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Some Developments in Nuclear Magnetic Resonance of Solids

B. F. CHEMELKA AND A. PINES

Nuclear magnetic resonance (NMR) spectroscopy continues to evolve as a primary technique in the study of solids. This review briefly describes some developments in modern NMR that demonstrate its exciting potential as an analytical tool in fields as diverse as physics, chemistry, biology, geology, and materials science. Topics covered include motional narrowing by sample reorientation, multiple-quantum and overtone spectroscopy, probing porous solids with guest atoms and molecules, two-dimensional NMR studies of chemical exchange and spin diffusion, experiments at extreme temperatures, NMR imaging of solid materials, and low-frequency and zero-field magnetic resonance. These developments permit increasingly complex structural and dynamical behavior to be probed at a molecular level and thus add to our understanding of macroscopic properties of materials.

NUCLEAR MAGNETIC RESONANCE (NMR) INVOLVES THE absorption and emission of radio-frequency energy by nuclear spins as they oscillate and reorient in the presence of internal and externally applied magnetic fields. The oscillation frequencies and reorientation times depend sensitively on the local environments and on the mobility of the atoms and molecules. The sensitivity of the resulting spectrum to local environment in the sample, together with a natural isotopic selectivity, enables NMR to provide detailed information about structure and dynamics for many classes of materials (1-4).

The interactions that determine an NMR spectrum depend, in general, on the microscopic orientation of the atomic or molecular species in a magnetic field. For molecules randomly oriented in a rigid lattice, the variety of possible orientations often leads to a correspondingly complicated spectrum. In liquids, by contrast, the

rapid and isotropic molecular motion averages the anisotropic interactions and thus narrows the spectral lines. The study of solids is therefore complicated because line broadening and low sensitivity frequently obscure the spectral features from which structural and dynamical details are to be extracted. Development of new instrumentation and analytical techniques that produce better resolved and more detailed spectra, however, continues to expand the application of NMR in various fields such as physics, chemistry, biology, medicine, geology, and materials science. In this review we describe a few recent developments in NMR (with selected references from the most recent literature) that demonstrate its exciting analytical potential in the study of solids. While the selection of topics and references is by no means comprehensive (or even democratic), we hope that it illustrates some of the novelty and diversity of modern NMR.

Line-Narrowing by Sample Reorientation

One way to narrow the broad lines in the NMR spectrum of a solid is to reorient the sample rapidly to average away the anisotropic effects artificially. Methods of this sort seek to resolve spectral details from which individual atomic sites can be identified and internuclear distances determined. Magic-angle spinning (MAS), in which a sample is rotated about an axis inclined at 54.7° (the "magic angle") with respect to the magnetic field, has been widely used, particularly for spin-1/2 nuclei such as ¹³C, ¹⁵N, ¹⁹F, ²⁹Si, and ³¹P, to diminish the broadening effects of chemical shift anisotropy and magnetic dipole-dipole coupling. High resolution spectra in complex solids have been obtained recently for ¹³C in biopolymers (5), for ²⁹Si in a zeolite (Fig. 1) (6), and for ¹⁵N in a protein (Fig. 2) (7), for example. Some recent advances in this area include development of fast MAS (with spinning speeds in excess of 20 kHz) (8), MAS in combination with multiple-pulse NMR (9), MAS with rotational resonance (10), and MAS with double resonance echoes (8). High-resolution structural information provided by NMR is generally short range in nature, and serves to complement the longer range periodicity to which diffraction techniques are sensitive. The ability to resolve structure over short distances is especially important for

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the study of polymers, amorphous materials, biological compounds, and other systems characterized by the absence of long-range order.

Sample spinning (at the magic and other angles) has also been applied to nuclei with spin $>1/2$, such as ^{11}B , ^{17}O , ^{23}Na , ^{27}Al , and ^{69}Ga , where an additional source of spectral broadening arises from anisotropic quadrupolar effects (12). Although some simplification and resolution can be achieved by combining MAS with quadrupolar nutation techniques (13) and by the use of oriented powders (14), second-order quadrupolar interactions often make it impossible to obtain NMR line widths sufficiently narrow to resolve the

Fig. 1. Room-temperature ^{29}Si magic-angle spinning NMR spectrum of the zeolite ZSM-5 obtained at a magnetic field of 9.4 Tesla. Most of the 24 crystallographically distinct Si sites in this highly siliceous polycrystalline sample are resolved. At higher temperatures the spectrum coalesces to one containing 12 peaks reflecting the transition to a structure with higher symmetry (14). The complexity of the structure is illustrated in the structural diagram of the (100) face of the ZSM-5 unit cell. [Adapted from (10) with permission; structural diagram courtesy of D. H. Olson, Mobil Research and Development Corp., Princeton, New Jersey]

