated in the whole volume and water molecules penetrate deeply into the layers of polymer. ^{13}C NMR revealed that hydrolysis lignin hydrates in both hydrophilic and hydrophobic regions of the macromolecule, and that the bulk of water concentrates around the hydroxyl and methoxy groups of lignin and polysaccharide residues.[155]

The complementary use of solid-state and solution NMR was employed to study the macromolecular structure and properties of lignin. ^{13}C-enriched lignin was prepared by administering [guaiacyl ring-5(G5)-^{13}C]-coniferin to a growing *Ginkgo biloba L.* shoot. The ^{13}C NMR spectrum derived from the G5 carbon was obtained as a difference spectrum based on the spectra of the G5-^{13}C enriched and un-enriched samples. The quantitative ratio of the condensed and uncondensed structures at G5 was found to be larger by solid-state CPMAS NMR than by solution NMR.[156]

4.6.4 Wood and other plant materials

As summarised by Terrett *et al.*, softwood from conifers is mainly composed of the polysaccharides cellulose (galactoglucomannan and xylan) and the phenolic polymer (lignin). The interactions between these polymers lead to wood mechanical strength and must be overcome in biorefining. Terrett *et al.* applied multidimensional solid-state ^{13}C NMR to analyse the polymer interactions in cell walls of the softwood. They proposed a model of softwood molecular architecture which explains the origin of the different cellulose environments observed in the NMR experiments.[157]

Hatakeyama *et al.* have studied the structural change in Japanese cedar powder from ring media pulverisation using solid-state NMR. Their results showed that Japanese cedar powder can be used as a cellulose nanomaterial.[158]

Acetylation and resin impregnation of Japanese cypress were also examined. The ^{1}H MAS NMR showed altered moisture balance after chemical and thermal modifications, while ^{13}C CPMAS NMR showed that acetylation occurred mainly for carbohydrates. The measured relaxation times suggested that molecular motions in the MHz frequency range were suppressed and those in the kHz frequency range were enhanced.[159]

^{1}H-detected NMR experiments were used to increase the spectral resolution, sensitivity and upper limit of measurable distances in plant cell walls consisting of a mixture of polysaccharides. Experiments for ^{1}H-^{13}C correlations at both moderate and fast MAS frequencies of 10–50 kHz were employed to resolve and assign ^{1}H chemical shifts of matrix polysaccharides in *Arabidopsis* primary cell walls.[160]

Structural characteristics of triacylglycerol, polysaccharides and trace elements in coffee beans (Indonesian green beans, roasted beans and spent coffee grounds) have been studied using solid-state ^{1}H and ^{13}C NMR measurements, so that coffee residues can be reutilised as biodiesel oils. Liquid-like triacylglycerol-containing linoleic acids were detected, based on observed signals of the –CH=CH–CH_2–CH=CH– fragment. It was found that triacylglycerol was still abundant in the spent coffee grounds. The chemical structure of triacylglycerol in coffee beans was presented and it was shown that the amount of extracted triacylglycerol can be quantified using solid-state NMR.[161]

4.7 Metal organic frameworks

Fluorescent metal-organic frameworks (MOFs) are promising materials for sensing applications. Fluorescent $Sc_2(NH_2\text{-BDC})_3$ crystals were prepared (BDC = 1,4-benzenedioic acid) and studied using solid-state ^1H, ^{13}C and ^{45}Sc NMR. It was shown that the "as-prepared" $Sc_2(NH_2\text{-BDC})_3$ crystals contained some defects, with the formation of scandium hydroxyls in the crystal structure.[162]

Metal-organic frameworks have shown great potential in gas separation and storage. Recent advances in solid-state NMR investigations of small gas molecules (i.e., carbon dioxide, carbon monoxide, hydrogen gas and light hydrocarbons) adsorbed in MOFs have been discussed by Wong *et al*. The breadth of information that can be obtained by solid-state NMR has been demonstrated, such as the number and location of guest adsorption sites, host-guest binding strengths and guest mobility.[163]

The metal-organic framework ZIF-8 is known for its adsorption and separation properties. A detailed solid-state ^2H NMR investigation of large guest molecules (xylene isomers, benzene, toluene and isobutane) confined inside ZIF-8 has been reported by Khudozhitkov *et al*. The evolution of the ^2H lineshape and T_1/T_2 relaxation times with temperature were interpreted in terms of the existence of different motional states for diffusing guest molecules.[164]

