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Solid State NMR Spectroscopy

BY A.E. ALIEV AND R.V. LAW

1 Introduction

Solid state NMR spectroscopy has now become an enormous field of research: in excess of 1500 publications used this technique in one way or another in the past year. This review takes highlights from all areas of research which we have for clarity's sake divided into subject and further sub-divided by nucleus type.

2 Reviews

Review papers covering theoretical aspects of SSNMR include numerical simulation techniques of SSNMR experiments[1] and application of Lie algebra to NMR.[2]

The condition for an echo formation has been reviewed in the context of half-integer quadrupole system.[3] The common features of the classical echo phenomena and the coherence transfer echo have been highlighted. The article also explains how the measurement of a series of coherence transfer echoes achieves the HR feature of the MQ MAS experiment.

SSB manipulation techniques in MAS NMR have been reviewed by Anzutkin.[4]

Various methodological aspects of half-integer quadrupolar nuclei have been extensively reviewed. Recent advances in experimental developments have been reviewed by Smith and van Eck.[5] The basic theoretical aspects underlying HR MQ MAS NMR experiment, as well practical aspects involved in the optimisation of its sensitivity, have been presented.[6] Also discussed has been the occurrence of unusual SSB patterns along the MQ domain; additional references to ongoing progress in the area that has appeared in the recent literature have also been presented. The advantages and drawbacks of various techniques that utilise MQ MAS NMR for studying molecular sieves and related materials have been reviewed.[7] The techniques reviewed include z-filtered MQ MAS with rotor synchronisation, MQ MAS with CP and MQ MAS with REDOR. Examples of applications include studies of various types of aluminophosphate. ^{59}Co NMR of tetrahedric clusters in solution and in the solid state at high fields has been reviewed.[8] Some recent progress in solid state

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^{47,49}Ti NMR of inorganics and gels has been reviewed.[9] Some complementary data from ^{17}O and ^{13}C NMR and powder XRD has also been included.

The application of SSNMR techniques for the structural determination of polysaccharide[10] and wood and other lignocellulosic materials has been reviewed.[11] Published spectroscopic observations pertaining to the crystal structure of native celluloses have been reviewed with emphasis placed on observations from ^{13}C SSNMR.[12] Considerable discussion has been devoted to the allomorphic composition of cellulose crystallites in higher plants. Published methods of NMR lineshape analysis for the higher plant celluloses have been reviewed and critiqued, both from the point of view of lineshape theory and from the point of view of self-consistency of inferences that are based on lineshape analyses for different carbons.

Review articles on SSNMR applications to biological materials have included MAS studies of oriented membrane proteins.[13] Advantages, practical aspects, and general perspective of MAS on oriented proteins have been presented. Characterisation of polymorphism in pharmaceuticals by SSNMR has also been reviewed.[14]

An overview has been given on recent NMR structural studies of phosphorus chalcogenide glasses and melts.[15] It has been shown that MAS in combination with DQ NMR provides detailed quantitative information on the network structural features present in ionically conducting thiophosphate glasses, spectroscopic and diffraction studies of simple phosphate glasses,[16] comparative studies of amorphous phosphates by HPLC, NMR and XPS,[17] and applications of SSNMR in microstructure studies of glasses.[18] DQ NMR measurements exploiting the dipole coupling between the phosphorus atoms as well as a novel 2D exchange experiment using the scalar coupling have been described for measuring the connectivities of phosphate tetrahedra in glasses.[19] It has been shown that bonding scenarios of up to four connected tetrahedra and the relative orientations of CS tensors can be determined by 2D NMR. This determination provides an additional verification of connectivities and can enable access to bonding angle data in future.

Reviews covering applications of SSNMR techniques to materials of catalytic importance have included.[20,21,22,23,24,25,26] Finally, developments in SSNMR and analytical TEM for advanced understanding of the nature of the nearly amorphous calcium silicate hydrate phases in hardened cement pastes have been reviewed by Richardson.[27]

3 Theory

The CP dynamics between ^{1}H and ^{19}F in a Viton-type fluoroelastomer have been studied using ^{19}F MAS and ^{1}H→19F CP MAS NMR at 188.29 MHz.[28] The phenomenological theory of spin thermodynamics based on the spin temperature hypothesis was employed to describe the polarisation transfer between the ^{1}H and ^{19}F spin baths. Simultaneous fitting of the evolution of magnetisation in the standard CP and a modified CP(TORQUE) experiment, using the exact solutions of the equations for the spin thermodynamics, gave unique sets of the parameters T_{HF}, $T_{1\rho}(^1H)$ and $T_{1\rho}(^{19}F)$ for five separate peaks in the ^{19}F spectra. The values of $T_{1\rho}(^1H)$ and $T_{1\rho}(^{19}F)$ obtained are consistent with those independently measured by spin-locking experiments.

Theoretical description and experimental observation of residual dipolar couplings between quadrupolar nuclei in HR SSNMR have been reported.[29] Nonsecular dipolar couplings between spin-$^1/_2$ nuclei that are in close proximity to quadrupolar spins have been extensively documented in SSNMR, particularly when involving directly bonded S = ^{13}C, I = ^{14}N spin pairs. The most notable characteristic of residual dipolar couplings is that they cannot be entirely averaged away by conventional MAS. Nonsecular dipolar couplings can also be expected to arise when both I and S are quadrupolar nuclei. Theoretical and numerical analysis have been presented for homo- or heteronuclear quadrupolar spin pairs in the high field limit. Variable field MQ MAS NMR results have also been presented for a variety of compounds possessing ^{11}B–^{14}N, ^{11}B–^{11}B and ^{55}Mn–^{55}Mn spin pairs, that validate these theoretical predictions and illustrate the valuable information that can be extracted from analysing these residual dipolar couplings. The research potential as well as resolution limitations that according to theoretical calculations these effects will impart on MQ MAS spectra recorded at low or moderate magnetic fields have thus been evidenced.

The ^{29}Si and ^{27}Al NMR chemical shifts of the two crystallographic sites of the zeolite mazzite have been evaluated from the NMR shielding tensors calculated using the SOS-DFPT method.[30] The calculations were carried out on one-site and two-site models, including from one to three coordination shells around each site. The effects of the cluster size, basis set extension, and choice of the exchange and correlation functional have been analysed. The effect of geometrical and electronic factors on the NMR chemical shifts have been analysed, showing their dependence on the cluster size and also on the shape of the zeolitic system.

The SOS-DFPT has been used to calculate ^{29}Si shielding constants and chemical shifts in zeolites.[31] The calculations were carried out on one-site (1T) $Si(OSiH_3)_4$ and two-site (2T) $R_3SiOSiR_3$ (R = $OSiH_3$) models, including three coordination shells around each site. The ^{29}Si NMR chemical shifts have been shown to be very sensitive to the local geometry. A linear correlation between chemical shifts and average SiOSi angles has been established, taking into account two different zeolites, *i.e.* mazzite and zeolite-beta. The use of 1T models allows the assignment of the experimental spectra, whereas that of 2T models, containing eventually four-membered rings, improves considerably the calculation of the absolute ^{29}Si chemical shifts, including those of silicon sites in aluminated zeolites.

To assist in the assignment and interpretation of ^{23}Na NMR spectra in silicate and aluminosilicate minerals and glasses the ^{23}Na NMR shieldings and the EFGs at the Na for a number of Na-containing species have been calculated.[32] Included are $Na(H_2O)_n^+$, n = 1, 2, 4, 5, 6 and 8, and Na^+ complexes with SiH_3OH, SiH_3ONa and $O(SiH_3)_2$ shieldings and EFGs for Nacentred clusters extracted from crystalline Na_2SiO_3 and anhydrous sodalite have also been evaluated. Based on 6-31G* SCF optimised geometries and the GIAO method with a 6-31G* basis set a calculated increase in shielding with coordination number (CN) for the $Na(OH_2)_n^+$, $n = 4, 6, 8$ series was found. This agrees with experimental trends. Calculated changes in the Na shielding as water is replaced by bridging or nonbridging silicate O atoms were also consistent with experimental observations. Theoretical studies, based on calculation of deshielding contributions for individual O-containing ligands and experimental values for the Na–O distances, were further extended to 12 different Na sites in silicate and aluminosilicate minerals which have recently been studied experimentally.

Experimental and theoretical evidences of enhanced effects of CSA on the DQ dipolar SSB patterns have been presented.[33] The DQ MAS NMR response to a five-pulse sequence of dipolar coupled spin-$^1/_2$ pairs in a powder sample of barium chlorate monohydrate has been investigated for different spinning frequencies and different durations of excitation and reconversion periods. It has been shown that the basic understanding of the effect of chemical shift interaction on MQ SSB patterns will be useful in the quantitative analysis of MQ spectra for structural purposes and may be exploited for measurements of ^1H CSA.

Analytical expressions for MQ signal generation of quadrupole nuclei have been derived.[34] Combined with numerical simulation of the double rotor motion, a strategy has been suggested for partial SSB suppression in MQ NMR spectra. Synchronisation of MQ excitation and selective flip pulses with outer rotor motion increases outer rotor speed effectively two times. This has also been demonstrated experimentally by TQ-SQ correlation spectra of ^{23}Na and ^{67}Rb.

The mathematical foundation of the determination of protein structure from orientational constraints has been described.[35] The tools used are vector algebra, gram matrices, and determinants. The report describes methods applied to the determination of protein structure by SSNMR. Examples have been given relating to the structure of the peptide gramicidin A.

The phenomenological theory of spin thermodynamics based on the spin temperature hypothesis has been employed to describe the CP dynamics between two abundant nuclei, ^{19}F and ^1H, when the number of fluorine atoms is not substantially less than the number of hydrogens.[36] The influence of $T_{1\rho}$s of both nuclei and the relative magnitude (heat capacity) of the two spin baths have been incorporated explicitly into the analysis in order to derive values for the parameters involved in the CP dynamics. Numerical calculations have been performed to clarify the difference in the evolution of magnetisation in variable contact time CP experiments between the $^1H \rightarrow {}^{13}C$ and $^1H \rightarrow {}^{19}F$ cases. A new type of CP-drain experiment has been developed for observing the residual ^1H magnetisation after $^1H \rightarrow {}^{19}F$ CP. Direct polarisation ^{19}F MAS, $^1H \rightarrow {}^{19}F$ CP, and $^1H \rightarrow {}^{19}F$ CP-drain MAS NMR spectra have been measured for a fluorinated polyimide, 6FDA/ODA. The CP dynamics between ^1H and ^{19}F for the polyimide have been analysed on the basis of the spin thermodynamics theory. The constant for polarisation transfer has been determined by the analysis using the effective CP parameters, which were directly obtained from the CP and CP-drain experiments, together with independently measured values of $T_{1\rho}(^1H)$ and $T_{1\rho}(^{19}F)$.

CP from a spin I = $^1/_2$ nucleus (*e.g.* ^{1}H) to a spin S = 3/2 nucleus (*e.g.* ^{23}Na) or a spin S = 5/2 nucleus (*e.g.* ^{27}Al or ^{17}O) in static powder samples has been investigated. The results of conventional SQ, TQ and five-quantum CP experiments have been presented and discussed. Based on a generalisation of an existing theory of CP to quadrupolar nuclei, computer simulations have been used to model the intensity and lineshape variations observed in CP NMR spectra as a function of the rf field strengths of the two simultaneous spin-locking pulses.[37] These intensity and lineshape variations can also be understood in terms of the spin S = 3/2 or 5/2 nutation rates determined from experimental quadrupolar nutation spectra. The results of this study are intended as a preliminary step towards understanding single and MQ CP to quadrupolar nuclei under MAS conditions and the application of these techniques to the MQ MAS NMR experiment.

The spin-locking mechanism of the spin I = 3/2 nuclei under MAS has been theoretically and experimentally investigated, and the criterion of adiabatic passage around zero-crossings of the quadrupole splitting was inferred from the time-dependent Schrödinger equation.[38] It has been shown that SOQ interaction and off-resonance play important roles in the spin-locking of the quadrupolar nuclei, and they were responsible for the great loss of the spin-locking signals. The spin-locking might be achieved by minimising the effect of the SOQ interaction by using a rf offset.

A formalised many-particle nonrelativistic classical quantised field interpretation of MAS RFDR has been presented.[39] A distinction has been made between the MAS spin Hamiltonian and the associated quantised field Hamiltonian. The interactions for a multispin system under MAS conditions have been described in the rotor angle frame using quantum rotor dynamics. In this quasiclassical theoretical framework, the chemical shift, the dipolar interaction, and rf terms of the Hamiltonian have been derived. The effect of a generalised RFDR train of π pulses on a coupled spin system has been evaluated by creating a quantised field average dipolar-Hamiltonian formalism in the interaction frame of the chemical shift and the sample spinning. This derivation shows the analogy between the Hamiltonian in the quantised field and the normal rotating frame representation. The magnitude of this Hamiltonian peaks around the rotational resonance conditions and has a width depending on the number of rotor periods between the π pulses. Its interaction strength can be very significant at the $n = 0$ condition, when the CS anisotropies of the interacting spins are of the order of their isotropic chemical shift differences.

The representation of second-order broadening effects in SSNMR by general fourth-degree surfaces has been presented.[40] Static SOQ and 'dipolar-quadrupolar' interactions have been treated in a unified way. Most experiments involving the fast reorientation of samples such as MAS, variable-angle spinning, DAS, and DOR and MQ MAS have also been illustrated by using averaged fourth-degree surfaces. The equations of the surfaces have been derived analytically and allow the derivation of most results concerning these experiments.

A general formalism has been developed for describing the effects of restricted rotational diffusion on ^{2}H MAS NMR spectra.[41] The approach is based on the Smoluchowski model that describes restricted rotational diffusion in an arbitrary ordering potential with an arbitrary diffusion tensor. It has been shown that the Smoluchowski model gives a physically more reasonable description of molecular motion than the discrete Markov (jump) model. The models have been shown to be mutually consistent for high ordering potentials and low temperatures provided the diffusion coefficient is sufficiently high. However, for low ordering potentials and high temperatures the discrete Markov model is not a useful approximation and the spectra can only be simulated with restricted rotational diffusion. This is also the case for small diffusion coefficients independent of the ordering potential and the temperature. The formalism is based on finite difference solutions to the stochastic Liouville-von Neumann equation. This defines a linear homogeneous system of coupled parabolic partial differential equations which includes both first- and second-order spatial derivatives. Numerical solutions are very difficult to obtain and some useful finite difference methods have been presented. The results have been elaborated for ^{2}H MAS NMR spectroscopy. Solutions have been obtained both in the presence and absence of rf irradiation and effects of finite pulse width have been included. The method has been applied to the investigation of motional effects on ^{2}H MAS NMR spectra of L-alanine-N,N,N-$^2H_3$. The orientational dependence of the ordering potential and the quadrupole parameters has been determined from the Smoluchowski model. The activation energies have been found to be temperature dependent. These effects have not previously been observed and give new information on molecular motion in this system. The rotational diffusion results have been compared with the discrete Markov model and it has been found that in this case the two models are consistent. The most important difference is that the Markov model does not map out the orientational dependence of the ordering potential and the quadrupole parameters. Another advantage of the rotational diffusion model is that it is physically more reasonable than the Markov model and that the parameters may be interpreted in terms of molecular properties.

A diffusion equation appropriate to the NMR spin diffusion experiments has been analysed using a periodic lattice model.[42] Effects of disorder in polymer morphology on spin diffusion has been discussed.

A simple model to describe heteronuclear spin decoupling in SSNMR under MAS conditions has been proposed.[43] It is based on a coherent description of two heteronuclear dipolar-coupled spins (I and S) and an incoherent description of the interaction of the I-spin with a large number of other I-spins. The abundant and strongly coupled I-spins are irradiated. The selected I-spin is coupled by a spin-diffusion type superoperator to the I-spin bath, and this coupling is described by a single spin-diffusion rate constant. Such a model allows to simulate efficiently the behavior of a spin system under heteronuclear decoupling in the case of CW irradiation as well as in the case of phase-modulated sequences such as TPPM.

A general treatment of NMR spectra under MAS conditions has been provided that is applicable both to homogeneously and inhomogeneously broadened lines.[44] It is based on a combination of Floquet theory and perturbation theory, and allows the factorisation of the spin system response into three factors that describe different aspects of the resulting MAS spectrum. The first factor directly reflects the Floquet theorem and describes the appearance of SSBs, the other two terms give the integral intensities of the resulting SSBs and their lineshapes and depend on the specific features of the considered interaction. From numerical simulations and the analysis of experimental MAS NMR spectra it was found that for typical spin systems, spinning frequencies of the order of the strongest couplings are sufficient to allow the analysis of the SSB intensities within the approximation of two-spin terms. This scaling of the different contributions together with the strong distance dependence of the dipolar interaction thus leads to a considerable simplification in the fast spinning limit and provides the basis for using the dipolar interaction in HR MAS spectra to obtain local structural information.

An interesting phenomenon of ^{1}H–^{13}C CP induced by temporary adsorption in nanocapsule dispersions have been reported.[45] A special mechanism of CP which is initiated by a temporary adsorption of mobile molecules to the more rigid capsule surface has been proposed.

The concept of MQ CP between an $I = 3/2$ and an $I = {}^{1}/_{2}$ spin during MAS have been described.[46] Experimental and theoretical results for ^{23}Na–^{1}H pairs have been presented that elucidate the transfer mechanism and the beneficial effect of adiabatic amplitude modulations of the CP field. The MQ CP approach has been shown to be beneficial for improving the sensitivity of CP MQ MAS experiments and for detecting dipolar correlations.

Procedures for processing data in rotor-synchronised 2D MAS NMR exchange measurements for both structural and dynamic studies have been presented.[47] It has been shown that there are two distinct data processing procedures that lead to 2D MAS exchange spectra with purely absorptive crosspeaks and processing of 2D MAS exchange data using both procedures may enhance the information content of 2D MAS exchange measurements.

An efficient algorithm for spectral simulations in NMR of rotating solids has been proposed.[48] Averaging over the γ powder angle has been shown to be generally equivalent to a cross correlation of two periodic functions. This together with the frequency-domain simulation procedure COMPUTE allows to reduce the computation time for spectral simulations by typically a factor of 10–30 relative to the original COMPUTE algorithm. The advantage and the general applicability of the new simulation procedure, referred to as γ-COMPUTE, have been demonstrated by simulation of single- and multiple-pulse MAS NMR spectra of ^{31}P–^{31}P and ^{1}H–^{1}H spin pairs influenced by anisotropic CS and homonuclear dipolar interactions.

Reintroduction of the quadrupolar interaction under MAS NMR has been investigated.[49] The anisotropy in the dipole–dipole and quadrupole couplings are averaged out in MAS NMR experiments and under conditions of axial symmetry ($\eta = 0$), the homologous forms of the respective coupling Hamiltonians have been exploited to show that the quadrupole coupling can also be resurrected by a simple adaptation of a rotor-synchronised pulse sequence previously proposed for the recovery of dipole–dipole couplings. The theory for the recovery of the quadrupole couplings has been developed. Numerical simulations of the quadrupolar (DQ) dephasing observed in the ^{2}H MAS NMR spectra of lipid systems have been used to extract the quadrupolar splitting.

A new assignment method based on the periodic *ab initio* calculation of ^{23}Na quadrupole coupling information using the CRYSTAL95 code has been described and applied to the multisite problem posed by $Na_5P_3O_{10}.6H_2O$.[50]

The detailed mechanism of coherence transfer in ^{2}H MAS NMR spectroscopy has been investigated in the presence of molecular motion.[51] An elaborate theoretical formalism has been developed that exploits the properties of Lie algebras to characterise the states of nuclear spin ensembles and to identify the allowed coherence transfer pathways. The functional form of the coherence transfer functions has been investigated within the Floquet-Poincare formalism. Based on these principles a general methodology has been described for evaluating the optimum pulse parameters consistent with maximum sensitivity. The intensity and phase distortions induced by the optimum pulse parameters have been discussed and the importance of incorporating these effects in theoretical simulations has been examined. The results have been verified by experimental spectra of polycrystalline thiourea-$^{2}H_4$ that have been analysed in terms of a discrete motional model. A theoretical description of CW high frequency LG CP MAS NMR experiments has been presented.[52] The full time-dependent LG CP MAS Hamiltonian has been replaced by its zero order time-independent Hamiltonian in the interaction representation. Carbon signal enhancements of LG CP MAS experiments have been calculated for spin systems consisting of six ^{1}H nuclei coupled to one ^{13}C nucleus. These simulations have been based on Floquet theory calculations, explicitly taking into account the time dependence because of MAS, and calculations based on the zero-order Hamiltonian. The good agreement between these calculations justifies the use of the zero-order Hamiltonian. The time-dependent intensities of the cross peaks in heteronuclear ^{13}C–^{1}H correlation spectra, extracted from 3D LG CP MAS experiments on a natural abundant D,L-alanine sample with increasing CP mixing times, are in good agreement with the theoretical intensities simulated by using the zero-order Hamiltonian. The approximated LG-CP MAS Hamiltonian can be used to obtain structural information about a proton coupled to a single carbon. The simulated intensities of the carbon signals of an isolated ^{13}C–^{1}H group and a ^{13}C–^{1}H group that is coupled to additional protons, measured by LG-CP MAS experiments with increasing CP mixing times, have been compared. This study suggests that the buildup curve of each LG CP MAS carbon signal and its Fourier transformed CP spectrum can be interpreted in terms of a single distance between the observed ^{13}C and its nearest proton, if the additional protons are removed from this carbon by at least 1.2 times this distance.

Using numerical optimisation procedures it has been shown that it is possible to design composite π rf pulses for MAS NMR spectroscopy by explicitly taking into account the variation of the resonance offset of each crystallite during the application of the rf pulses.[53] When using composite rf pulses in experiments such as TOSS, where the delays between the pulses have to be critically adjusted, an optimisation of these delays can lead to the desired performance characteristics. Using molecular cluster models a theoretical *ab initio* study of the ^{27}Al and ^{31}P NMR chemical shieldings aimed at obtaining short-range structural information on the aluminophosphate oxynitride (AlPON) catalyst system has been undertaken.[54] Orthophosphate-like molecular models with P/Al ratio equal to one and varying N/O ratios were used to simulate the experimentally obtained compositions. The computed NMR chemical shieldings reproduce quantitatively the observed features in the ^{31}P MAS NMR spectra. The comparison of ^{27}Al isotropic chemical shieldings and the experimental spectra allow to conclude that N/O substitution does not happen in the first coordination shell of aluminum atoms.

A numeric algorithm has been proposed that is suitable to calculate spectral lineshapes influenced by isotropic and anisotropic tumbling under sample spinning conditions.[55] It is based on the stochastic Liouville equation and a rotational diffusion process described by a stationary Markov operator. An example has been presented demonstrating the potential of off-MAS as a tool to analyse slow tumbling motions.

Ab initio HF and DFT calculations, based upon both cluster and periodic modelling approaches, have been reported for the EFG tensor at sodium in $NaNO_2$.[56] Calculations based on different-sized clusters have been compared and it has been shown that resonable agreement with experiment can be obtained for a symmetrical cluster that extends beyond the immediate coordination environment of Na^+. It has been suggested that periodic *ab initio* HF calculations using the standard 6-21G basis set, with suitable basis set optimisation to take into account the cationic nature of sodium, can provide a routine and consistent method for predicting sodium EFG tensor information for ionic sodium compounds.

Ab initio HF MO calculations have been applied to the crystalline imidazole and its derivatives in order to examine systematically the effect of possible N–H···N type H-bonding on the nuclear quadrupole interaction parameters.[57] The ^{14}N QCC and the asymmetry parameter (η) of the EFG were found to depend strongly on the size of the molecular clusters, from single molecule, to dimer, trimer and to the infinite molecular chain, *i.e.*, crystalline state, implying that the intermolecular N–H···N hydrogen bond affects significantly the electronic structure of imidazole molecule. A certain correlation between the ^{14}N QCC and the N–H bond distance R was also found and interpreted on the basis of the MO theory. A re-examination of the observed N–H distances in imidazole derivatives was suggested.

The use of rotational–resonance experiments to achieve homonuclear polarisation transfer between half-integer quadrupolar spins has been proposed.[58] A theoretical description for a homonuclear two-spin system in the framework of Floquet theory has been given. Numerical simulations, as well as analytical Floquet calculations, were performed to analyse the behaviour of such a system. It has been shown that while a rotational–resonance experiment at fixed spinning speed leads only to a partial polarisation transfer, an adiabatic passage through the rotational–resonance condition, achieved by a spinning-speed ramp, promotes polarisation transfer for all components of the SOQ broadened lineshape.

The assignment of SSNMR spectra has been studied by the use of model systems computed with *ab initio* methods.[59] Hexabenzocoronene derivative has been used. It has been shown that the combination of experimental NMR data with quantum chemical calculations can be employed as a useful tool in determining the structure of solid-state systems in general, especially where other experimental techniques fail.

A theoretical framework for the use of continuously phase modulated rf pulses for homonuclear decoupling in SSNMR has been presented.[60] Within this framework, new families of decoupling sequences have been derived using numerical optimisation. One of the sequences has been tested experimentally on an ordinary organic solid, and its performance has been compared with standard multiple-pulse sequences. A theoretical and experimental study of the spin dynamics in PISEMA (Polarisation Inversion Spin Exchange at the Magic Angle) to investigate the line-narrowing mechanism has been presented.[61] The study focuses on the effect of neighbouring protons on the spin exchange of a strongly coupled spin pair. The spin exchange has been solved analytically for simple spin systems and has been numerically simulated for many-spin systems. The results show that the dipolar couplings from the neighbouring protons of a strongly coupled spin pair perturb the spin exchange only in the second order and has little contribution to the linewidth of PISEMA spectra in comparison to the separated-local-field spectra. The effects from proton resonance offset and the mismatch of the Hartmann-Hahn condition have also been discussed along with experimental results using model single-crystal samples.

A selectively ^{2}H labeled osmium dihydride has been studied by ^{2}H MAS NMR.[62] It was found that the interference between the quadrupolar and homonuclear dipolar interaction results in a characteristic lineshape of the SSBs. The basic properties of the interference of homonuclear dipolar and quadrupolar coupling on the ^{2}H NMR lineshape were elucidated, using average Hamiltonian theory, and exact simulations of the experiments were achieved by stepwise integration of the equation of motion of the density matrix. These simulations show that it is possible to determine the size of the dipolar interaction and thus the ^{2}H–^{2}H distance from the lineshape of the SSBs.

4 Experimental Aspects

4.1 New Technique Developments. – It has been demonstrated that through-space recoupling can be achieved in dipolar coupled quadrupolar spins in the presence of an appropriate rf field.[63] Experimental and theoretical results for ^{23}Na–^{23}Na pairs have been presented that elucidate the experimental conditions leading to homonuclear dipolar transfer. The effect of adiabatic amplitude modulation on spin-3/2 systems has been compared to spin-$^1/_2$ cases and applications of this approach in the context of HR MQ MAS for dipolar filtering and correlation have been discussed. Lithium spin-alignment spectroscopy has been presented as an NMR technique for studying slow translational motions in solid and solid-like ionic conductors.[64] Phase cycling that allows to measure translational correlation functions *via* the generation of a pure quadrupolar ordered state has been used. Correlation functions of the crystalline electrolyte $Li_3Sc_2(PO_4)_3$ have been recorded for times ranging from about 0.1 ms to more than 10 s, implying that translational diffusion coefficients smaller than 10^{-20} m^2/s become accessible.

The miscibility of two macroscopic phase separated polymers, a propylene-ethylene-diene terpolymer and an atactic polypropylene, has been investigated by a combination of several SSNMR techniques.[65] Carbon-detected proton $T_{1\rho}(^1H)$ and $T_1(^1H)$ in systems conditioned by 2D heteronuclear WISE have been used. Both techniques are sensitive to spin diffusion between phases, with WISE being suited to making it stand apart from the basic relaxation process. These two techniques yield similar but different assessments of the presence and amount of phase separation present. An additional comparison has been made with differential scanning calorimetry and xenon NMR results, which also address this problem.

