NMR of Solids

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Symbols

B_0	magnetic flux density
D	dipolar interaction tensor
$\mathscr{H}$	interaction Hamiltonian
p	order of multiquantum coherence
P_i	rotation about the i-axis
R	dipolar coupling constant
T_1, T_2	relaxation times
γ	nuclear gyromagnetic ratio
η	asymmetry parameter
ν_Q	quadrupole frequency
ν_L	Larmor resonance frequency
σ_{zz}	shielding constant
τ	time interval between pulses

Introduction

NMR spectra cannot normally be measured in solids in the same way in which they are routinely obtained from liquids. For example, the width of the ^{1}H NMR line in the spectrum of water is $\sim 1\,$Hz, while the line from a static sample of ice is $\sim 100\,$kHz wide. The reason for this is the existence of net anisotropic interactions which in the liquid are exactly averaged by the rapid thermal tumbling of molecules. A typical high-resolution spectrum of an organic compound in solution contains a wealth of information. The frequency of the radiation absorbed by the various non-equivalent nuclei in the molecule depends subtly on their chemical environments, giving rise to very sharp spectral lines. The parameters derived from such a spectrum (positions, widths, intensities and multiplicities of lines, relaxation mechanisms and rates) provide detailed information on the structure, conformation and molecular motion. This is not the case in a solid, where the nuclei are static and a conventional NMR spectrum is a broad hump which conceals most structural information. Although certain solids have sufficient molecular motion for NMR spectra to be obtainable without resorting to special techniques, we are concerned here with the general case, where there is no motion of nuclei and where conventional NMR, instead of sharp spectral lines, yields a broad hump which conceals information of interest to a chemist. Although the study of moments of such spectra and of various temperature-dependent parameters can still yield information on the degree of crystallinity, interatomic distances and molecular motion ('wide-line NMR'), we shall be primarily interested in ways of achieving high-resolution spectra, i.e. spectra which enable magnetically non-equivalent nuclei of the same spin species (e.g. ^{13}C) to be resolved as individual lines.

The interactions to be considered in the solid state and their Hamiltonians are as follows:

(1) Zeeman interaction with the magnetic field, $\mathscr{H}_Z$;
(2) chemical shielding, $\mathscr{H}_{CS}$;
(3) dipolar interaction, $\mathscr{H}_D$;
(4) J-coupling, $\mathscr{H}_J$;
(5) quadrupolar interaction, $\mathscr{H}_Q$.

The total Hamiltonian is a sum of all these contributions:

$$\mathscr{H} = \mathscr{H}_Z + \mathscr{H}_{CS} + \mathscr{H}_D + \mathscr{H}_J + \mathscr{H}_Q \qquad [1]$$

with the quadrupolar term $\mathscr{H}_Q$ non-zero only for nuclei with $I > \frac{1}{2}$. In general, $\mathscr{H}_Z$, $\mathscr{H}_{CS}$, $\mathscr{H}_D$ and $\mathscr{H}_Q$ are much larger than $\mathscr{H}_J$. J-Coupling is rarely observed in solids so that $\mathscr{H}_J$ will henceforward be neglected.

The interaction Hamiltonians have the general form

$$\mathscr{H} = \boldsymbol{I} \cdot \mathbf{A} \cdot \boldsymbol{S} = \begin{bmatrix} I_x & I_y & I_z \end{bmatrix} \begin{bmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yz} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{bmatrix} \begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix} \qquad [2]$$

where $\boldsymbol{I}$ and $\boldsymbol{S}$ are vectors and $\mathbf{A}$ is a second-rank Cartesian tensor. We shall consider the various interactions in turn.