Khudozhitkov *et al*. have also reported solid-state ^2H NMR spectroscopic studies, which revealed the dynamics of pyridine interacting with coordinatively unsaturated metal sites in catalytically active MIL-100(Al) MOFs.[165]

Rauche *et al*. have shown that selective ^{13}C-labelling of carboxylate carbons in the linker molecules of flexible MOFs makes solid-state NMR spectroscopy suitable for investigating solvent-induced local structural changes. This was demonstrated using ^{13}C and ^1H NMR techniques on the pillared layer MOF DUT-8(Ni).[166]

The host–guest interaction between methanol and MOF $Cu_{3-x}Zn_x(BTC)_2$ has been comprehensively studied using solid-state NMR methods combined with quantum chemical calculations. It was found that methanol could be readily coordinated with metal sites Zn^{2+} and Cu^{2+} separately. The ^1H and ^{13}C NMR chemical shifts of methanol coordinated with the distinct metal ions were extracted from hetero- and homonuclear correlation experiments. It was confirmed that Zn^{2+} is likely to be the primary methanol adsorption site according to the experimental observations and theoretical calculations.[167]

The acid strength of MOFs plays a key role in their catalytic performance, such as activity and selectivity during catalytic reactions. Solid-state NMR studies of MOFs with probe molecules 2-^{13}C-acetone and pyridine-d_5 were employed to characterise the acid strength of MOF UiO-66-X (X = H, 2COOH, SO_3H). It was found that after introduction of the functional groups, the acid strength of UiO-66-2COOH and UiO-66-SO_3H was considerably enhanced compared with that of the parent MOF, UiO-66. Theoretical calculations were employed to further confirm the acid strength of UiO-66-SO_3H and UiO-66-2COOH.[168]

4.8 Organometallic and coordination compounds

Lithium cyclopentadienide has been investigated by ^{6}Li and ^{13}C CPMAS NMR and by B3LYP GIAO calculations. From spectral simulations, the axially symmetric ^{13}C shift tensor components were identified to be $\delta_{11} = \delta_{22} = 151.5$ ppm and $\delta_{33} = 15.5$ ppm. The ^{6}Li tensor components were $\delta_{11} = \delta_{22} = +1.0$ ppm and $\delta_{33} = -43.0$ ppm. B3LYP GIAO calculations were found to agree remarkably well with the experimental data.[169]

The structure and thermal reactivity of powdered lead squarate tetrahydrate, $Pb(C_4O_4)\cdot 4H_2O$, have been investigated using solid-state NMR and XRD. It was shown that $Pb(H_2O)(C_4O_4)$ and two polymorphs of anhydrous PbC_4O_4 can be formed under different conditions. The elimination of water was found to lead to the condensation of initial inorganic chains into 2D- or 3D-type crystal structures. The full decomposition of the squarate ligand provided lead oxides.[170]

Four hydrogenated intramolecular phosphane-borane frustrated Lewis pair (B/P FLP) compounds bearing unsaturated cyclic or aromatic carbon backbones have been structurally characterised using solid-state ^{31}P, ^{11}B, ^{2}H and ^{1}H NMR. A comparison of the spectra with those of the free B/P FLPs showed that ^{11}B isotropic chemical shifts and quadrupolar coupling constants decrease upon FLP hydrogenation, revealing the breakage of the partial B−P bond present in the starting materials. From ^{11}B{^{31}P} REDOR experiments, the B−P distance was estimated to be ~3.2 Å. The experimental NMR parameters were reproduced well using DFT methods, and the geometries obtained from energy optimisations or single-crystal structures.[171]

Ke *et al.* have reported solid-state ^{13}C NMR spectra of urea-loaded copper benzoate, $Cu_2(C_6H_5CO_2)_4 \cdot 2$(urea), which was used as a simplified model for copper paddlewheel-based MOFs. Paramagnetic NMR chemical shifts were also calculated using DFT methods. Using the proposed assignments of the signals, the mean absolute deviation between computed and observed ^{13}C chemical shifts was found to be below 30 ppm over a range of more than 1100 ppm.[172]