Three exchange NMR techniques have been presented that yield ^{13}C NMR spectra exclusively of slowly reorienting segments, suppressing the often dominant signals of immobile components.[66] The first technique eliminates the diagonal ridge that usually dominates 2D exchange NMR spectra and that makes it hard to detect the broad and low off-diagonal exchange patterns. A modulation of the 2D exchange spectrum by the sine-square of a factor which is proportional to the difference between evolution and detection frequencies is generated by fixed additional evolution and detection periods of duration τ, yielding a 2D pure-exchange (PUREX) spectrum. Smooth off-diagonal intensity has been obtained by systematically incrementing τ and summing up the resulting spectra. The related second technique yields a static 1D spectrum selectively of the exchanging site(s), which can thus be identified. Efficient detection of previously almost unobservable slow motions in a semicrystalline polymer has been demonstrated. The third approach, a 1D pure-exchange experiment under MAS, is an extension of the exchange-induced sideband (EIS) method. A TOSS spectrum obtained after the same number of pulses and delays, with a simple swap of *z* periods, is subtracted from the EIS spectrum, leaving only the exchange-induced sidebands and a strong, easily detected centreband of the mobile site(s).

An NMR experiment has been presented which allows the relative orientation of nuclear quadrupole and dipole coupling tensors to be determined.[67] The experiment uses a 4I quantum filter to select dipolar-coupled spin I pairs, and the relative tensor orientations have been determined by lineshape analysis. It selects dipolar-coupled spin pairs, even in a multi-spin system, and leads to data which are straightforward to interpret. The same approach has been used to perform a 2D correlation experiment showing which spins are close in space.

When observing spin $I = {}^1/_2$ nuclei with important CSA in disordered materials, the distribution of isotropic shift can become so large that no accessible spinning rate is able to provide a resolved spectrum. This is the case of ^{207}Pb in glasses where static and high-speed MAS spectra are nearly identical. The possibility of rebuilding an SSB free spectrum using a shifted echo modified PASS sequence has been demonstrated.[68] This makes it possible to discuss isotropic and anisotropic chemical shifts of lead in phosphate glasses, to characterise its structural role and its chemical bonding state.

DQ heteronuclear local field spectroscopy has been used to determine a molecular torsional angle in the *meta*rhodopsin-I, which is the 41 kDa integral membrane protein.[69] The result obtained is consistent with current models of the photo-induced conformational transitions in the chromophore.

Isotropic NMR spectra of half-integer quadrupolar nuclei using satellite transitions and MAS have been reported.[70]

A novel MQ MAS spin counting experiment based on the C7 recoupling sequence has been described.[71] The new experiment is applicable at fast MAS rates and can be used to follow the MQ excitation dynamics with fine time resolution. It has been illustrated by experiments on adamantane at spinning speeds comparable to the nonspinning dipolar linewidth.

A new type of fast amplitude modulated pulse scheme has been presented that yields a significant sensitivity enhancement in the TQ MAS NMR spectrum of a spin-5/2 nucleus.[72] Enhancement is achieved by fast phase alternation of the TQ-to-SQ conversion pulse, which transfers TQ-to-SQ coherence in a direct, non-adiabatic manner.

REDOR and θ-REDOR experiments for recovering the ^{13}C–^{2}H dipolar interaction during MAS NMR have been compared.[73] It has been found that limited ^{2}H rf power may severely compromise the performance of the REDOR experiment whereas the θ-REDOR experiment can be designed to work well. Results have been presented for an isolated ^{13}C–^{2}H spin pair with a large ^{2}H QCC and for a ^{13}C coupled to three methyl deuterons undergoing fast methyl rotation.

New modified spectral editing methods for ^{13}C CP MAS experiments for separating nonprotonated C and CH_3 peaks have been reported.[74] Examples have been provided for 3-methylglutaric acid, fumaric acid monoethyl ester, and two complex natural products: methyl o-methylpodocarpate and 10-deacetylbaccatin III.

The 2D anisotropy-correlated NMR spectra of half-integer quadrupolar nuclei may be recorded by using an exchange sequence in conjunction with

MAS during evolution and detection, and off-MAS during mixing.[75] Application to boron oxides has been described, in addition to an analysis of the spin diffusion rates in such materials.

The use of double frequency sweeps (DFSs) consisting of two sidebands generated by a time-dependent amplitude modulation of the rf-carrier frequency has been demonstrated in NMR of spin 3/2 nuclei.[76] This can be used for signal enhancement in both static and MAS spectra, as shown for a number of model compounds. DFSs prove to be efficient for the conversion of TQ-to-SQ coherence in MQ MAS spectroscopy. This relieves the rf-power requirements and as a result undistorted MQ MAS lineshapes are obtained (demonstrated for the four ^{23}Na resonances in $Na_4P_2O_7$).

A strategy of designing new heteronuclear broadband decoupling sequences for SSNMR has been presented.[77] The new technique involves a phase modulation of the decoupler as a function that is a sum of several cosine terms (abbreviated as CPM $m-n$ for cosine phase modulation with m harmonics and having frequency intervals of ω_{rf}/n, where m and n are integers). Experimental results show that their performances are considerably better than those of the existing decoupling methods, under conditions of moderate spinning rate and decoupling power.

The MQ MAS NMR experiment and a sensitivity enhanced variant detecting the SOQ powder pattern through a train of quadrupolar CPMG refocusing pulses have been analysed with respect to the effects of finite rf pulse irradiation and the MAS frequency.[78] Taking these effects explicitly into account, it is possible to determine optimum conditions for excitation of MQ coherences and reconversion of these into detectable SQ coherences as well as simulate the SOQ lineshape necessary to extract quadrupolar parameters and isotropic chemical shifts. These are important for the exploitation of MQ MAS experiments for quantitative determination of site populations. The various effects have been described analytically and demonstrated by numerical simulations and by ^{87}Rb MQ and MQ CPMG MAS experiments on $RbNO_3$.

The MQ MAS has been used to evaluate the individual lineshape of the Al signals in the 1D ^{27}Al MAS NMR spectrum of zeolite materials.[79] By the application of these real lineshapes, an improved deconvolution of the 1D MAS NMR spectrum has been achieved. This methodology has been applied to the two tetrahedrally coordinated Al sites in mazzite zeolite. Changes in the TQ CP matching profiles and ^{27}Al/^{23}Na SOQ lineshapes, have been observed as a function of the I = $^1/_2$ rf field strength for both static and MAS conditions.[80] It has been shown that only a fraction of the spins in the powder, with specific orientations of the EFG tensor, can match the Hartmann-Hahn condition at the same time, for a fixed I = $^1/_2$ rf field strength.

Magnetic field gradients have proven useful in NMR for coherence pathway selection, diffusion studies, and imaging. Recently they have been combined with MAS to permit HR measurements of semi-solids, where MAS averages any residual dipolar couplings and local variations in the bulk magnetic susceptibility. First examples of coherence pathway selection by gradients in dipolar coupled solids have been presented.[81] It has been shown that when the gradient evolution competes with dipolar evolution the experiment design must take into account both the strength of the dipolar couplings and the means to refocus it. Examples of both homonuclear and heteronuclear experiments have been shown in which gradients are used to eliminate the need for phase cycling. The target field method of designing gradient coils has been extended to the case where the gradient producing currents lie on cylinders of a general orientation with respect to the polarising magnetic field.[82] This provides a general approach for designing coils that require unusual sample geometries such as those required for MAS applications. A detailed example of a magic angle gradient coil set has been presented.

One of the main problems in the performance of the MQ MAS experiment is the poor efficiency of the rf pulses used in converting MQ coherences to the observable SQ signals. As the MQ MAS is an echo experiment this problem can be related to the efficiency with which CW pulses can normally achieve the MQ-to-SQ conversion for different crystallites in a spinning powdered sample. An improved MQ MAS NMR experiment using amplitude modulated pulses has been reported.[83] These pulses were found to yield MQ MAS NMR signals that are 2–3 times stronger than the ones arising from the usual CW pulse schemes by virtue of a superior efficiency of the TQ-to-SQ conversion. Numerical simulations and experimental results for ^{23}Na and ^{87}Rb have been presented that corroborate the usefulness of the new approach. Various aspects involved in this MQ-to-SQ conversion have been investigated further,[84] in order to devise new experimental schemes that can lead to significant MQ MAS signal enhancements. A new MQ MAS experiment employing amplitude-modulated rf pulses and the mechanisms of operation of CW and of amplitude-modulated pulses have been examined. Experimental results highlighting the utility of this scheme in samples possessing multiple quadrupolar sites with varying quadrupolar anisotropies and chemical shift offsets have been demonstrated.

A pulse scheme for achieving HR ^{1}H NMR spectra in solids by coherent averaging of spin–spin interactions called phase-modulated LG has been reported.[85]

Rotationally induced excitation of TQ coherences has been demonstrated for $I = 5/2$ nuclei from comparison of the variation of the observed and simulated lineshapes as a function of spin-lock time.[86] A new pulse sequence producing purely absorptive lineshapes has been reported. Rotation-induced 5Q↔1Q coherence transfer (RIACT) for 5Q MAS NMR experiments has been reported for ^{17}O for compounds with quadrupolar interactions in the range 3–7 MHz.[87] It has distinct advantages over the methods used to excite 5Q MAS NMR hitherto through much reduced sensitivity to the EFG. The 2D 5Q RIACT ^{17}O spectrum of zeolite Na-A has been reported, which is better resolved than the higher field TQ spectrum.

A new technique for measurements of dipolar interactions in rotating solids has been presented that combines the capabilities of MQ MAS with the REDOR.[88] This new technique exhibits improved sensitivity toward weak dipolar interactions. WISE NMR with windowless isotropic mixing (WIM) has been developed as a method to study the dynamics of polymers and blends.[89] This experiment has been designed to measure the dynamics of polymers through the ^{1}H lineshapes that are correlated with the ^{13}C chemical shifts in 2D NMR experiments. 2D WIM/WISE has been used to measure the main-chain and side-chain dynamics in poly(*n*-butyl methacrylate) and blends of polystyrene and poly(vinyl methyl ether).

A new pulse sequence for heteronuclear DQ MAS NMR spectroscopy of dipolar-coupled spin-$^1/_2$ nuclei has been introduced.[90] The heteronuclear DQ SSB patterns produced by this experiment have been shown to be sensitive to the heteronuclear distance, as well as the relative orientations of the CS and dipolar tensors. The isolated ^{13}C–^{1}H spin pair in deuterated ammonium formate with ^{13}C in natural abundance has been chosen as a model system, and the perturbing influence of dipolar couplings to surrounding protons on the ^{13}C–^{1}H DQ coherence has been discussed. The pulse sequence can also be used as a heteronuclear DQ filter, hence providing information about heteronuclear couplings, and thus allowing the differentiation of quaternary and CH bonded carbons.

A new heteronuclear chemical shift correlation technique of abundant spins (*e.g.* ^{1}H) with rare spins (*e.g.* ^{13}C) has been reported.[91] HR is provided by ultra-fast MAS and high magnetic fields, high sensitivity being ensured by a direct polarisation transfer from the abundant protons to ^{13}C. In a rotor-synchronised variant, the method can be used to probe heteronuclear through-space proximities, while the heteronuclear dipolar coupling constant can quantitatively be determined by measuring MQ SSB patterns. By means of recoupling, even weak heteronuclear dipolar interactions are accessible. The capabilities of the technique have been demonstrated by measurements on crystalline L-tyrosine hydrochloride salt.

^{13}C ZQ MAS NMR spectroscopy for paramagnetic solids has been proposed to obtain both highly resolved isotropic peaks and accurate values of shift anisotropies by removing line broadening due to bulk magnetic susceptibility (BMS) shifts.[92] Several pulse sequences for ZQ NMR experiments under fast MAS have been presented which are based on homonuclear J couplings between a pair of ^{13}C spins. For determining paramagnetic shift anisotropies, ZQ SSB (SSB) patterns have been observed which are free from the distortion due to the BMS shifts. To enhance ZQ SSB intensities, a π pulse was inserted during the t_1 period of 2D experiments. A selective excitation scheme has also been developed which leads to the improvement of the SNR of ZQ NMR spectra.

The 2D PASS experiment is a useful technique for simplifying MAS NMR spectra that contain overlapping or complicated SSB manifolds. The pulse sequence separates SSBs by their order in a 2D experiment. The result is an isotropic/anisotropic correlation experiment, in which a sheared projection of the 2D spectrum effectively yields an isotropic spectrum with no SSBs. The original 2D PASS experiment works best at lower MAS speeds (1–5 kHz). At higher spinning speeds (8–12 kHz) the experiment requires higher rf power levels so that the pulses do not overlap. In the case of nuclei such as ^{207}Pb, a large CSA often yields too many SSBs to be handled by a reasonable 2D PASS experiment unless higher spinning speeds are used. Performing the experiment at these speeds requires fewer 2D rows and a correspondingly shorter experimental time. New PASS pulse sequences have been implemented that occupy multiple MAS rotor cycles, thereby avoiding pulse overlap.[93] A version of the multiple-rotor-cycle 2D PASS sequence that uses composite pulses to suppress spectral artifacts has also been presented. These sequences have been demonstrated on ^{207}Pb test samples, including lead zirconate, a perovskite-phase compound.

Different approaches to obtain pure absorption-mode lineshapes in MQ MAS experiments employing a train of π phase-alternating pulses for the MQ-to-SQ mixing period have been investigated.[94] Four pulse sequences have been presented and their improved performance has been experimentally demonstrated by ^{87}Rb MQ MAS of $RbNO_3$.

A simplified method for acquiring pure-phase 2D exchange spectra under slow MAS has been introduced. It combines rotor-synchronised 2D exchange spectroscopy with whole-echo acquisition leading to a simplification in data acquisition and processing.[95] The proposed method is applicable to samples where an echo of the FID can be obtained, *i.e.*, where the inhomogenous linewidth is larger than the homogeneous linewidth. This is the case in rare-spin spectroscopy of samples with natural isotopic abundance. The usefulness of the new method has been demonstrated, using ^{13}C spectroscopy. Layered paramagnetic compounds, such as $La_2Li_{0.5}Ni_{0.5}O_4$ with a perovskite structure, the ^{7}Li NMR spectrum is broadened by anisotropic quadrupolar as well as paramagnetic dipolar interactions. A 2D spin echo (SE) experiment to separate the quadrupolar interaction and obtain a clean quadrupolar spectrum along the w_1 dimension has been suggested.[96] This has been demonstrated through 2D SE experiments conducted in static samples as well as those in spinning at the magic angle. A quadrupole coupling constant of 92 kHz has been estimated for paramagnetic $La_2Li_{0.5}Ni_{0.5}O_4$. It has been shown that the same information may be obtained from the C–H dipolar couplings using 2D experiments correlating ^{13}C chemical shifts and H–C dipolar couplings.[97] The order parameters of C_4–H_a and C_4–H_e vectors calculated from this experiment are in agreement with those previously determined on the same sample from ^{2}H NMR. This experiment opens the way to the simultaneous determination of order parameters of all C–H vectors without the need of specific labelling.

New 1D, 2D and 3D SSNMR spectroscopic methods designed for structural studies of uniformly ^{15}N- and ^{13}C-labeled peptides and proteins in oriented samples have been described.[98] These methods provide a means of obtaining resolved spectra, sequential resonance assignments, and structural constraints. Experimental results for model single-crystal peptides and amino acids demonstrate that HR 1D ^{13}C spectra can be obtained for signals from carbonyl or carboxyl carbons in uniformly labelled samples by applying phase-modulated selective homonuclear (PSH) decoupling at aliphatic carbon resonances, in addition to heteronuclear proton and ^{15}N decoupling. ^{13}C-detected 2D ^{15}N/^{13}C chemical shift correlation spectroscopy has been made possible by a combination of PSH decoupling and broadband heteronuclear polarisation transfer sequences such as WALTZ-5 CP. Experimental 2D spectra of uniformly ^{15}N- and ^{13}C-labelled AlaGlyGly crystals show that resolution and sequential assignment of (CO)-^{13}C and ^{15}N NMR signals is possible. Comparisons of experimental spectra and simulations verify the assignments and the accuracy of structural information contained in the 2D spectra in the form of the orientation-dependent (CO)-^{13}C and ^{15}N chemical shifts. ^{13}C-detected 3D spectroscopy has also been demonstrated by adding a ^{1}H–^{15}N dipolar dimension to the 2D methods. Results of experiments at fields of 9.39 and 17.6 T have been reported.

Enhancement of sensitivity in ^{15}N NMR by indirect detection through ^{1}H NMR signals under high-speed MAS and high-field conditions has been demonstrated experimentally on two ^{15}N-labelled peptides, polycrystalline AlaGlyGly and the helix-forming 17-residue peptide.[99] Sensitivity enhancement factors ranging from 2.0 to 3.2 have been observed experimentally, depending on the ^{15}N and ^{1}H linewidths and polarisation transfer efficiencies. The ^{1}H-detected 2D ^{1}H/^{15}N correlation spectrum of AlaGlyGly illustrates the possibility of increased spectral resolution and resonance assignments in indirectly detected experiments, in addition to the sensitivity enhancement.

A procedure for structural characterisation based on XRD and on a set of 2D SSNMR experiments has been proposed.[100] It has been applied to a new gallophosphate oxyfluorinated compound. A set of three NMR experiments – RFDR for ^{19}F, DQ for ^{31}P and HETCOR between ^{19}F and ^{31}P – facilitate the analysis of the topology of homoatomic and heteroatomic sub-networks of fluorine and phosphorus included in the inorganic framework of this material. The efficiency of this combination of NMR experiments in assigning all NMR signals to their crystallographically sites has also been demonstrated.

4.2 NMR Parameters: Experimental and Quantum Mechanical Studies. – *4.2.1 Spin-$^{1}/_{2}$ Nuclei: Isotropic Shifts and CS Tensors.* [1] – Determination of ^{1}H CS tensors is crucial for protein structure determination by SSNMR. The ^{1}H chemical shift is particularly important in spectra obtained on oriented samples of membrane proteins as a mechanism for providing dispersion among resonances that are not resolved with the ^{1}H–^{15}N dipolar coupling and ^{15}N chemical shift frequencies. This has been demonstrated with 3D experiments on uniformly ^{15}N-labeled samples of Magainin antibiotic peptide and the protein Vpu from HIV-1 in oriented lipid bilayers.[101] These experiments enable resonances in 2D ^{1}H–^{15}N dipolar coupling/^{15}N chemical shift planes separated by ^{1}H chemical shift frequencies to be resolved and analysed.

It has been shown that the magnitude and absolute orientation of ^{1}H CS tensors may be determined from polycrystalline powders using CRAMPS by simultaneous evolution under CS and heteronuclear dipolar coupling interactions.[102] An experimental approach based on the broadband high-order truncating MSHOT-3 homonuclear decoupling sequence has been demonstrated for the H-bonded proton within the ^{31}P–^{1}H–^{31}P three-spin systems of a powder of KH_2PO_4.

^{13}C – The polymorphic structures of silk fibroins in the solid state were examined on the basis of a quantitative relationship between the ^{13}C chemical shift and local structure in proteins.[103] To determine this relationship, ^{13}C chemical shift contour plots for C_α and C_β of Ala and Ser residues, and the C_α chemical shift plot for Gly residues were prepared using atomic coordinates from the Protein Data Bank and ^{13}C NMR chemical shift data reported for 40 proteins.

Possibilities and limitations of iterative lineshape fitting approaches for the complete determination of magnitudes and orientations of NMR interaction tensors in a four-^{13}C-spin system from MAS NMR experiments have been investigated.[104] The model compound chosen for this investigation is the monoammonium salt of maleic acid. Various selectively and fully ^{13}C-labelled versions of this compound permit a stepwise reduction of the number of unknown parameters, necessary to fully describe the four-^{13}C -spin system in the uniformly ^{13}C-labelled maleate moiety. It has been demonstrated that assumptions about 'typical' CS tensor orientations, even if not deviating much from the real orientations, lead to severe errors in internuclear distance determinations. The principal values of the ^{13}C CS tensors were measured for coronene and corannulene, both at room temperature and at approximately 100 K.[105] A comparison of the principal values between the room temperature motionally averaged pattern and the low-temperature static pattern provides information about the orientation of the principal axis system of the CS tensor for the bridgehead carbons in these molecules. The results show that the motion is not constrained to simple in-plane rotation, but must also have an out-of-plane component. Quantum chemical calculations of the CS tensors were also completed using both experimental and optimised molecular geometries.

^{19}F - Experimental measurements of ^{19}F isotropic chemical shifts on a large set of mainly ionic fluoride compounds (from simple metal fluorides to transition metal fluoride glasses) obtained by MAS NMR at 15 kHz have been investigated.[106] First, Ramsey's theory of die chemical shift with MOs obtained by Lodwin's orthogonalisation method has been used to evaluate the isotropic part of the ^{19}F chemical shift in ionic fluorides for which the crystallographic structure and the atomic radial wavefunctions are known. Assuming that the paramagnetic part of the ^{19}F shielding in a given material is simply the summation of the paramagnetic contributions due to all the cations in the neighbourhood of the considered fluorine, a superposition model of the ^{19}F isotropic chemical shift has been developed. This empirical approach has been applied to complex fluoride compounds of unknown structure and it has been shown that it allows to obtain reliable structural informations.

The sensitivity of the ^{19}F isotropic chemical shift to the environment of the fluorine atom has been used to investigate transition metal fluoride glass networks.[107] From the chemical shift values, it has been shown that three F sites can be identified shared and unshared Fs between two MF_6 octahedra and free Fs which are not implied in these MF_6 octahedra. The proportions of these different fluorines in the glasses have been obtained and the connectivity of the MF_6, octahedra which constitute the networks has been deduced. It has been shown that the structure of the alkali fluoride glasses is quite different from the other fluoride glasses.

^{31}P - Local structure of phospholipid/amine polyion complexes in lyophilised powders of dipalmitoylphosphatidic acid/poly-L-lysine and DPPA/poly-L-arginine has been investigated.[108] The intermolecular interactions in the polyion complexes were detected by ^{31}P–^{1}H HETCOR. The complete information about the ^{31}P CS tensor components and the mutual orientation of CS tensor with respect to a molecular fixed frame was determined by both CP MAS and spin-echo separated local field measurements. From the *ab initio* ^{31}P CS calculation, the behaviour of the principal components of ^{31}P CS tensor in the phosphate group in DPPA has been found to be dominated by a change in the electronic state in association with phosphate/amine complexation.

The ^{31}P CS surface of phosphinoborane R_2PBR_2' has been investigated *via* MO calculations and experimental measurements.[109] *Ab initio* calculations of ^{31}P CS tensors were determined for the phosphinoboranes H_2PBH_2 and Me_2PBMe_2. Changes in the angle from planarity, *i.e.* that between the P–BR_2' plane and the bisector of the RPR angle, are reflected in the orientations and magnitudes of the three principal components of the ^{31}P CS tensor. To determine the validity of the calculated ^{31}P CS surface, three phosphinoborane compounds with different angles from planarity were studied by ^{31}P SSNMR spectroscopy. The experimental magnitudes of the principal components and orientations of the ^{31}P CS tensor compared well to the calculated predictions. The combined experimental and theoretical results provide a good description of the effects on changes in bond angle on ^{31}P CS as the molecule is distorted from a planar to folded geometry.

31P 1D NMR spectra of a stationary powder sample of a phosphole tetramer containing two phosphorus spin pairs have been obtained at 4.7 T and 9.4 T.[110] In order to separate ^{31}P–^{31}P spin–spin coupling from anisotropic CS, 2D spin-echo NMR spectra have been acquired. ^{31}P CP MAS NMR experiments indicate that the two spin pairs of the tetramer are equivalent and each may be treated as an isolated spin pair. Within a given spin pair, the difference between the isotropic chemical shifts of two directly bonded ^{31}P nuclei is 1.7 ppm. They are spin–spin coupled by both the indirect ($^{1}J = -362$ Hz) and direct interactions (1.80 kHz). The principal components and relative orientation of the two ^{31}P CS tensors have been determined using the dipolar-chemical shift technique. Ambiguities in the CS tensor orientation relative to the molecular framework have been resolved using *ab initio* calculations and simulations of the 2D spin-echo spectra. The spans and skews of the ^{31}P CS tensors for all 4 three-coordinate ^{31}P nuclei are the same within experimental error, 115 ppm and 0.70, respectively.

^{31}P CS and spin–spin coupling tensors have been characterised for tetramethyldiphosphine disulfide (TMPS) by analysis of ^{31}P CP NMR spectra obtained for a single crystal and powder samples have been acquired at 4.7 and 9.4 T.[111] A 2D spin-echo NMR spectrum was obtained to independently determine the effective ^{31}P–^{31}P dipolar coupling constant. The subtle difference between two particular inequivalent phosphorus sites in TMPS were examined using ^{31}P CS tensors obtained from both single-crystal and dipolar-chemical shift NMR methods.

^{109}Ag - It has been shown that ^{109}Ag NMR signals in $Ag_xCu_{1-x}I$ crystals are shifted to a low field relative to that in solid AgI with decreasing the unit cell constant analogous to ^{63}Cu MAS NMR signals.[112] The observed chemical shieldings were analysed using *ab initio* calculations of ^{109}Ag and ^{63}Cu CS tensors for tetrahedral $AgI_4{}^{3-}$ and $CuI_4{}^{3-}$ ions.

^{119}Sn - The effects of powder granule size on parameters such as chemical shift, linewidth, and spin-lattice relaxation have been studied using ^{119}Sn MAS NMR of SnO_2 powders.[113] Linewidth showed a general broadening as size decreased, but there was evidence in the anisotropy of the chemical shift and in the spin-lattice relaxation.

^{199}Hg - The ^{199}Hg MAS NMR spectra of Hg_2X_2 (X = Cl, SCN, NCO, CH_3CO_2, CF_3CO_2) have been reported.[114] SSB analysis has been used to determine the ^{199}Hg CS parameters, $\Delta\sigma$ and η. In contrast to the case of the corresponding Hg(II) compounds, the shielding anisotropy has been found to be relatively insensitive to the nature of the X group. This is consistent with the view that the electronic environment of the Hg atom in the Hg(I) compounds is dominated by the Hg–Hg bond. The changes in the ^{199}Hg CS parameters from the Hg(II) to the corresponding Hg(I) compounds, as well as the changes in these parameters in the Hg(I) compounds with changes in X, can be interpreted as variations in the local paramagnetic contribution to the CS tensor.

^{207}Pb - The isotropic chemical shift of ^{207}Pb has been used to perform structural investigations of crystalline fluoride compounds and transition metal fluoride glasses.[115]

Using ^{207}Pb CP MAS with ^{19}F decoupling, it has been shown that the $\delta_{iso}(^{207}Pb)$ varies on a large scale (1000 ppm) and that the main changes of its value are not due to the nearest neighbour fluorines but may be related to the number of next nearest neighbour Pb^{2+} ions. α-PbO and β-PbO have been studied with ^{207}Pb MAS NMR.[116] The ^{207}Pb NMR CS tensor in α-PbO is axial, with $\delta_\perp = 3030$ and $\delta_\| = -270$ ppm. In β-PbO, the ^{207}Pb NMR powder spectrum has been represented by a single non-axial tensor with $\delta_{11} = 2820$, $\delta_{22} = 2760$ and $\delta_{33} = -1000$. Using normal-coordinate analysis, the ^{207}Pb CS tensor has been represented as a sum of contributions from separate Pb–O and Pb–Pb interactions. It has been shown that Pb–O and Pb–Pb contributions are of the same order of magnitude. Pb_3O_4 has been studied with ^{207}Pb NMR.[117] The ^{207}Pb CS tensor of the Pb^{2+} site has principal values of $\delta_{11} = 1980$, $\delta_{22} = 1540$ and $\delta_{33} = 1108$ ppm. The CS tensor of the Pb^{4+} site is axial, with principal values $\delta_\| = 1009$ ppm and $\delta_\perp = 1132$ ppm. The Pb^{4+}–Pb^{2+} spin–spin coupling constant is 2.3 kHz.

207Pb NMR powder pattern analysis has been applied to several lead-containing inorganic and organic compounds.[118] The CS tensors obtained are less susceptible to systematic error than earlier studies employing MAS SSB analysis. Since the lead atom is very sensitive to its local environment, a correlation between the chemical shift and structure was investigated. An increase in Pb–O interatomic distance tends to shift the isotropic chemical shift to lower frequency, whereas conversely an increase in Pb–halogen interatomic distance tends to increase the chemical shift. As a consequence of the electronic structure of Pb^{2+}, almost all ^{207}Pb shielding tensors of Pb^{2+} species have a negative anisotropy.