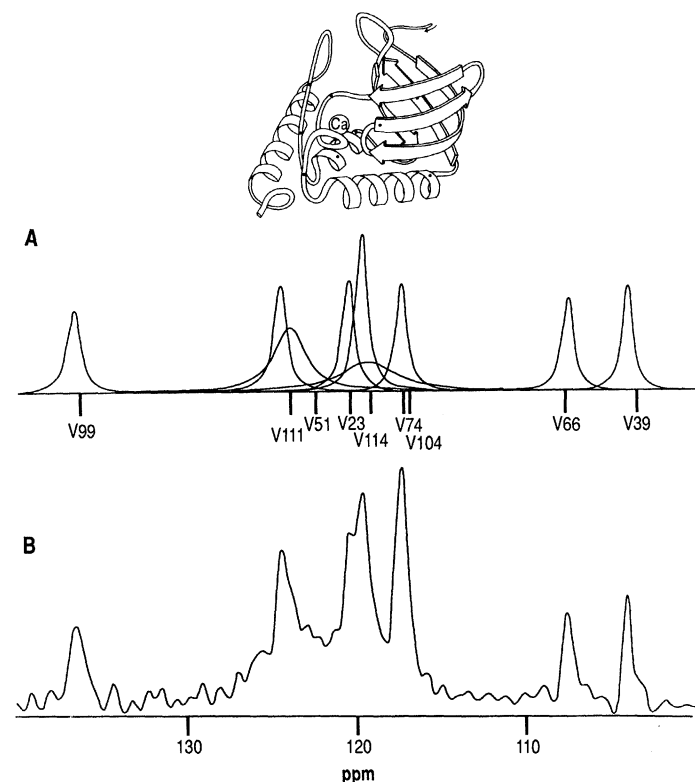
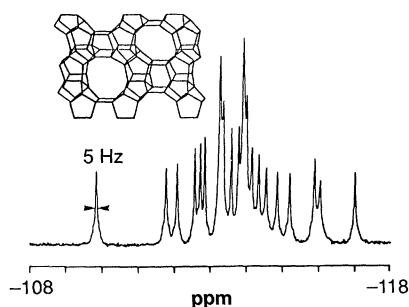


Fig. 2. Simulated (A) and experimental (B) cross-polarization-magic-angle spinning ^{15}N NMR spectra of wild-type staphylococcal nuclease in the solid state showing contributions from the nine inequivalent ^{15}N sites associated with valine residues in the protein structure (shown as black dots in the structural diagram at the top). The NMR spectrum of this protein in solution displays the same ^{15}N chemical shifts, indicating that the conformations are similar in solution and in the crystal. [Adapted from (11) with permission; structural diagram courtesy of J. S. Richardson, Duke University]

isotropic peaks necessary for unambiguous identification of different atomic sites. Second-order broadening can, however, be averaged with new sample reorientation techniques in which the sample is rotated about more than one axis (15). In double-rotation (DOR) NMR the sample rotates simultaneously about two axes inclined at two "magic angles" and thus follows a continuous trajectory that eliminates not only first-order effects, such as chemical shift anisotropy and secular dipole-dipole couplings, but second-order quadrupolar effects as well. In dynamic-angle spinning (DAS) NMR similar results are obtained by rotating the sample about two axes in succession. Recently demonstrated for ^{17}O in silicate minerals (Fig. 3) (16, 17), DOR and DAS make it possible to obtain spectra of improved resolution from many NMR-active nuclei of the periodic table. Such improvements in resolution now open the door to structural and motional investigations of a wide range of solid materials containing quadrupolar nuclei.

Multiple-Quantum and Overtone Spectroscopy

Whereas conventional Fourier transform NMR experiments involve transitions between spin levels differing by 1 in magnetic quantum number (the selection rule $\Delta m = 1$), there are at least two ways (Fig. 4) to extend NMR to transitions with $\Delta m \neq 1$. Additional structural and dynamical information can be obtained in such instances because the intensities and frequencies of the transitions depend on spin-spin couplings and on the relative orientations of internal and external magnetic fields. In liquid NMR, multiple-quantum spectroscopy is used routinely to filter transitions arising from groups of coupled spins and thereby to simplify considerably the interpretation of the resulting spectra (18). In solids and liquid crystals, multiple-quantum experiments, in which many quanta (more than 100) of radio-frequency energy can be coherently absorbed or emitted, have been used for studies of clustering and molecular conformations (19).