The Zeeman Interaction

The Zeeman Hamiltonian, which determines the resonance frequency of an NMR-active nucleus in the magnetic field B_o, is

$$\mathscr{H}_Z = \boldsymbol{I} \cdot \boldsymbol{Z} \cdot \boldsymbol{B}_o \qquad [3]$$

where $\boldsymbol{Z} = -\gamma \hbar \mathbf{1}$, $\boldsymbol{I} = [I_x, I_y, I_z]$, $\boldsymbol{B}_o = [B_x, B_y, B_z]$ and $\mathbf{1}$ is a unit matrix. When the magnetic field is aligned with the z-axis of the laboratory frame of reference, $\boldsymbol{B}_o = [0, 0, B_o]$. The Zeeman interaction, which is directly proportional

to the strength of the magnetic field, is thus entirely under the operator's control.

Magnetic Shielding

The effect known as the chemical shift, central to the application of NMR in chemistry, is caused by simultaneous interactions of a nucleus with surrounding electrons and of the electrons with the static magnetic field B_o. The field induces a secondary local magnetic field which opposes B_o, thereby 'shielding' the nucleus from its full effect. The shielding Hamiltonian is

$$\mathscr{H}_{CS} = -\gamma\hbar \, \mathbf{I} \cdot \boldsymbol{\sigma} \cdot \mathbf{B}_o \qquad [4]$$

The shielding is anisotropic, which is quantified in terms of a second-rank tensor $\boldsymbol{\sigma}$ ('the chemical shielding tensor'):

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \qquad [5]$$

In strong magnetic fields $\boldsymbol{\sigma}$ is axially symmetric. When transformed into its principal reference system (PAS) by using rotation matrices, the tensor is described by three principal components $\boldsymbol{\sigma}_{ii}$ ($i = 1, 2, 3$):

$$\begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \xRightarrow{\text{Rotation}} \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$

and three direction cosines, $\cos\theta_i$, between the axes of PAS and the laboratory frame.

The observed shielding constant, σ_{zz}, is a linear combination of the principal components:

$$\sigma_{zz} = \sum_{i=1}^{3} \sigma_{ii} \cos^2\theta_i = \frac{1}{3}\text{Tr}\,\sigma + \frac{1}{3}\sum_{i=1}^{3}\left(3\cos^2\theta_i - 1\right)\sigma_{ii} \quad [6]$$

where $\text{Tr}\,\sigma$ stands for the trace of the tensor. Since the average value of each $\cos^2\theta_i$ is $\frac{1}{3}$, the average value of σ_{zz} in the NMR spectra of liquids (where there is random molecular tumbling) is the isotropic value:

$$\overline{\sigma_{zz}} = \tfrac{1}{3}\text{Tr}\,\sigma = \sigma_{iso} \qquad [7]$$

In solids the angle-dependent second term on the right of eqn [6] survives, giving rise to a spread of resonance frequencies, i.e. line broadening.

Dipolar Interactions

The Hamiltonian for the dipolar interaction between a pair of nuclei i and j separated by the internuclear vector $\mathbf{r}$ is given by

$$\mathscr{H}_D = R\mathbf{I}_i \cdot \mathbf{D} \cdot \mathbf{I}_j = R\begin{bmatrix} I_{ix} & I_{iy} & I_{iz} \end{bmatrix}$$
$$\times \begin{bmatrix} r^2 - 3x^2 & -3xy & -3xy \\ -3xy & r^2 - 3y^2 & -3yz \\ -3xz & -3yz & r^2 - 3z^2 \end{bmatrix} \begin{bmatrix} I_{jx} \\ I_{jy} \\ I_{jz} \end{bmatrix} \qquad [8]$$

where $R = \gamma_i\gamma_j\hbar\mu_o/4\pi\,r^3$ is the dipolar coupling constant, γ the nuclear gyromagnetic ratio and $\mathbf{D}$ the dipolar interaction tensor. In the PAS of the tensor, with the internuclear vector aligned along one of the coordinate axes, we have $xy = yz = zx = 0$, $r^2 = x^2 + y^2 + z^2$ and the tensor becomes

$$\mathbf{D} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad [9]$$

It is clearly traceless ($\text{Tr}\,\mathbf{D} = 1 - 2 + 1 = 0$).