Static and MAS ^{207}Pb NMR spectra of a series of lead oxides, including various electronic materials have been reported.[119] The chemical shift parameters and the spin–lattice relaxation times have been determined. The symmetry of the local environment of the Pb(II) site and the covalency of the Pb–O bonds have been determined to be the best indicators of the ^{207}Pb chemical shift parameters.

4.2.2 Quadrupolar Nuclei: Isotropic Shifts, CS and EFG Tensors. *$^{6,7}Li$* – Two nitrogen ceramic phases, the oxynitride LiSiON and the nitride $LiSi_2N_3$, have been studied by $^{6,7}Li$ MAS at 7 and 14 T.[120] The EFG tensor of both phases has been determined by iterative fitting of the $^{6,7}Li$ lineshapes at the two field strengths. Due to the fact that for ^7Li the quadrupolar interaction is much larger than the chemical shift interaction, it has been shown that neither the small CSA nor the relative orientation of the two interaction tensors can be determined accurately by ^7Li MAS NMR. For ^6Li, the two interactions are comparable and the value of these parameters obtained from the fits of the ^6Li experimental MAS lineshapes are therefore much more reliable.

$^{6,7}Li$ MAS NMR has been used to investigate the local coordination environment of Li in a series of $xLi_2O{\cdot}(1-x)P_2O_5$ glasses.[121] Both the ^6Li and ^7Li show chemical shift variations with changes in the Li_2O concentration, but the observed ^6Li NMR chemical shifts closely approximate the true isotropic chemical shift and can provide a measure of the lithium bonding environment. The ^6Li NMR results indicate that, in this series of lithium phosphate glasses, the Li atoms have an average coordination between four and five. An increase in the ^6Li NMR chemical shift with increasing Li_2O correlates with increased cross-linking of the phosphate tetrahedral network by O–Li–O bridges.

^9Be - Despite the favourable NMR properties of ^9Be (I = 3/2), NMR spectroscopy of this nucleus in the solid state remains comparatively unexplored.[122] An integrated experimental and theoretical study of the Be CS and EFG tensors in bis(2,4-pentanedionato-O,O′)beryllium [$Be(acac)_2$] has been presented. Interpretation of the ^9Be NMR data was facilitated by XRD results, which indicate two crystallographically unique sites. ^9Be NMR spectra acquired at 4.7 and 9.4 T for MAS and stationary samples have been fitted in order to extract the QCC (χ), asymmetry parameter (η), and isotropic chemical shift (δ_{iso}). The best-fit quadrupole parameters for the two sites were determined to be $\chi(1) = -294$ kHz, $\eta(1) = 0.11$; $\chi(2) = -300$ kHz, $\eta(2) = 0.15$. Analyses of the stationary samples also reveal a definite anisotropy in the beryllium CS tensor and allow to place upper and lower limits on the spans of 7 and 3 ppm. This is the first evidence for anisotropic shielding in beryllium. *Ab initio* calculations of the ^9Be CS tensors in $Be(acac)_2$ indicate spans ranging

from 7 to 9 ppm; this represents a substantial fraction of the total known chemical shift range for ^{9}Be (<50 ppm). Calculations of the beryllium CS tensors for a series of compounds encompassing the known range of ^{9}Be chemical shifts have also been presented. The calculations are in accord with experimental data from the literature. On the basis of calculations for linear molecules, it has been shown that the assumption that the ^{9}Be chemical shift is governed essentially by the diamagnetic term is erroneous. For some of these molecules, the calculated Be CS tensor spans are greater than the total known chemical shift range.

^{17}O - NMR determinations of the ^{17}O CS and EFG tensors for a series of ^{17}O-enriched organic compounds containing various functional groups have been reported.[123] In several cases, analysis of the ^{17}O MAS and static NMR spectra yields both the magnitude and relative orientations of the ^{17}O CS and EFG tensors.

The feasibility of ^{17}O SSNMR as a potentially useful technique for studying molecular structure and H-bonding has been demonstrated. ^{17}O NMR parameters (χ, η, δ_{iso} and T_1) have been reported for both Si–O–Si and Si–OH fragments within a silica gel.[124] The Si–OH units have a wide spread of parameters but are typically characterised by a very short T_1 (~ 0.1 ms) and χ < 200 kHz. These observations have important implications for the quantification of such units in these gels and related glassy materials.

The static, MAS and MQ ^{17}O NMR experiments have been optimised to observe a distinct resonance from the OH group. The ^{17}O NMR spectra of L-alanine-residue containing polypeptides were measured by MAS at 25 kHz.[125] NMR parameters such as χ, η and δ_{iso} have been obtained from the spectra. The relationship between the H-bonded structure and these NMR parameters has been clarified. The H-bonding structures have been related to the χ and δ_{iso} values.

^{23}Na - The ^{23}Na MAS, DOR and MQ MAS MR spectra of $Na_4P_2O_7$, measured at five different Larmor frequencies (ν_L) ranging from 105.8 MHz to 211.6 MHz have been analysed and the complete set of NMR parameters (χ, η and δ_{iso}) of the four crystallographically inequivalent Na sites were determined with high accuracy.[126] Different approaches of spectra evaluation have been discussed and their results have been compared. It has been shown that $Na_4P_2O_7$ may serve as a useful reference material for experimental set-up and reliability tests of the various NMR experiments.

Ag-impurity effects on the first- and second-order quadrupole interaction at ^{23}Na site in an isomorphic mixed system, $Na_{1-x}Ag_xNO_2$ ($x = 0$, 0.0084, 0.026, 0.079, 0.094, 0.16), have been investigated by employing ^{23}Na MAS NMR.[127] The quadrupole parameter and its distribution width have been obtained as a function of Ag concentration.

The QCC (χ) and the spin–lattice relaxation rate ($1/T_1$) of ^{23}Na NMR in the $NaNO_2$ powder have been investigated by employing MAS and wideline probes at 9.4 T in the range of 300–458K.[128] The linearity between χ and the squared spontaneous polarisation was obeyed up to near the critical temperature (T_c = 437 K), which is consistent with the previous reports. The reorientational motion of NO_2^- ion in powder samples has been found to have an activation energy, $\Lambda U = 0.22$ eV, which is in good agreement with the value obtained with single crystals.

^{27}Al - The well-characterised minerals kyanite and andalusite have long presented great challenges in using ^{27}Al NMR to determine the χ, η and δ_{iso} values for each of the inequivalent Al sites in these minerals. Recent advances in magnet technology (up to 18.8 T) and in MAS probe technology (spinning up to 35 kHz and considerably stronger rf) and refinements of the 2D MQ MAS technique suggested that these developments could be used to study kyanite and andalusite. The benefit of being able to study kyanite both by MAS and MQ MAS techniques on 400, 500 and 800 MHz spectrometers has been demonstrated.[129] The two octahedral Al with the largest (and nearly equal) χ values give overlapping 1D MAS or 2D TQ MAS signals at all three field strengths. Nevertheless, quantitatively accurate 34 signal intensities at 9.4 T for all four octahedral Al sites (with χ values up to 10 MHz) allow more detailed analysis. For andalusite, 34 kHz MAS on the 800 MHz spectrometer significantly narrows the extremely broad signal for the octahedral aluminum, and only slight difficulties have been encountered in quantitating the relative amounts of AlO_5 and AlO_6 present. Even with $\chi = 15.3$ MHz, the octahedral Al in andalusite gives a signal in a MQ MAS experiment. Some of the benefits and limitations of these advances in instrumentation and of different experimental approaches for studying non-integral spin quadrupolar nuclei in solids have been discussed.

The chemical shift tensor has been measured for the five- and six-coordinate sites in andalusite, Al_2SiO_5.[130] The experimental results agree well with those calculated by the full-crystal density functional theory, differing by only 0.17° for the six-coordinate site and 1.56° for the five-coordinate site. The calculated value of χ is in error by -0.254 MHz for the five-coordinate site. The embedded cluster MO results are significantly less accurate, with orientation errors exceeding 45°.^{27}Al satellite transition NMR spectroscopy has been used to probe the quadrupolar interaction of NaA, NaX and NaLSX (low silica X) zeolites.[131] The χ and η values have been obtained by computer simulations of the SSBs. These parameters represent the local electronic environments around the Al and have been used for structural correlations.

^{35,37}Cl- Values of χ, η and δ_{iso} have been determined for a series of inorganic perchlorates from ^{35}Cl MAS NMR spectra at 14.1 T.[132] Illustrative ^{37}Cl MAS NMR spectra have been obtained and analysed for some of the samples. For perchlorate anions with $\chi < 1$ MHz, the ^{35,37}Cl NMR parameters are most precisely determined from the full manifold of SSBs observed for the satellite transitions while lineshape analysis of the central transition has been employed for the somewhat larger χ values. The environments for the individual perchlorate anions are best characterised by the quadrupole coupling parameters (*e.g.* χ ranges from 0.3 to 3.0 MHz), while the dispersion in the isotropic ^{35}Cl chemical shifts is small (1029 ppm $< \delta_{iso} <$ 1049 ppm). Due to the variation in quadrupole coupling parameters, ^{35}Cl MAS NMR may be employed for identification of anhydrous and hydrated phases of perchlorates,

in studies of phase transitions, hydration reactions, and the composition of mixed phases. The ^{35}Cl MAS NMR spectra of $LiClO_4$, $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$, for which the crystal structures are unknown, reveal that each of these salts possesses a single perchlorate site in the asymmetric unit; the ^{35}Cl NMR data for $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ suggest that they are isostructural.

^{51}V - Static and MAS ^{51}V NMR spectra of BiVO4 were recorded at three different held strengths (2.3, 9.4 and 14.1 T) and give evidence of the relative effects of the quadrupolar interaction and electronic shielding at the nucleus.[133] The experimental powder spectra were fitted to ascertain both the magnitude and orientation of CS and EFG tensors.

^{51}V EFG and CS tensors have been determined from for nine divalent metal metavanadates.[134] The manifold of SSBs from the central and satellite transitions, observed in the ^{51}V MAS NMR spectra have been analysed using least-squares fitting and numerical error analysis. This has led to a precise determination of the eight NMR parameters characterising the magnitudes and relative orientations of the EFG and CS tensors. The optimised data demonstrates that different types of *meta*vanadates can easily be distinguished by their anisotropic NMR parameters. The CS parameters for orthovanadates and mono- and di-valent metal *meta*vanadates have been compared.

^{63,65}Cu - Direct NMR observation of ^{63,65}Cu in solid $K_3Cu(CN)_4$ provides the first experimental example of anisotropic copper CS.[135] Axially symmetric by virtue of the space group symmetry, the CS tensor spans 42 ppm, with the greatest shielding when the unique axis is perpendicular to the applied magnetic field. The nuclear quadrupole coupling constant is also appreciable, $\chi(^{63}Cu) = -1.125$ MHz, reflecting a deviation of the $Cu(CN)_4{}^{3-}$ anion from pure tetrahedral symmetry. Spin-spin coupling to ^{13}C nuclei in an isotopically enriched sample has been quantified by lineshape simulations of both ^{13}C and ^{63,65}Cu MAS spectra to be 300 Hz. It has been shown that this information is also directly available by ^{63,65}Cu TQ MAS NMR. Spin–spin couplings $^{2}J(^{63,65}Cu,^{15}N)$ detected in ^{15}N MAS experiments have been found to be 19 and 20 Hz for the two crystallographically distinct cyanide ligands.

^{67}Zn - A ^{67}Zn NMR study of compounds containing zinc ions coordinated by oxygen, nitrogen and sulfur ligands have been reported.[136] New information concerning ^{67}Zn quadrupole coupling constants and chemical shifts has been obtained from MAS spectra of solid compounds.

$^{69/71}$Ga - Owing to the implementation of acquisition techniques specific for nuclei with very large quadrupolar interaction, NMR spectra of ^{69}Ga and ^{71}Ga have been obtained in crystallised and glassy gallium fluorides.[137] Simulations of both static and MAS spectra allow to obtain consistent determinations of isotropic chemical shifts and very large quadrupolar parameters (up to 14 MHz). In the crystalline compounds whose structures are unknown, the number and the local symmetry of the different gallium sites are tentatively worked out. For the glassy systems, a continuous Czjzek's distribution of the NMR quadrupolar parameters accounts for the particular shape of the NMR spectrum. New measurements of NMR parameters for ^{71}Ga in gallium bearing oxide reference compounds, ranging from perfectly ordered

systems to disordered crystalline structures and their aluminate counterparts have been reported.[138] Static, MAS and QPASS spectra have been obtained at magnetic fields ranging from 7.0 to 18.8 T. The new results enhance the previously established correlation between $\delta_{iso}(^{71}Ga)$ and $\delta_{iso}(^{27}Al)$. A correlation between ^{71}Ga and ^{27}Al EFGs has been proposed. This correlation shows that the EFG at ^{71}Ga sites are generally three times greater than those at equivalent ^{27}Al sites.

^{87}Rb - A remarkable sensitivity of the ^{87}Rb nucleus to its physical environment in alkali metal halides has been reported.[139] When Rb^+ is incorporated into different cubic halide lattices at very low concentrations, the ^{87}Rb NMR chemical shift becomes more shielded by as much as 282 ppm when the cation is changed from Na^+ to Cs^+. Similarly, in mixed crystals of KCl and RbCl, the average resonance frequency shifts with the degree of incorporation. The ^{87}Rb chemical shift data for each halide show a near-linear correlation with the average alkali metal–halide interionic distance in the different crystals studied, in good agreement with *ab initio* calculations which show that indeed the chemical shielding has a strong dependence on the nearest neighbor shell of halide anions and their distance from the Rb^+. Temperature dependencies of χ, η and δ_{iso} have been observed for RbCl, $RbClO_4$, Rb_2SO_4 and $RbNO_3$ by ^{87}Rb MAS NMR in the temperature range -100 – $+165\,^{\circ}C$.[140] The results demonstrate that χ (^{87}Rb) and $\delta_{iso}(^{87}Rb)$ are highly temperature-dependent for all samples. Linear correlations of $\delta_{iso}(^{87}Rb)$ with temperature have been observed. ^{87}Rb NMR spectra for a powder and single crystal of $RbVO_3$ have been acquired for the central transition at two magnetic field strengths (9.4 and 14.1 T).[141] The powder spectra have been obtained using spin-echo techniques without sample spinning because the widths of the spectra are in the range 100–150 kHz, The spectra have been analysed in terms of the CS and EFG tensors. Parameters of high precision including the relative orientation for the two tensors have been obtained from the single-crystal spectra at 14.1 T. Finally, the orientations of the two tensors in the crystal frame have been deduced from the crystal symmetry and an XRD analysis.

^{95}Mo - The Chevrel-phase pseudo-binary solid solution Mo_6Se_8–Mo_6Te_8 has been studied by ^{95}Mo NMR.[142] The experimental spectra were fitted by an anisotropic central line of axial symmetry corresponding to the Mo atoms of the Mo_6 metallic cluster. Quadrupolar effects due to the chalcogen network were neglected since the shape and width of the resonant line ($+^1/_2 \rightarrow -^1/_2$ transition) have been shown to be independent of the chalcogen substitution. The Knight shift varies linearly with the Se/Te ratio and it was found to be proportional to the room-temperature susceptibility, implying the existence of polarisation mechanisms between *d* and *s* electron spins.

4.2.3 Multinuclear Studies. The principal components of the ^{13}C, ^{15}N and ^{77}Se CS tensors for several solid selenocyanate salts have been determined.[143] Within experimental error, all three CS tensors are axially symmetric, consistent with the expected linear geometry of these anions. The spans of the ^{13}C and ^{77}Se CS tensors for the $SeCN^-$ anion are approximately 300 and 800 ppm, respectively, much less than the corresponding values for CSe_2. This difference is a consequence of the difference in the CS tensor components perpendicular to the C infiniti symmetry axes in these systems. *Ab initio* calculations show that the orbital symmetries of these compounds are a significant factor in the shielding. For CSe_2, efficient mixing of the σ and π orbitals results in a large paramagnetic contribution to the total shielding of the CS tensor components perpendicular to the molecular axis. Such mixing is less efficient for the $SeCN^-$, resulting in a smaller paramagnetic contribution and hence in greater shielding in directions perpendicular to the molecular axis.

^{77}Se and ^{13}C CP MAS experiments have been employed to study the structure and dynamics of DL-selenomethionine and L-selenomethionine in the solid state.[144] The ^{77}Se principal elements of CS tensors for both compounds were calculated by means of the graphical method of Herzfeld and Berger. From ^{77}Se and ^{13}C NMR it has been concluded that the unit cell of L-selenomethionine contains two molecules and it is isomorphous with L-methionine. The results of first principles Hartree-Fock (HF) and DFT calculations on the ^{1}H, ^{29}Si and ^{17}O NMR chemical shifts of hydroxyl groups in silica have been reported.[145] Quantitative agreement with the available experimental data has been obtained at the DFT level. The CP SSMAS ^{29}Si, ^{119}Sn and ^{207}Pb NMR spectra of $(Ph_3E)Mn(CO)_5$ (E = Si, Sn, Pb), have been analysed to give the chemical shifts, ^{1}J(E-Mn) couplings, the 'effective-dipolar' coupling constants ($D-\Delta J/3$), the CS tensors, and the spin–spin anisotropy (ΔJ).[146] For the Sn and Pb compounds, three and four sets of chemical shifts, respectively, were observed, and two different polymorphs occur for the Pb complex. The average values of the reduced coupling constants, ^{1}K(Mn–E) showed a linear correlation with the *s*-electron densities at the respective metal nuclei. The principal components of the CS tensors have been determined for the tin and lead compounds.

The two anhydrous polymorphs of $Na_5P_3O_{10}$ have been characterised by ^{23}Na and ^{31}P MAS NMR spectroscopy.[147] The ^{23}Na MQ MAS spectrum of the low-temperature form (phase II) displays three resonances for which the quadrupole coupling parameters and isotropic chemical shifts have been determined. Discrepancies between recently reported ^{23}Na MQ MAS spectra of this phase and the crystal structure have been clarified. The ^{23}Na resonances observed for the low-temperature form have been assigned to the crystallographically inequivalent Na sites in the crystal structure using point-monopole calculations of the EFG tensors. Three ^{23}Na resonances have also been observed for the high-temperature form (phase I), with two signals having very similar quadrupolar couplings and isotropic chemical shifts indicating similar coordination environments for the corresponding Na sites, in disagreement with the reported single-crystal structure. Point-monopole calculations of the EFG tensors based on the crystal structure fail to reproduce the experimental values. The ^{31}P CS anisotropies, obtained from ^{31}P MAS NMR spectra, show that the terminal P atoms of the $P_3O_{10}{}^{5-}$ ions have a negative shielding anisotropy parameter ($\Delta\sigma = \delta_{iso} - \delta_{33}$) in agreement with similar observations reported for diphosphates.

Based on the MP2/SCF optimised geometry of the FCO_2^- anion, the shielding both at the ^{13}C and ^{19}F nuclei have been calculated by the IGLO-method.[148] The different contributions to the shielding, stemming from the respective bonds, lone pairs and inner electron shells have been reported. The calculated chemical shifts have been compared to the experimentally observed ^{13}C and ^{19}F shifts. The shielding depends on the C–F bond length and the corresponding O–C–O bond angle. C–F bond lengthening is accompanied with a decrease of the magnetic shielding of the ^{19}F nucleus, mainly caused by the fluorine lone pairs, and an increase of the magnetic shielding of the ^{13}C nucleus which is mainly affected by the C–F bond electrons. Finally, this study confirms the expected geometric particularity of the ion: that is a weak C–F bond and open O–C–O bond angle of a planar entity. The interpolated C–F bond lengths derived from the experimental chemical shifts by this methodology is 1.55 Å (^{13}C NMR) and 1.60 Å (^{19}F NMR) and are thus close to that of 1.505 Å from an *ab initio* calculation.

A 2D NMR method for characterising the principal values and relative orientations of the EFG and the CS tensors of half-integer quadrupolar sites has been presented.[149] The technique exploits the different contributions that quadrupolar and shielding interactions impart on the evolution of MQ and SQ coherences, in order to obtain 2D powder lineshapes that are highly sensitive to these nuclear spin coupling parameters. Different spinning variants of this experiment were assayed, but it was concluded that a static version can yield the highest sensitivity to the values of the principal components and to the relative geometries of the local coupling tensors. Good agreement between data obtained on ^{87}Rb and ^{59}Co samples and ideal theoretical lineshape predictions of this experiment was obtained.

^{51}V static and MAS NMR of central transition has been shown to be an effective method for the characterisation of strongly bonded V(V) species in supported vanadia catalysts.[150] Determination of EFG and CS tensors parameters from both static and MAS NMR spectra of central transition permits the extraction of all NMR parameters with a reasonable accuracy. A large ^{51}V quadrupolar constant (14–16 MHz) has been obtained for strongly bonded V(V) species, whereas CSA tensor components were found to be close to those for bulk V_2O_5.

4.2.4 Indirect and Residual Dipolar Interactions. The ^{13}C CP MAS NMR spectra of various nitroanilines have been measured, and the origin of the differential broadening observed between the signals split by the residual dipolar interaction with ^{14}N has been clarified experimentally.[151,152] The dipolar interaction between ^{1}H and ^{14}N is responsible for the ^{13}C differential broadening, while the direct dipolar interaction with ^{1}H is neglected. A molecular motion can eliminate the differential broadening, which is presumably the π flip of the NH_2 group around the C–N axis.

VT ^{13}C single-pulse and CP MAS NMR spectra of homochiral tetrahydro-2*H*-1,3-oxazines have been reported.[153] Asymmetric multiplets observed for the carbons directly bonded to the nitrogen have been interpreted using

$^{13}C,^{14}N$ indirect and residual dipolar interactions. ^{14}N quadrupolar parameters and $^1J(^{13}C,^{14}N)$ have been determined from numerical simulations of ^{13}C lineshapes.

The cobaltocenium ions were studied by ^{13}C CP MAS NMR.[154] The ring carbon signals showed splitting patterns which are due to $^{59}Co,^{13}C$ dipolar coupling. The dependence of the patterns on the field, the rotor spinning rate and the temperature was investigated, and full-matrix diagonalisation treatment was used to fit the spectra. The patterns were better resolved at lower fields and to some extent at lower spinning rates. Lineshape fitting yielded dipolar and indirect isotropic $^{59}Co,^{13}C$ coupling constants of 530 and 40 Hz, respectively. When the counter ion was changed from PF_6^- to Cl^- the dipolar coupling pattern was not present, probably because of self-decoupling.

^{31}P CP MAS spectra of 2 phosphite- and 17 phosphine-substituted cobaloximes have been reported at two applied magnetic fields.[155] In the majority of cases, eight-peak multiplets arising from $^1J(^{59}Co,^{31}P)$ coupling have been observed. The spacings between adjacent peaks gradually increase or decrease from low to high frequency, due to the presence of residual $^{59}Co,^{31}P$ dipolar coupling. Values of $^1J(^{59}Co,^{31}P)$ range from 225 to 372 Hz, while in the phosphite derivatives this coupling is considerably larger, from 420 to 615 Hz. The magnitudes of $^1J(^{59}Co,^{31}P)$ and dipolar shifts have been shown to be dependent upon the nature of the axially-substituted ligands.

The first observation of residual dipolar couplings in MAS and MQ MAS NMR spectra of half-integer quadrupolar nuclei has been reported.[156] The fine spectral splittings observed in the ^{11}B MAS spectrum of crystalline triethanolamine borate have been attributed to the residual ^{11}B–^{14}N dipolar coupling, which is not completely averaged by MAS. This interpretation has been corroborated by the observation of an asymmetrical doublet in the ^{11}B MQ MAS spectrum.

4.3 Other Experimental Aspects. – *4.3.1 Single Crystal Studies.* The construction of a single-crystal NMR probe with a new two-axis geometry for the goniometer has improved the sensitivity of the NMR response from small crystals.[157] This allows studies of the smallest crystals used so far in single-crystal NMR. The goniometer of the probe uses only two different mountings of the crystal, and the rotation axis of the goniometer is tilted 45 degrees with respect to the direction of the magnetic field. By moving the goniometer outside the rf coil, the filling factor and the probe sensitivity increase. The improved sensitivity for the probe has been illustrated by the ^{31}P–{^1H} CP spectrum of a 0.088 mm^3 crystal of $(NH_4)_2HPO_4$ and a ^{87}Rb single-pulse spectrum of a 0.048 mm^3 crystal of $RbZn_2(HPO_4)PO_4$. The capability to determine precise parameters for the SSNMR interactions using the new probe has been demonstrated by ^{23}Na and ^{87}Rb single-crystal studies of $NaNO_3$ and $RbClO_4$.

A gain in detection sensitivity of more than three orders of magnitude has been achieved in HR ^2H SSNMR of monocrystalline fluorene-$^2H_{10}$ by applying optical nuclear polarisation *via* excited tripler states of acridine guest molecules.[158] The sensitivity gain has been utilised to measure the angular dependence (rotation pattern) of the ^{2}H nuclear magnetic resonance lines. In this way the principal values and orientations of all ^{2}H quadrupolar tensors have been determined.

The orthorhombic-to-hexagonal phase transition for constrained ultradrawn polyethylene fibres has been investigated ^{13}C CP (MAS and static).[159] The calculation of the ^{13}C chemical shift has revealed that 7% *gauche* defects are included in the hexagonal phase. In the CP ^{13}C NMR spectra measured by setting the orientation axis perpendicular to the static magnetic field, two resonance lines assignable to σ_{11} and σ_{22} for the CH_2 carbons that appear in the orthorhombic phase merge to a single resonance line at an upfield position compared to the average of σ_{11} and σ_{22} in the hexagonal phase. When the orientation axis is set parallel to the static magnetic field, no remarkable change has been observed in the hexagonal phase for the resonance line appearing at σ_{33}. These experimental results indicate that gauche defects such as kinks should be introduced at random along each molecular chain, and independent jump rotations occur around the molecular chain axis for the sequences between the gauche defects in the hexagonal phase. It has also been found that the π jump rotation around the molecular chain axis is induced in the orthorhombic phase at temperatures near the orthorhombic-to-hexagonal phase transition.

With nutation NMR for a spin $I = 5/2$ system, the relative line intensities of the central and the inner- and outer-satellite transitions have been calculated as functions of quadrupolar coupling and rf pulse strength.[160] The method has been illustrated in α-Al_2O_3 crystals (ruby and corundum) with the single-crystal ^{27}Al nutation NMR spectra. The new feature that the rf pulse strength shows reduced effect on the satellite transition lines according to the quadrupolar coupling has been discussed by using a fictitious spin-$^{1}/_{2}$ operator.

Single-crystal ^{95}Mo NMR spectra for a crystal of $Mo(CO)_6$ have been acquired for the central and satellite transitions.[161] The spectra have been analysed in terms of the EFG and CS tensors. The orientations of the two tensors have been obtained without any *a priori* knowledge of the crystal symmetry of the $Mo(CO)_6$ octahedron. The data from single-crystal NMR fully confirm the magnitudes and relative orientation of the EFG and CS tensors determined in a recent ^{95}Mo powder NMR study of $Mo(CO)_6$. Finally, it has been shown that slow-speed spinning ^{95}Mo MAS NMR at 14.1 T allows determination of the NMR parameters with good precision for the two tensorial interactions, despite the small CS anisotropy.

31P and ^{13}C CS tensors in the phosphoenolpyruvate moiety have been determined from rotary resonance recoupling ^{13}C and ^{31}P MAS and single crystal ^{31}P NMR.[162] The ^{31}P CS tensors have been assigned using the orientation-dependent ^{31}P–^{31}P dipolar splittings of the resonance lines. From ^{13}C MAS NMR experiments with ^{31}P rotary resonance recoupling on polycrystalline powder samples the orientations of the ^{31}P CS tensors have been determined.

4.3.2 Relaxation, Spin Diffusion and Polarisation Studies. ^{19}F NMR spin-echoes and free induction decays (FIDs) have been observed from samples of fluoridated trabecular canine bone powder, with varying fluoride concentrations.[163] Curve fitting of echo envelopes and FIDs was performed using a two-component model function, where one of the components incorporates the effects of dipolar coupling. This function provides a good match for both echo envelopes and FIDs. Based on the second moment measurements, it has been argued that ^{19}F spins in bone mineral typically experience weaker heteronuclear dipolar coupling than those in the mineral hydroxyapatite, which is often considered to be a prototype for bone mineral.