More recently, overtone NMR spectroscopy, involving absorption of single radio-frequency quanta at a multiple of the fundamental NMR frequency, has been used to determine distances and bond angles in molecules. For a quadrupolar nucleus, the parameters (for example, intensities and frequencies of transitions) extracted from

Fig. 3. Oxygen-17 NMR spectra (central transition) of the mineral cristobalite, SiO_2 , enriched to 37% in ^{17}O . (A) The static spectrum of a polycrystalline sample has a line width of 20 kHz. (B) Second-order quadrupolar interactions ($e^2qQ/h = 5.8$ MHz, $\eta = 0$) are incompletely averaged by magic-angle spinning, yielding a signal that is still about 4 kHz wide. (C) The dynamic-angle spinning (DAS) spectrum shows a narrowed (about 200-Hz line width) ^{17}O resonance at its isotropic shift, -16.7 ppm with respect to the ^{17}O resonance in enriched water. Spinning side bands accompany the isotropic peak at multiples of 2.5 kHz (one-half the rotor frequency); 1 ppm corresponds to 54.2 Hz for ^{17}O in a magnetic field of 9.4 Tesla. [Adapted from (17) with permission]

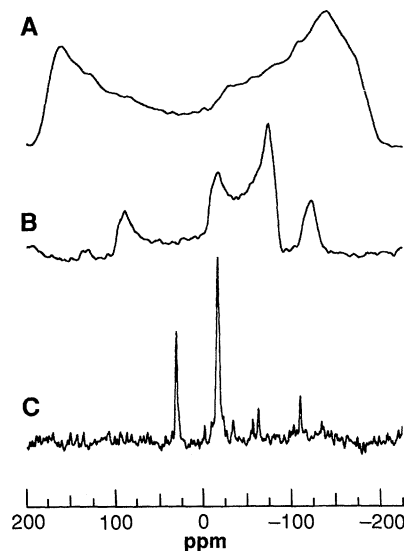
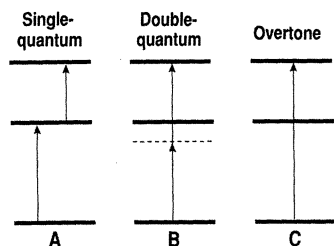


Fig. 4. Spin energy levels for a quadrupolar spin $s = 1$ nucleus, illustrating the transitions observed in different NMR experiments. (A) The conventional single-quantum transitions occur near the fundamental (Larmor) frequency. (B) The double-quantum transition connects the $m = 1$ and $m = -1$ levels by means of two quanta at the fundamental frequency. In multiple-quantum NMR, in general, transitions of higher order (Δm) can be involved. (C) Overtone NMR involves excitation or detection by means of a direct one-quantum transition with $\Delta m > 1$ near a multiple of the fundamental frequency. [Courtesy of S. J. Opella, University of Pennsylvania]



overtone spectroscopy are quite sensitive to the relative orientation of the internal and external fields in molecules or functional groups. Measurements of anisotropic spin interactions for ^{14}N in peptide linkages, for example, have been used to establish the relative orientations of individual peptide planes in single crystals of simple proteins (20). Recent work also has combined overtone spectroscopy with cross-polarization from proton spins to yield a substantial enhancement in the sensitivity of this technique in powdered samples (21). The application of multiple-quantum and overtone NMR should be valuable for studying molecular structures and organizations in polycrystalline and disordered samples.

Guest Atoms and Molecules in Porous Solids

Sorption, reaction, and thermal stability properties of porous solids are tied closely to the structure and function of the framework and guest materials. A relatively inert probe like xenon (with two NMR-active isotopes, ^{129}Xe and ^{131}Xe) can provide structural information about the host matrix and the symmetry of its internal cavities. The Xe atom has a high polarizability, which makes it sensitive to the intracrystalline environment of molecular sieves and other ordered porous materials. Interactions between Xe atoms and

Fig. 5. NMR spectra of ^{129}Xe occluded in the 0.57 nm and 0.75 nm diameter cavities of $136\text{SiO}_2 \cdot 16(\text{CH}_2)_4\text{O} \cdot 8\text{Xe}$ (dodecasil-3C). In the clathrasil pores, Xe atoms (0.44-nm diameter) interact with the cage wall; this interaction results in a downfield (higher frequency to the left) shift of the ^{129}Xe resonance relative to a low-pressure gaseous Xe reference. The line shapes reflect the symmetry of the cage environments at temperatures above and below the clathrasil phase transition at ~ 298 K. The upfield peak (spectral feature to the right) at 376 K (A) arises from Xe trapped inside the large cage structure; the line is narrow because of the cubic symmetry. The downfield ^{129}Xe line shape (spectral feature to the left) is dominated by the anisotropic chemical shift; the axial symmetry of the chemical shift is consistent with the threefold axis of the small cage. When the temperature is lowered to 251 K (B), the isotropic upfield peak is unchanged because no significant alteration occurs in the large cage structures. The resonance from Xe in the small cavities, however, changes to one characteristic of a shielding tensor that is not axially symmetric; this change indicates that in the small cavity, the environment of the confined ^{129}Xe probe has departed from axial symmetry. [Adapted from (23) with permission]