The truncated dipolar interaction Hamiltonian may be written in the form

$$\mathscr{H}_D = \frac{\gamma_i\gamma_j\,\hbar^2}{2r^3}\left[\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{iz}\,I_{jz}\right]\left(3\cos^2\theta - 1\right) \qquad [10]$$

where θ is the angle between $\mathbf{r}$ and the external magnetic field $\mathbf{B}_o$. Since the average value $\overline{\cos^2\theta_{ij}} = \frac{1}{3}$, the isotropic average of the Hamiltonian is $\overline{\mathscr{H}_D} = 0$ so that the dipolar interaction does not affect the NMR spectrum in solution. In the solid the interaction remains, greatly increasing the spectral line width.

Quadrupolar Interactions

Some 74% of all NMR-active nuclei have $I > \frac{1}{2}$ so that, in addition to magnetic moment, they possess an electric quadrupole moment brought about by non-spherical distribution of the nuclear charge. The quadrupole interaction broadens and shifts the NMR lines, and also affects their relative intensities.

When the quadrupolar Hamiltonian is considered as a perturbation on the Zeeman Hamiltonian, there is no general analytical solution for the eigenvalues of $\mathscr{H}_Z$ in the (very rare) case when $\mathscr{H}_Z$ and $\mathscr{H}_Q$ are of comparable magnitude. When $\mathscr{H}_Q \gg \mathscr{H}_Z$, the splitting of the nuclear states is very large and 'pure quadrupole resonance' (NQR) is observed even in the absence of a magnetic

field. In the usual 'high field' case, $\mathscr{H}_Z \gg H_Q$, the quadrupole Hamiltonian in the PAS of the electric field gradient tensor is

$$\mathscr{H}_Q = \frac{e^2 qQ}{4I(2I-1)}\left[3I_z^2 - I^2 + \eta\left(I_x^2 - I_y^2\right)\right] \quad [11]$$

where η is the asymmetry parameter which describes the symmetry of the electric field gradient. The definitions of η and of the 'quadrupole frequency', v_Q, which describes the magnitude of the interaction, are

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \qquad v_Q = \frac{3e^2 qQ}{2I(2I-1)h} \quad [12]$$

Perturbation theory allows us to calculate the energy levels $E^{(0)}_m$, $E^{(1)}_m$ and $E^{(2)}_m$ (superscripts denote the order). Because of the first- and second-order shifts in energy levels, instead of a single (Larmor) resonance frequency $v_L = [E^{(0)}_{m-1} - E^{(0)}_m]$, as with spin-$\frac{1}{2}$ nuclei, there are now several resonance frequencies:

$$v_m = \frac{E_{m-1} - E_m}{h} = v_L + v_m^{(1)} + v_m^{(2)} \quad [13]$$

Detailed calculations reveal that:

(1) The first-order frequency shift is zero for $m = \frac{1}{2}$ so that the central transition for non-integer spins (such as ^{27}Al with $I = \frac{5}{2}$) is not affected by quadrupolar interactions to first order. It is thus advantageous to work with such nuclei, especially since the central transition is normally the only one which is observed: other transitions are so broadened and shifted as to be unobservable.
(2) The first-order shift is scaled by $\frac{1}{2}(3\cos^2\theta - 1)$.
(3) The second-order shift increases with v_Q^2 and is inversely proportional to the magnetic field strength. Since the dispersion of the chemical shift, which is what we normally wish to measure, is proportional to B_o, it is advantageous to work at high fields, where the chemical shift effects make the maximum contribution to the spectrum. As the second-order frequency shift is always present for all transitions, the feasibility of obtaining useful spectra depends on the magnitude of v_Q.

The very small quadrupole interactions of ^{2}H and their sensitivity to molecular motion at a wide range of frequencies make this integer spin nucleus very useful for chemical studies. ^{2}H NMR experiments normally use static samples, and dynamic information is extracted by comparing spectra measured at different temperatures with model computer simulations.