Relaxation calculations for rapidly spinning samples show that spin–lattice relaxation time (T_{1Z}) anisotropy varies with the angle between the rotor spinning axis and the external field.[164] When the rate of molecular motion is in the extreme narrowing limit, the measurement of T_{1Z} anisotropies for two different values of the spinning angle allows the determination of linear combinations of the static spectral densities, which are sensitive to molecular geometry and the rate and trajectory of motion. The utility of these phenomena has been demonstrated with ^{13}C NMR experiments: for ferrocene-^{2}H$_{10}$ deuteron T_{1Z} and T_{1Q} anisotropies and the relaxation time of the ^{13}C MAS peak provide sufficient information to determine the orientation dependence of all individual spectral densities.

Paramagnetic effects of Fe(III) species on T_1 of fluid protons in porous media has been studied.[165] In the absence of paramagnetic impurities, surface relaxivities of quartz sand and silica gel samples of known porosity and surface area at any pH were lower than any previously reported values. It has been shown that relaxation rate of the bulk pore fluid increased linearly with increasing Fe(III) concentration and varied with speciation of the ion.

^{1}H NMR spin-diffusion experiments have been carried out in order to investigate the domain structure of semicrystalline poly(vinylidene fluoride) by means of ^{1}H–^{19}F NMR dual-channel CP MAS.[166] The ^{19}F NMR detection of ^{1}H spin-diffusion gives a much higher discrimination of the effect due to the large chemical shift differences between the signals of the crystalline and amorphous regions. Different mobility filters were applied in order to create a magnetisation profile which allowed the measurement of the transfer from the crystalline regions to the mobile parts and *vice versa*. The data for the magnetisation transfer of the spin-diffusion process support the two-component model of the polymer.

Relatively efficient spin diffusion among unprotonated carbons can be achieved by a ^{13}C NMR multiple-pulse sequence with a low-duty cycle.[167] The spin diffusion occurs among transverse-magnetisation isochromats, while the total transverse magnetisation is a conserved quantity under the average Hamiltonian. The 'flip-flop' term of the dipolar-coupling average Hamiltonian is the same as in the full dipolar coupling. For a sample of 40% (COO)-^{13}C-labeled poly(vinyl acetate), with ^{13}C in ester groups accounting for 7% of all heavy atoms, magnetisation equilibrates within 20 ms, while the T_2 relaxation time of the total transverse magnetisation is similar to 40 ms. The spin diffusion coefficient has been estimated as $D = 3\ nm^2/s$.

19F→^{23}Na TQ CP experiments and numerical simulations have been performed on the oxyfluoride $NaMoO_3F$.[168] Due to the orientation dependence of the EFG tensor, only a fraction of the spins in the powder can match the Hartmann-Hahn condition at the same time, for a fixed ^{19}F rf field strength. Numerical simulations of the static TQ CP process, for different single crystallite orientations, demonstrate that the most efficient TQ CP occurs for parts of the powder where the quadrupolar splitting is largest. The TQCP matching profiles vary significantly with crystallite orientation and with spinning speed, due to the different time dependences of the quadrupolar interaction for the different orientations. The efficiencies of the SQ CP, MQ MAS and TQ CP MQ MAS experiments were compared and were found to be very similar for $NaMoO_3F$. The 2D TQ CP-MQ MAS experiment was illustrated.

Cross relaxation and CP from laser-polarised xenon to surface species have been studied.[169] The high polarisation of optically pumped ^{129}Xe was transferred to surface C and Si species under MAS conditions. ^{29}Si MAS spectra of fumed silica and ^{13}C spectra of chemisorbed methanol on silica were obtained using a steady flow of hyperpolarised xenon adsorbed onto the surface at 135 K. CP to ^{29}Si from SPINOE enhanced hydroxyl protons and to ^{13}C from enhanced methyl protons is observed with good efficiency. A direct SPINOE transfer from ^{129}Xe to ^{13}C without CP is observed to give the highest enhancement under these conditions.

The lateral dimensions of cellulose crystallites have been estimated using ^{13}C NMR signal strengths.[170] Differences in $T_{1\rho}(^1H)$ were exploited to edit the ^{13}C NMR spectra of solid lignocellulosics, separating signals assigned to cellulose crystallites from signals assigned to amorphous material.

Relative signal areas were used to estimate the weight-averaged lateral dimensions of crystallites. Silicalite crystals have been studied using $T_1(^{29}Si)$.[171] Loading of *p*-xylene into the silicalite channel reduces the $T_1(^{29}Si)$ compared to that of empty silicalite. The relaxation time is unaffected when *p*-xylene-$^2H_{10}$ was used. This indicates that dipole–dipole couplings between ^{1}H and ^{29}Si atoms does not contribute significantly to $T_1(^{29}Si)$. A method employing aromatic endoperoxide has been used for controlled addition of O_2 into silicalite samples. The results showed that interaction with O_2 is not the only relaxation mechanism for ^{29}Si, and that zeolite structural changes caused by guest molecules play an important role in determining $T_1(^{29}Si)$.

4.3.3 New (Less Studied) NMR Phenomena. Hartmann-Hahn match conditions for two half-integer quadrupolar nuclei, spin-lock signal as a function of effective nutation frequency, and the correlation of effective nutation frequency and rf field strength have been reported for three samples: sodium diborate ($Na_2B_4O_7$), aluminum boride (AlB_2), and lithium aluminate ($LiAlO_2$).[172] The observation of a new decoupling-induced recoupling phenomenon in MQ MAS spectra of half-integer quadrupolar nuclei has been reported.[173] The origin of the effect is identical to the second-order recoupling between dipolar and anisotropic CS interactions under CW spin decoupling, which is first observed by Ernst *et al.* in the SSNMR spectra of spin-$^1/_2$ nuclei [*J. Chem. Phys.*, 1996 **105,** 3387].

Negative cross-peaks have been observed in the ^{19}F 2D magnetisation-exchange MAS NMR spectra of $Ba_2MoO_3F_4$ under fast-spinning conditions.[174] The polarisation transfer dynamics have been studied as a function of the spinning frequency and the frequency separation of the resonances. The results are consistent with a novel mechanism, in which four spins simultaneously exchange Zeeman magnetisation with each other, in an energy-conserving process. 2D ^{27}Al/^{31}P CP MAS NMR experiments have been performed on sodium aluminophosphate glasses, providing direct detection of particular Al species connected to specific P species.[175] The spectral-editing capabilities of 2D experiments allow the elucidation of ^{31}P resonances that are strongly correlated to four-, five-and six-coordinate Al species. Results from 2D contour plots and projections of spectra along the ^{31}P dimension allow the assignment of phosphate structures that cannot be directly assigned from 1D ^{31}P MAS spectra. Changes in the phosphate/aluminate ordering have also been monitored by inspection of the ^{31}P subspectra of the 2D CP MAS, demonstrating a change in Al/P connectivity correlated to changes in molar composition.

Second-order perturbation theory predicts the existence of a 'cross term' between the quadrupolar and dipolar interactions of two spin $I = 3/2$ nuclei.[176] This cross term manifests itself as a broadening in SSNMR spectra of spin $I = 3/2$ nuclei which cannot be fully removed by MAS and has on inverse dependence on the Larmor frequency, ω_0. In these attributes, the SOQ-dipolar broadening does not differ from pure SOQ broadening. It has been shown that the recently developed 2D MQ MAS technique, designed originally to suppress SOQ broadening, allows the two broadening interactions to be separated and quantified. 1D HETCOR experiments have been utilised to determine local structural changes in sodium phosphate glass compositions with ratios of Na/P of 0.25, 0.78, 1 and 1.3.[177] Glasses containing only Q^2 (metaphosphate composition), Q^2 and Q^1 (between meta- and pyro-phosphate compositions), and Q^3 and Q^2 (ultraphosphate region) have been investigated using ^{23}Na → ^{31}P CP MAS NMR to detect direct interactions between distinct P sites and Na nuclei in the second coordination sphere. Variable-contact CP MAS experiments provide additional information about association of ^{23}Na nuclei with specific phosphate sites. Time constants describing the transfer of magnetisation ^{23}Na → ^{31}P have been found to be affected by Na ion concentration in ultraphosphate glasses, and an important finding of these investigations is the degree of correlation of Na ions with Q^3 sites in ultraphosphate glasses.

The feasibility of ^{2}H-{^{1}H} CP MAS and its implementation in HETCOR experiments has been studied using as-made all-silica zeolites.[178] The results presented show that ^{2}H-{^{1}H} CP MAS can be employed successfully in 2D correlation spectroscopy experiments. The effects of experimental and physical parameters on the NMR spectra have been studied in detail. In the limit of small QCCs and weak proton homonuclear dipolar coupling, the CP behavior of the deuterons is similar to spin I = $^1/_2$ systems and ^1H spin-diffusion is minimal. Samples with larger QCCs and strong proton dipole–dipole coupling exhibit less efficient spin-locking of the deuterons and ^1H spin-diffusion is more prevalent. In this case, it is necessary to perform proton spin-diffusion experiments in conjunction with the correlation spectroscopy. Minimising ^1H spin-diffusion is crucial for correct interpretation of the multidimensional correlation spectroscopy experiments, which can be achieved by using short contact times. ^2H-{^1H} CP MAS HETCOR experiments could find uses for b0th organic and organic–inorganic solids where selective deuteration can be achieved.

A novel mechanism for ^{13}C–^{13}C polarisation transfer under MAS has been presented.[179] By applying a recently proposed ^{13}C–^1H recoupling sequence under MAS, the spin part of the ^{13}C–^1H dipolar interaction is modulated with a particular frequency so that non-commutable time-dependent ^{13}C–^1H and ^{13}C–^{13}C dipolar interactions interfere with each other. This novel polarisation-transfer approach has been theoretically explained and experimentally demonstrated using [1,3-^{13}C] L-alanine.

4.3.4 Distance and Angle Measurements. – The viability of SSNMR distance determinations in multiple spin systems of unknown geometry using REDOR and TEDOR has been investigated.[180] These techniques can provide distances which compare very well with those obtained by XRD if the samples contain isolated heteronuclear spin pairs and are currently being used in structural investigations of solids including peptides, polymers and inorganic materials. However, in most cases the spin system geometry was known before analysis of the NMR data, thus it is unclear whether reliable distances can be determined when the geometry of the spin system is completely unknown. To investigate the uniqueness of distance determinations from fitting of multispin REDOR and TEDOR data, theoretical calculations have been carried out. These indicate that it is highly unlikely that reliable distances can be obtained directly from REDOR and TEDOR experiments on multiple spin systems when the number of spins and their geometrical arrangement is completely unknown. Furthermore, it is possible to obtain incorrect distances if isolated spin pairs are assumed and multiple spins are present.

SSNMR distance determinations using CP between ^{19}F and ^{29}Si have been presented.[181] Three analytical functions that allow efficient nonlinear least-square regression analyses of the experimental data to determine the internuclear distances for non-spinning powder samples as well as at the ± 1 and ± 2 MAS sideband matching conditions have been reported. Using these functions, a ^{19}F–^{29}Si distance of 2.53 ± 0.04 Å was determined for the T_1 silicon in octadecasil from fitting of the oscillatory behaviour. This distance is in good agreement with that known from the XRD structure and the previous $^{19}F/^{29}Si$ REDOR and TEDOR distance measurements. The advantages and limits of the different dipolar-based NMR techniques for heteronuclear distance determinations have been examined and discussed.

While an HR monomer structure of the ion channel forming polypeptide, gramicidin A, has been solved with 120 orientational constraints, the precise geometry of the dimer interface has not been characterised.[182] Using both ^{13}C and ^{15}N labelled gramicidin A samples in hydrated phospholipid bilayers, both inter- and intra-molecular distances have been measured with a recently developed simultaneous frequency and amplitude modulation (SFAM) SSNMR scheme. Using this approach ^{15}N–$^{13}C_1$ residual dipolar couplings across a H-bond as small as 20 Hz have been characterised. While such distances are on the order of 4.2 ± 0.2 Å, the spectroscopy is complicated by rapid global motion of the molecular structure about the bilayer normal and channel axis. The intermolecular distance confirmed the previously described monomeric structure.

19F/^{29}Si CP has been applied under fast MAS to a powder sample of octadecasil.[183] The magnitude of the dipolar coupling constant has been deduced directly from the line splitting between the intense singularities of the Fake-Like patterns obtained by Fourier transformation of the oscillatory polarisation transfer. The corresponding Si–F internuclear distance, $r = 2.62 \pm 0.05$ Å, is found to be in agreement with the XRD structure and the value of 2.69 ± 0.04 Å reported from REDOR and TEDOR experiments. Furthermore, the CP technique is still reliable under fast MAS where both REDOR and TEDOR sequences suffer from severe artefacts due to finite pulse lengths.

The distance between the host and guest molecular components of the supramolecular inclusion compound *p*-*tert*-butylcalix[4]arene-fluorobenzene has been examined by REDOR.[184] No isotopic enrichment is required for either interacting nuclei. REDOR curves using internuclear distances derived directly from the XRD structural unit cell fail to match those determined experimentally. When a structural model incorporating both multiple spin interactions and molecular reorientation is used, the REDOR curve approaches the experimental curve. A mathematical treatment of the angular and distance dependence of a generalised SI_n system of *n*-spins under motional conditions has been developed. These results extend the scope of distance-determining NMR techniques such as REDOR to systems complicated by disorder, molecular reorientation and multiple-spin interactions.

Constraints on the proximity of the carboxyl carbons of the Asp-85 and Asp-212 side chains to the 14-carbon of the retinal chromophore have been established for the bR(555), bR(568) and M-412 states of bacteriorhodopsin (bR) using SSNMR spectroscopy.[185] Distances were examined *via* ^{13}C–^{13}C magnetisation exchange, which was observed in 2D RFDR and spin diffusion experiments. The NMR distance constraints are in agreement with the results from diffraction studies on intact membranes and with theoretical simulations.

Magnetic dipolar couplings between the ^{15}N atom (labeled) and neighboring ^{13}C atoms (natural abundance) in three solid modifications of *N*-octyl-*d*-gluconamide have been measured using REDOR.[186] The dipolar couplings in the range 45 to 1220 Hz have been converted into C–N distances. These distances have been employed in conjunction with the ^{13}C chemical shieldings of the CP MAS spectra to determine sets of possible torsion angles, which define the molecular conformation in the neighbourhood of the amide group.

The potential of the variable contact time ^{13}C CP MAS experiment for obtaining geometrical information has been demonstrated using the partially deuterated stearic acid.[187] It was found that the cross relaxation rate $1/T_{CH}$ values for the methylene carbons are proportional to $r_{av}{}^{-6}$, which is the averaged atomic distance between any specified carbon and protons.

Retinylidene ligand structure in bovine rhodopsin and 10-methylrhodopsin have been determine from internuclear distance measurements using ^{13}C-labeling and 1-D rotational resonance MAS NMR.[188] These results represent the first highly precise distance determinations in a ligand at the active site of a membrane protein. Overall, the MAS NMR data indicate a tight binding pocket, well defined to bind specifically only one enantiomer out of four possibilities and providing a steric complement to the chromophore in an ultrafast isomerisation process.

13C–^{27}Al REDOR and TRAPDOR experiments on several Al organic compounds have been presented with the aim of detecting ^{13}C–^{27}Al dipolar couplings and distances in solids.[189] The ^{13}C and ^{27}Al pulses have been applied to the same probe channel because their resonance frequencies are in close proximity. The different possibilities of controlling the efficiency of the TRAPDOR approach (by varying the ^{27}Al rf amplitude and the MAS frequency) have been investigated. The results indicate that TRAPDOR is superior to REDOR in resolving differences in ^{13}C–^{27}Al distances when choosing the proper experimental conditions. A method to determine r_{CH} with high precision from LG CP with fast MAS and continuous LG decoupling on uniformly ^{13}C-enriched tyrosine · HCl has been presented.[190] When the CP amplitudes are set to a sideband of the Hartmann-Hahn match condition, the LG-CP signal builds up in an oscillatory manner, reflecting coherent heteronuclear transfer. Its Fourier transform yields an effective ^{13}C frequency response that is sensitive to the surrounding protons. This ^{13}C spectrum can be reproduced in detail with MAS Floquet simulations of the spin cluster, based on the positions of the nuclei from the neutron diffraction structure. Measurement of CH distances is straightforward, since the separation between the maxima for a single ^{1}H-^{13}C pair is related to r_{CH}. The method offers an attractive route for collecting long-range distance constraints and for the characterisation of intermolecular H-bonding.

DQ heteronuclear local field NMR has been applied to two ^{13}C$_2$-labelled carbohydrate samples [1,2-^{13}C$_2$]-glucose and methyl-α-D-[1,3-^{13}C$_2$]-glucose.[191] The geometry of the H–^{13}C–^{13}C–H moeity was estimated using the evolution of DQ coherences under correlated heteronuclear dipolar interactions. The torsion angles in crystalline glucose were measured. The influence of anisotropic rotational diffusion, CSA, and ^{1}H–^{1}H spin diffusion on the torsion angle estimate has been assessed. These techniques may be applied to other structural problems such as the determination of glycosidic linkage conformations and the conformation of sugar rings in nucleotides.

A spectrum-inversion approach to extract information from MQ MAS NMR spectra in glasses has been presented.[192] This allows the reconstruction of the underlying 2D distribution of the δ_{iso} correlated to the quadrupolar interaction. Correlation of the distributions of each interaction to structural local information has been attempted. A borosilicate and a basaltic-like glass have been studied using ^{27}Al and ^{23}Na TQ MAS NMR. The interpretation of the different site distributions has been discussed in terms of topological disorder (the distribution of specific geometrical parameters such as bond distances and angles). Using the semiempirical relationships previously established with crystalline silicate compounds, the distributions of the Na–O distance and the Al–O–Si bond angle have been determined from the extracted distributions of the δ_{iso}.

The Al–O–Si bond angles were investigated in aluminosilicate glasses by the ^{27}Al MQ MAS spectrum inversion to infer quantitative distributions of isotropic chemical shifts, enabling to estimate an angular distribution.[193] The experimental data were compared with MD simulations.

13C–^{15}N distances in uniformly ^{13}C labeled biomolecules have been measured using *J*-decoupled REDOR.[194] SSNMR methods and *ab initio* calculations have been employed to investigate the structure of the trimethylphosphine (TMP)-Bronsted acid site complex in zeolite HY.[195]

^{27}Al/^{31}P and ^{27}Al/^{1}H rotational echo double-resonance NMR experiments were utilised to measure Al–P and Al–H–B distances, where H–B is the Bronsted acid site proton. A P–H–B distance was obtained by fitting the SSBs in the ^{1}H MAS NMR spectrum. The experimental internuclear distances are within the range of the Al–P, Al–H–B, and P–H–B distances obtained from *ab initio* calculations. Bronsted and Lewis acidity in zeolites has been characterised by the ^{29}Si and ^{27}Al REDOR NMR to provide the spatial arrangement of the base with respect to either the Si/Al distribution in the lattice or the coordination in the nonframework Al nano-particles.[196]

Pigments of titanium dioxide rutile, coated with SiO_2–Al_2O_3, have been characterised by ^{27}Al TQ MAS NMR, REDOR ^{27}Al–^{1}H and CP ^{1}H–^{29}Si experiments to provide longer range distance information.[197] Two types of surface treatment can be distinguished from ^{27}Al–^{1}H REDOR by the presence of proton free alumina domain in the surface treatment.

4.3.5 Exotic and Troublesome Nuclei. ^{14}N NMR spectra of solids are usually very broad due to the presence of large quadrupole coupling constants; however, even partial excitation of the whole spectrum can give valuable information.[198] With MAS, the spectrum consists of a number of peaks, but normally the centreband cannot be readily distinguished from the SSBs. Multiple pulse methods of SSB elimination, such as TOSS and PASS, cannot be used for ^{14}N because of its short spin–spin relaxation time. The SSBs can be eliminated by systematic data treatment: the SNR is enhanced by co-adding all the peaks in a MAS spectrum in a periodic way and then several spectra obtained at different spinning rates are added or multiplied together to identify the centerband. In the centreband region of the spectrum obtained from the addition method, the residual SSBs can be distinguished from the weak signals by the use of logical or digital filtering. Results obtained by using these methods to treat the spectra of two mixtures of KNO_3, $Pb(NO_3)_2$ and NH_4Cl have been shown. The experimental requirements are not very stringent, the SNR is good, and peaks covering a large range of chemical shifts can be readily observed with HR.

^{25}Mg NMR has been applied to study inner-sphere Mg^{2+} binding complexes in the solid state.[199]

^{39}K MAS NMR spectra of $KNiF_3$ were measured between 180 and 450 K.[200] In the paramagnetic state (450–270 K), a shift of the ^{39}K resonance to lower frequency is observed with decreasing temperature which is due to an isotropic hyperfine interaction. This is in contrast to theory which predicts zero unpaired electron density at the potassium. In the antiferromagnetic state (below 250 K), a reduction of the shift contribution from the unpaired electrons has been observed. The temperature dependence of the ^{39}K shifts parallels that of the magnetic susceptibilities over the whole temperature range measured.

HR ^{73}Ge SSNMR spectra of organogermanium compounds have been observed for the first time; the chemical shifts and half-widths of tetraphenylgermane and tetrabenzylgermane have been reported.[201]

^{137}Ba MAS NMR spectra at 11.7 T have been presented for 10 ceramic materials and related inorganic compounds.[202] The spectra of compounds in which Ba occurs in highly symmetric sites show sharp resonances, with a well-resolved quadrupolar lineshape in the case of $BaTiO_3$. In other Ba-containing ceramics and ceramic precursor compounds, the Ba typically occurs in irregular polyhedral sites, giving spectra which are considerably broader. Some of the present spectra show evidence of an expected negative trend in the resonance positions with increasing Ba coordination number. The results suggest that ^{137}Ba MAS NMR spectroscopy has potential value for studying some types of Ba-containing ceramics and ceramic precursors.

VT ^{89}Y MAS NMR studies on some yttrium-dihydride phases have been reported and yield evidence that ^{89}Y CP MAS techniques are an experimentally feasible route to investigate order–disorder phenomena in metal-hydride phases.[203] ^{89}Y MAS NMR has been investigated to study the local environment of Y sites in a red phosphor and Eu doped-Y_2O_2S (Eu-Y_2O_2S).[204] Despite the presence of paramagnetic Eu^{3+} ions, HR spectra have been acquired and a number of local environments have been detected. The assignment of the resonances to different Y local environments has been made on the basis of signal intensities, chemical shifts, and spin–lattice relaxation times (T_1) in conjugation with the crystal structural data. T_1 reduction and a line-broadening due to paramagnetic Eu^{3+} ions have been discussed in relation to the distribution of Eu ions.

^{93}Nb NMR of polycrystalline $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ solid-solution relaxor ferroelectrics have been reported.[205] The ^{93}Nb static and MAS NMR spectra of $Pb(Mg_{1/3}Nb_{2/3})O_3$ have two major resonances due to the central transition ($^1/_2 \leftrightarrow -^1/_2$), a sharp peak at -902

ppm and a broad resonance centered at -980 ppm. The sharp peak has been assigned to Nb(V) B-sites. The broad resonance at -980 ppm has been assigned to a range of $Nb(ONb)_{6-x}(OMg)_x$ site configurations. $Pb(Mg_{1/3}Nb_{2/3})O_3$ and a related pyrochlore phase have also been studied by single- and TQ ^{93}Nb MAS NMR.[206]

4.3.6 Quantification Aspects. A method that can yield quantitative MQ MAS spectra by correcting experimental spectra with numerical simulations has been presented.[207] This method does not require intensive rf fields, extensive pulse optimisation or high spinning speeds, *etc.* Its effectiveness has been verified by treating the ^{23}Na MQ MAS spectra of a series of sodium compounds to yield almost the XRD site quantification.

Short-range order and local atomic configuration in charge-balanced aluminosilicate glasses as functions of composition have been studied using ^{17}O and ^{27}Al MAS and TQ MAS NMR.[208] Enhanced resolution in ^{17}O and ^{27}Al TQ MAS spectra allows the quantification of the spectra and the extent of disorder using a semiempirical function relating TQ MAS efficiency to a quadrupolar coupling constant. In the ^{17}O TQ MAS spectra, variations of populations of three clearly resolved oxygen sites (Al–O–Al, Si–O–Al and Si–O–Si) are consistent with the predictions from ^{29}Si MAS NMR. The method provides improved prospects for the quantitative application of TQ MAS NMR and add to a more complete understanding of framework site connectivity in aluminosilicate glasses.

A new method for quantitation of solid-phase synthesis using ^{19}F NMR spectroscopy has been presented.[209]

Quantification aspects of humic acid composition in the solid state by ^{13}C MAS and CP/T_1 TOSS NMR techniques have been reported.[210] Quantitative multinuclear MAS NMR studies of zeolites have been performed using ^{1}H, ^{27}Al, and ^{29}Si MAS NMR investigations combined with elemental analysis.[211] Because in fully protonated samples the number of Bronsted protons equals the number of tetrahedral Al atoms in the framework. The framework Si/Al ratio of the samples was estimated from ^{1}H MAS NMR in combination with chemical analysis. To quantify the true Si/Al ratio of the zeolite framework, an unambiguous assignment of the peaks due to the Bronsted acid sites in the ^{1}H MAS NMR spectra was made. The results obtained from the quantification of the ^{1}H MAS NMR spectra were confirmed by those of the ^{27}Al MAS NMR spectra. In addition, the number of defect sites in the framework was determined by comparing the true Si/Al framework ratio with the Si/Al ratio derived from ^{29}Si MAS NMR.

A new method to extract quantitative information from poorly resolved ^{29}Si MAS NMR spectra of natural mixed-layer illite–smectite (I–S) clays has been presented.[212] The Si–Al distribution in layered aluminosilicates have been used to link the intensities of ^{29}Si resonances from all $Q^3(n\mathrm{Al})$ sites ($n = 0$–3) to the tetrahedral layer Al substitution by applying Loewenstein's aluminum avoidance principle (no Al–O–Al linkages). In addition, correlations between ^{29}Si chemical shifts and the Al substitution have been established for illite resonances by computer fitting of well-resolved phyllosilicate spectra. Combination of these two constraints led to a general procedure for iterative fitting of ^{29}Si MAS NMR spectra of clay minerals containing high- and low-charge sites. The applicability of the new method has been demonstrated for two I–S samples.

4.3.7 Novel Applications. It has been shown that local residual dipolar broadening of ^{1}H coupled to ^{13}C is a sensitive way to observe motional constraints from networks and entanglements in cross-linked and uncross-linked rubber systems, and this may be easily obtained from the indirect observation of proton spin system through ^{13}C resonance in the conditions of slow MAS.[213] The method has been used to visualise the changes in the amount of physical constraints induced during mechanical treatment, which precedes the vulcanisation process. Polymorphic behavior has a broad impact on chemical technology influencing the solid-state properties of many materials from pigments to pharmaceuticals. The simultaneous presence of two or more polymorphs may introduce ambiguities in the characterisation of materials using spectroscopy, diffraction or scattering techniques.

A ^{13}C SSNMR method combined with the direct exponential curve resolution algorithm has been presented,[214] that allows the elucidation of component spectra from the total spectrum of a mixture of polymorphs, previously characterised by XRD.

High-speed 2D CP MAS NMR has been applied to study polymorphs of uniformly ^{13}C-labeled aspartame.[215] Three forms of crystalline aspartame have been observed. The ^{13}C CP MAS NMR spectra of two of the forms of aspartame showed that certain carbons have up to three resonances due to different conformations/arrangements of molecules in the asymmetric unit cell. 2D exchange experiments on uniformly ^{13}C-labeled aspartame were used to assign the spectra of aspartame. Increasing the spinning rate to 28 kHz and the ^{1}H decoupling power to 263 kHz allowed to observe crystallographically inequivalent sites. 2D RFDR and exchange experiments using very high spinning speed and decoupling power gave complimentary assignment information for short (1–2 bond) and long (>3 bonds) range interactions in the polymorphic forms.

The use of MAS (>30 kHz) in tandem with delayed echo acquisition has been shown to yield very HR ^{1}H MAS NMR spectra of complex natural organic materials: cork and wood components.[216] The effect of the spinning rate on the ^{1}H NMR spectra was evaluated with single-pulse acquisition and delayed-echo acquisition. The delayed-echo acquisition spectra presented linewidths as sharp as 67 and 25 Hz. The narrow peaks, characterised by proton T_1 and T_2 relaxation, were assigned to the isotropic chemical shifts and the general spectral features were shown to correlate with the sample chemical structure.