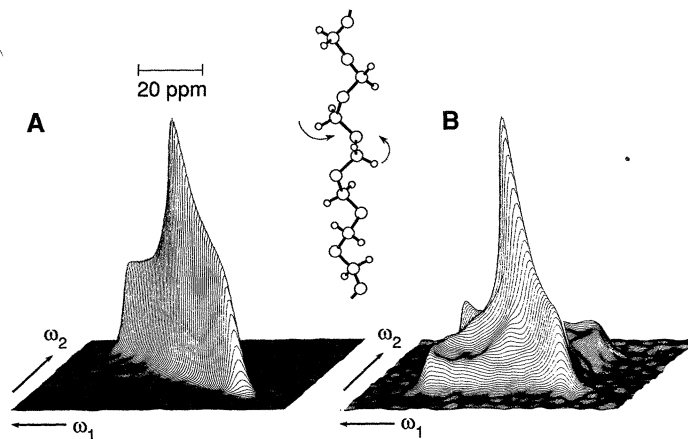
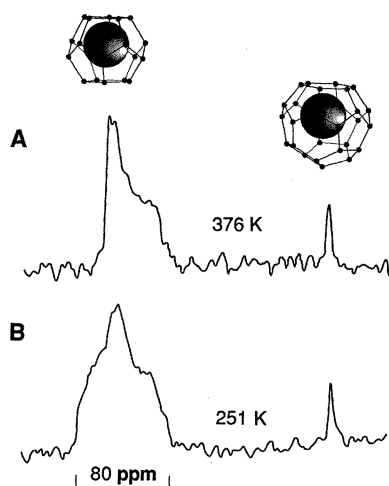


Fig. 6. Experimental two-dimensional ^{13}C NMR spectra of polyoxymethylene at 7.1 Tesla. Motions are measured by a two-dimensional correlation map of initial and final orientations separated by a mixing time t_m during which the molecular orientations change. (A) At 252 K, a spectrum along the two-dimensional diagonal is observed that indicates the absence of molecular reorientation on the time scale $t_m = 1$ s. (B) At 370 K, the effect of chemical exchange is observed in the form of an elliptical ridge pattern that reflects the symmetry of the reorientation process. Such sharp features are characteristic of discrete molecular jumps. Simulations of these spectra indicate that the carbon atoms undergo 200° rotational jumps during $t_m = 4$ s, consistent with rotational jumps of the helical polyoxymethylene structure. At later times, multiples of the fundamental rotational jumps occur. [Adapted from (30) with permission]

the host matrix perturb the Xe electron cloud, deshielding the nucleus and thereby expanding the range of the observed chemical shift. It is this large chemical shift range that permits subtle structural and chemical effects to be studied with high sensitivity (22).

Guest atoms and molecules introduced during synthesis or by adsorption are particularly useful in the study of intracrystalline environments in zeolites and clathrates. For example, Xe atoms can be used to probe porous solids because the ^{129}Xe NMR line shape varies in response to changes in the pore symmetry of the framework host (23, 23a). Xenon atoms are occluded in dodecasil-3C because they are too large to pass through the windows separating cavities in the clathrasil compound. Changes in the symmetry of the ^{129}Xe line shape allow temperature-dependent changes (for example, phase transitions) in clathrasil structure to be observed (Fig. 5). A remarkable example of such symmetry effects on a macroscopic scale is the appearance of quadrupolar splittings in the NMR spectrum of optically polarized ^{131}Xe gas in containers with shapes of less than cubic symmetry (24). The distribution and temperature-dependent properties of Xe clusters trapped in the pores of a zeolite has allowed careful study of gas-solid interaction (25). Dynamics of the guest molecules in a porous matrix have been investigated with proton NMR to study diffusivity within zeolite channels (26) and with deuterium NMR to probe motions of hydrocarbons in clathrate and zeolite cavities (27).

Chemical Exchange and Spin Diffusion

When molecules reorient (by continuous rotation or discontinuous jumps, for example) their NMR frequencies usually change. This is an example of what is generally referred to as chemical exchange. Similarly, frequencies can also be affected by spin diffusion between sites having different NMR parameters. By monitoring the correlation among frequencies in the different time dimen-