The sensitivity of solid-state NMR to local environments in the presence of a transition metal has been demonstrated through ^{13}C and ^{1}H MAS NMR spectra of $Mn(acac)_3$. The spectral assignment was carried out using DFT calculations. It was shown that the paramagnetic interaction enhances the spectral resolution and offers the possibility of using these spectra as structural fingerprints.[173]

Crystalline heteroleptic bismuth(III) complexes have been shown to form 1D polymer structures using XRD, ^{13}C and ^{15}N CPMAS NMR measurements.[174]

Similarly, a new representative of mercury(II) dithiocarbamate complexes with a pseudo 1D polymeric structure has been characterised using ^{13}C and ^{15}N MAS NMR and XRD.[175]

4.9 Carbonaceous materials and soils

Twelve bituminous coal samples from China were studied using solid-state ^{13}C NMR techniques.[176]

Structural differences of spontaneous combustion prone inertinite-rich Chinese lignite coals have also been studied using solid-state ^{13}C NMR and other methods.[177]

The protonated nitrogen structure in coals has been studied using quantitative ^{15}N MAS NMR spectra of ^{15}N-labelled synthetic coals. From the 2D NMR results, it was established that there are not only pyrrolic nitrogen groups but also amide-type nitrogen functional groups in the ^{1}H-^{15}N bonded region of the model coal with a sub-bituminous-level degree of carbonisation.[178]

The difficulties and pitfalls with the interpretation of solid-state ^{13}C NMR spectra in graphitic materials have been discussed in detail by Freitas *et al*. The issues with the spectral simulation and the interpretation of the spectral parameters obtained by some arbitrary models reported in the recent literature were examined and alternative methods were presented.[179]

Amino acid derivatives of C_{60} have been studied by solid-state NMR, which showed that the fullerene core is attached to the amino acids via the amino group.[180]

The molecular structure of kerogen in the Longmaxi shale was characterised using solid-state ^{13}C NMR and other techniques.[181]

Humic extracts and humic acids of organic-rich peat soils have been examined by solid-state ^{13}C NMR and shown to be integral components of the peat, contrary to recent suggestions that humic materials are artifacts of alkali extraction. The authenticity of humic substances was demonstrated by recombining humic fractions and comparing NMR spectra of the recombined peat with the original sample.[182]

Humic fractions (fulvic acid, humic acid and humin) isolated from two representative soils (upland and paddy soils) in China under six long-term (>20 years) fertilizer treatments have been quantitatively characterised using CPMAS NMR combined with dipolar dephasing. The results showed that humic fractions reflected changes in environmental conditions and fertilizer treatments.[183]

4.10 Glasses and ceramics

The structural and microstructural properties of both homogeneous and phase-separated lanthanum aluminosilicate (La_2O_3-Al_2O_3-SiO_2) glasses have been investigated using solid-state NMR. A qualitative and simplified structure description was proposed, based on the deconvolution of ^{29}Si NMR spectra.[184]

^{27}Al MAS NMR spectroscopic studies of $Al_{23}Te_{77}$ glass have revealed the existence of 5-coordinated Al and its influence on electrical memory switching.[185]

The short-range structural features in lithium aluminosilicate glasses with various Al_2O_3/Li_2O ratios and the addition of P_2O_5 have been investigated using solid-state NMR. The phosphorus environment was determined quantitatively using ^{31}P MAS NMR constrained by results obtained from ^{31}P-^{27}Al MQ NMR techniques. It was found that phosphorus is mainly located as orthophosphate and pyrophosphate species in glasses with a low amount of Al_2O_3. The local environments of framework (Si and Al) and charge-balancing (Li) cations were also studied.[186]

Bradtmuller *et al.* have explored the beneficial effect of magnesium oxide upon the performance of crack-resistant oxide glasses in a series of aluminoborosilicate glasses. The simultaneous presence of both boron and aluminum oxides in these glasses has a synergetic effect upon crack resistance, the structural origins of which were studied by detailed ^{11}B, ^{23}Na, ^{27}Al and ^{29}Si single and double resonance solid-state NMR measurements. Aluminum was found to be 4-coordinated, whereas boron was found in both 3- and 4-coordinated states. $^{11}B/^{27}Al$ double resonance studies showed no evidence of the formation of new structural units.[187]