A simple but efficient ^{13}C MAS NMR method has been presented for the determination of the location of embedded molecules such as peptides relative to biological membrane surfaces by exploiting the interaction with paramagnetic lanthanide ions.[217] Tested on the membrane-embedded 50 residue long M13 coat protein,^{13}C labeled at its Val-29 and Val-31 residues, no paramagnetic quenching was observed for the peptide resonances by Dy^{3+}, suggesting that Val-29 and Val-31 are not in close proximity to the bilayer interface.

HR multidimensional NMR methods can be used to correlate many backbone and side-chain chemical shifts for hydrated micro-crystalline Basic Pancreatic Trypsin Inhibitor (BPTI).[218] Results from two homonuclear transfer methods, RFDR and spin diffusion, were compared. Typical ^{13}C peak line widths are 0.5 ppm, exhibiting many resolved peaks. 2D ^{13}C,^{13}C correlation spectra of BPTI have sufficient resolution to identify and correlate many of the spin systems associated with the amino acids. The agreement between shifts measured in the solid state and those in solution is typically good, although some shifts near the ion binding sites differ by at least 1.5 ppm. These studies were conducted with approximately 0.2 to 0.4 μmol of enriched material; the sensitivity of this method is also adequate for other biological systems.

The acquisition of 2D heteronuclear NMR local field spectra under moderately fast MAS conditions has been discussed.[219] It has been shown both experimentally and with the aid of numerical simulations on multispin systems that when sufficiently fast MAS rates are employed, quantitative dipolar SSB patterns from directly bonded spin pairs can be acquired in the absence of ^{1}H–^{1}H multiple-pulse homonuclear decoupling even for 'real' organic solids. The MAS speeds involved are within the range of commercially available systems (10–14 kHz) and provide SSBs with sufficient intensity to enable a reliable quantification of heteronuclear dipolar couplings from CH groups. Simulations and experiments show that useful information can be extracted even from more tightly coupled CH_2 moieties. Applications of this approach to the analysis of molecular motions in solids have been presented; characteristics and potential extensions of the method have also been discussed.

The structure of $AlPO_4$-CJ2 aluminophosphate has been reinvestigated by MAS, MQ MAS, CP MQ MAS and HETCOR techniques.[220] The CP MQ MAS method showed that the sample, when not allowed adequate time for crystallisation, included a substantial concentration of amorphous species and the crystalline component was cleanly singled out by this technique. The relative populations and the distributions of F and OH groups within the structural building units and their distribution of within the crystalline structure have been studied by the $^{19}F \rightarrow {}^{31}P$ HETCOR.

New structural strategies to access structure determination of microporous materials by SSNMR techniques have been presented.[221] A set of 2D experiments using RFDR (^{19}F), DQ (^{31}P) and HETCOR (^{19}F and ^{31}P) has been used to analyse the topology of the microporous network.

The biologically important compound, hydrated disodium adenosine 5′-triphosphate (ATP) has studied by ^{23}Na NMR (MAS, CP MAS and MQ MAS) at 4.7 and 9.4 T.[222] MQ MAS experiments enabled the resolution of all the four crystallographically different Na sites in the unit cell at 4.7 T, but not at 9.4 T. The four sites were successfully assigned and the principal elements of the quadrupolar tensors and isotropic chemical shifts of the ^{23}Na nuclei at each lattice site determined by analysing and computer simulating the experimental spectra.

The temperature dependence of ^{207}Pb chemical shift in MAS NMR spectrum of $Pb(NO_3)_2$ has been shown to provide a sensitive method to calibrate temperature in MAS NMR: the temperature dependence is uniform in the range 30–400 °C.[223]

Sample heating due to the friction between the rotor and the bearing gas at MAS frequencies up to 35 kHz has been studied using the ^{119}Sn NMR signal of the chemical shift thermometer $Sm_2Sn_2O_7$.[224] The frictional heating effect has been quantified, and a calibration of the sample temperature under ultrafast MAS conditions has been described. An empirical expression has been given which allows the determination of the sample temperature as a function of the bearing gas temperature and the spinning frequency.

5 Structural Applications

5.1 Organic Solids. –

Compound	*Nuclei*	*Comments*	*Ref.*
3,5-Bis(trifluoromethyl)pyrazole	^{1}H	Tetramers, N-H···N hydrogen bonds	225
Columnar hexabenzocoronene	^{1}H	π-π packing, ^{1}H–^{1}H proximities by DQ MAS	226
Triphenylene & hexabenzocoronene derivatives	^{1}H	π-π packing, 1H-1H proximities by DQ MAS	227
Hexabenzocoronene carboxylic acid derivative	^{1}H	π-π packing, H-bonding, DQ-filtered MAS	228
Pyridyl nitronyl nitroxides	^{1}H	Spin density distribution, MAS, DFT calculations	229
Nitronyl nitroxide radicals	^{1,2}H,^{13}C	Spin density distribution, MAS, *ab initio*	230
Conjugated nitroolefins in β-cyclodextrin	^{1}H,^{13}C	Inclusion complexes, MAS	231
Piroxicam in β-cyclodextrin	^{13}C	Inclusion complex, guest conformation,	232
Bisepoxide & α,ω-diamine in α-cyclodextrin	^{13}C	Inclusion complexes, CP MAS	233
β-D-glucopyranoside derivatives	^{13}C	Polymorphism, CP MAS	234
1-Arylpiperazine-4-alkylimides	^{13}C	Hydrochlorides and perchlorates, CP MAS	235
N-Benzoyl(-DL-)-L-phenylalanines	^{13}C	H-bonding, 2D EXSY & 1D ODESSA	236
2-hydroxy-5-methyl-isophthaldehyde, dianyl of	^{13}C	Intramolecular O–H···N H-bonding, CP MAS	237
Tetra(*C*-undecyl)calix[4] -resorcinarene	^{13}C	DMFA solvate, dimers, CP MAS, XRD	238
3′-Azido-3′-deoxythymidine (AZT)	^{13}C	Anti-HIV-1 agent, H-bonding, CP MAS	239

1,5-Dimethylsemibullvalene-2,6-dicarbonitrile	^{13}C	β form, VT CP MAS	240
p-Xylene clathrate of Dianin's compound	^{13}C	Single guest site, CP MAS, XRD	241
(Perilene)$_2$ PF$_6$·2/3(Tetrahydrofurane)	^{13}C	Organic conductor, Knight shifts, CP MAS	242
(−)-Scopolamine HBr/HCl salts	^{13}C	Conformational pseudopolymorphism, CP MAS	243
(−)-Scopolamine, hydrobromide 'trihydrate'	^{13}C	MAS induced phase-transition, CP MAS	244
1*H*,3*H*-pyrido[1,2-*c*] pyrimidine-1,3-diones	^{13}C	Dimers, CP MAS, XRD	245
Triphenylmethanol, Ph$_3$COH	^{13}C	H-bonded tetramers, MAS, Neutron Diraction	246
2-Methyl-4-(*p*-X-phenylazo)-imidazoles	^{13}C	N-H···N & C-H···O(N) interactions, CP MAS	247
Benzylideneanilines	^{13}C	H-bonding and tautomerism, CP MAS, XRD	248
Metacyclophane/C$_{60}$ complexes	^{13}C	π–π & σ–π interactions, CP MAS, XRD	249
2,2-Dimethylcyclohexane-1,3-dione dioximes	^{13}C	Intermolecular H-bonding, CP MAS, XRD	250
Tris(*o*-phenylenedioxy)-cyclotriphosphazene	^{13}C,^{31}P	Inclusion complexes, T$_1$(^{13}C), CP MAS	251
NH-Pyrazole derivatives	^{15}N	Intermolecular N–H···N bonds, CP MAS	252
Imidazole	^{15}N	Protonic conduction, 2D ^{15}N-exchange NMR	253
Diazadiphosphetidines with fluorine substituents	^{19}F,^{31}P	CS tensors by triple resonance ^{31}P-{^{19}F, ^{1}H}	254

5.2 Organometallics and Coordination Compounds. – *^{1}H* - Temperature dependence of ^{1}H NMR lineshapes and second moments in polycrystalline BF$_4$$^{-}$ salts of 1-propyltetrazole complexes of Fe(II) and Zn(II) have been reported.[255]

^{1}H,^{2}H,^{17}O - Diffusion and dynamic properties of hydration water in (+/−)-tris(ethylenediamine)cobalt(III) chloride hydrate have been studied by means of ^{1}H, ^{2}H, and ^{17}O NMR techniques.[256]

^{13}C - ^{13}C MAS has been applied to study strontium carbonate crystals strongly bound by H-bond to poly(carboxylate) ligand,[257] solid-state conformation of *N*-methylene(phenyl)phosphinic acid derivatives of cyclen and cyclam,[258] polymorphic structures of alkaline earth metal acetylides, MC$_2$ (M = Ca, Sr, Ba),[259] selenocyanogen and related compounds[260] and the stereochemistry of the LiNCS complex of 1,4,7,11-tetraoxacyclotetradecane.[261]

^{13}C,^{15}N - Combined ^{13}C and ^{15}N CP MAS studies have been undertaken to investigate rotation isomers of bis(diethyldithiocarbamato) zinc(II) adduct with pyridine,[262] the structural reorganisation of bis-(diethyldithiocarbamato)-pyridine-zinc(II) and -copper(II),[263] adduct-formation of diethyldithiocarbamate zinc(II) and copper(II) complexes with morpholine[264] and CCl$_4$,[265]

palladium(II) chloride complexes with 1,2,4-triazolo[1,5-a]-pyrimidines[266] and dicopper(I) analogues of disilver(I) iminocryptates.[267]

^{13}C,^{29}Si - ^{13}C and ^{29}Si CP MAS have been applied to study immobilisation of rhodium complexes in chiral organic-inorganic hybrid materials.[268]

^{13}C,^{31}P - ^{13}C and ^{31}P CP MAS studies have been used to study polymorphism of bis(dineopentoxyphosphorothioyl)diselenide.[269]

^{17}O - Titanium oxo-organo clusters and monodisperse nanoparticles of titania anatase having 20 Å and 30 Å oxide core diameters, have been characterised by ^{17}O NMR.[270] The ^{17}O NMR linewidths are dominated by chemical shift distribution with a minor contribution from SOQ broadening. ^{17}O MAS NMR has been applied to identify surface species.

^{31}P - ^{31}P CP MAS has been applied to study a complex obtained from Sb powder and diiodine activated by tetraphenyldithioimidodiphosphine,[271] triphenylphosphinecobaloximes,[272] complexes of octacarbonyldicobalt with bis(-diphenylphosphanyl)amine, bis(diphenylphosphanyl)methane, and 1,1,1-tris(diphenylphosphanyl)ethane,[273] complexes of copper(I) and silver(I) halides with trimethylphosphine,[274] tris(triphenylphosphine)-copper(I) and -silver(I) formates[275] and bis(trimethylphosphine)gold(I) halides.[276]

^{51}V - ^{51}V SSNMR has been used to study bis(acetylacetonate)oxovanadium(IV) and derivative.[277]

^{119}Sn - ^{119}Sn SSNMR techniques have been applied to characterise bis(trifluoroacetato)dibutyltin 1,10-phenanthrolin[278]e (antitumor agent).[277]

5.3 Natural Products. –*^{1}H* - The proton spin–lattice relaxation times, $T_1(^1\mathrm{H})$, for isolated cuoxam lignin and fully bleached cellulose have been measured as a function of pH in order to examine for possible macromolecular connectivities that may be present between lignin and carbohydrates within softwood.[279]

^{1}H,^{13}**C** - The effect of hydration on the mobility of polysaccharides in onion cell-wall material (CWM) has been studied by SSNMR. $T_{1\rho}(^1\mathrm{H})$ and $T_1(^{13}\mathrm{C})$ and 2D WISE experiments have been applied to characterise effects of hydration on polymer mobility in onion cell-wall material; the 2D WISE revealed a spatial heterogeneity of the polysaccharide dynamics across the sample, showing at least two different motional regimes for pectin and cellulose domains.[280] Combined ^{1}H and ^{13}C NMR study of cellulose metabolism by *Fibrobacter succinogenes* S85 has been reported.[281]

^{2}H,^{13}C - ^{2}H and ^{13}C NMR techniques have been applied to study structure and dynamics in fruit cuticle polyesters[282] and hydration of waxy and mealy potato starch cultivars.[283]

^{11}B - Boron-11 NMR imaging and MAS spectroscopy have been used to characterise the nature and distribution of boron compounds after preservative treatment of radiata pine wood with trimethylborate.[284]

^{13}C - Proton relaxation-induced spectral editing (PRISE) techniques have been applied in ^{13}C CP MAS studies of plant cell wall materials and model systems.[285] ^{13}C MAS techniques have been employed to investigate the cell walls of potatoes and Chinese water chestnuts,[286] polysaccharides in sugar beet cell walls,[287] modern resins,[288] acetylated and methylated derivatives of homo-

galacturonans,[289] a mixed-linked (1 → 3), (1 → 4)- β-D-glucan extracted from barley,[290] hydration capacity of scleroglucan,[291] insect chitin isolated from beetle larva cuticle and silkworm (*Bombyx Mori*) pupa exuvia,[292] natural fibre from sugar cane,[293] water-soluble/insoluble derivatives of hyaluronic acid chestnut starch, oil composition in transformed Canola seeds,[294] lignins from several Australian hardwoods,[295] ^{13}C-enriched human hair keratin,[296] crystallinity and structuring role of water in native and recrystallised starches,[297] the supermolecular structure of bast fibres and their changes by mercerisation,[298] ultrathin cellulose microfibrils,[299] cellooligosaccharide peracetates as a model for cellulose triacetate,[300] carboxyl content in oxidised celluloses[301] and cellulose I.[302] CPMAS spectroscopy was used to characterise the structural changes of cell wall polymers in beech wood *Fagus sylvatica* during drying processes.[303]

^{13}C,^{29}Si - The occurrence and thermal transformations of silicon-containing species in biomass materials (rice hulls and endocarp of babassu coconut) have been studied using ^{13}C and ^{29}Si MAS NMR.[304]

^{15}N - ^{15}N variable contact time CP MAS has been employed to investigate the reaction products formed in wood composites bonded with ^{15}N-enriched polymeric diphenylmethane diisocyanate based adhesives.[305]

^{31}P - ^{31}P MAS has been used to characterise the trabecular rat bone mineral.[306]

5.4 Biochemical, Medical and Pharmaceutical Applications. – *5.4.1 Proteins.* A new approach to efficiently determine the backbone conformation of solid proteins that utilises selective and extensive ^{13}C labeling in conjunction with 2D MAS NMR has been presented.[307] The selective ^{13}C labeling has been used to reduce line broadening and other multispin complications encountered in SSNMR of uniformly labeled proteins while enhancing the sensitivity of NMR spectra. Information on the secondary structure of a labeled protein has been obtained by measuring multiple backbone torsion angles ϕ simultaneously, using an isotropic–anisotropic 2D correlation technique, the HNCH experiment. Experiments for resonance assignment of a selectively ^{13}C labeled protein have been performed using ^{15}N–^{13}C 2D correlation spectroscopy. From the time dependence of the ^{15}N–^{13}C dipolar coherence transfer, both intraresidue and interresidue connectivities can be observed, thus yielding partial sequential assignment. The method has been demonstrated on a 8.5 kDa model protein, ubiquitin.

A new method for the site-resolved identification of the secondary structure of solid peptides and proteins has been presented.[308] This technique exploits the correlation between the backbone conformation and the C_α CSAs of proteins. The $^{13}C_\alpha$ CSAs have been measured under fast MAS using a new sequence of 16 π pulses with special timing to reintroduce the CSA selectively. Quantitative values of the CSAs have been determined from the magnetisation decay, as demonstrated for several amino acids. To achieve HR spectra, the CSA filter experiment has been combined with 2D ^{15}N–^{13}C correlation spectroscopy. Applied to selectively and extensively ^{13}C-labeled and uniformly ^{15}N-labeled ubiquitin the 2D experiment yields a spectral pattern that corresponds primarily to α-helical residues. This agrees with the previous finding that helical residues have smaller CSAs than sheet residues. However, the quantitative CSA differences between the helical and sheet conformations are less pronounced than indicated by solution-state NMR. This CSA filter technique provides an efficient and site-resolved method for characterising the secondary structure of extensively isotopically labeled proteins.

Several 2D and 3D MAS correlation techniques for resonance assignment have been described and applied at 7 T to ^{13}C and ^{15}N labeled ubiquitin to examine the extent of resonance assignments in the solid state.[309] Both interresidue and intraresidue assignments of the ^{13}C and ^{15}N resonances have been addressed. The interresidue assignment was carried out by an N(CO)CA technique, which yields N^{i}–$C_{\alpha}{}^{i-1}$ connectivities in protein backbones *via* two steps of dipolar-mediated coherence transfer. The intraresidue connectivities were obtained from a new 3D NCACB technique, which utilises the well resolved C_{β} shift to distinguish the different amino acids. Additional amino acid type assignment was provided by a ^{13}C spin diffusion experiment, which exhibits ^{13}C spin pairs as off-diagonal intensities in the 2D spectrum. To better resolve carbons with similar chemical shifts a dipolar-mediated INADEQUATE has been applied. The sensitivity and resolution of these experiments have been evaluated.

In order to clarify the difference between solution NMR and XRD analyses concerning the presence of α-helical structure in protein A, the conformation-dependent chemical shifts of the ^{13}C-labeled carbonyl carbons for selectively labeled protein A have been used.[310] In the ^{13}C CP MAS NMR spectra, the higher-field shifts of the carbonyl carbons of ^{13}C-labeled Thr and Val residues compared with the random coil chemical shifts both in solution and solid state imply the presence of the third helix in the polypeptide chain, in contrast to the crystal structure. Thus, a combination of selective isotope labeling and conformation-dependent chemical shifts has been shown to be a good probe to monitor the local structure of homologous protein in solution and solid state.

The ionisation state and H-bonding environment of the transition state analogue inhibitor, carboxymethyldethia coenzyme A, bound to citrate synthase have been investigated using ^{13}C MAS NMR.[311] The CS tensor values of the carboxyl groups of the inhibitor were obtained. 2D ^{1}H–^{13}C heteronuclear correlation spectra were obtained. Strong cross-peaks were observed from the carboxyl carbon to protons with chemical shifts of 22 ± 5 ppm. Both the ^{1}H chemical shift and the intensity of the cross-peak indicate a very short H-bond to the carboxyl group of the inhibitor, the C···H distance based upon the cross-peak intensity being 2.0 ± 0.4 Å.

Other ^{13}C NMR applications have encompassed studies of a conformational change of bacterio-opsin induced by binding of retinal during its reconstitution to bacteriorhodopsin,[312] hydrophobic core of [3-^{13}C]Ala labeled bacteriorhodopsin[313] and dynamic conformation of a triblock protein hydrogel.[314]

^{15}N NMR techniques have been used to investigate the protonated Schiff base linkage in the [α,ε-$^{15}N_2$]Lys-rhodopsin[315] and the protonated retinylidene Schiff base nitrogen in rhodopsin.[316]

REDOR NMR has been applied for the direct identification of enzyme active site residues in KDO8P synthase.[317]

5.4.2 Peptides. The tetrapeptide Ala *n*-lle-Gly-Met bound to a Wang resin *via* the methionine residue has been studied by ^{1}H MAS NMR and compared to the same peptide in solution.[318] The origin of the residual NMR linewidth observed for the bound form has been investigated. The dynamics of the peptide has been shown to be only marginally responsible for the increased linewidth; the major cause of the line broadening appears to be nonaveraged magnetic susceptibility differences.

^{13}C SSNMR techniques have been applied to investigate the conformation of an N-terminal peptide of salivary statherin both free and adsorbed on hydroxyapatite crystals.[319] The ^{1}H MAS, ^{2}H static, ^{15}N CPMAS and ^{15}N–^{1}H dipolar CSA NMR spectra of two different modifications of C-α-deuterated ^{15}N-polyglycine, namely PG I and PG II (-CO-CD$_2$- (NH)-^{15}N-)(*n*) have been measured. The data from these spectra have been compared to previous NMR, IR, Raman and inelastic neutron scattering work.[320] The torsion angle ϕ was determined at three positions by measuring distances between the backbone carbonyls carbons in the indicated adjacent amino acids using dipolar recoupling with a windowless sequence. Global secondary structure was determined by measuring the dipolar coupling between the ^{13}C backbone carbonyl and the backbone ^{15}N in the I → i + 4 residues using REDOR. The measured average ϕ angle and the observed high conformational dispersion suggest a random coil conformation. REDOR measurements confirm the presence of helical content. These results support a structural model where the N-terminus is disordered, potentially to maximise interactions between the hydroxyapatite surface and the negatively charged side-chains.

The orientation of the insect antibiotic peptide cecropin A in the phospholipid bilayer membrane has been determined using ^{15}N NMR.[321] The ^{15}N chemical shift from these uniaxially oriented samples display a single ^{15}N chemical shift frequency for each labeled residue. Both frequencies are near the upfield end of the ^{15}N chemical shift powder pattern, as expected for an α-helix with its long axis in the plane of the membrane and the NH bonds perpendicular to the direction of the magnetic field.

The secondary structure and membrane-associated conformation of a synthetic peptide corresponding to the putative membrane-binding 38 C-terminal residues from bovine PP3 has been determined using ^{15}N NMR.[322] ^{15}N SSNMR shows that the peptide is associated to the membrane surface with the amphipathic helix axis oriented parallel to the bilayer surface.

5.4.3 Lipids and Membranes. ^{2}H SSNMR has been used to investigate the properties of bicelles,[323] the equimolar complex of the lipid-like chelating agent with Tm^{3+},[324] membrane properties of archaeal macrocyclic diether phospholipids[325] and the orientation of the deuterated methyl group in [18-

CD_3]-retinal in oriented bacteriorhodopsin.[326] ^{13}C SSNMR has been applied to probe membrane surfaces and location of membrane components,[327] structure of the membrane embedded M13 coat protein,[328] and chlorpromazine interaction with glycerophospholipid liposomes.[329] Conformation and dynamics of melittin bound to magnetically oriented lipid bilayers have been studied by ^{31}P and ^{13}C SSNMR.[330]

5.4.4 Biomedical Applications. The technique of ^1H MAS NMR applied to intact tissues provides excellent peak resolution and thus much biochemical information. The use of computer-based pattern recognition techniques to classify human renal cortex tissue samples as normal or tumour based on their ^1H MAS NMR spectra has been investigated.[331] This technique has also been used for prognostication in patients with liposarcoma.[332] ^1H relaxation rates were related to the composition of unloaded human intervertebral disks.[333] The solid signal fraction depended on collagen and residue protons. The data led to a model of disk architecture in which the collagen and residue were largely solid, forming distinct water compartments; the remaining water was present in a proteoglycan gel. Limits of detection for neat poly(dimethylsiloxane) have been detected by ^{29}Si MAS NMR.[334] The limit of detection is three orders of magnitude higher than silicon levels found in human blood.

^{31}P MAS NMR spectra have been measured for several oxides, such as Al_2O_3, SiO_2, TiO_2 and Ta_2O_5, which were soaked in a simulated body fluid.[335] The chemical states of phosphate anions deposited on these oxides were determined. The surface Ta(V) species supported on the oxides induced a bone-like apatite nucleus, even though the base oxides did not deposit apatite.

^{29}Si and ^{31}P MAS NMR were used to analyse $20Na_2O.80SiO_2$ glass particles before and after soaking in a simulated body fluid.[336] The structure of the bulk glass and the glass surface, as well as the chemical states of the calcium phosphates adsorbed on the glass surface, have been examined. The chemical shifts show that the local structural environment of P atoms and ions is similar to that of hydroxyapatite.

^{19}F MAS NMR has been used to study dental restorative materials.[337,338]

5.4.5 Pharmaceutical Compounds. Multidimensional SSNMR techniques have been applied to study structure and dynamics of linear peptide antibiotics isolated from amphibians, insects and humans and used as templates to design cheaper analogues for medical applications.[339] Many of them have been prepared by solid-phase peptide synthesis with isotopic labels incorporated at selected sites. Structural analysis by SSNMR spectroscopy indicates that these peptide antibiotics strongly interact with lipid membranes. In bilayer environments they exhibit amphipathic α-helical conformations and alignments of the helix axis parallel to the membrane surface. This contrasts the transmembrane orientations observed for alamethicin or gramicidin A.

The structures of four crystalline forms of double ^{13}C-labeled cimetidine, three anhydrates and a monohydrate, have been examined using ^{13}C CP MAS NMR methods.[340] Rotational resonance magnetisation exchange curves have been used to measure interatomic distances. DQ heteronuclear local field NMR was used to determine the relative orientations of the ^{13}C–H bonds at the two ^{13}C-labeled sites. These results demonstrate the feasibility of determining the complete solid-state structures of pharmaceutical compounds, and other materials not amenable to crystallography, using CP MAS NMR combined with a minimal isotope labeling strategy.

^{13}C CP MAS NMR was used to identify and quantify delavirdine form changes in tablets.[341]

Multinuclear SSNMR methods (^{13}C, ^{15}N, ^{31}P and ^{59}Co) were applied to the structural and dynamic analysis of cyanocobalamin (vitamin B-12) polymorphs.[342] Two polymorphs could be identified in these studies. Most informative about the molecular differences characterising these forms were the ^{13}C NMR data, which showed sharp and well-resolved resonances indicative of high sample crystallinity.

^{27}Al MAS NMR has been explored to characterise aluminum hydroxyphosphate vaccine adjuvants.[343] All the adjuvants were found to contain both tetrahedrally and octahedrally coordinated Al. The octahedral form was always predominant. The chemical shifts corresponding to octahedral aluminum were at values intermediate between that of Al hydroxide -9 ppm) and those of phosphate-containing Al minerals (-9 ppm) and varied with the phosphate content of the adjuvant. Aside from the presence of tetrahedral and octahedral Al, there was no evidence in any of the adjuvants of distinct, structurally defined phases.

The SSNMR spectra of 3,4-methylenedioxy-*N*-methylamphetamine (MDMA) hydrochloride and a number of illicitly manufactured tablets containing this material and marketed as ‘Ecstasy’ have been reported. Excipients detected include lactose, cellulose, stearate salts, sucrose, starch, polyvinylpyrrolidone and sodium croscarmellose. Two samples were found to contain 3,4-methylenedioxy-*N*-ethylamphetamine, rather than MDMA.[344]

5.5 Coal, Soil Organic Matter and Other Related Materials. – *5.5.1 Coals and Related Materials*. A ramped-amplitude CP (RAMP CP) has been applied to coal measurement by ^{13}C SSNMR.[345] In the RAMP CP pulse sequence ^{13}C spin-lock amplitude was changed linearly during CP while ^{1}H spin-lock amplitude constant. The parameters for RAMP CP MAS measurement were optimised for the Upper Freeport coal sample. The results show that the sensitivity of the RAMP CP MAS is better than that of the single-amplitude CP MAS.