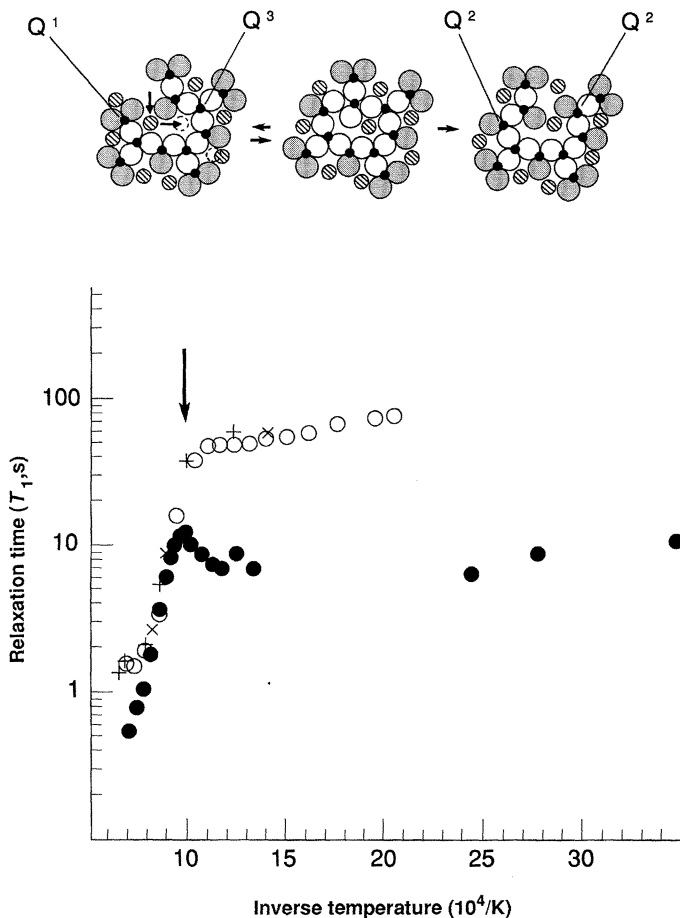


Fig. 7. Spin-lattice relaxation times (T_1) versus reciprocal temperature for ^{29}Si in albite glass at 4.2 and 9.4 Tesla. Temperatures in these studies approached 1500 K and special cooling features were required to permit in situ heating of the sample in the bore of the superconducting magnet. After radiofrequency excitation, ^{29}Si spins relax toward equilibrium because of interactions with local fluctuating fields. The relaxation times depend on atomic mobility, which changes during a phase transition. In the case of molten silicates, chemical exchange at elevated temperature modulates the ^{29}Si signal, thereby decreasing the relaxation time T_1 . The markedly different T_1 trends on each side of the glass transition (denoted by the arrow) reflect different motional behavior in the liquid and vitreous regimes of the mineral albite ($\text{NaAlSi}_3\text{O}_8$). The diagram at the top summarizes the diffusive dynamics that have been postulated to account for high-temperature silicate relaxation behavior. Shown are Si cations (black), alkali metal cations (cross-hatched), bridging oxygen atoms (unpatterned), and nonbridging oxygen atoms (shaded). Two Si sites with different numbers of bridging oxygens (Q^1) are interconverted during oxygen exchange. [Adapted from (39) with permission]

sions of a multidimensional NMR experiment (18, 28), it is possible to learn about the mechanisms and rates of reorientation and diffusion processes in solids. The mechanical properties of polymeric materials, for example, are closely related to microstructure and molecular reorientation dynamics. By means of two-dimensional spectroscopy applied to solid polymers, measurement of slow molecular reorientational motions and determination of the size of heterogeneous domains have been possible. The quadrupole coupling of deuterium and the anisotropic chemical shift of ^{13}C are particularly useful NMR interactions that have been used to probe the reorientation of molecular segments. The sensitivity of these interactions to orientation permits one to follow the molecular dynamics that influence polymer impact strength, flexibility, and thermal processing properties (Fig. 6) (29, 30). Different motional mechanisms, such as discrete reorientation jumps or angular diffu-

Fig. 8. Spin-echo NMR images of water in glass-reinforced epoxy polymer fibers. The polymer phase contains differing amounts of water in the samples shown: (from top to bottom) 5% (top), 10% (middle), and 20% (bottom) H_2O . The pixel resolution is $130\ \mu\text{m}$ in the 1-mm-thick slices taken along the length of the 5-mm-diameter fibers. The glass fibers are visible as the blue-white features. [Courtesy of W. Kuhn, Bruker Analytical Instruments Karlsruhe, Federal Republic of Germany]

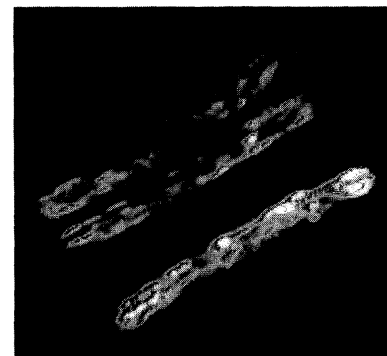
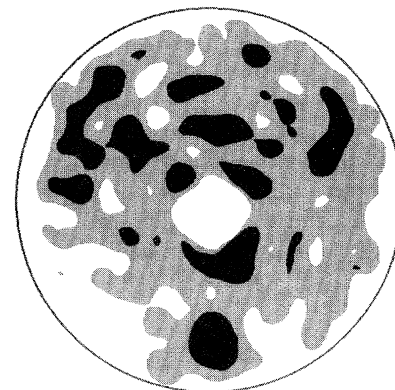