The structural evolution of the glass matrix and the formation of crystalline fluoride phases in KF-ZnF_2-SiO_2 glasses has been investigated using XRD and solid-state NMR. A significant amount of SiF_6^{2-} units was detected by employing ^{29}Si MAS and $^{29}Si\{^{19}F\}$ CPMAS NMR. Using dipolar NMR techniques, $^{29}Si\{^{19}F\}$ REDOR and $^{29}Si\{^{19}F\}$ CPMAS NMR, the presence of Si-F connectivity was ruled out.[188]

Precipitation of Er^{3+}-doped $Na_5Y_9F_{32}$ crystals from fluoro-phosphate glasses has been studied using solid-state 2D *J*-resolved, REDOR and HMQC NMR methods by Zhang *et al*. On the basis of luminescence and solid-state NMR spectra, a novel structure evolution model during crystallisation was suggested.[189]

Various compositions of lead bismuth titanate borosilicate glasses doped graphene nanoplatlets have been characterised using ^{29}Si and ^{11}B MAS NMR spectral analysis. The solid-state NMR analysis for five glass samples with different fractions of PbO revealed that the silicate and borate network becomes more polymerised on increasing the content of PbO.[190]

Cao *et al.* have reported in-situ studies of microstructure of CaF_2-Al_2O_3-MgO electroslag by Raman spectroscopy and ^{27}Al MAS NMR.[191]

Short- and medium-range order in photothermal refractive glass has been characterised using ^{19}F MAS NMR, supported by ^{19}F{^{27}Al} and ^{19}F{^{23}Na} dipolar recoupling experiments. Most fluoride within the glass was found within Na-dominated local environments, which also interact strongly with the aluminum. ^{23}Na{^{19}F} rotational echo double resonance revealed that about 1/3 of the Na^+ ions have fluoride ions in their first coordination spheres.[192]

Kim and Lee applied high-resolution ^{29}Si and ^{17}O solid-state NMR techniques to establish the degree of polymerisation and structural disorder in $(Mg,Fe)SiO_3$ glasses and melt. Though qualitative, the NMR methods shed light on the structures of iron-bearing natural volcanic glasses and are expected to improve the understanding of the transport properties of the basaltic melts.[193]

A comprehensive study of the Na environments in a large ensemble of 32 silicate-based glass compositions from the borosilicate, phosphosilicate and borophosphosilicate systems has been presented. The spatial distribution of Na in the glasses was examined using ^{23}Na NMR. The relative propensities of Na to associate with the BO_3 and BO_4 structural moieties in B-bearing glasses were probed by heteronuclear dipolar-based ^{11}B{^{23}Na} MAS NMR. The experimental NMR data agreed well with the results from MD simulations.[194]

Fluoroapatite formation in a new bioactive glass composite for orthodontic adhesives has been studied using solid-state ^{19}F and ^{31}P MAS NMR.[195]

The process of nucleation and crystal formation in lithium disilicate-apatite glass-ceramic SiO_2-Al_2O_3-CaO-Li_2O-K_2O-P_2O_5-F has been investigated using a combination of techniques, including solid-state NMR.[196]

One of the most common bioceramics widely applied in bone cements and implants, β-tricalcium phosphate, was characterised using solid-state ^{31}P NMR and other techniques by Boanini *et al*.[197]

Various structural models of β'-sialons were characterised and distinguished using a combined solid-state ^{29}Si/^{27}Al NMR, powder XRD and computational approach.[198]

Similarly, a combined experimental-computational approach was employed by Pavon *et al.* to gain insight into the atomic structure of designed micas. In particular, natural-abundance ^{17}O MAS NMR and DFT simulations were used.[199]

4.11 Micro- and mesoporous solids

Amorphous aluminophosphates have been synthesised and analysed by ^{27}Al/^{31}P MAS NMR and other techniques. The NMR studies showed the presence of variable contents of tetra- and penta-coordinated Al species, which were correlated with the catalytic activity of $AlPO_4$.[200]

The temperature dependent morphologies of co-existing solid ice and interfacial water within two classic mesoporous materials, MCM-41 and SBA-15, have been investigated below the Gibbs-Thomson transition temperature using NMR spin-diffusion and second moment calculations. This work demonstrated an approach based on the combination of NMR techniques applicable to studies of the porous material surface via probing the interfacial water layers.[201]

