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MAGIC ANGLE SPINNING

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ABSTRACT

Rapid specimen rotation about an axis inclined at the magic angle of $54^{\circ} 44'$ to the direction of the applied magnetic field can remove many sources of broadening from the NMR spectrum of a solid and enable finer features to be revealed.

The review commences with a discussion of the basic principles of magic angle spinning and an examination of the effects on magnetic dipolar interactions, the chemical shift interaction, pseudo-dipolar interactions and electric quadrupolar interactions. The anisotropic parts of these interactions are removed from the central spectrum and appear as spinning sidebands. The interactions that remain are the isotropic shifts and J couplings as in isotropic fluids; however some essential differences between solids and fluids remain.

Examples of the effects of magic angle spinning on a variety of interactions and materials are given. When applied to metals the anisotropy of Knight shift is removed, isotropic Knight shifts may be measured with precision, and the Ruderman–Kittel interaction may be determined in the presence of much larger dipolar interactions. The effects of spinning on homogeneous and inhomogeneous spectra are distinguished. Sources of residual broadening are identified and discussed.

Magic angle spinning may be used on its own, and may also be successfully combined with other line-narrowing techniques. Examples are given of the combination of magic angle spinning with multiple pulse methods to obtain high-resolution NMR spectra, especially of protons, from solids. The combination of magic angle spinning with cross-polarization has been particularly fruitful in enabling high-resolution NMR spectra to be obtained for ^{13}C and other nuclei in polycrystalline and amorphous specimens, including polymers, peptides, proteins and viruses. Magic angle spinning has also been used in combination with multiple quantum NMR to remove residual broadening from chemical shift anisotropy in ^2D spectra.

Finally a section is devoted to turbines for spinning specimens at high speeds about the magic axis.

1. INTRODUCTION

It is a well-known and highly characteristic feature of nuclear magnetic resonance (NMR) that the spectral lines from liquid specimens are very much narrower than those from solids. An immediate example is provided by water whose proton NMR response is of the order of 0.1 Hz wide at room temperature, while that from ice at low temperatures is of the order of 10^5 Hz, a million times broader. This very substantial difference in behaviour arises from the static anisotropic interactions to which the nuclei are subjected in the solid state. By contrast, in fluids the rapid isotropic motions of the nuclei average the anisotropic interactions and effectively remove them from the spectrum. Consequently a rich

high-resolution NMR spectrum is often revealed which is of great value in the structural and dynamic analysis of molecules and is now a standard spectroscopic technique in all chemical laboratories.

At first sight it might therefore seem that applications of high-resolution NMR spectroscopy are inevitably confined to liquid specimens. Such a restriction would be a serious limitation since there are an enormous number of solid materials which cannot be examined in the liquid state either because they will not dissolve in any suitable solvent, or do not melt without decomposition, or significantly change their structure in the liquid state. Consequently, there has been great interest in pursuing ways in which high-resolution NMR spectra might be obtained from solid specimens also.

First of all we may notice that a solid does not present a completely rigid atomic architecture. Often in the solid state there is sufficient motion of the nuclei to narrow the NMR spectra substantially, and sometimes the spectrum is sufficiently narrowed to resolve a high-resolution NMR spectrum. An example is the ^{31}P NMR spectrum of polycrystalline P_4S_3 at 420 K, which is 26 K below its melting point, shown in Fig. 1 (Andrew *et al.*, 1974c, 1978). An AB_3 spectrum is resolved, the doublet arising from the three basal phosphorus nuclei in the molecule and the quartet coming from the apical nuclei. The J coupling constant and the chemical shift separation were determined. At 420 K the P_4S_3 molecules are performing rapid isotropic reorientations and are diffusing from site to site fast enough to give the lines a liquid-like narrowness.

Although in more general cases sufficient motion is not present in solids to narrow the NMR lines, we may try to emulate nature by imposing a motion on the nuclei. This was first done by rapidly spinning the solid specimen (Andrew, Bradbury and Eades, 1958a,b, 1959; Andrew, 1959; Lowe, 1959). As we shall see later this is most completely effective when the angle between the spinning axis and the applied magnetic field has the 'magic' value $54^\circ 44'$. By this means substantial narrowing of NMR lines from solids was achieved and the first spin multiplets from solid specimens were resolved (Andrew, Farnell and Gledhill, 1967).

Several years later an alternative approach was developed to NMR line narrowing in solids by imposing a motion on the nuclei in spin space with a suitable sequence of resonant pulses (Mansfield and Ware, 1966; Ostroff and Waugh, 1966). At one time the two

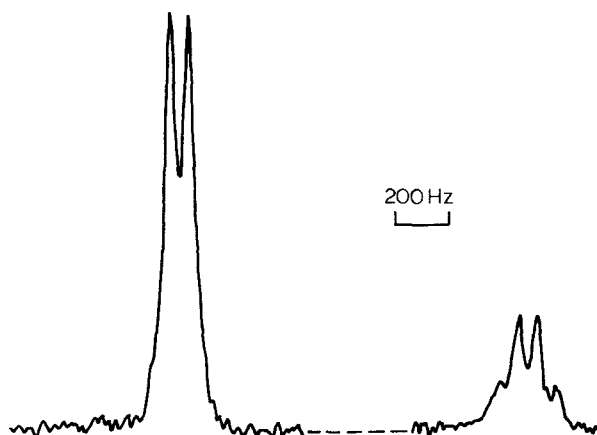


FIG. 1. ^{31}P NMR spectrum of polycrystalline P_4S_3 at 420 K (melting point 446 K). The spectrum is strongly narrowed by molecular motion in the solid and displays an AB_3 type fine structure (Andrew, Hinshaw and Jasinski, 1974c).

techniques of magic angle spinning and multiple pulse irradiation were seen as competitive approaches, but now they are seen very much as complementary methods. Multiple pulse methods do not remove line broadening which arises from anisotropic chemical shift interactions, but, as we shall see later, magic angle spinning does. Consequently for polycrystalline and amorphous materials, which cover most solid materials of practical interest, sharp highly-resolved NMR spectra, comparable with those from fluids, can only be obtained with the use of magic angle spinning which removes anisotropic sources of broadening which resist averaging in spin space.