Magic-Angle Spinning

Magic-angle spinning (MAS) is by far the most powerful tool in solid-state NMR. The technique averages anisotropic interactions by acting on the factor $(3\cos^2\theta - 1)$ in the Hamiltonians, which in solids is not averaged to zero by rapid molecular motion. MAS was first introduced to deal with the dipolar interaction. It can be shown that when the sample is rapidly spun around an axis inclined at the angle β to the direction of the magnetic field, the time-averaged value of the angle θ, which an arbitrary internuclear vector makes with B_o, is

$$\overline{3\cos^2\theta - 1} = \tfrac{1}{2}\left(3\cos^2\beta - 1\right)\left(3\cos^2\chi - 1\right) \quad [14]$$

where χ, the angle between the internuclear vector and axis of rotation, is constant for each vector, because the solid is rigid. The result is that the term $\frac{1}{2}(3\cos^2\beta - 1)$ scales the spectral width, and that for $\beta = \cos^{-1}(1/\sqrt{3}) = 54.74°$ (the 'magic angle'), $\overline{3\cos^2\theta - 1} = 0$. The dipolar Hamiltonian in eqn [10] is averaged to zero.

For MAS to be effective, the sample must be spun at a rate greater than the static spectral width expressed in Hz. As the homonuclear ^{1}H–^{1}H interactions may lead to spectra which are as much as 50 kHz wide, it is not possible to spin the sample fast enough. Thus high-resolution solid-state ^{1}H spectra of most organic compounds, where protons are generally close together, cannot be obtained with the use of MAS alone, but require the additional use of multiple-pulse techniques (see below). However, MAS is successful in removing homonuclear interactions for ^{13}C, ^{31}P and nuclei of small gyromagnetic ratios.

The chemical shift anisotropy is also reduced by MAS, because the tensor interactions controlling all anisotropic interactions in solids all have a common structure and may be expressed in terms of Wigner rotation matrices which are scaled by MAS.

High-Power Decoupling

When dilute spins, such as ^{13}C, interact via the dipolar interaction with ^{1}H or other abundant nuclei, the large heteronuclear broadening of an already low-intensity spectrum is a considerable problem. High-power decoupling, used to remove heteronuclear coupling effects, applies a continuous, very highpower pulse at the ^{1}H resonance frequency in a direction perpendicular to B_o. The ^{13}C pulse is then applied, and the ^{13}C free induction decay measured while continuing the ^{1}H irradiation. The powerful decoupling pulse stimulates rapid ^{1}H spin transitions, so rapid that the ^{13}C spins experience only the time-average of the ^{1}H magnetic

moment, i.e. zero. Since the technique relies on selective excitation of the abundant and dilute nuclei, it can only remove heteronuclear interactions.

Cross-Polarization

Dilute nuclei, such as ^{13}C and ^{15}N, are more difficult to observe than abundant nuclei, such as ^{1}H or ^{31}P, particularly when they also have a low gyromagnetic ratio. However, the dilute and abundant nuclei are often in close proximity, and coupled via the dipolar interaction. Cross-polarization (CP) exploits this interaction to observe dilute nuclei, at the same time overcoming two serious problems often encountered in solid-state NMR: (i) because of a very small population difference in the polarized sample, NMR actually observes very few dilute spins and consequently the sensitivity of the experiment is low; (ii) spin–lattice relaxation times of spin-$\frac{1}{2}$ nuclei in solids are often very long so that long delays are required between experiments and the spectral signal-to-noise ratio is poor.

The sequence of events during the ^{13}C–^{1}H CP experiment is as follows. After the end of the 'preparation period', during which the sample polarizes in the magnetic field, a $\pi/2$ pulse is selectively applied to ^{1}H along the x-axis of the rotating frame, aligning the ^{1}H magnetization with the y-axis. A long pulse of amplitude B_{1H} is then applied along the y-axis. Since the ^{1}H magnetization is now aligned with the effective field in the rotating frame, it becomes 'spin locked' along this direction. At the same time, a long pulse of amplitude B_{1C} is selectively applied to ^{13}C along the x-axis. The amplitudes B_{1H} and B_{1C} are adjusted so as to satisfy the Hartmann–Hahn condition:

$$\gamma_H\,B_{1H} = \gamma_C\,B_{1C} \qquad [15]$$

The energies of ^{1}H and ^{13}C in the rotating frame are thus equal, and the two spin reservoirs can transfer magnetization in an energy-conserving manner during the 'contact time'. Finally, the ^{13}C radiofrequency field is turned off and a free induction decay observed in the usual way. During the observation time the ^{1}H field is still on, but serves as the high-power decoupling field to reduce the ^{1}H–^{13}C dipolar broadening.