Structural characterisation of vanadium environments in MCM-41 molecular sieve catalysts by solid-state ^{51}V NMR has also been reported.[202]

The structure of mesoporous silica encapsulated Pt and PtSn nanoparticles has been established by ^{29}Si MAS NMR. In particular, the connectivity of the –Si–O–Si– network was revealed by DNP-enhanced 2D ^{29}Si-^{29}Si correlation spectroscopy.[203]

Wu *et al.* have reported the results of their solid-state NMR and EPR studies of the mechanism of the direct conversion of methane into methanol over Cu/Na-ZSM-5 zeolite. It was found that the copper methoxy species and the adsorbed methanol transform into free methanol through the process of hydration.[204]

A metakaolinite-rich brick after zeolitisation by alkaline treatments has been characterised by ^{27}Al and ^{29}Si MAS NMR. ^{27}Al MQ MAS NMR was employed to study the Al coordination. ^{23}Na and ^{1}H MAS NMR measurements were performed on the alkali brick to evaluate the abundance of hydrated Na^+ ions.[205]

The adsorption and interaction of *n*-hexane in acidic zeolites have been investigated using ^{1}H MAS NMR. It was shown that *n*-hexane adsorbed on zeolite ZSM-5 is not exclusively interacting with acidic Si(OH)Al groups, but is also affected by the zeolitic framework.[206]

4.12 Surface science and catalysis

As indicated by Mance *et al.*, heterogeneous catalysts fulfil a vital role in industrial processes, while the nature of the catalytic surfaces makes it difficult to study the structure of the active sites. It has been demonstrated that solid-state fast MAS NMR allows well-resolved ^{1}H-detected spectra of heterogeneous catalysts to be detected efficiently. This approach was applied to study the structure of surface species resulting from grafting VO(O*i*Pr)$_3$ onto a partially dehydroxylated silica.[207]

Kobayashi and Pruski have demonstrated the advantages of conventional and DNP-enhanced solid-state NMR methods for detailed studies of the spatial distribution of silica-bound catalytic organic functional groups.[208]

Solid-state ^{1}H and ^{93}Nb NMR studies of the acidity of nanodisperse $Nb_2O_5{\cdot}nH_2O$ have been reported by Yakovlev *et al*.[209]

The local structure of $TiCl_4$ adsorbed onto the surface of $MgCl_2$ has been investigated by solid-state ^{47}Ti/^{49}Ti MAS NMR at 21.8 T along with DFT calculations. The electric field gradient and chemical shielding tensors of ^{49}Ti were obtained via DFT calculations of model molecules.[210]

^{51}V NMR was applied to reveal the mechanism behind the selective catalytic reduction of NO_x with NH_3 to N_2 by V_2O_5(-WO_3)/TiO_2 catalysts. Long-standing uncertainties in the molecular structures of surface vanadia were clarified.[211]

Klimavicius *et al.* have studied room temperature CO oxidation catalysed by supported Pt nanoparticles using DNP-enhanced solid-state NMR.[212]

Solid-state ^{1}H, ^{13}C and ^{29}Si NMR studies of various depolymerised organosiloxanes on silica surfaces have also been reported. The spectral changes observed in solid-state NMR spectra allowed the major products of the reaction of various organosiloxanes to be characterised.[213]

Solid-state ^{1}H, ^{13}C, ^{27}Al and ^{35}Cl NMR measurements were employed to gain insights into surface interactions on grafting bis-silylamido aluminum species on silica. ^{27}Al MAS NMR spectra showed the presence of two types of species where the Al centre adopts a tetracoordinated coordination sphere. Further DFT calculations improved understanding of the grafting mechanism and the spectroscopic properties of the material.[214]

The polar surface structure of oxide nanocrystals has been revealed using solid-state ^{17}O and ^{1}H NMR spectroscopy and DNP, combined with DFT calculations.[215]

As reported by Batista *et al.*, the structural and spectroscopic features of edge sites on γ-Al_2O_3 crystallite surfaces can be unravelled by DFT calculations coupled with high-field ^{1}H MAS NMR measurements.[216]