Fig. 9. Solid-state proton NMR image (pixel resolution $\approx 50\ \mu\text{m}$) of the polybutadiene component in a 1:1 polybutadiene-polystyrene blend cast from toluene. The sample is a solid disk 3.5 mm in diameter and 0.75 mm thick. The image shows variations in polybutadiene concentration in the disk ranging from regions devoid of polybutadiene (white) to regions of essentially pure polybutadiene (blue). It is clear that the immiscible polymer phases are not homogeneously mixed in this sample. [Adapted from (43) with permission]



sion, can be readily distinguished by analysis of the two-dimensional NMR lineshape.

In the well-known process of spin diffusion, nonuniform spin order (for example, magnetization) is transported through a solid by means of mutual spin "flip-flops" that can occur even in the absence of atomic or molecular motion. From measurements of the time required for the spin order to come to a uniform state, the size and intimacy of microstructural domains in a heterogeneous sample can be established. Proton spin diffusion experiments are useful for studying solid structures with domain sizes of up to 30 nm (the time required for spin diffusion to occur over these distances is typically on the order of 1 s). Such studies are particularly valuable when the domains are smaller than $\approx 5\ \text{nm}$, near the resolution limit of electron microscopy techniques. For example, the phase heterogeneities of polymer blends, block copolymers, semicrystalline polymers, and even natural polymers such as wood fall in this range and are thus amenable to study. Recent spin-diffusion experiments have aided in discerning 2.5-nm morphological heterogeneities in a 1:1 polybutadiene-polystyrene blend (31) and 1.0-nm domains in polysaccharide compounds (32). In cases where spin diffusion is slow, for example between inequivalent naturally abundant ^{13}C sites in an amino acid, it can be enhanced by rotational resonance (7, 33). In systems where spin diffusion and chemical exchange are both present, NMR with MAS and cross-polarization has been used to distinguish between competing polarization transfer dynamics (34). Finally, spin diffusion plays an important role in the distribution of spin order for polarized nuclear targets (35). Such polarized samples are also used to observe nuclear spin ordering (for example, antiferromagnetism) by means of spin-dependent scattering between neutrons and nuclei (36).

Experiments at High and Low Temperatures

When the temperature of a sample is varied, phase transitions and changes in molecular motion can be studied through their effects on spectra and relaxation times. At the extreme of low temperature, recent experiments have been performed on solids and adsorbed molecules at spin temperatures in the nanokelvin to millikelvin range (36, 37). At the other extreme, high-temperature capabilities (approaching 2000 K) have been combined with NMR to study dynamic behavior in otherwise rigid solids of interest in geology (38). As an example, static and MAS ^{29}Si NMR results from silicate melts and glasses at high temperature have provided a better understanding of microscopic processes that govern the macroscopic properties of magmas (Fig. 7) (39). The relation between NMR relaxation measurements and molecular melt dynamics can be used to investigate magma transport behavior, in particular the diffusive processes on the atomic scale that control crystal growth, crystal dissolution, and viscous flow. The close link between local diffusive motions, as manifested by ^{29}Si relaxation data, and bulk thermodynamic properties can be probed sensitively by the study of NMR parameters at elevated temperatures.

Imaging in Solid Materials

Mapping of NMR data into spatial images (magnetic resonance imaging and magnetic resonance microscopy) provides a noninvasive means of characterizing the internal structure of intact objects (40). Having been adopted for routine use in medicine, imaging techniques are now being extended to problems in materials science. Imaging techniques yield planar or three-dimensional pictures from selected regions of an object by measuring parameters such as nuclear spin density, chemical shift, or relaxation time in the presence of externally applied magnetic field gradients. This infor-