Detailed arguments show that the magnetization of ^{13}C nuclei is theoretically increased by the factor of $\gamma_H/\gamma_C \approx 4$. After the ^{13}C free induction decay signal has been measured, the magnetization of carbons is again almost zero, but the loss of proton magnetization is small. The CP experiment can be repeated without waiting for the carbons to relax. The only limitations are the gradual loss of polarization by the ^{1}H spin reservoir, and the decay of the ^{1}H magnetization during spin locking. The latter process proceeds on a time-scale ('spin–lattice

relaxation in the rotating frame') which is much shorter than the ^{13}C spin–lattice relaxation time.

Multiple-Pulse Line Narrowing

Although homonuclear dipolar couplings are in principle removable by MAS, with abundant nuclei they are often very strong. For example, the removal of the ^{1}H–^{1}H interaction in most organic compounds requires spinning rates far in excess of what is practically feasible. The alternative to MAS is to manipulate the nuclear spins themselves using 'multiple-pulse line narrowing' so as to average the dipolar interaction. The method uses specially designed sequences of pulses with carefully adjusted phase, duration and spacing. The result is that, when the signal is sampled at a certain moment during the sequence, the dipolar interaction is averaged to zero.

WAHUHA, the simplest multiple pulse sequence, is composed of four 90° pulses:

$$\left(P_x - 2\tau - P_{-x} - \tau - P_y - 2\tau - P_{-y} - \tau\right)n \text{ times} \quad [16]$$

where P_i represents rotation about the particular i-axis of the rotating frame and τ is the time interval between pulses. Over the sequence, the magnetic moments spend equal amounts of time along each of the three principal axes. The NMR signal is sampled in one of the 2τ windows. Sequences have been developed involving from 4 to as many as 52 pulses. The entire sequence must be short relative to the relaxation time T_2, and the pulses themselves must also be very short.

Multiple pulse sequences not only average the dipolar Hamiltonian but also affect other Hamiltonians to an extent which depends on the particular sequence. For example, the WAHUHA sequence scales chemical shift anisotropies by a factor of $1/\sqrt{3}$.

Moments of an NMR Line

Even when the dipolar ^{1}H–^{1}H interaction is not removed from the spectrum, the method of moments can provide important structural information. The mth moment of the line shape $f(\omega)$ about ω_0 is defined as

$$M_n = \frac{\displaystyle\int_0^\infty (\omega - \omega_0)^n f(\omega)\,d\omega}{\displaystyle\int_0^\infty f(\omega)\,d\omega} \qquad [17]$$

where

$$M_0 = \int_0^\infty f(\omega)\,d\omega$$

is the area under the line (the zeroth moment). For a normalized function, $M_0 = 1$. The second moment is

physically analogous to the moment of inertia of an object with the same shape as the line. If $f(\omega)$ is an even function of ω, $M_n = 0$ for all odd values of n. It is convenient to calculate moments about the centre of gravity of the line shape, i.e. the value of ω_0 for which the first moment is zero.