^{13}C MAS NMR has been used to characterise Indonesian coal,[346] demineralisation in native and air-oxidised coals,[347] structural changes of coal density-separated components during pyrolysis,[348] amber samples from different geographical locations,[349] the amorphous and crystalline phases in asphalts[350] and and the mobility of various asphaltene samples.[351] Coal solubilisation through ‘ionic’ oxidation and base-promoted alkylation have been studied using ^{1}H and ^{13}C CP MAS NMR.[352] Petroleum coke samples of different origins and heat treated at different temperatures below 3100 K have been studied by spectroscopic and electrochemical procedures. According to ^{13}C and ^{1}H MAS NMR, IR, and ESR data, aromatic compounds and surface OH groups are present in green coke samples. The results of ^{6}Li MAS NMR and ESR have been correlated with the experimental determination of lithium diffusion coefficients and surface properties.[353]

5.5.2 Soils. ^{2}H - ^{2}H MAS NMR studies of TNT/soil adsorption have been reported.[354]

^{13}C - ^{13}C MAS NMR has been employed to study straw decomposition in soil,[355] carbon transformations during decomposition of plant leaves in soil,[356] soil organic carbon dynamics under long-term sugarcane monoculture,[357] condensed domains in soil organic matter,[358] effects of added paramagnetic ions in a de-ashed soil,[359] chemical removal of magnetic materials,[360] slow desorption of PCBs and chlorobenzenes from soils and sediments,[361] poly(-methylene) crystallites in humic substances,[362] correlation of soil and sediment organic matter polarity to aqueous sorption of nonionic compounds.[363] relationship of soil organic matter characteristics to organic contaminant sequestration and bioavailability,[364] and an elemental composition of humic substances.[365]

^{15}N - The nature of organic carbon and nitrogen in physically protected organic matter of some Australian soils[366] and in fine particle size separates of sandy soils of highly industrialised areas.[367]

^{19}F - It has been shown that ^{19}F SSNMR observation of the sorptive uptake of hexafluorobenzene by two peat samples gives direct spectroscopic evidence for the existence of dual-mode sorption to soil organic matter.[368]

^{31}P - Various aspects of ^{31}P SSNMR spectra of peat and mineral soils, humic acids and soil solution components have been presented.[369] Iron is often a major component in soil and it has been thought that the presence of paramagnetic Fe and Mn in soil components is responsible for loss of resolution in NMR spectra. It has been shown that the resolution of signals in the ^{31}P NMR spectra of an Fe- and Mn-rich soil was no worse than that for a series of peat soils with a comparable concentration of P. Removal of up to 50% of the Fe produced little change in spectral resolution. It was concluded that the limitations to resolution in ^{31}P SSNMR spectroscopy of soil humic substances do not stem from the presence of paramagnetic substances, but from the variable ways P species are physically held in the amorphous milieu of the organic phase.

5.6 Polymers. – *^{1}H* - A series of UF resins and one MUF resin were studied by low-resolution ^{1}H NMR. The mobility of the resin during curing have been followed by measuring the T_2 with curing time.[370]

The SSNMR spin diffusion technique has been employed to study polymer morphologies with a unique emphasis on interface structures. The use of ^{1}H detected experiments has been shown to provide high sensitivity for a fraction of the time needed to acquire the signal compared to the widely used ^{13}C detection experiments of rigid and mobile polymer components.[371]

The mobility of distant methyl side groups in poly(hexyl methacrylate)-block-poly(sodium acrylate) and poly(dodecyl methacrylate))-block-poly(sodium acrylate) micelles, dispersed in D_2O and characterised by SANS, has been studied using ^{1}H single and DQ HR and MAS NMR.[372]

^{1}H,^{2}H - The properties of polymer films prepared from latex dispersions are influenced by the drying or film formation process. The role of water in these films has been investigated using ^{1}H and ^{2}H SSNMR spectroscopy. Different types of water could be distinguished in the spectra.[373]

^{1}H,^{13}C - SSNMR techniques have been used to characterise cyclomaltoheptaose (β-cyclodextrin, β-CD) polymers. These insoluble materials have been investigated by SSNMR. These NMR spectra allow the assignment of the principal ^{1}H and ^{13}C signals. The presence of two distinct components (cross-linked β-CD and polymerised epichlorohydrin) in the materials has been clearly demonstrated.[374] Conformational conversion and molecular dynamics of the amorphous poly(ethylene terephthalate) annealed above T_g have been investigated by SSNMR and DSC.[375] The miscibility and thermal properties of poly(*N*-phenyl-2-hydroxytrimethylene amine)/poly(*N*-vinyl pyrrolidone) blends have been examined by using DSC, SSNMR techniques, and TGA.[376] Time dependence of the gel formation in toluene solutions of polycarbonate has been investigated by 2D FTIR correlation and SSNMR spectroscopy.[377] Blends of poly(vinyl chloride) with poly(*N*-vinyl pyrrolidone) have been investigated by FTIR and CPMAS spectroscopy.[378] The phase behavior and segmental mobility in binary blends of polystyrene and poly(vinyl methyl ether) have been investigated.[379]

Solvent dynamics and polymer–solvent interactions in syndiotactic polystyrene/ethylbenzene clathrates, as well as polymer–salt interactions in the poly(ethylene oxide)/$LiCF_3SO_3$ complex, have been characterised by ^{1}H and ^{13}C SSNMR.[380]

The structure of ultradrawn ultra-high molecular weight polyethylene fibres has been investigated by SSNMR. A crystallinity of (88 ± 2)% has been determined by traditional ^{1}H NMR lineshape decomposition, and by a new adaptation of ^{13}C NMR crystallinity determination for polyethylenes with extremely long crystalline T_1 relaxation times.[381] A new approach to characterise the reverse osmosis permeability in conjunction with the macromolecular structures and inherent polymer properties for crosslinked and linear model aromatic polyamides has been proposed.[382] The combination of ^{13}C solution NMR and SSNMR has been used to reveal the relative amount of crystalline PVC in two (50/50 wt % of poly(vinyl chloride)/di-2-ethylhexyl phthalate) samples.[383]

^{7}Li,^{13}C - Gel-type electrolytes based on fluorinated polymers of interest for electrochemical devices have been studied by ^{7}Li-^{13}C SSNMR.[384] To study compositional dependent conductivity of Li^+ ions in lithium perchlorate/poly(ethylene oxide) ($LiClO_4$/PEO) electrolytes, mobility of the Li^+ ions and morphology of the electrolytes have been investigated by examining the T_1 of ^{7}Li and by SSNMR methods.[385]

^{13}C - $T_{1\rho}$(^{1}H) and CPMAS have been employed to investigate the compatibility of a polymeric blend formed by high-density polyethylene and a synthetic petroleum resin of low molecular weight.[386]

A collection of SSNMR spectra on polymer blends, block copolymers, or polymeric latexes has been made available *via* the internet at http://www.mpip-mainz.mpg.de/documents/aksp/spektrensammlung.[387]

Employing CPMAS spectroscopy, the existence of immobile regions in natural rubber (cis-1,4-polyisoprene) have been shown.[388] The CPMAS NMR spectrum of solid poly(γ-benzyl L-glutamate) (PBLG) has been measured at the slow spinning rate. The exact principal values of the ^{13}C CS tensor for the main-chain carbonyl carbons of PBLG have been obtained.[389] SSNMR measurements have been carried out on poly(aspartic acid) sodium /poly(vinyl alcohol) blends over a wide range of temperatures.[390] The effect of drawing on the structure and molecular orientation of polyamide fibers has been investigated by ^{13}C SSNMR. The molecular orientation in the fibres has been determined using a 2D rotor synchronised MAS experiment.[391]

Poly(furfuryl alcohol) structures have been determined by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum indicated the predominance of linear sequences and the absence of -CH$_2$–O–CH$_2$- bonds in the polymer.[392] ^{13}C-enriched polyethylene was subjected to γ-irradiation in the presence of air. Significant quantities of hydroperoxides have been detected in the 25 °C irradiated sample by MAS NMR spectroscopy.[393] Solid structures of the compositionally fractionated bacterial poly(3-hydroxybutyric acid-co-3-hydroxypropionic acid)s have been studied by CPMAS.[394] The miscibility of poly(epichlorohydrin)/poly(vinyl acetate) blends have been investigated by DSC and CPMAS.[395] The spectral features in the CPMAS NMR of poly (1,1,6,6-tetraphenylhexadiyn diamine) (poly(THD)) have been compared with XRD.[396] An analysis of the structure of syndiotactic copolymers of propene with l-butene prepared with a single-centre metallocene-based catalyst in a whole range of comonomer composition by CPMAS spectroscopy has been presented.[397]

The cure reactions of phenylethynyl end-capped polyimides have been investigated using SSNMR. A ^{13}C-labeled model compound (^{13}C-PEPA-3,4′-ODA) and an imide oligomer (^{13}C-PETI-5) have been synthesised and characterised.[398]

Styrene-crosslinked mixed polyesters derived from maleic anhydride, 2,2-di(4-hydroxypropoxyphenyl)propane, oligo(propylene oxide) and 1,2-propylene glycol have been investigated by SSNMR spectroscopy.[399]

The styrene-crosslinked mixed polyesters derived from maleic anhydride, 2,2-di-(4-hydroxypropoxyphenyl)propane and 1,2-propylene glycol have been studied by means of CPMAS.[400]

In order to improve the stability of high-density polyethylene as a thermal energy storage medium, HDPE was cross-linked by electron beam irradiation. The observed increase of amorphous phase was attributed to a result of crystalline to amorphous phase transition of perturbed regions in the crystalline phase close to defect sites occupied by oxidation products or EG molecules.[401] The structure in the solid state of two optically active polyamides obtained from 2,3-*O*-methylene-L-tartaric acid and linear α,ω-alkanediamines with 9 and 12 carbon atoms has been investigated.[402] SSNMR analyses of the structure and chain conformation have been carried out for a main-chain thermotropic liquid crystalline polyether which was polymerised with 4,4′-dihydroxy-alpha-methylstilbene and 1,9-dibromononane.[403] The phase-separated structure and molecular mobility for core-shell type polymer particles composed of poly(butyl acrylate) and poly(methyl methacrylate) have been examined by SSNMR.[404] The observed ^{13}C NMR chemical shifts of poly(-phenylacetylene) (PPA) in the solid state before and after *cis-trans* isomerisation have been investigated on the basis of NMR chemical shift calculations within AM1 for the *cis-transoidal* and deflected *trans-transoidal* forms.[405] SSNMR spectra of (ethylene-vinyl alcohol) copolymers with various ethylene contents in the solid-state.[406] The structure and variations in dynamic motions of three polyguanidines possessing different side-chains have been studied by CP MAS.[407]

The solid state dynamics of three helical polyguanidines differing only in their stereochemistry has been investigated by CPMAS NMR.[408] Poly(2-hydroxyethyl methacrylate) and poly(2-hydroxyethyl methacrylate) interpenetrated with 5% SiO_2 have been studied by CPMAS.[409] The structure and dynamic motions of the polycarbodimide has been studied by CPMAS NMR.[410] The structure and rigidity of the backbone of two polycarbodiimides as a function of the side-chains have been studied by CPMAS NMR.[411] The chain conformation and H-bonding in the crystalline and noncrystalline regions have been characterised for atactic poly(vinyl alcohol) films prepared under different conditions by CPMAS analyses developed recently.[412] Structure development in silica filled polyisoprene composites has been investigated by wide line pulsed NMR and HR SSNMR combined with transmission electron microscopy.[413] NMR spectroscopies have been employed to investigate the cure-acceleration effects of three carbonates propylene carbonate, sodium carbonate, and potassium carbonate on liquid and cured phenol-formaldehyde resins.[414]

^{15}N - As demonstrated on different nitrogen-containing polysilanes and polysilazanes, the CP MAS technique spectra can be obtained in good quality and within acceptable measuring time without ^{15}N enrichment.[415]

^{19}F - ^{19}F SSNMR using high-speed MAS has been applied to investigate the structural changes resulting from irradiation of poly(tetrafluoroethylene) (PTFE) with high-energy electrons under vacuum.[416] Radiation effects on molecular structure of PTFE have been studied by ^{19}F high speed MAS NMR spectroscopy. Samples used for the NMR studies were prepared by electron beam irradiation of PTFE with a wide range of irradiation doses in the molten state.[417] The SSNMR ^{19}F of poly(trifluoroethylene) study has concentrated on the detection of heterogeneities in the polymer. Transient oscillations in $^{1}H \rightarrow {}^{13}C$ CP curves have been used in order to determine effective bond distances and, consequently, to detect motion of the polymer chain.[418]

^{29}Si - Poly[(4-oligodimethylsiloxanyl)styrene]s were synthesised by radical polymerisation of the corresponding monomers. Quantitative evaluation of T_1

has been made at each silicon atom of the side-chains by ^{29}Si SSNMR. It was found that the closer the silicon atoms were to the main-chain, the more the motion was correlated to the gas permeation. Such local mobility of side chains behavior through the polymer membrane has been observed.[419]

^{31}P – A novel phosphorus-containing carbonaceous sorbent has been prepared by pyrolysis of phosphorylated phenol–formaldehyde resin. The surface properties of the material have been characterised by nitrogen adsorption-desorption isotherms and ^{31}P MAS.[420]

Multinuclear – Symmetric diblock copolymers in the lamellar phase have been studied by NMR. ^{2}H NMR spectra obtained in macroscopically oriented monodomains show an absolute frequency shift of a few ppm, which depends of the orientation of the sample with respect to the magnetic field.[421]

5.7 Glasses and Amorphous Solids. – *^{11}B* - ^{11}B MAS NMR has been applied to study the structural role of PbO in pseudoternary glasses Li_2O–PbO–B_2O_3,[422] xV_2O_5–B_2O_3 and xV_2O_5–B_2O_3–PbO glasses,[423] BaO–B_2O_3–SiO_2 and BaO–B_2O_3–TiO_2 glasses[424] and amorphous networks in the Si–B–N(–C) systems.[425]

^{11}B,^{17}O - MAS and TQ MAS ^{11}B and ^{17}O NMR has been employed to characterise non-bridging oxygens in borate glasses.[426]

^{11}B,^{29}Si - ^{11}B and ^{29}Si MAS NMR spectra have been used to investigate the spinodal phase separation of sodium borosilicate glasses.[427]

^{11}B,^{31}P - ^{11}B and ^{31}P SSNMR have been used to study glasses SiO_2–B_2O_3–P_2O_5[428] and V_2O_5–P_2O_5–B_2O_3.[429]

^{17}O - MAS and static ^{17}O NMR spectra, from amorphous germania and quartz-like GeO_2, have been used to estimate the range of ^{17}O quadrupolar parameters in the glass for different bond angle distributions.[430] ^{17}O MAS NMR data for crystalline $NaAlO_2$ and $CaAl_2O_4$ at 9.4 and 14.1 T, as model compounds for Al–O–Al sites in tetrahedral networks have been reported.[431]

^{19}F - ^{19}F ultrafast MAS NMR spectra for Na and Ca silicate and aluminosilicate glasses have been presented. Several distinct fluoride ion sites are well resolved and can be assigned to various coordination environments based on clear similarities to crystalline model compounds.[432]

^{23}Na - The spatial arrangements of Na cations for a series of sodium phosphate glasses, $x\text{Na}_2\text{O}$–$(100-x)\text{P}_2\text{O}_5$ ($x \leq 55$), have been investigated using ^{23}Na spin-echo NMR. The spin-echo decay rate has been related to the spatial proximity of neighboring Na nuclei. It increases non-linearly with higher sodium number density in the sodium phosphate glasses and provides a measure of the Na–Na extended range order.[433]

^{23}Na,^{71}Ga - The cationic coordinations of phosphate based gallium sodium glasses in the system Na_2O–Ga_2O_3–P_2O_5 have been studied by ^{23}Na and ^{71}Ga MAS NMR in order to study the relationship between the structure and the chemical composition.[434]

^{27}Al - ^{27}Al MAS NMR techniques have been applied to study gibbsite,[435] lanthanum-aluminates of the composition $(1 - x)\text{Al}_2\text{O}_3.\ x\text{La}_2\text{O}_3$ ($0 < x <$

0.7)[436] and the local structures of Sm and Al in Sm-doped aluminosilicate glasses.[437]

^{27}Al,^{29}Si - Glass samples from the neapolitan yellow tuff,[438] β-eucryptite ($LiAlSiO_4$),[439] a swelling mica, $Na_2Mg_3(Al_2Si_2)O_{10}F_2 . xH_2O$[440] and Ag^+/Na^+ ion-exchanged $R_2O–Al_2O_3–SiO_2$ glasses[441] have been investigated using ^{27}Al and ^{29}Si MAS NMR techniques.

^{27}Al,^{31}P - The ^{31}P MAS NMR spectra have been analysed for the two phosphate glasses[442] that contain distinct metals (In or Ba), different amounts of PbO, and the same content of P_2O_5 and Al_2O_3. The ^{31}P isotropic peaks at -3.8 or -4.8 ppm indicate that orthophosphate species are the dominant P sites. The ^{27}Al MAS NMR spectrum measured for the lead–barium–aluminum phosphate glass shows that the Al ions are in four-, five- and six-fold coordination with oxygen and that the $Al(OP)_4$ is the dominant moiety for the glass.

^{29}Si - The effect of paramagnetic impurity in the structure of sodium disilicate glass has been investigated using ^{29}Si MAS NMR.[443] The ^{29}Si chemical shifts and full widths at half maximum in $Na_2O–2SiO_2–xMnO$ for $0 < x < 0.8$ glasses have been measured. The large space varying magnetic field of the paramagnetic centres increases the line width and moves the chemical shift to a lower frequency, *i.e.* more shielded, with the increase of Mn^{2+}. The T_1 relaxation time falls rapidly and the relaxation rate has been shown to be proportional with the concentration of MnO. ^{29}Si MAS NMR spectra have been reported for the monoclinic and triclinic crystalline phases of $CaSi_2O_5$,[444] two series of aluminosilicate glasses $SiO_2–NaAlO_2$ and $SiO_2–CaAl_2O_4$,[445] products of nitridation of silicon powder[446] and silanol-group minerals and hydrous aluminosilicate glasses.[447]

^{29}Si,^{31}P - ^{29}Si and ^{31}P MAS NMR measurements have been used to study the glass structure of ionically conductive $Li_2S–SiS_2–Li_2O–P_2O_5$ oxysulfide glasses,[448] and the influence of the CaO/MgO ratio on the structure of phase-separated glasses.[449]

^{31}P - The local environment of phosphorus in aluminosilicate glasses $xNa_2O–(1-x)Al_2O_3–2SiO_2$ of variable Na/Al ratio has been investigated using TRAPDOR NMR.[450] The studied glasses contain approximately 4 mol% P_2O_5. The short-range dipolar couplings of P atoms to Al and Na have been used to deduce the connectivities of PO_4 units to AlO_4 tetrahedra and/or Na by observing the effects on a ^{31}P MAS echo spectrum caused by simultaneous irradiation of the ^{27}Al or ^{23}Na. In this way, different P environments have been identified. The observed resonances can be assigned to Na_3PO_4 and $Na_4P_2O_7$ units, as well as PO_4 tetrahedra coordinated to nAl atoms in the aluminosilicate framework (with n = 1–3). The results provide unambiguous evidence for the interaction of P with Al even in peralkaline compositions, confirming a recently proposed model describing the solution of phosphorus in aluminosilicate melts. ^{31}P SSNMR techniques (mainly HR) have been applied to investigate the structures of binary lead phosphate glasses,[451] extruded $Ca(PO_3)_2$ glass,[452] zinc polyphosphate glasses,[453] GeAs thiophosphate glasses,[454] $Na_2O–Ga_2O_3–P_2O_5$ glasses,[455] $Na_2O–Al_2O_3–P_2O_5$ glasses[456] and phosphorus oxynitride glasses.[457]

^{113}Cd - ^{113}Cd SSNMR has been used to identify possible Cd^{2+} adsorption sites in montmorillonite.[458]

^{125}Te - ^{125}Te static and MAS NMR rechniques have been applied to study the structure of TeO_2 and $M_2O–TeO_2$ (M = Li, Na, K, Rb and Cs) glasses.[459]

Multinuclear - Hydrous aluminosilicate glasses of composition $NaAlSiO_{18}$, $NaAlSi_3O_8$, $NaAlSi_2O_6$ and $NaAlSiO_4$ have been studied with ^{1}H MAS, ^{1}H/^{27}Al and ^{1}H/^{23}Na TRAPDOR NMR.[460] Two different environments for molecular water have been identified. Three ^{1}H OH resonances (1.5, 3.5 and 5–6 ppm) have been observed in all the glasses. The resonance at 1.5 ppm shows a large ^{1}H–^{27}Al dipolar coupling and has been assigned an Al(Q^3)–OH group; the concentration of this species increases with increasing Al content in the glass. The resonance at 3.5 ppm has been assigned to Si(Q^3)–OH units, on the basis of its chemical shift, proximity to Na and Al, and the change in the relative intensity of the three resonances, with varying Al/Si ratio. The resonance at 5–6 ppm has been assigned to a Q^3-OH unit that is H-bonded to another oxygen atom. These assignments imply that the aluminosilicate framework undergoes depolymerisation as an outcome of water dissolution. A variety of ^{1}H, ^{17}O, ^{23}Na, ^{27}Al and ^{29}Si NMR data consistent with the formation of Q_3 AlOH and SiOH groups upon dissolution of H_2O into aluminosilicate glasses have been reported.[461] ^{29}Si single-pulse and ^{29}Si CP MAS data has been shown to present more direct evidence for the formation of Q^3 Si species.

The ^{11}B, ^{29}Si, and ^{31}P MAS NMR spectra of $30Na_2O–5SiO_2–65[(1-x)P_2O_5–xB_2O_3]$ glasses have been examined.[462] The six-coordinated Si atoms have been observed in glasses with $x < 0.25$. The three-coordinated B atoms begin to appear in glasses with $x > 0.50$. The distribution curves derived from the deconvolution of the spectra by component signal of each phosphate and berate species agree with those calculated using species with different Na_2O/P_2O_5 ratios. The ^{11}B,. ^{27}Al, ^{29}Si and ^{31}P MAS NMR have been used to study alkaline earth phosphosilicate and aluminoborosilicate glasses.[463] Five binary borosilicate glasses and 54 ternary sodium borosilicate glasses covering the glass-forming regions have been examined by ^{11}B, ^{23}Na and ^{29}Si MAS NMR.[464] Linear dependencies of the chemical shifts on compositional parameters have been observed.

5.8 Cements. – *^{27}Al* - ^{27}Al MAS NMR has been used to study the substitution of Si by Al in calcium silicate hydrates (C–S–H), the main component of hydrated portland cement[465] and to characterise the aluminum incorporation in calcium silicate hydrates (C–S–H) depending on their Ca/Si ratio.[466]

^{27}Al,^{29}Si - ^{27}Al and ^{29}Si MAS NMR techniques have been applied to investigate the influence of cement constitution and temperature on chloride binding in cement paste,[467] the interaction between salts (NaCl, CsCl) and calcium silicate hydrates (C–S–H)[468] and electronic and structural properties a series of reduced-charge montmorillonites.[469]

^{29}Si - ^{29}Si MAS NMR has been used to study the room-temperature

hydration of C_3S, β-C_2S and reactive β-C_2S mixed with different amounts of silica fume (SF).[470] NMR has also been used to quantify the remaining starting materials and the resulting hydration products of different species. A broad peak assigned to Q^3, increases in intensity with increased SF content. A Q^4 species also appeared in the CP MAS spectra of samples with large SF additions after extended hydration and has been attributed to CP by adjacent hydroxylated Q^3 species at the surface of amorphous SiO_2. ^{29}Si NMR has been used to characterise an amorphous silica by-product as a possible supplementary cementing material,[471] mullite in silicoaluminous fly ash,[472] to study kinetics of the hydration reactions in the cement paste[473] with mechanochemically modified cement and to follow the hydration of metakaolin-blended ordinary Portland cement pastes.[474]

5.9 Micro- and Meso-porous Solids. – *^1H* - ^{1}H MAS spectra of perfluorotributylamine adsorbed on HZSM5 zeolites has been used for distinguishing the internal and external acidic sites in zeolites as well as for determining the position of silanols and some non-framework Al species.[475] Titanium aluminophosphate molecular sieves have been synthesised hydrothermally and their acidic properties characterised by FTIR and proton NMR.[476] The temperature dependence of the line width of ^{1}H MAS NMR reveals that the acidic protons in HZSM5 become mobile at temperatures as low as 370 K, though they are not mobile at 298 K. Substitution of a small part of the protons with Na^+ or K^+ ions sharply decreases the mobility as well as the catalytic activity of the remaining protons, suggesting that a long-range interaction exists among the acid sites.[477] MAS NMR and ESR spectroscopies have been employed to investigate Mo-modified HZSM5 catalysts prepared by impregnation.[478] The IR and ^{1}H MAS spectroscopy of zeolite H-β in interaction with CD_3CN has been described; two families of strong Si(OH)AI Bronsted sites have been clearly distinguished.[479]

^1H,^{27}Al - Sorption of oxygen in the pores of zeolite HY and ^{1}H MAS NMR has been used to determine which Bronsted acid sites are accessible to oxygen. Large increases in the ^{1}H SSB manifolds have been observed at low temperatures for the supercage protons that can directly interact with the oxygen molecules; a much smaller increase in SSB intensity is seen for the sodalite protons.[480]

$^{6,7}Li$ - ^{6}Li and ^{7}Li MAS NMR spectra of the dehydrated zeolites LiX–1.0 $[(SiAlO_4)_{96}Li_{96}]$ and LiX–1.25 $[(Si_{106}Al_{86}O_{384})Li_{86}]$ have been shown to contain three peaks belonging to cations in the different crystallographic sites.[481]

^{11}B,^{29}Si - Titanium-containing MEL zeolites (Ti-ZSM-11) have been prepared. XRD, FTIR, ^{11}B and ^{29}Si MAS NMR techniques have been used to characterise these materials.[482]

^{13}C - CPMAS evidence for arylmethyl carbocations formed from a series of ^{13}C-labeled precursors adsorbed at room temperature on heat-pretreated zeolite HY has been reported and discussed. The reactivities of precursors of three binds of arylmethyl carbocations, have been compared, and evidence for

the chemical transformations of arylmethylium precursors on zeolite HY has been provided by analysing $CDCl_3$ extracts.[483] Silica gel, dealuminated zeolite USY and cesium-exchanged zeolite Y were impregnated with alkali metal hydroxides or acetates followed by calcination. Surface groups formed on these samples were used as ^{13}C NMR spectroscopic probes to investigate the formation of well dispersed basic guest compounds.[484]

^{13}C, ^{129}Xe - A combination of ESR, CPMAS NMR, ^{129}Xe NMR, xenon adsorption, and TGA techniques have been employed to examine the preferred location of coke formation in the conversion of ethylbenzene under various conditions, such as reaction temperature, space velocity, and carrier gas to ethylbenzene molar ratio.[485]

^{17}O - In framework aluminosilicate materials (*e.g.*, feldspars, zeolites and many others), it is generally assumed that AlO_4 tetrahedra do not share corners, *i.e.*, that Al–O–Al oxygen sites are avoided when stoichiometry permits. This assumption plays a key role in models of thermodynamic properties and of reaction kinetics a new approach has been presented to directly test this assumption, based on ^{17}O TQ MAS NMR.