Surface-enhanced DNP solid-state NMR has been employed to shed light on Bronsted-Lewis acid synergy during zeolite-catalysed methanol-to-hydrocarbon conversion. It was shown that the inclusion of Lewis acidity prevents the formation of carbene/ylide species, directly affecting the equilibrium between arene and olefin cycles, and hence regulating the ultimate product selectivity and catalyst lifetime.[217]

The mechanism and contribution of various oil components to asphaltene adsorption on solid surfaces have been investigated using ^{1}H and ^{13}C solution and solid-state NMR techniques.[218]

4.13 Cements

The hydration of the most important hydraulic phase in calcium aluminate cement, $CaAl_2O_4$, has been studied by Hughes *et al.* by high-field in-situ solid-state NMR, using time-resolved ^{27}Al NMR measurements during the early stages of the reaction. A variant of the NMR technique, involving alternate acquisition of direct-excitation and MQMAS ^{27}Al NMR spectra, was used to monitor the ^{27}Al species present in both the solid and liquid phases as a function of time. The results provided quantitative information on the changes in relative amounts of ^{27}Al sites with tetrahedral (the anhydrous reactant phase) and octahedral coordinations (the hydrated product phases) as a function of time, and revealed significantly different kinetic and mechanistic behaviour of the hydration reaction at 20 ºC and 60 ºC.[219]

The chemical composition of cement pastes exposed to accelerated carbonation using different concentrations of CO_2 has been compared with those of natural carbonation using quantitative XRD and ^{29}Si MAS NMR. The results revealed that complete carbonation was hardly attained. Calcite, aragonite and vaterite were in co-existence after accelerated carbonation, with vaterite being dominant.[220]

^{29}Si and ^{27}Al MAS NMR techniques were employed to study the structure of C-S-H gels of slag cement-hardened paste. It was found that the silicate tetrahedron $[SiO4]^{4-}$ was present in the Q^0, Q^1 and Q^2 states in the hardened paste of Portland cement, and the C-S-H gel mainly existed as the dimer Q^1. After hydration for 3 days, Al^{3+} replaced some of the Si^{4+} in the tetrahedra. The Al/Si ratio was found to reach 0.11 for the slag-cement blend with 50% slag replacement.[221]

4.14 Inorganic and other related solids

The question of whether the broad $^{69/71}$Ga NMR signal of hexagonal gallium nitride (*h*-GaN) at 530–330 ppm is related to the Knight shift was investigated by Tansho *et al.* ^{71}Ga MQ MAS NMR revealed that the quadrupolar interaction products of nanocrystalline *h*-GaN are almost constant (~1.7 ± 0.1 MHz) in the entire shift range investigated. Since this parameter is sensitive to the local chemical symmetry around the Ga atom, the NMR shift distribution was considered not to be related to that of the chemical environment.[222]

Solid-state ^{17}O NMR has been used to study the structure of monoclinic and tetragonal zirconia nanoparticles together with DFT calculations. It was shown that surface oxygen species can be detected selectively using ^{17}O-labelled water to enrich surface oxygen sites. The high-frequency ^{17}O NMR signals arising from low coordinated oxygen ions on the surface of monoclinic and tetragonal zirconia nanoparticles were observed.[223]

High-resolution solid-state ^{19}F NMR has been applied to TiF_4, which bears both bridging and terminal fluorines. The observed 12 isotropic signals were assigned to 6 terminal and 6 bridging fluorines. The isotropic chemical shift for terminal Fs appeared at high frequency (~420–480 ppm from $CFCl_3$ at 0 ppm) with large shielding anisotropy (~850 ppm). For bridging Fs, the isotropic chemical shifts were ~0–25 ppm with moderate CSAs of ~250 ppm. The origin of the observed high-frequency shift for terminal fluorines is ascribed to the second-order paramagnetic shift with increased covalency, shorter Ti−F bonds and smaller energy difference between the occupied and vacant orbitals. Examination of the orientation of the shielding tensor showed that the most deshielded component of the shielding tensor is oriented along the Ti−F bond.[224]

The YTB_4 borides (T = Cr, Mo, W, Re) showed four crystallographically distinct boron sites in their solid-state ^{11}B spectra at 14.1 T. Partial site assignments were possible based on comparisons with electric field gradient calculations using the WIEN2k code. ^{89}Y MAS NMR spectroscopic studies suggested substantially weaker Knight shift contributions to the resonance frequencies compared to other intermetallic yttrium compounds, including other ternary yttrium boride compounds measured previously.[225]