The second moment can be calculated from the interatomic distances in the solid containing pairs i, j of dipolar-coupled nuclei. Van Vleck has shown that, for a polycrystalline powder composed of randomly oriented crystals in which we observe identical spin-$\frac{1}{2}$ nuclei, the second moment is

$$M_2^{\text{homo}} = \frac{9}{16} \gamma^4 \hbar^2 \left(\frac{\mu_0}{4\pi}\right)^2 \sum_j \frac{1}{r_{ij}^6} \qquad [18]$$

while for pairs of unlike nuclei the second moment is different:

$$M_2^{\text{hetero}} = \frac{1}{4} \gamma_i^2 \gamma_j^2 \hbar^2 \left(\frac{\mu_0}{4\pi}\right)^2 \sum_j \frac{1}{r_{ij}^6} \qquad [19]$$

Thus, even when the interacting nuclei have very similar gyromagnetic ratios, the homonuclear second moment is larger by a factor of $\frac{9}{4}$ than the heteronuclear moment. This is because dipolar coupling between unlike spins cannot lead to an energy conserving mutual spin flip. The second moment is thus very sensitive to the kind of neighbour.

The method of moments has further advantages. First, since the second moment is inversely proportional to the sixth power of the internuclear distance, it is a very sensitive means of determining interatomic distances. Second, it can provide insights into the structure. For example, it was used to demonstrate the presence of groups of three equivalent protons in solid hydrates of strong acids, thus proving the presence of hydronium ions, H_3O^+. Third, it is useful for the study of motion, because the moments are dramatically reduced when the dipolar interaction is partly or completely averaged out by an onset of a specific motion.

DOR, DAS and MQ-MAS

We have seen that the second-order quadrupolar interaction, which affects all quadrupolar nuclei, is reduced, but not removed, by MAS. Its complete removal is clearly of importance in solid-state NMR. Three different techniques have been proposed to achieve this aim.

When the second-order quadrupole interaction is expanded as a function of Wigner rotation matrices, and we consider the case of a sample rapidly rotated about an angle β with respect to B_o, the average second-order quadrupolar shift of the central transition becomes

$$\nu_{\frac{1}{2}}^{(2)} = \frac{\nu_Q^{(2)}}{\nu_L}\left[I(I+1) - \frac{3}{4}\right][A_0 + B_2 P_2(\cos\beta) \\ + B_4 P_4(\cos\beta)] \qquad [20]$$

where ν_Q is the quadrupole frequency, ν_L is the Larmor frequency, A_0 and B_0 are constants and the $P_n(\cos\beta)$ terms are the Legendre polynomials

$$P_2(\cos\beta) = \tfrac{1}{2}(3\cos^2\beta - 1)$$

$$P_4(\cos\beta) = \tfrac{1}{8}(35\cos^4\beta - 30\cos^2\beta + 3) \qquad [21]$$

There is no value of β for which both the $P_2(\cos\beta)$ and the $P_4(\cos\beta)$ terms can be zero so that the angle-dependent terms cannot be averaged by spinning about a single axis. Instead, in the ingenious 'double-rotation' (DOR) experiment the sample is spun *simultaneously* about two different axes β_1 and β_2 so that

$$P_2(\cos\beta_1) = 0 \qquad P_4(\cos\beta_2) = 0 \qquad [22]$$

with solutions $\beta_1 = 54.74°$ (the conventional magic angle) and $\beta_2 = 30.56$ or $70.12°$. As a result, only the A_0 term remains in eqn [20]. This is accomplished by a rotor-within-a-rotor probehead in which the centres of gravity of the two rotors, each spinning at a different angle with respect to B_o, exactly coincide. Although the daunting engineering problems posed by the design of a DOR probehead have been overcome, it is very difficult to spin the two rotors simultaneously at sufficiently high spinning speeds, and the spinning rates are limited to ~ 6 and $1\,\text{kHz}$ for the inner and outer rotors, respectively, compared with $\sim 30\,\text{kHz}$ achievable with MAS. This is an unfortunate limitation, since multiple spinning sidebands appear in the spectra if the rate of the rotation is lower than the strength of the quadrupolar interaction.

The technique known as 'dynamic-angle spinning' (DAS) adopts an alternative approach to DOR: the sample is rotated *sequentially* about two different axes, β_1' and β_2', which are chosen so that

$$P_2(\cos\beta_1') = -P_2(\cos\beta_2') \\ P_4(\cos\beta_1') = -P_4(\cos\beta_2') \qquad [23]$$

with the solutions $\beta_1' = 37.38°$ and $\beta_2' = 79.19°$. The rotation axis is switched very rapidly, which poses technical problems, given that the minimum time required for changing the spinning angle must be shorter than the relaxation time of the nucleus being observed. As a result, DAS often cannot be applied to many nuclei, including ^{27}Al, and is limited to the study of nuclei with long relaxation times (for example in amorphous samples, such as glasses).