^{17}O, ^{29}Si - HR ^{17}O NMR spectra of siliceous ferrierite have been collected and the ^{29}Si and ^{17}O isotropic chemical shifts and the EFGs of oxygen have been calculated from first principles. The theoretical ^{29}Si MAS NMR spectrum has been found to be in excellent quantitative agreement with the experimentally determined spectrum. However, theoretical predictions of the chemical shifts, QCCs and asymmetry parameters show only qualitative agreement with the experimental ^{17}O NMR spectra obtained by DOR and MQ MAS as the spectra are much more complex (10 peaks within a shift range of less than 15 ppm, and the quadrupolar coupling constants only differ by 0.4 MHz) and hence higher accuracy is required from the shift calculations (>0.5 ppm), which is currently not possible. These findings also demonstrate the current limitations of the experimental techniques and show that no simple correlation appears to exist between the zeolite structure, such as the Si–O–Si bond angles or lengths, and the ^{17}O NMR parameters.[486]

^{19}F - Interactions between PFA molecules and MFI structure type zeolites have been studied by FTIR and ^{19}F MAS NMR spectroscopies. In the purely siliceous ZSM5 sample, PFA molecules were physisorbed. In the acid samples, the interactions implicated the carbonyl group of the PFA molecules and the Bronsted acid sites of HZSM5. This interaction could be an H-bond or a protonation of the carbonyl group. The complementarity of the IR and ^{19}F NMR spectroscopies has been shown.[487]

^{19}F, ^{29}Si - Pentacoordinated silicon units, $SiO_4/2F^-$, have been found by SSNMR experiments in various as-made high-silica zeolites (Beta, SSZ-23, ITQ-3, ITQ-4, ZSM-12, Silicalite-l) that have been prepared in the presence of fluoride ions as mineralising agents.[20]

^{23}Na - SOQ broadening has rendered the study of cation sites in microporous materials almost impossible until the recent advent of the 2D MQ NMR experiment. Strong evidence has been given for preferential potassium cation siting.[488] The framework structure of calcined and dehydrated cancri-

nite have been characterised by powder neutron diffraction and ^{23}Na NMR spectroscopy. QCC obtained by a simple point-charge model agree well with the simulation of the ^{23}Na MAS spectra.[489]

^{23}Na,^{29}Si - A variety of SSNMR techniques have been applied in order to assign resonances in the ^{29}Si and ^{23}Na NMR spectra of a new crystalline silicate Mu-11 to crystallographically distinct silicon and sodium sites, respectively. A preliminary assignment based on the electronegativities has been carried out and ^{29}Si CP experiments confirmed the assignments. The two crystallographically different sodium atoms have been resolved by ^{23}Na TQ MAS NMR, and an assignment for these two sites has been proposed.[490]

^{27}Al 1D and 2D SSNMR techniques, in conjunction with elemental analyses, IR, and powder XRD, establish that high concentrations of Al have been incorporated into the aluminosilicate MCM-41 frameworks, with retention of mesoscopic order.[491] The nature and concentration of the acid sites of MCM-41 material as a function of Si/Al ratio have been monitored by *in situ* IR using pyridine as a probe molecule. The thermal stability of aluminium in the framework of these materials has been studied using ^{27}Al MAS NMR spectroscopy.[492] Aluminium-containing mesoporous molecular sieves (Al-MCM41) with different Al contents have been prepared and characterised by XRD and MAS NMR studies. ^{27}Al NMR studies reveal that the Al is present in Td coordination in the samples.[493] FTIR and multinuclear NMR spectroscopy and catalytic test reaction have been applied to investigate acid sites in mesoporous MCM-41 materials.[494] The distribution of aluminum in MCM-22 zeolite has been studied by ^{27}Al SSNMR.[495] Aluminosilicate mesoporous molecular sieves exhibiting excellent structural ordering have been examined by ^{27}Al MAS.[496]

^{27}Al,^{29}Si IR, NMR, and NH_3-stepwise temperature-programmed desorption (STPD) have been used to study the acidity characteristics of de-aluminated ZSM-12. ^{27}Al NMR data which indicate mostly the presence of tetrahedral sites for ZSM-12. ^{29}Si NMR data can be described by at least three distinctly different Si sites.[497] MnAPO-11, MnAPO-41 and MnSAPO-41, have been prepared and characterised by the techniques of XRD, SEM, TGA/DTA, ^{31}P and ^{27}Al MAS NMR and ESR spectroscopy.[498] CXN zeolite, a natural zeolite in China, has been modified by ion exchange and calcination. The structural properties have been characterised by chemical analysis, powder XRD, TG/DTA, ^{27}Al and ^{29}Si MAS NMR and nitrogen adsorption.[499] Combined 1D and 2D MQ ^{27}Al NMR results together with ^{29}Si NMR data provide interesting information on the siting of Al in levyne zeolite. It is clearly shown that the distribution of Al is random in the structure, as the relative intensity of the two tetrahedral species is equal to two, corresponding to the ratio of T_1 and T_2, the crystallographically different tetrahedral sites.[500] Combination of ^{27}Al, ^{29}Si MAS and TQ MAS NMR provide interesting information on the siting of aluminium in levyne zeolites. It is clear that aluminium is randomly distributed in the LEV structure during synthesis. Indeed, the relative intensity of the two tetrahedral species is equal to two, which corresponds to the ratio between the crystallographically different

tetrahedral sites T_1 and T_2.[501] The application of ^{27}Al and ^{29}Si MAS NMR has provided a direct probe of alkali metal cluster formation and distribution in the alpha-cages of zeolite A.[502]

^{27}Al,^{31}P - Three different molecular sieves have been characterised using ^{31}P and ^{27}Al MAS NMR spectroscopy and acidity measurement techniques. The synthesised solids were a silicoaluminophosphate sample, a chromium-substituted silicoaluminophosphate sample and a chromium-supported SAPO-11 sample. Significant differences were observed between the CrAPSO-11 MAS NMR spectra and the spectra for the other two solids.[503] A layered aluminophosphate, Mu-4, has been investigated by various SSNMR techniques. In particular, ^{27}Al–^{31}P 2D heteronuclear correlation experiments were useful to evidence the P–Al connectivities present in this new layered aluminophosphate.[504] Highly crystalline aluminophosphate molecular sieve $AlPO_4$-41 has been synthesised and have been characterised by SSNMR spectroscopy using ^{27}Al and ^{31}P MAS, 2D ^{27}Al SQ MAS, and ^{27}Al→^{31}P CP MAS techniques. Both ^{31}P MAS and ^{27}Al SQ-MAS spectra of the as-synthesised $AlPO_4$-41 exhibit several resonances, all of them being assigned to framework atoms.[505]

^{29}Si - The sensitivity of 1D and 2D MAS NMR experiments to the local order of framework T atoms and energy-minimisation calculations for the geometrical analysis of the complete zeolite framework structure have been combined to provide a most detailed view of their structural properties.[506] ^{29}Si NMR and IR spectra have been measured for as-prepared and annealed porous silicon samples to characterise their structure.[507] A SAPO-11 molecular sieve was dealuminated to different Al content. Dealuminated samples have been characterised by catalytic transformation of butene, *o*-xylene and cumene, IR analysis of adsorbed pyridine and ^{31}P and ^{29}Si-MAS-NMR. The reaction kinetics and mechanism have been discussed.[508] SAPO-11 and SAPO-31have been characterised ^{29}Si MAS NMR studies.[509] A high-quality Si-MCM-41 was prepared. The ^{29}Si MAS NMR results demonstrated that the water treatment promoted the wall polymerisation or local atomic arrangement.[510] The aluminum coordination state of the molecular sieve SAPO-37 has been studied by ^{27}Al MQ MAS NMR spectroscopy. Although the 1D ^{27}Al MAS NMR spectra of the aluminum sites show complex patterns, the 2D TQ MAS NMR spectra of SAPO-37 samples, submitted to different treatments, lead to the detection of four distinct framework Al species in the as-synthesised sample. By use of ^{1}H spin echo editing MAS NMR experiments, a new proton signal at 3.4 ppm has been observed in the calcined H-SAPO-37. By ^{1}H{^{27}Al} and ^{1}H{^{31}P} spin echo double-resonance experiments, this new signal has been assigned to a kind of framework Al–OH hydroxyls caused by partially broken Al–O bonds.[511] The iii coordination state of molecular sieve SAPO-37 has been studied by ^{27}Al MQ MAS NMR spectroscopy, although the 1D ^{27}Al MAS NMR spectrum of the aluminum sites show a complex pattern, the TQ MAS NMR spectra of SAPO-37, submitted to different treatments, lead to the detection of four different Al species in the as-synthesised sample.[512] ^{27}Al TQ MAS NMR spectroscopy has been applied to study the coordination state of the species giving the 30 ppm Al NMR signal in the ^{27}Al MAS NMR spectrum

of activated mordenite materials. From the ^{27}Al TQ MAS NMR measurements it is evident that the broad peak at 30 ppm in the ^{27}Al NMR spectrum of the mordenite calcined at high temperatures comes mainly from the distorted four-coordinated Al.[513] Alumina has been incorporated in the cavities of mordenite and has been assessed on the basis of the data of MAS ^{27}Al NMR measurements and powder XRD.[514] Crystalline galliosilicates with the β structure have been synthesised ^{29}Si MAS-NMR and. ^{71}Ga NMR spectra confirm that Ga(IV) is the dominant species and that Ga(VI) formation depends, in part, on the thermal pretreatment applied to the crystals.[515]

^{1}H,^{13}C,^{15}N - Multinuclear SSNMR has been applied to investigate the use of chloroform as a probe molecule to characterise the basic properties of zeolites. The characteristics of the ^{1}H signals of adsorbed chloroform are consistent with highly mobile molecules leading to an average chemical shift that reflects the interaction of the molecule with the host zeolite through H-bonding with basic framework oxygen atoms. The use of $^{13}CHCl_3$ has allowed to establish that the ^{13}C chemical shift position is also a measure of framework basicity for zeolites X and Y.[516]

^{1}H,^{27}Al,^{29}Si - The thermal behaviors of five differently prepared samples (A–E) of the very-large-pore aluminophosphate molecular sieve VPI-5 have been investigated. ^{27}Al, ^{31}P and ^{1}H MAS NMR experiments for the two samples yielded almost identical spectra. The ^{27}Al spectra confirmed that all Al were tetrahedral, the ^{1}H spectra showed that no water was present, and the ^{31}P spectra contained seven peaks, indicating that the symmetry was much lower than the expected topochemical space group.[517] The Si/Al ratio of the framework and the number of defect sites in the framework of zeolites have been investigated by means of SSNMR, ^{1}H MAS NMR showed that the extent of dealumination increased with the number of Bronsted acid sites interacting with the zeolite framework and ^{29}Si MAS NMR showed that at the same time the number of defect sites in the samples increased.[518] Variations in the structure and acidity properties of HZSM-5 zeolites with reduction in crystal sizes down to nanoscale (less than 100 nm) have been investigated by XRD, TEM and SSNMR with a system capable of *in situ* sample pretreatment. As evidenced by a combination of ^{27}Al MAS, ^{29}Si MAS, CP MAS and ^{1}H MAS techniques.[519] The variations in structure and acidity on the internal and external surfaces of HY zeolites modified by MgO and SiO_2 have been studied by MAS NMR, together with the selective adsorption of perfluorotributylamine. ^{27}Al and ^{29}Si MAS NMR spectra revealed that the modifications led to significant changes of the framework owing to the migration of some non-framework Si and Al into the framework in the course of the modifications. ^{1}H MAS NMR spectra showed that the modifications decreased the acidity of the zeolite surfaces.[520]

^{7}Li,^{27}Al,^{133}Cs - A study on the modification of the surface acidity of β-zeolite exchanged with Cs and Li has been carried out by means of XRD, ^{27}Al, ^{133}Cs and ^{6}Li MAS. The ^{133}Cs and ^{6}Li MAS technique suggested that Cs cations were located in accessible sites, while Li cations were inaccessible and possibly located in cavities within the channels network.[521]

^{27}Al,^{29}Si,^{31}P - The hydrothermal transformation of silico-aluminophosphate gel with cyclohexylamine to SAPO-34 has been examined. The hydrothermal crystallisation products of the SAPO have been investigated by XRD, FTIR, nitrogen and water adsorption, thermogravimetric analysis, surface analysis and ^{27}Al, ^{31}P and ^{29}Si MAS NMR. The ^{27}Al MAS NMR signal of tetrahedrally coordinated Al observed in the silico-aluminophosphate gel without the organic template was changed to octa-, penta- and tetrahedrally coordinated aluminium upon the addition of the cyclohexylamine template to the SAPO gel. After 3 h of hydrothermal treatment at 473 K however, the ^{27}Al MAS NMR signals of the octahedral and pentacoordinated aluminium were removed. This has also been confirmed by ^{31}P and ^{29}Si MAS NMR.[522]

^{29}Si,^{27}Al,^{113}Cd,^{207}Pb - NMR studies of Pb- and Cd-exchanged LTA zeolites have been reported.[523]

^{13}C, ^{23}Na,^{27}Al,^{29}Si - Multinuclear MAS NMR techniques were used for investigation of surface reaction of Y-type zeolites with CFCs and HCFC.[524]

^{27}Al,^{29}Si,^{23}Na,^{133}Cs - The NaY zeolites exchanged with other alkali cations have been characterised by HR SSNMR. The chemical shifts of the various Si(nAl) n = 0, 1, 2, 3 and 4 configurations show particular changes as a function of the alkali counter-cations.[525]

^{27}Al,^{29}Si,^{71}Ga - A wide range of sodalite framework materials, $M_8[TT'O_4]_6X_2$ where T = Al, Ga, Si, T′ = Be, Al, Si, Ge, have been characterised using MAS NMR spectroscopy. Structural parameters, such as functions of the framework T–O–T′ angle, correlate linearly with the determined chemical shift values and provide relationships, as a function of T′, which will facilitate characterisation of more complex zeolitic compounds containing such species.[525] Gallioaluminosilicate hydrogels were prepared at different temperatures to yield crystals with the faujasite or gmelinite structure. This finding has been proved by ^{27}Al, ^{71}Ga and ^{29}Si MAS NMR spectroscopic results. The ^{29}Si NMR spectra of samples exchanged are poorly resolved and their quantitative analysis indicates substantial loss of Al and Ga from the faujasite framework. Consistent with this interpretation, ^{27}Al MAS NMR spectra reveal large amounts of octahedrally coordinated species. Moreover, the ^{71}Ga spectra show no evidence of tetrahedrally coordinated framework Ga.[526]

^{29}Si,^{71}Ga - The hydrothermal transformation of galliosilicate hydrogels were prepared from colloidal silica and sodium gallate mixtures, yields crystals with the faujasite or natrolite structure. Raising the crystallisation temperature causes the formation of analcime crystals. ^{71}Ga MAS NMR spectra have shown that in both GaY and H(Ga,La)Y, no extraframework Ga(VI) species are present.[527]

5.10 Surface Science and Catalysis. – A VT isolated flow and large-volume MAS NMR probes for heterogeneous catalysis studies has been developed.[528]

^{1}H - The chemisorbed state of hydrogen on partially reduced Ag^{+}- exchanged Y zeolite has been studied by means of ^{1}H MAS NMR spectroscopy. When AgY was reduced with hydrogen, a peak appeared at -0.1 ppm besides

peaks at 4.6 ppm and 4.0 ppm. The latter two peaks have been attributed to bridging hydroxyl groups in sodalite cages and supercages, respectively. The peak at -0.1 ppm has been ascribed to atomic hydrogen species adsorbed on cationic silver clusters.[529] The isomerisation of 2-methyl-2-pentene has been studied on boron phosphate catalysts with different P/B ratios. ^{1}H MAS NMR has been employed to provide supplementary evidence of the variation in acidity with composition.[530] CdS nanoparticles precipitated from aqueous solution have been studied by ^{1}H NMR. The nanoparticles were deliberately not capped by any surface termination agent. The samples had a porous structure. ^{1}H, ^{113}Cd MAS NMR spectra revealed that there are three abundant proton species in nanoparticle samples prepared with an excess of Cd, having different chemical shifts: a relatively narrow peak due to OH groups and two broader lines resulting from adsorbed water molecules with different chemical environments. The exchange between different lines has been studied by 2D exchange MAS spectroscopy. The analysis of the ^{1}H-^{1}H elation spectra as a function of the mixing time led to the conclusion that the nanocrystalline surface is covered by clusters of water.[531] Substitution of the protons in 12-tungstophosphoric acid by monovalent cations of the Groups 1B and 3B, in particular Ag$^+$ and Tl$^+$, respectively, produces high surface area microporous solids whose morphological properties and numbers of residual protons are dependent upon the relative amounts of the preparative reactants. ^{1}H MAS NMR and the isomerisation of 1-butene have been employed to demonstrate that both the numbers of protons and the distribution of the acidic strengths present.[532] Co-Nb(2)Q(5)–SiO$_2$ catalysts have been examined by ^{1}H MAS NMR.[533]

^{1,2}H - The regioselective ^{1}H/^{2}H exchange taking place between isobutane and acidic OH groups of strong solid acids has been investigated both by *in situ* ^{1}H MAS NMR with perdeuteroisobutane and H-ZSM5.[534]

^{1}H,^{51}V - A series of vanadia catalysts supported on sol-gel derived mixed oxide Al_2O_3–TiO_2 have been synthesised with a V_2O_5 varying content. The catalysts have been characterised by employing ^{51}V, ^{27}Al, ^{1}H MAS NMR. In the calcined catalysts ^{51}V NMR studies indicated the peaks corresponding isolated and distorted tetrahedral vanadia species at low V_2O_5 contents and octahedral vanadia species at high vanadia loadings. The ^{1}H MAS NMR studies showed the presence of terminal and bridged hydroxyl groups of alumina and titania.[535] A series of supported vanadia catalysts with different V_2O_5 contents were prepared using the ZrO_2–SiO_2 support. ^{51}V NMR studies indicated the presence of tetrahedally coordinated vanadate species at lower vanadia contents and octahedral vanadyl species at higher V_2O_5 loadings. ^{1}H MAS NMR spectra showed peaks corresponding to hydroxyl groups of zirconia and silica.[536] Alumina-silica mixed oxide has been used as a support for dispersing and stabilising the active vanadia phase. The catalysts have been characterised employing ^{51}V and ^{1}H MAS NMR. ^{51}V SSNMR studies on the calcined catalysts showed the peaks corresponding to both tetrahedral and distorted octahedral vanadia species at low vanadia loadings and with an increase in V_2O_5 content, the ^{51}V chemical shifts corresponding to amorphous

V_2O_5 like phases have been observed.[537] A series of catalysts with varying vanadia contents have been characterised employing ^{51}V, ^{1}H MAS NMR. ^{51}V NMR studies indicated the presence of tetrahedral vanadate species at all the loadings. The ^{1}H MAS NMR studies showed the peaks corresponding to hydroxyl groups of alumina and zirconia.[538]

^{2}H - The effect of carbon modifications and oxygen surface groups on the hydrophobicity of activated carbons has been described. ^{2}H SSNMR experiments showed that the presence of toluene decreases the mobility of water, either due to a stronger interaction with the surface sites or to an enhanced adsorption in the smallest pores.[539]

^{11}B - The acidity and surface structure of pure γ-alumina and a berated alumina (AB), containing a low amount of boria have been investigated by a variety of techniques. The coordination states of AB, and the distribution of hydroxyls on the surface, have been studied by ^{11}B MAS NMR. Partially hydrated AB has trigonal boron on the surface, as found in B_2O_3, and a small part of the boron nuclei exhibit ^{11}B resonances narrowed by exchange with water. In situ ^{13}C NMR has been also used to study the acid/base strength.[540]

^{11}B, ^{27}Al - Boria-alumina mixed oxides have been studied by MAS NMR.[541]

^{13}C - The temperature dependent effective catalytic pore size can be determined by the comparison of ^{13}C MAS spectra of heterogeneously catalysed, shape selective reactions and data collected from GC analysis of the product stream of reactions under similar reaction conditions.[543] Powder neutron diffraction and ^{13}C MAS methods have been used in the structural parameters determinations of the NaX and NaY zeolites with chemisorbed methyl groups CD_3 or CH_3.[543] The mechanism of propane conversion into butanes over H-MFI as catalyst has been investigated using controlled atmosphere ^{13}C MAS NMR spectroscopy. The labelled reactant was propane 2-^{13}C. The nature of the primary labelled products has been found to depend on the propane partial pressure.[544]

^{13}C MAS NMR have been performed *in situ* to investigate the mechanism of *n*-hexane conversion over Pt/alumina, Pt/ceria and Pt/ceria-alumina composite oxides, prepared by laser assisted Pt deposition. *n*-Hexane conversion has been studied at 653 K. n-Hexane 1-^{13}C was used as the labelled reactant.[545] ^{13}C NMR spectra and relaxation parameters ($T_1(^1H)$, $T_1(^{13}C)$, $T_{1\rho}(^1H)$, T_{CH}) have been measured *via* CP MAS and DP MAS techniques as a function of acetone loading level in acetone/SiO_2 samples at 25 °C. $T_1(^1H)$ and $T_{1\rho}(^1H)$ values have also been measured *via* ^{29}Si CP MAS experiments. Peak positions and relaxation parameters are averaged by rapid exchange between different acetone interaction sites on the surface.[546]

^{13}C,^{19}F - The adsorption of benzenoid aromatic compounds on porous silica has been studied by ^{13}C and ^{19}F NMR. Small chemical shifts between the resonances of methyl groups or fluorine substituents in the microcrystalline bulk material and the adsorbed species can be used to monitor the degree of adsorption.[547]

^{13}C,^{29}Si - The molecular metallasiloxanes Mo((NBu)-Bu-*t*)$_2$(OSiMe$_3$)$_2$ and Ti(OSiMe$_3$)$_4$ have been studied by ^{13}C and ^{29}Si CP MAS NMR.[548] Meso-

porous titania–silica mixed oxides with covalently bound 3-chloropropyl, 3-acetoxypropyl, and *N*,*N*-dimethyl-3-aminopropyl groups have been characterised by ^{29}Si and ^{13}C NMR. ^{29}Si MAS NMR measurements indicated covalent incorporation of the modifying group.[549] Titania-silica mixed oxides with covalently bound methyl or phenyl groups have been studied by ^{29}Si and ^{13}C MAS NMR.[549]

^{13}C,^{31}P - ^{31}P and ^{13}C MAS NMR spectra have been used to characterise pure bisphosphonates and also bisphosphonates adsorbed on hydroxyapatite. The molar ratio of phosphonates adsorbed on hydroxyapatite determined by ^{31}P spectra without CP is approximately two times larger for geminal bisphosphonates than for ol,w-bisphosphonates and phosphonoacetic acid. ^{13}C CP MAS spectra of pure and adsorbed bisphosphonates recorded in two cases for identification of adsorbed compounds give additional information about the state of adsorbed compounds.[550]

^{15}N - NaX and CaX zeolite samples were dehydrated under controlled conditions and $^{15}N_2$ was adsorbed on the zeolites. The water content has been determined by quantitative ^{1}H-NMR. The gas and adsorbed nitrogen phases were fully characterised by ^{15}N NMR. The partition coefficients and relaxation times T_1 and T_2 of the N_2 phases were then studied as a function of temperature. ^{15}N-NMR measurements were performed under static and MAS conditions. Two different types of adsorbed nitrogen molecules were also found on the zeolites.[551]

^{19}F - KF/alumina catalysts containing different amounts of KF have been characterised by ^{19}F MAS NMR to elucidate the catalytically active sites, whose appearance varies much with the pretreatment temperature. Although the main species containing F was K_3AlF_6 formed by the reaction of KF with alumina, which has been observed by both XRD and ^{19}F MAS NMR, it was not related to the formation of active sites.[552] Some reactions that control the dissolution of bayerite [β-Al(OH)$_3$] and boehmite [γ-AlOOH] have been identified by comparing the adsorption chemistry, the dissolution rates, and ^{19}F spectra of the reacting surfaces. The ^{19}F spectra of bayerite distinguish two sites for fluoride reaction that vary in relative concentration with the total adsorbate density. One resonance at -131 ppm has been assigned to fluoride bridges and the other resonance at -142 ppm has been assigned to fluoride at terminal sites.[553]

^{23}Na,^{51}V - Sodium-doped binary vanadia–titania catalysts have been studied using modern HR SSNMR techniques, including fast MAS and 2D TQ MAS NMR. NMR and powder XRD data brought together allow identification of sodium- and vanadium-containing species formed in the course of the preparation of the catalysts.[554]

^{27}Al - ^{27}Al MQ MAS has been used to characterise the oxide Mo-P-Al hydrotreating catalysts.[555] ^{27}Al NMR MAS has been used to study the surface aluminium compounds forming during the treatment of supported $TiCl_4$/$MgCl_2$ catalyst with organoaluminium compounds of various composition.[556] By means of ^{27}Al TQ MAS NMR and ^{27}Al{^{19}F} WISE MAS NMR, three different Al–F sites on the surface of fluorinated γ-alumina have been detected.

Three ^{19}F resonances at 9, 20, and 33 ppm (from C_6F_6) correlated to ^{27}Al resonances in the octahedral range. While the positions of the maxima in the ^{27}Al dimension were ill-defined due to the inherently low efficiency of the $^{27}Al\{^{19}F\}$ CP MAS process, the centre of gravity of the lines shifted significantly upfield in that dimension with increasing wt.% F. At F contents above levels corresponding to the full fluorination of the γ-Al_2O_3 surface, neoformation of an AlF_3. $3H_2O$ phase was also evidenced ^{19}F resonance at -8 ppm and with an ^{27}Al resonance at -17 ppm.[557]

^{27}Al,^{29}Si - An increasing demand for 2,6-dialkylnaphthalene has spurred interest in shape-selective naphthalene alkylation. This process has been examined by other techniques including ^{27}Al and ^{29}Si MAS NMR.[558]

^{11}B,^{27}Al,^{31}P - The synthesis of isoprene from the dehydration of 2-methylbutanal has been described using boron phosphate, aluminium phosphate and mixed boron/aluminium phosphates as catalysts. It has been investigated by ^{31}P, ^{27}Al, and ^{11}B MAS NMR spectroscopy shows that B and Al are in the same lattice in these mixed phosphate catalysts.[559]

^{29}Si - A series of highly crystalline silicoaluminophosphates having the AFI topology (SAPO-5) have been synthesised with varying silicon. These have been studied by the ^{29}Si MAS NMR technique.[560] X-Ray amorphous ZnO nanoparticles homogeneously dispersed in a silica matrix were evidenced in ZnO-SiO2 nanocomposites obtained by a sol-gel method. Through a comparison of the ^{29}Si MAS NMR data of the nanocomposites and silica samples, obtained by the same method, it was possible to observe that reaction occurs between ZnO and silica on heating, which causes a depolymerisation of the host matrix with the formation of low condensation groups.[561]

^{31}P - Zirconium-pillared layered phosphates were prepared from a-zirconium phosphate and zirconium phosphate phenylphosphonate by colloid manipulation method. IR and ^{31}P MAS spectroscopic studies show that P–O–Zr linkages are formed after calcination as a result of this strong interaction.[562] The room temperature decompositions of the nerve agent simulant diisopropyl fluorophosphate sorbed on γ-alumina, polydivinylbenzene, and Ambergard, have been studied *in situ* using ^{31}P MAS NMR.[563] Ruthenium complexes having bidentate phosphine ligands were incorporated into an amorphous silica matrix *via* chemical anchoring using a silylether bridge. The integrity of the complexes after immobilisation has been confirmed by CP MAS ^{31}P NMR.[564] Different compositions of $Ca_{10.5-x}Cu_x(PO_4)_7$ ($0 \leq x \leq 1$) and $Ca_{10-x/2}Na_xCu_{0.5}$ $(PO_4)_7$ ($0 \leq x \leq 1$) belonging to the Whitlockite-type structure have been characterised. ^{31}P MAS NMR investigations of $Ca_{10.5}(PO_4)_7$ and $Ca_{10}Na(PO_4)_7$ showed that the occupancy level of the Ca sites does not modify notably the symmetry of the $(PO_4)^{3-}$ groups.[565] The heterogenisation of the zwitterionic Rh(I) catalysts (sulfos)Rh(cod) and (sulfos)$Rh(CO)_2$ [sulfos = $-O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$; cod = cycloocta-1,5-diene] has been performed by controlled adsorption on partially dehydroxylated high surface area silica. Experimental evidence of the $-SO_3\cdots HOSi$-interaction with silica has been obtained from CP MAS ^{31}P NMR studies.[566] The hydroformylation of styrene over Rh/SiO_2 has been studied by FTIR and

^{31}P CP MAS NMR.[567] A new family of vanadium phosphorus oxides (VPO) catalysts have been identified by XRD and ^{31}P NMR. ^{31}P NMR by spin echo mapping and ^{31}P MAS NMR have confirmed an interaction of the VPO precursor with Nb and of the NbPO amorphous material with V.[568] ^{31}P MAS NMR characterisation of zirconium phosphate/phosphonate (ZP) multilayer assemblies grown on SiO_x. The reaction of silica with excess $POCl_3$ and treatment with collidine results in both physisorbed and chemisorbed $H_xPO_{4(x-3)}$ being present at the SiO_x, surface was reported. The ^{31}P NMR spectrum of zirconium phosphate grown from silica shows no residual Cl-containing species, indicating essentially complete hydrolysis.[569] The change in chemical shift of a chemisorbed probe molecule is an informative tool for the characterisation of solid acids. This work demonstrates that the ^{31}P isotropic chemical shift of the probe triethylphosphine oxide (TEPO) can be used to identify the acidity of multiple acid sites on a surface.[570] The bonding of triethylphosphine oxide to the acid site of a surface has been shown to produce a systematic change in the ^{31}P isotropic chemical shift that is proportional to the acid strength of the adsorption site.[571]

^{51}V - Vanadium–cerium oxide samples with different V/Ce atomic ratios have been characterised by XRD and ^{51}V MAS NMR. ^{51}V MAS NMR study has shown the presence of different V sites in solids.[572] Wideline ^{51}V SSNMR spectra of supported V_2O_5–WO_3/TiO_2 catalysts were obtained under ambient conditions.[573] Milling of V_2O_5 in a ball mill increased the surface area. After milling in a ball mill it has been characterised by the combination of wideline and MAS ^{51}V NMR techniques together with theoretical simulations of NMR spectra.[574] The fresh catalyst V_2O_5–WO_3/TiO_2 and catalyst have been studied by the ^{51}V SSNMR spectroscopy in static and MAS conditions. According to ^{51}V NMR in both samples the majority of vanadium sites are in a distorted octahedral environment similar to that in V_2O_5.[572]