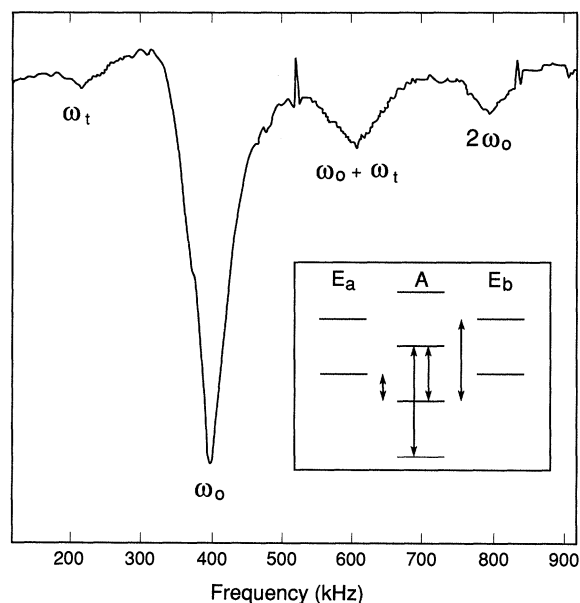


Fig. 10. Low-field (15 gauss) NMR spectrum of solid propionic acid, obtained at 4.2 K by direct detection with a dc-SQUID spectrometer and use of circularly polarized radio-frequency saturation. In addition to the NMR transitions at the Larmor frequency and twice the Larmor frequency (ω_0 and $2\omega_0$), absorption induced by quantum tunneling of the methyl group is observed (ω_t and $\omega_0 + \omega_t$). The peaks correspond to the transitions shown in the inset. The labels A, E_a , and E_b refer to the classification of the methyl proton spin states according to the irreducible representations of C_3 . [Adapted from (48) with permission]

mation is encoded and interpreted to transform spatially dependent NMR parameters into highly resolved images of complex solids or of fluids in solid materials. As in medical imaging methods, NMR can probe structural features in solids containing intercalated water by providing images of the spatial distributions of the mobile fluid (Fig. 8) (41).

The usual NMR imaging techniques, which are sensitive to fluids, are of little use for solid materials lacking mobile components. The spatial resolution in images of such solids is severely compromised by the effects of homonuclear dipole-dipole coupling and other anisotropic interactions. Multiple-pulse and sample spinning methods can diminish the effects of these interactions and enable images to be obtained for heterogeneous solid materials. Indeed, with such techniques, NMR images of rotating samples can be obtained (42) that provide spatial resolution in the range of 50 μm in solid polymer blends (Fig. 9) (43). Methods that employ sample spinning together with rotating field gradients are suitable for probing domains of chemical interest not amenable to acoustic or optical observation. Imaging of solid samples is now well under way with both multiple-pulse (static) and sample spinning NMR techniques (44).

Low Frequencies and Zero Field

Removal of the magnetic field typically present in a solid-state NMR experiment restores the isotropy of space, and many of the broadening effects are therefore absent. For this reason, dipolar couplings (which depend on intermolecular distances) in disordered samples can often be better studied at low or zero magnetic field. Several techniques are used to overcome the accompanying problem of low sensitivity, among them field cycling with magnetic field pulses (19, 45) and the use of a superconducting quantum interference device (SQUID) (46). For example, quantum tunneling of the methyl group in polycrystalline propionic acid can be detected directly: in a high field, the relevant NMR transitions are strongly forbidden by symmetry, but they have been observed indirectly by field cycling (47); with the use of a dc-SQUID spectrometer, however, methyl group tunneling is evident in a directly detected low-field NMR spectrum (Fig. 10) (48). Zero-field magnetic reso-

Fig. 11. Conventional high-field (A) and fictitious zero-field (B) proton NMR spectra of polycrystalline deuterated benzene (meta- $\text{C}_6\text{H}_2\text{D}_4$). In high-field NMR (A) spins are quantized in the direction of the external magnetic field, and a broad spectrum with no resolved dipole couplings between spins is produced. In the presence of a fictitious zero field (B), induced by rotating the sample and applying a synchronized sequence of pulses, the spins are effectively quantized along local fields in the rotating frame and the spectrum collapses to the characteristic zero-field, three-line pattern from which the proton dipolar couplings is easily determined. [Adapted from (51) with permission]

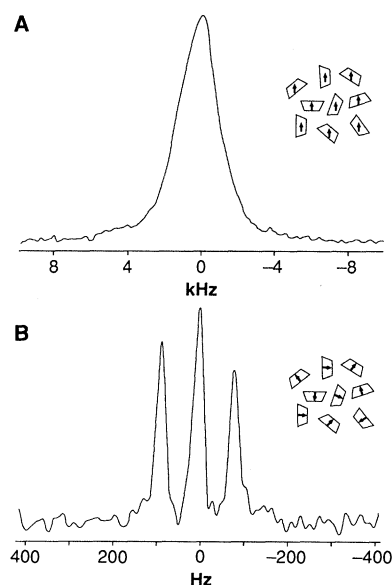
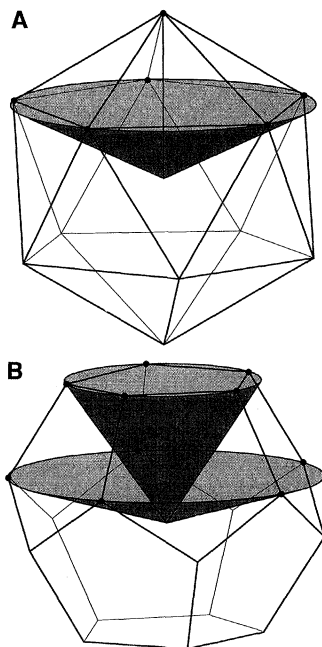