Yet another solution to the problem, known as 'multiple-quantum magic-angle spinning' (MQ-MAS), relies on the fact that B_2 and B_4 are functions of I, p, η, α and β, where p is the order of the multiquantum coherence and α and β are the Euler angles corresponding to the orientation of each crystallite in the powder with respect to the rotor axis. Under fast MAS, the chemical shift anisotropy, heteronuclear dipolar interactions and the term proportional to P_2 in eqn [20] are removed so that

$$v_{\frac{1}{2}}^{(2)} = \frac{v_Q^{(2)}}{v_L}\left[I(I+1) - \frac{3}{4}\right]\left[A_0 + B_4 P_4(\cos 54.74°)\right] \quad [24]$$

Although the second term, proportional to P_4, still causes substantial line broadening, it can be eliminated by using

p-quantum transitions. A p-quantum transition (with $p = 3$ or 5 for ^{27}Al) is excited and the signal allowed to evolve during time t_1. As multiple quantum transitions are not directly observable by NMR, a second pulse converts the signal into a single-quantum transition, which is observable. The technique enables a two-dimensional representation of the spectra, with a regular increment of t_1 providing a 'p-quantum dimension', free of quadrupolar interactions. Although the optimal conditions for MQ-MAS are difficult to establish, the technique is being increasingly used for the study of quadrupolar nuclei of half-integer spin, such as ^{27}Al, ^{85}Rb, ^{23}Na, ^{11}B and ^{93}Nb.

Note that DOR, DAS and MQ-MAS do not remove the A_0 term in eqns [20] and [24]. Thus the position of
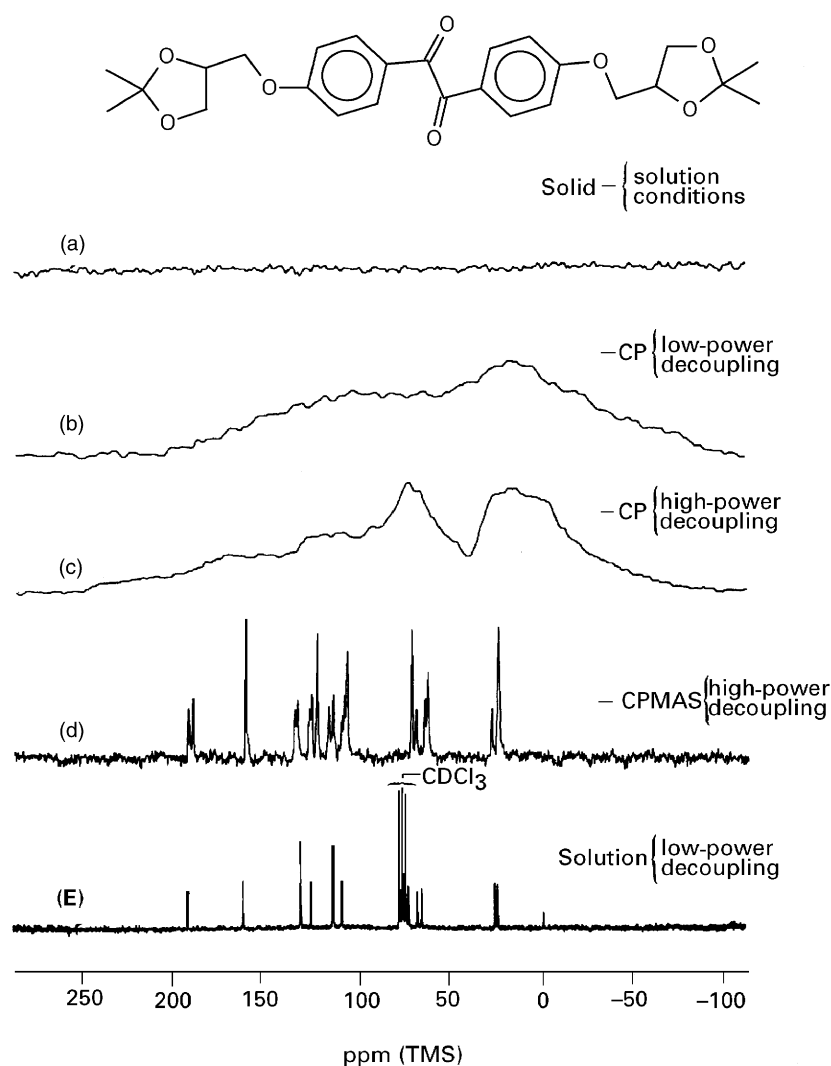
Figure 1 ^{13}C NMR spectra of solid 4,4'-bis[(2,3-dihydroxypropyl)oxy]benzil. (a) Solution conditions using 60° ^{13}C pulses and 10 s recycle delays; (b) as in (A) but with 1H–^{13}C cross-polarization, low-power proton decoupling and 1 s recycle delays; (b) as in (b) but with high-power proton decoupling; (d) as in (c) but with the addition of magic-angle spinning; (e) high-resolution spectrum of a solution in CDCl$_3$ with the same NMR parameters. Reproduced with permission of the American Chemical Society from Yannoni CS (1982) *Accounts of Chemical Research* **15**: 201–208. Copyright 1982 American Chemical Society.