^{1}H,^{27}Al,^{29}Si - The interaction between Mo species and a conventionally microsised and particularly nanosised HZSM-5 support has been studied by HR SSNMR techniques. As proved by ^{27}Al and ^{29}Si MAS as well as CP MAS NMR investigations, this interaction was so strong that the framework aluminum of both microsised and nanosised HZSM-5 zeolites could be extracted. With increasing Mo loading, more nonframework aluminum, resonanced at 30 ppm, appeared in the ^{27}Al MAS NMR spectrum of the Mo-loaded nanosized HZSM-5 catalyst.[575]

^{1}H,^{2}H,^{31}P - Spectroscopic techniques in controlled atmosphere, such as ^{1}H, ^{2}H and ^{31}P MAS and inelastic neutron scattering (INS), have been used to investigate the effect of dehydration on structural modifications and acidic properties of solid 12-tungstophosphoric acid $H_3PW_{12}O_{40}$ and its cesium salt $Cs_{1.9}H_{1.1}PW_{12}O_{40}$. MAS spectra have been recorded as a function of the degree of dehydration/rehydration and allowed to characterise the protonic species present.[576]

5.11 Inorganic and Other Related Materials. – *^{1}H* - ^{1}H MAS NMR at high magnetic fields and high spinning speeds provides a powerful means of identifying the different proton sites in smectites and affects information on the octahedral nature.[577] ^{1}H MAS NMR experiments have been used to characterise the non-acid protons of the anions in polycrystalline paratungstates by means of the measured isotropic chemical shift values. The investigation of various hydrates of ammonium paratungstate allows a direct proof of protons in NH_4 ions and in water molecules while protons of the anions are not detectable. However, for both the potassium and the sodium paratungstates ^{1}H MAS NMR investigations detected the protons of water molecules and the non-acid protons of the paratungstate anions. Additional ^{1}H broadline NMR experiments at 173 K support the interpretation of the results.[578]

^{6,7}*Li* - $LiMnO_2$ with orthorhombic structure was synthesised, a spectrum of solid-echo ^{1}H-NMR on γ-MnOOH became diminished, while a spectrum of solid-echo ^{7}Li-NMR emerged with three different kinds signals which is accompanied by SSB at around 37 ppm, 74 ppm and 1 ppm, respectively.[579] ^{6}Li and ^{7}Li MAS NMR and in situ XRD have been used to study lithium manganate cathode materials ($Li_xMn_2O_4$, $0 < x \leq 1$) during and following charging and discharging. Only one major local environment has been observed by ^{6}Li MAS NMR from lithium in the tetrahedral sites of the spinel structure, the resonance shifting by no more than 8 ppm in this range (from its original position).[580] Samples of Li_xCoO_2 (0.5 x 1) have been prepared by electrochemical deintercalation from high temperature $LiCoO_2$ and are characterised by XRD, electrical measurements and ^{7}Li MAS NMR spectroscopy. ^{7}Li MAS NMR suggests that the metal–non-metal transition is the driving force for the existence of the biphasic domain.[581] ^{7}Li MAS NMR studies have been performed for both the spinel compounds before and after Li^+ intercalation.[582]

^{13}*C* - Jahn-Teller distortion in the $C_{60}^{\ -}$ ion has been studied by ^{13}C NMR spectroscopy in the solid samples $KC_{60}(THF)$ and $KC_{60}(THF)_x$ ($0 < x < 1$). Solvating the K^+ ion by THF can change electronic states of $C_{60}^{\ -}$ ion.[583] The microstructure of carbonaceous matter prepared from copper acetylide, by a coupling reaction promoted by air, hydrogen peroxide or $Cu(NH_3)_n^{\ 2+}$ oxidation has been studied by SSNMR, FT-IR and Raman spectroscopy. SSNMR provides additional evidence on the presence of small cumulenic moiety 'allenic or cumulenic carbyne (polyethylenediylidene). SSNMR in conjunction with Raman spectroscopy show sp^3-hybridised carbon moieties known also as 'diamond-like carbon', formed by a crosslinking reaction of acetylenic carbyne chains; additionally sp^2-hybridised carbon atoms have been detected and assigned to amorphous and graphitic carbon.[584]

^{17}*O* - Three- and five-quantum ^{17}O MAS NMR experiments are used to resolve fully the three crystallographically distinct oxygen species in forsterite (Mg_2SiO_4). The chemical shift and quadrupolar parameters extracted from these spectra are compared with the literature values obtained using conventional ^{17}O MAS and DAS NMR.[585] Powder XRD and electron single-crystal diffraction of crystals of $Li_2TiOSiO_4$ and $Li_2TiOGeO_4$ showed them to be tetragonal, space group. ^{17}O NMR spectra of the two compounds, isotopically enriched with ^{17}O, showed peaks due to the apical titanyl, Ti–O, and basal, bridging, Ti–O–Si or Ti–O–Ge, oxygen atoms of the title compounds.[586]

^{23}Na - The structure of NASICON-type compounds, $Na_{1+x}Sc_xTi_{2-x}(PO_4)_3$ ($0 \leq x \leq 2$), and the dynamics of Na^+ have been investigated by ^{23}Na NMR spectroscopy. It was found that the ^{23}Na 1D and 2D MQ MAS spectra depend on the Na concentration, suggesting strongly that the Na^+ ions are distributed between two crystallographically nonequivalent sites, one is a special position with axial symmetry, and the other a position of low symmetry.[587]

^{27}Al - The kaolinite–mullite reaction process has been studied by SQ and TQ ^{27}Al MAS NMR. All materials have also been characterised by ^{29}Si MAS NMR and powder XRD. It has been shown that in order to record reliable ^{27}Al MAS NMR spectra it is important to use very fast sample spinning rates. The conflicting values previously reported in the literature for the four-, five- and six-coordinated Al metakaolinite populations are due to the relatively modest and different MAS rates and magnetic fields used. TQ ^{27}Al MAS NMR provides hard evidence for the presence in metakolinite of distorted (and distributed) four-, five-, and six-coordinated Al local environments.[588] The structure of $Bi_2Al_4O_9$ has been refined using a combination of X-ray and HR neutron powder diffraction. Iterative simulation of the ^{27}Al SSNMR data confirms the presence of two Al sites, one octahedral and one tetrahedral, in an approximate 1:1 ratio.[589] Investigations on the hydrothermal formation and the crystal structure of nitrate cancrinite have been carried out in the system Na_2O–$x$$SiO_2$–$Al_2O_3$–$NaNO_3$–$H_2O$, $1 < x < 6$. Structural investigations of nitrate cancrinite have been performed by IR and MAS NMR spectroscopy of the nuclei ^{29}Si, ^{27}Al and ^{23}Na. The results confirmed the alternating Si, Al ordering of the alumosilicate framework for a Si/Al ratio of 1.0 for all samples, independent of the Si/Al ratio of the educts as well as the temperature and pressure of crystallisation. A distribution of the quadrupolar interaction of the sodium cations caused by the enclathrated water molecules and motional effects can be suggested from the ^{23}Na MAS NMR spectrum.[590] A series of bentonite illite/smectite with a range of Fe content and illite composition has been analysed by means of FTIR, ^{27}Al MAS NMR and theoretical calculations.The calculated distributions have then been analysed in comparison with the experimental ^{27}Al NMR results.[591]

^{29}Si - The microstructure of silicon carbide has been characterised by XRD and ^{29}Si SSNMR.[592]

^{31}P - A ^{31}P SSNMR study of TiP_2O_7 has been reported. The combined constraints from 1D and 2D ^{31}P MAS NMR experiments probing through-bond P–O–P connectivities *via* homonuclear *J* coupling interactions, positively identify the cubic space group. 2D SQ-DQ correlation ^{31}P MAS NMR experiments subsequently lead to complete assignment of the distinct crystallographic P sites in the structure of TiP_2O_7 to the corresponding eight resolved resonances in ^{31}P MAS NMR spectra of TiP_2O_7, while ^{31}P ZQT and C7 DQT MAS NMR experiments confirm that TiP_2O_7 and the cubic phase of SiP_2O_7 are isostructural.[593] The compound $P_2I^{5+}AlI^{4-}$ and the novel compounds $P_2I^{5+}GaI^{4-}$ and $P_2I^{5+}InI^{4-}$ have been prepared in two different ways either from PI_3 and EI_3 or from P_2I_4 and I_2/EI_3 (E = Al, Ga or In). The products have been characterised by ^{31}P MAS SSNMR, Raman and IR spectroscopy.

The ^{31}P MAS SSNMR spectra are compared with NMR studies of related PI_4^+ salts and alkylphosphorus tetraiodides.[594]

^{113}Cd - Semiconductor nanocrystals doped with transition metals has been studied ^{113}Cd MAS spectra; the observed paramagnetic shift and decreased longitudinal relaxation time are consistent with Mn incorporated in the quantum dots.[595]

^{13}C,^{29}Si,^{31}P - The SSNMR characteristics of unsupported and silica-supported H-4[$SiMo_{12}O_{40}$] and H-3[$PW_{12}O_{40}$] heteropoly acids after (i) calcination or (ii) reaction with 2,3-butanediol are described. The supported and unsupported acids have been studied by ^{29}Si or ^{31}P MAS NMR spectroscopy and the supported catalysts, which became steady-state in a 2,3-butanediol flow, have been probed by ^{13}C CP MAS NMR measurements as well. The position of Si signal corresponding to the heteropoly acid in $H_4[SiMo_{12}O_{40}]/SiO_2$ could be distinguished from the Si signals of the support. The ^{31}P NMR spectrum of $H_3[PW_{12}O_{40}]$ revealed that the material contains two species: one is somewhat dehydroxylated, but fully protonated, the other has been further dehydrated and probably proton deficient too.[596]

^{23}Na,^{31}P - ^{23}Na and ^{31}P MAS and powder XRD have been used in combination to study the structure of the model phosphate phases $NaMg(PO_3)_3$ and $NaZn(PO_3)_3$. The ^{23}Na and ^{31}P SSNMR data confirm the similarities between the two structures, while the ^{23}Na also suggested three sodium sites in a 2:1:1 ratio, consistent with the proposed crystallographic model.[597]

^{27}Al, ^{29}Si - MAS NMR studies on building stones from historical monuments have been reported.

^{7}Li,^{23}Na - Two new non-metallic filled beta-manganese phases $M_2Ga_6Te_{10}$ (M: Li, Na) have been characterised by MAS NMR, including MQ NMR.

6 Molecular Dynamics Studies

6.1 Organic Solids: – Hydrogenated oligocyclopentadiene has been investigated by means of ^1H and ^{13}C NMR in the solid state.[598] The dynamic behavior has been investigated through the measurements of $T_{1\rho}(^1H)$ and $T_1(^1H)$, as well as $T_1(^{13}C)$, highlighting the presence of two major motional processes.

^2H NMR techniques have been employed to study phenyl ring dynamics of enkephalin molecules and behaviour of bound solvents in the crystalline states,[599] the methyl group dynamics in aspirin and in the inclusion complex aspirin/β-cyclodextrin,[600] symmetry, disorder, and dynamics in solid crown ether complexes[601] and the molecular motional modes in sucrose octapalmitate.[602]

Dynamics of the benzene and pyridine *p-tert*-butylcalix[4]arene inclusions has been studied using wideline ^2H NMR lineshapes and ^{15}N NMR CS tensor components.[603] The absence of short contacts rules out a C-H···N hydrogen bonding interaction of the host to the guest.

Dynamics of aromatic ring flipping in solid 4,4′-diphenoxydiphenylether has been studied by ^{13}C time-reverse ODESSA NMR.[604]

Conformational dynamics in the solid state has been studied by ^{13}C techniques for *S*-alkyl-1,4-dithianium salts (a persistent solid degradation product of mustard),[605] triisopropyl(aryl)silanes,[606] triisopropylsilanes,[607] tris-(trimethylsilyl)methanes,[608] homochiral dicarvone[609] and 9-*tert*-butylanthracene[610] Tautomerism and H-bonding of benzylideneanilines in the solid state has been studied by ^{13}C CP MAS.[247] Molecular dynamics of C_{60} in cocrystals of C_{60} and *p*-bromocalix[4]arene propyl ether[611] and of ferrocene in deoxycholic acid/ferrocene inclusion compound have been studied by ^{13}C NMR.[612]

^{15}N CP MAS has been employed to study the kinetics of degenerate intermolecular triple proton and deuteron transfers in the cyclic trimers of ^{15}N-labeled polycrystalline 4-nitropyrazole and 4-bromopyrazole[613] and the proton transfer thermodynamics and dynamics and the proton locations in polycrystalline ^{15}N-labeled porphycene.[614]

The rate of ring inversion of fluorocyclohexane in its thiourea inclusion compound has been studied using ^{19}F NMR, 2D EXSY and selective polarisation inversion, triple-channel ^{13}C-{^{1}H,^{19}F} spectra. The superiority of the ^{19}F measurements over the use of ^{13}C spectra has been emphasised.[615]

6.2 Organometallics and Coordination Compounds. – H-migration and carbonyl mobility in $(NMe_4)_{4-x}[H_xNi_{12}(CO)_{21}] \cdot S$ ($x = 1$, S = Me_2CO; $x = 2$, S = 2THF) have been studied VT ^{1}H and ^{13}C SSNMR.[616]

Wideline ^{2}H NMR has been used to probe the motion of the η^2-dideuterium ligand in the solid state.[617]

Representative examples of large-amplitude dynamic phenomena in various classes of solid metallorganic compounds and their study by VT ^{13}C CP MAS have been presented.[618] Dynamics of monohaptocyclopentadienyl rings of hafnium and titanium tetracyclopentadienyl in the solid state has been investigated by 2D ^{13}C CP MAS.[619] 1D and 2D ^{13}C and ^{29}Si MAS NMR have been employed to demostrate that crystalline $(Ph_3Si)Si(SiMe_3)_3$ lacks all molecular symmetry and that internal $2\pi/3$ reorientation of all three crystallographically inequivalent $SiMe_3$ groups in the molecule occurs.[620]

Modes of molecular reorientation in solid $C(SnMe_3)_4$ have been investigated by 1D and 2D ^{13}C and ^{119}Sn static and MAS NMR.[621] The pseudo-five-fold disorder previously observed by single-crystal XRD has been shown to be dynamic. A dynamic-disorder model where each tin atom in a $C(SnMe_3)_4$ molecule occupies the twenty sites of a nearly perfect pentagonal dodecahedron with equal probability has been suggested.

Intermolecular H-bonds of the type N-H⋯N in crystals of imidazole and its 4-substituted and 4,5-disubstituted derivatives have been studied by ^{15}N CP MAS NMR and an *ab initio* calculation.[622]

6.3 Biological and Biomedical Applications. – ^{1}H $T_1/T_{1\rho}$ and ^{13}C CP MAS studies have been used to study molecular dynamics of poly(lactide-co-glycolide) controlled pharmaceutical release polymers.[623] Results suggest that around the broad glass transition at about 50 °C slow polymer backbone motions (on the 10 to 100 μs timescale) become significant.

Lipid dynamics in the annexin V – membrane complex has been studied by ^{2}H NMR.[624] Details of backbone motions in a crystalline protein have been derived from field-dependent ^{2}H NMR relaxation and lineshape analysis.[625] ^{2}H NMR has also been applied to study dynamic properties of phospholipid model membranes[626] and mobility of the tyrosine side chain in Bombyx mori and Samia cynthia ricini silk.[627] ^{13}C NMR studies of dynamic properties of 14 residue antifreeze glycopeptide have been reported.[628]

Effects of hydration on molecular mobility in dormant Bacillus subtilis spore samples have been investigated by ^{31}P and ^{13}C SSNMR.[629] Superslow backbone dynamics of the protein barstar and the polypeptide polyglycine has been studied by time-reverse ODESSA technique that can detect reorientation of nuclei carrying anisotropic chemical shift tensors.[630] Experiments have been performed on carbonyl ^{13}C in polyglycine and backbone ^{15}N nuclei. Two exchange processes have been observed in the experiments: molecular reorientation and spin diffusion. It has been shown that the application of MAS exchange spectroscopy provides new opportunities in studying slow biomolecular dynamics that is important for the biological function of proteins.

6.4 Polymers. – Temperature dependent ^{2}H quadrupole echo lineshapes have been reported for polyamidoamine dendrimer salts.[631] The spectra are characteristic of amorphous materials undergoing broad glass transitions. The estimated average H-bond lengths are 2.2 Å. Three-fold rotation and asymmetric cone libration model has been used to explain the observed temperature dependent asymmetry parameters of terminal ND_3^+ groups.

^{13}C 2D exchange NMR has been applied to investigate dynamic alternation among three forms of H-bonds in the poly(acrylic acid)/poly(ethylene oxide).[632] The ^{13}C CP MAS signal for carboxyl carbon in the complex is split into three peaks corresponding to three forms of H-bonds: the complex form, the dimeric form and the free form. These three peaks coalesce into a single peak at temperatures above 346 K, showing that dynamic alternation of H-bonds occurs in the complex. 2D exchange NMR spectra directly show that the dissociation-association of H-bonds occurs at temperatures, higher than T_g. The exchange rates are on the order of Hz and have a wide distribution. It was found that the H-bonding dynamics is coupled to the segmental motion of poly(acrylic acid) in the complex.

^{13}C NMR has also been employed to study the local motions in aryl-aliphatic copolyamides by following the temperature dependence of ^{13}C CSAs and ^{13}C-^{1}H dipolar couplings.[633]

6.5 Microporous Solids and Related Materials. – ^{1}H MAS tecniques have been used to study the dynamic properties of acidic protons in metallosilicate molecular sieves.[634] Results of the first pulsed field gradient NMR studies of H-diffusion in zeolites have been presented and compared with corresponding measurements by quasielastic neutron scattering.[635] The results of the two techniques were in satisfactory agreement. The H-diffusivity is generally found to decrease with decreasing free apertures of the zeolite pore structure.

HR ^{1}H MAS NMR investigations (including ^{1}H NOESY NMR and ^{1}H–^{13}C cross-relaxation studies) of the mobility of 1-butene and 1-pentene molecules adsorbed in zeolite NaX have been presented.[636] The mobility of the adsorbed species can be characterised by a fast libration motion of the molecules and an overall reorientation–translation motion with a correlation time which is comparable to the lifetime of the molecules in a cavity with respect to their jump into a neighbouring cavity.

^{2}H NMR spectroscopy have been used to examine the structure and rotational dynamics of CD_3 groups pointing into the unidimensional channels of the β-polymorph of the hybrid organic/inorganic microporous solid aluminium methylphosphonate, $Al_2(CD_3PO_3)_3$.[637]

1D and 2D exchange ^{13}C NMR techniques have been used to show that *n*-pentane translation in zeolite ZK-5 occurs by hopping between neighboring α and γ cages.[638] Owing to the structure of the ZK-5 pore network, these techniques give direct information about the translational part of molecular intercage motion, which represents the elementary step of sorbate self-diffusion.

6.6 Other Materials. – The dynamic behaviour of *n*-octylammonium ions intercalated into tetrasilicicfluormica has been investigated by measuring ^{1}H and ^{2}H NMR lineshape and $T_1(^{1}H)$ measurements. Uniaxial rotation of cations has been found to take place above *ca*. 200 K among non-equivalent potential wells made by clay sheets.[639]

^{2}H and ^{15}N NMR has been used to measure the ^{2}H EFG and ^{15}N CS tensors in solid hydroxylammonium chloride and to study the NH_3 and OH dynamics. There was no evidence for OH reorientation up to 405 K, indicating a rather strong OH···Cl H-bond.[640] The rotational dynamics of P_4O_6S and P_4O_7 in the solid state have been studied by means of ^{31}P spin-echo and ^{31}P MAS NMR.[641] All spectra have been simulated to confirm the type of the motion and to extract the time scales as a function of the temperature. Good agreement between experimental and theoretical data was obtained on the basis of a three-site jump model.

^{31}P NMR measurements have been reported for solid Li_3P_7 under both nonspinning and MAS conditions.[642] At low temperatures the spectra correspond to a static situation, exhibiting a superposition of three subspectra due to the epical, equatorial, and basal P atoms in the P_7-cage. Analysis of these spectra provided information on the CS tensors of the various P atoms. Their orientations in the molecular frame have been obtained from quantum mechanical calculations. At high temperatures a bond shift rearrangement model (similar to the Cope rearrangement process in bullvalene) has been used to interpret the lineshape changes.

7 Phase Transitions. – *^{1}H* - ^{1}H T_1 and $T_{1\rho}$ have been measured as a function of temperature in order to investigate order–disorder phase transitions in layer crystals with a rotator phase, $(n\text{-}C_5H_{11}NH_3)_2ZnCl_4$ and $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$.[643] The highest-temperature solid phase in both compounds was found to be the rotator phase, where rod-like cations perform uniaxial reorientations about the molecular long axes accompanied by conformational disordering and translational self-diffusion of the cations. These rotator phases have been shown to be quite analogous to those reported in *n*-alkylammonium chlorides. $(n\text{-}C_5H_{11}NH_3)_2ZnCl_4$ undergoes four structural phase transitions, while $C1_2H_{25}NH_3)_2ZnCl_4$ exhibits a single transition above *ca.* 120 K. All of these transitions have been shown to be of order-disorder type.

^{1}H NMR measurements have been performed to study thermally induced rearrangement of H-bonded helices in 4-isopropylphenol below the melting point.[644] Energetically inequivalent Me group reorientations have been observed in differently prepared samples and this suggested that a high-temperature polymorph occurs below the transition point as a metastable phase. It has been proposed that thermally induced molecular rearrangements enable proton transfer in H-bonds and this stimulates protonic conduction.

^{13}C - ^{13}C MAS NMR studies have been untertaken to study the low temperature phase transition in fullerene C_{60}.[645] At the phase transition near 262 K, the $T_1(^{13}C)$ in static samples of pure C_{60} decreases from 31 to 0.8 s as the temperature decreases by less than 8 K, while XRD patterns change little. Under MAS $T_1(^{13}C)$ decreases from 46 to 0.8 s over only 2 K, while the onset of the phase transition is lowered to 255 K. It has been suggested that uniaxial cage motion cannot average the CSA to the value observed in static samples, and nutation must be present.

The deoxycholic acid inclusion complex 2DCA:ferrocene has been shown to undergo a ‘gradual’ phase transition above ambient temperature, ‘completed’ by similar to 360 K.[646] The phase transition has been characterised by using XRD and ^{13}C CP MAS. The transition, most clearly observed in the positions of the DCA molecules, is largely dominated by the dynamic behaviour of the guest ferrocene molecules.

^{13}C,^{15}N - Polymorphism and phase transitions in 2-(2,4-dinitrobenzyl)-3-methylpyridine have been investigated using single-crystal ^{13}C and ^{15}N NMR. The spectral observations have been interpreted in terms of a distribution of mesoscopic domains within the crystal, differing in their local pressure. The presence of dynamic processes on time scales shorter than minutes has been excluded by both NMR measurements and tautomerisation kinetics.[647]

^{15}N - The phase transitions within the three phases of potassium nitrate (α-, β-, and γ-KNO_3) have been investigated in detail by VT ^{15}N MAS. The stability of the metastable γ-KNO_3 phase has been found to be highly influenced by the thermal history of the sample. The spectral appearance for the room-temperature α-KNO_3, phase has been found to change after excursions of the sample into the high-temperature β-KNO_3 phase.[648]

^{29}Si - The different polymorphs of $Y_2Si_2O_7$ have been studied by ^{29}Si MAS NMR. ^{29}Si NMR spectra for the α, β, γ and δ polymorphs are consistent with accepted structural data from the point of view of the number of sites, the populations and the chemical shifts.[649]

^{31}P - The order-disorder ferrielectric-paraelectric transition in lamellar $CuInP_2S_6$ has been studied using VT ^{31}P MAS NMR.[650] Two centrebands have been observed at the lowest measured temperature while only one has been detected at the highest temperature. The former two represent the inequivalent positions for the P atoms of the P_2S_6 group which reflect the antiparallel displacements of the polar Cu and In sublattices in the ferrielectric phase. The latter corresponds to the appearance of a 2-fold axis through the P–P bond as the Cu ions undergo double-well hopping motions, and the In ions occupy on-centre sites in the paraelectric phase. The presence of the ferrielectric type resonance in the paraelectric regime has been ascribed to the nucleation of polar order, while the persistence of the paraelectric signal well below the transition temperature implies residual hopping motions occurring in the ferrielectric regime.

^{71}Ga - The melting-freezing phase transition of gallium confined within Vycor glass has been studied by ^{71}Ga NMR. A single broad ^{71}Ga NMR line corresponding to melted gallium was observed in contrast to lineshapes found until now for liquid gallium in porous matrices. A difference between results obtained using the three methods was explained by formation of various confined solid gallium modifications.[651]

^{133}Cs - Crystalline $Cs^+(18\text{-crown-}6)_2e^-$ is a linear chain Heisenberg antiferromagnet undergoing a slow, irreversible transition above 230 K from a crystalline low temperature phase to a disordered Curie-Weiss paramagnetic high temperature (HT) phase. A 100 ppm diamagnetic shift of the ^{133}Cs MAS NMR peak accompanies this transition. The HT phase undergoes an additional first-order reversible transition upon cooling below 220 K accompanied by the observation of two peaks in the ^{133}Cs NMR spectrum.[652]

8 *In situ* Reactions

8.1 Polymerisation. – The solid-state formation of a centrosymmetric cage dimeric 4-aryl-1,4-dihydropyridine has been monitored by ^{13}C CP MAS NMR.[653] The spectra of the photodimerising derivatives show the changes in symmetry during the reaction and the reaction progress and clearly reflect conformational properties of the molecules. Starting from centrosymmetric pairs of monomeric molecules, dimerisation proceeds to non-symmetrical syn-dimers, that subsequently cyclise to centrosymmetric cage dimers.

The thermally induced solid-state polymerisation reactions in sodium chloroacetate and sodium bromoacetate, leading to poly(hydroxyacetic acid) (polyglycolide) and NaCl and NaBr, respectively, have been studied by isothermal *in situ* ^{23}Na and ^{13}C MAS NMR with a time resolution of the order of 5 to 25 min. For sodium chloroacetate, there is no evidence for the involvement of intermediate phases during the reaction whereas this cannot be excluded for sodium bromoacetate. The mechanistic and kinetic information obtained from *in situ* solid-stale NMR investigations has been compared and contrasted with information obtained from other *in situ* probes of the polymerisation reactions in these materials.[654]

8.2 Heterogeneous Catalysis. – An isolated flow MAS NMR probe have been developed to enable simultaneous observation of events occurring on a catalytic surface with characterisation of the effluent gas using an external analytical instrument.[655] The probe uses ceramic ball bearings to support the rotor. The spinning and spectroscopic capabilities of the probe have been proven by obtaining a ^{13}C CP MAS spectrum of hexamethylbenzene at 2 kHz. The flow capabilities of the probe have been demonstrated by observing methanol adsorption onto HZSM-5. The VT capabilities have been shown by monitoring the change in the ^{207}Pb chemical shift of $Pb(NO_3)_2$ with temperature. Temperatures >300 °C have been achieved for the probe. The reaction of methanol to dimethyl ether on zeolite HZSM-5 has been used to demonstrate the ability of the probe to study heterogeneous catalysis reactions *in situ*. Under flow conditions only dimethyl ether was observed. In previous studies under sealed (*i.e.* batch) conditions, an equilibrium was observed between methanol and dimethyl ether.

A new technique has been introduced allowing simultaneous *in situ* MAS NMR investigations of hydrocarbon conversions on solids under flow conditions and on-line gas chromatography.[656] The new *in situ* technique has demonstrated its advantage for a simultaneous investigation of compounds with a long residence time on the catalyst surface and of compounds rapidly leaving the catalyst surface. *In situ* ^{13}C MAS NMR techniques have been employed to study the conversion of methanol to dimethyl ether on zeolite HZSM-5,[657] the methanol-to-gasoline conversion,[658] the formation of methyl-*tert*-butyl ether on zeolites HY, HBeta, HBeta/F and HZSM-5,[659] the photocatalytic oxidation of ethanol over two TiO_2-based catalysts,[660] the photocatalytic oxidation of ethanol over a TiO_2-coated optical microfiber catalys[661]t and the propene polymerisation under the conditions of continuously flowing propene through a supported Ziegler catalyst.[662]

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