Two-dimensional solid-state ^{19}F MAS NMR exchange spectroscopy was applied by Lunghammer *et al.* to reveal the site preference of the F^- anions when hopping through nanocrystalline solid solutions of PbF_2 and CaF_2. The F^- anions located in sites coordinated by Pb cations were more mobile than those residing near or in Ca-rich environments.[226]

The structures of stable phases in the Cu-Zn-Sn-S system have been investigated using solid-state NMR, XRD and Raman spectroscopy. The NMR results aided in distinguishing octahedral versus tetrahedral Sn^{4+} coordinations.[227]

Solid-state ^{27}Al and ^{39}K NMR studies were used to determine the coordination environments of the Al^{3+} and K^+ cations in layered copper thioaluminate $K_2Cu_3AlS_4$.[228]

The feasibility of high-resolution solid-state ^{175}Lu NMR spectroscopy in intermetallic compounds crystallising with cubic crystal structures was explored by Benndorf *et al.* Sources of the observed line broadening were discussed based on field-dependent static and MAS NMR spectra, providing guidance with respect to measurement conditions, and leading to reliable results.[229]

4.15 Electrolytes and battery materials

Reaction mechanisms have been explored by Kitada *et al.* for silicon monoxide, which is a promising alternative anode material due to its much higher capacity than graphite. An in-depth analysis of the lithium silicide (Li_xSi) phases that form during lithiation/delithiation of SiO was presented, and the results compared with pure-Si anodes, using XRD and solid-state ^{7}Li and ^{29}Si NMR spectra.[230]

Solid-state NMR was employed by Shimoda *et al.* for the structural characterisation of the lithiation/delithiation behaviour of amorphous VS_4, which is a promising positive electrode material for next-generation rechargeable lithium-ion batteries because of its high theoretical capacity.[231]

Marbella *et al.* have used ^{7}Li NMR chemical shift imaging for detecting the early stages of Li microstructural growth in all-solid-state batteries.[232]

As indicated by Dunstan *et al.*, many different chemical controls, such as aliovalent doping, have been attempted to stabilise δ-Bi_2O_3, a material with exceptionally high oxide-ion conductivity which is only stable over a narrow temperature range. A multinuclear NMR approach was applied to characterise and measure oxide-ion motion in V- and P-substituted bismuth oxide materials showing excellent ionic conduction properties. Two main ^{17}O NMR resonances were distinguished, corresponding to O in the Bi–O and V–O/P–O sublattices. Using measurements ranging from room temperature to 923 K, the ionic motion experienced by these different sites was studied. Variable-temperature ^{51}V and ^{31}P NMR experiments showed high rates of tetrahedral rotation.[233]

Ion mobility in $K_{0.45}Bi_{0.55-x}In_xF_{2.1}$ solid solutions has been studied at different temperatures using ^{19}F NMR and conductivity data.[234]

Local structural changes due to the substitution of Na^+ by the larger K^+ ion in piezoelectric ceramic compositions $Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3$ have been studied using ^{23}Na solid-state NMR spectroscopy.[235]

As discussed by Hu *et al.*, magnesium batteries are potential alternatives to lithium-ion batteries because of their lower cost, higher safety and enhanced charge density. However, magnesium readily oxidizes to form a thin MgO surface layer that blocks the transport of Mg^{2+} across the solid electrode-electrolyte interface. A combination of in-situ ^{13}C single-pulse, surface-sensitive ^{1}H-^{13}C CPMAS and quantum chemical calculations was employed to study the adsorption and thermal decomposition of diglyme and electrolytes containing $Mg(TFSI)_2$ in diglyme on 10 nm-sized MgO particles (TFSI = trifluoromethane sulfonyl imide). The results showed that electrolyte composition has a directing role in the species present on the electrode surface.[236]

Ultra-wideline high-field natural abundance solid-state ^{33}S NMR spectra of the Li-ion battery conversion electrode NbS_3 have been reported by Halat *et al.* The observed large quadrupolar coupling (~31 MHz) was consistent with the value obtained from DFT calculations, and the spectra provided evidence for a linear Peierls distortion that doubles the number of ^{33}S sites.[237]