the line in the spectrum, however narrow, does not correspond to the pure chemical shift, but includes the effect of the quadrupole interaction.

Modern Solid-State NMR

Magic-angle spinning has greatly enhanced our knowledge of a wide range of materials used in chemical, physical, biological and earth sciences and in the technology of glass and ceramics. It took nearly twenty years, since its discovery in 1958, for MAS to become a routine tool of structural investigation. The reasons were the difficulty of spinning the sample at the very high speeds required and the insufficiently high magnetic fields. However, the introduction of Fourier-transform NMR, cross-polarization and superconducting magnets during the 1960s and 1970s greatly improved the sensitivity of the spectra and enabled virtually all NMR-active nuclei to be observed in solids. ^{1}H MAS NMR was used to examine polymers as early as 1972, and Schaefer and Stejskal were the first to combine CP and MAS in ^{13}C NMR studies of organics. Much important work, at first mostly with ^{13}C but later with other nuclei, has been done since. Since the early 1980s great progress has been made in the study of ^{29}Si and ^{27}Al in natural and synthetic molecular sieve catalysts and minerals, which is particularly significant since nearly a half of all known minerals are silicates or aluminosilicates.

High-resolution spectra of solids are now routinely obtained using a combination of CP and MAS (see **Figure 1**), and it is fair to say that CP-MAS has revolutionized materials science. The otherwise weak signals from dilute nuclei (such as ^{13}C or ^{29}Si) are enhanced by cross-polarization, heteronuclear dipolar interactions are removed by high-power decoupling, chemical shift anisotropy and the weak dipolar interactions between dilute nuclei are averaged by fast MAS, and the signal-to-noise ratio is increased further, thanks to the more frequent repetition of the experiment and the availability of high magnetic fields. Although the line widths in such high-resolution spectra are still greater than those measured in liquids, the various non-equivalent nuclei can in most cases be separately resolved.

See also: ^{13}C NMR, Methods, ^{13}C NMR, Parameter Survey, High Resolution Solid State NMR, ^{1}H, ^{19}F, High Resolution Solid State NMR, ^{13}C, Magnetic Field Gradients in High Resolution NMR, NMR in Anisotropic Systems, Theory, NMR Principles, NMR Pulse Sequences, Polymorphism Studied by Solid-state NMR, Solid State NMR, Methods, Solid State NMR Using Quadrupolar Nuclei, Solid State NMR, Rotational Resonance.

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