Fig. 12. Orientations of the magnetic field (with respect to a coordinate system fixed in the sample) over which the spherical harmonics (Y_{lm}) that characterize the transformations of first- and second-order NMR interactions are averaged away. Motions conforming to the 12 directions defined by the vertices of an icosahedron (**A**), or its 20 faces, the vertices of a dodecahedron (**B**), remove harmonics of ranks $l = 1, 2, 3, 4, 5, 7, 8, 9, 11, 13, \dots$. In the case that only even l values (for example, 2, 4, 8) need to be removed, the center of the icosahedral symmetry is unnecessary, and half of the directions suffice. These directions can be accommodated by discontinuous jumps or by continuous trajectories that involve rotations about two axes. Trajectories of this type can be employed for dynamic-angle spinning NMR (15–17) in which case the magnetic field reorients relative to the space coordinates of the sample, and for fictitious zero-field NMR (50) in which case the field reorients relative to both space and spin coordinates. [Adapted from (52) with permission]



nance is also sensitive to molecular reorientation through effects on lineshape and relaxation (49). Both pulsed-field cycling and SQUID detection should allow more widespread application of zero-field NMR and low-frequency nuclear quadrupole resonance to the study of solid materials by increasing the sensitivity to low-frequency transitions.

A recent alternative approach to zero-field NMR makes it possible to conduct experiments entirely in a high magnetic field by rapid sample reorientation together with a train of synchronously applied radio-frequency pulses (50). Such a “fictitious zero-field” experiment has the advantages of zero-field NMR (for example, the measurement of internuclear distances and radial distribution functions in amorphous and polycrystalline solids) but with the full sensitivity of high-field NMR (Fig. 11). Furthermore, this new method allows the study of materials with short relaxation times and preserves the isotopic selectivity of high-field NMR and thus permits the application of heteronuclear spin decoupling experiments and other selective spin excitation schemes not easily accomplished in zero field.

It has been pointed out (51, 52) that the optimal trajectories imposed on spin and spatial variables in fictitious zero-field NMR are identical to those involved in reorientation of the sample when second-order effects are removed by (say) double rotation or dynamic-angle spinning (15–17). In both cases, second- and fourth-rank tensors are being averaged. In dynamic-angle spinning the symmetry underlying the motional averaging is that of the icosahedral group. Icosahedral symmetry is relevant because, in the rotation group, only irreducible representations of dimensions $2l + 1$ with $l = 0, 6, 10, 12, \dots$ contain the totally symmetric (scalar) representation of the icosahedral subgroup. In order to realize this symmetry, motion involving at least six discrete orientations or rotation around two axes is necessary (Fig. 12). Symmetry considerations of this type offer exciting possibilities for multiple-pulse and iterative schemes (53), as well as for applications of NMR to study the high-rank tensor order parameters that characterize condensed systems such as blue phases (54) and icosahedral quasicrystals and glasses (55).

Conclusion

Modern NMR techniques are now able to produce images of the insides of intact objects, to probe structure, molecular order, and clustering in solids, and to monitor the effects of motion over an enormous range of time scales, from picoseconds to megaseconds. One of the primary challenges in the ongoing development of NMR as an analytical tool for solid materials is to increase sensitivity further. Traditionally, magnetic resonance signal intensities are low because of the low equilibrium spin polarizations at room temperature and the low frequencies (energies) of the electromagnetic radiation involved. Signal-to-noise limitations place constraints on the sizes of samples and the concentrations of species that can be studied, and also restrict the spatial resolution achievable by imaging. The recent exploitation of low-temperature spin polarization and superconductive detectors is one step in the direction of increased sensitivity. Other developments such as optical pumping and detection (24, 56) and the recent use of spin order arising from quantum symmetry (in pure parahydrogen, for example) (57) can contribute to the analytical capability of solid-state NMR. Perhaps we are closer to the ideal of observing single nuclear spins, an accomplishment recently reported for processing electron spins detected by means of a scanning tunneling microscope (58).

NMR continues to reverse the onset of rigor mortis and remains a lively area of research both in fundamental developments and in applications. We anticipate an exciting future in the study of a wide range of solid materials including polymers, catalysts, semiconductors, proteins, minerals, alloys, and ceramic superconductors. The possibility of correlating macroscopic material properties with microscopic structure and motion is one exciting outcome of continuing developments in the NMR of solids.

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"The greenhouse certainly seems to have its effect on Hobbs."