Using ^{1}H and ^{23}Na NMR studies of solid-solution $Na_2(CB_9H_{10})(CB_{11}H_{12})$, Soloninin *et al.* have studied ion dynamics in a carbon-substituted closo-hydroborate salt. It was found that the diffusive motion of Na^+ ions can be described as two jump processes: a fast localised motion within the pairs of tetrahedral interstitial sites of the hexagonal close-packed lattice formed by large anions, and a slower jump process via octahedral sites leading to long-range diffusion.[238]

4.16 Synthetic and natural minerals

Grube *et al.* have applied multinuclear solid-state NMR techniques to identify hydrogen species in alunite-type minerals. The results confirmed the previously proposed defect mechanism for alunite and allowed structural defects to be quantified. Analysis of ^{1}H and ^{27}Al MAS NMR spectra showed that the synthetic ammonioalunite contained small amounts of hydronium (5–10%). The close structural relationship between hydronium and gallium alunite was reflected in the ^{27}Al and ^{71}Ga quadrupole coupling parameters.[239]

Solid-state ^{23}Na MAS NMR spectroscopy of the smectite mineral hectorite acquired at temperatures from –120 ºC to 40 ºC, in combination with the results from MD simulations, have showed the presence of complex dynamic processes in the interlayer galleries that depend significantly on their hydration state. It was found that the average hydration state of Na^+ increases with increasing relative humidity and water content of the clay.[240]

As indicated by Mckay *et al.*, the Earth's transition zone, while being composed of nominally anhydrous magnesium silicate minerals, may be subject to significant hydration. Little is known about the mechanism of hydration, despite the vital role this plays in the physical and chemical properties of the mantle. Mckay *et al.* have presented an ab initio random structure searching investigation of semihydrous (1.65 wt% H_2O) and fully hydrous (3.3 wt% H_2O) wadsleyite. Selected structures from this search were subjected to further geometry optimisation with tighter constraints prior to NMR calculations. The fully hydrous models produced by ab initio random structure searching were able to explain the observed NMR signals, providing detailed insight into the structure of this important mineral.[241]

A solid-state NMR study of local ^{31}P and ^{1}H environments in monetite [$CaHPO_4$; dicalcium phosphate anhydrous (DCPA)] has been presented by Yu *et al.* The three observed ^{1}H NMR peaks were assigned to the crystallographically distinct H sites of monetite, while their pairwise spatial proximities were probed by homonuclear ^{1}H-^{1}H DQ-SQ NMR at the MAS frequency of 66 kHz. The relative ^{1}H-^{31}P proximities were also examined among the inequivalent sites in monetite. The measured shortest internuclear ^{1}H-^{31}P distances agreed well with those from the neutron diffraction study.[242]

Using solid-state ^{19}F NMR spectroscopy, Ren *et al.* have studied the mechanism of fluoride sorption by nanosized hydroxyapatite. The experimental results showed that F^- sorption mechanisms depend on solution pH and fluoride concentration. $^{1}H\{^{19}F)$ REDOR analysis indicated the involvement of a dissolution-precipitation process in the F^- sorption.[243]

4.17 Perovskites

Milic *et al.* have applied solid-state NMR methods to study structure and dynamics in formamidinium-based layered 2D perovskites.[244]

The phase transition, structure and dynamics of mixed lead-free zinc-based perovskites $(MA)_2Zn_{1-x}Cu_xCl_4$ (x = 0, 0.3, 0.5, 0.7 and 1; MA = methyl ammonium) have been investigated using $T_{1\rho}$ measurements by ^{1}H and ^{13}C MAS NMR.[245]

The effects of Co addition on the chemical and electronic structure of $PbTiO_3$ were studied using computational and experimental techniques. ^{207}Pb NMR revealed a growing isotropic component in the presence of Co. Consistent with the experiments, DFT calculated chemical shifts confirmed isotropic coordination of Pb, suggesting the formation of cubic Pb_2CoTiO_6 domains.[246]

Finally, formamidinium-based perovskite solar cells stabilised by 5-ammonium valeric acid iodide have been characterised using multinuclear solid-state MAS NMR measurements and DFT calculations.[247]

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