Another important development has been the use of cross-polarization methods to provide high-resolution NMR spectra of rare spins such as ^{13}C , ^{15}N and ^{29}Si in solids (Pines, Gibby and Waugh, 1972). Under strong irradiation the magnetization of abundant spins in the solid, for example protons, is transferred to the rare spins and their heteronuclear anisotropic interactions are suppressed. Because the rare spins are so dilute their homonuclear dipolar and other interactions are weak. Nevertheless in polycrystalline and amorphous materials substantial broadening due to anisotropic shift interactions remains. Here again high-resolution NMR spectra from solid specimens is only obtained by the addition of magic angle spinning of the specimen.

More recently it has been shown that multiple-quantum NMR spectra, for example of ^2D in polycrystalline samples, have a residual breadth arising from chemical shift anisotropy (Eckman *et al.*, 1980b). These residual sources of broadening may be removed rather simply by magic angle spinning, and thus we are provided with another avenue for high-resolution NMR spectroscopy from solid specimens.

Thus high-resolution NMR spectra may be obtained from polycrystalline and amorphous specimens either by magic angle spinning alone, or by magic angle spinning in combination with multiple-pulse irradiation, in combination with cross-polarization double-resonance procedures, or in combination with multiple-quantum spectroscopy. For these reasons modern commercial NMR spectrometers for work with solids nowadays include a magic angle spinning facility as an essential part of their operation.

In this paper we set out the essential features of magic angle spinning. Examples will be given of its effectiveness in NMR line-narrowing when used alone, and when used in conjunction with the other techniques just mentioned. Earlier reviews of magic angle spinning and its effects in solid state NMR have been given by Andrew (1970, 1971, 1975); the subject is also discussed in the books on high-resolution NMR in solids by Haeberlen (1976) and by Mehring (1976). At a recent Royal Society meeting in London (18 to 19 June 1980) on NMR Spectroscopy in Solids, the proceedings of which were published in *Phil. Trans. Roy. Soc. A*, 299 (1981), a number of papers were concerned directly or indirectly with magic angle spinning (Andrew, 1981; Gerstein, 1981; Griffin *et al.*, 1981; Schaefer *et al.*, 1981; Garroway, VanderHart and Earl, 1981; Balimann *et al.*, 1981; Opella *et al.*, 1981).

The anisotropic nuclear interactions which are of interest in solid-state NMR spectroscopy are the following:

1. Direct magnetic dipolar: (a) homonuclear
(b) heteronuclear
2. Indirect electron-coupled: (a) homonuclear
(b) heteronuclear
3. Electron quadrupolar (for nuclei with spin $I > \frac{1}{2}$)
4. Electron shielding (chemical shift, Knight shift).

Consideration will now be given to the effect of magic angle spinning on each of these interactions.

2. MAGIC ANGLE SPINNING AND DIPOLAR INTERACTIONS

We begin by examining the effect of rapid specimen rotation or nuclear magnetic dipolar interactions since these interactions are always present to some degree and were historically the first to be considered and removed; moreover this gives good insight into the operation of the method.

The truncated dipolar interaction Hamiltonian, for all nuclear pairs i, j in a solid, both like and unlike, is given by (Abragam 1961):

$$\mathcal{H}_D = \sum_{i < j} \frac{1}{2} \gamma_i \gamma_j \hbar^2 r_{ij}^{-3} (\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{iz} I_{jz}) (3 \cos^2 \theta_{ij} - 1), \quad (1)$$

where γ_i, γ_j are the nuclear gyromagnetic ratios, \mathbf{r}_{ij} is the internuclear displacement, and θ_{ij} is the angle between \mathbf{r}_{ij} and the Zeeman field \mathbf{H}_0 , which is directed along the z -axis in the laboratory frame of reference. The NMR spectrum is in principle calculated by treating \mathcal{H}_D as a perturbation on the Zeeman term \mathcal{H}_Z , where:

$$\mathcal{H}_Z = - \sum_i \gamma_i \hbar \mathbf{I}_i \cdot \mathbf{H}_0. \quad (2)$$

Since the isotropic average $\overline{\cos^2 \theta_{ij}} = \frac{1}{3}$, it follows from (1) that the isotropic average of the dipolar Hamiltonian $\overline{\mathcal{H}_D} = 0$, and rapid isotropic motion in fluids therefore eliminates the dipolar interaction from the NMR spectrum.

If we take a solid specimen, whether monocrystalline, polycrystalline or amorphous, and rotate it uniformly with angular velocity ω_r about an axis inclined to \mathbf{H}_0 at angle β , every internuclear vector \mathbf{r}_{ij} in the solid describes a motion illustrated in Fig. 2. The angle θ_{ij} becomes time-dependent, and the factor $(3 \cos^2 \theta_{ij} - 1)$ in (1) runs through a range of values which may be either positive or negative. Its average value may be made zero by judicious choice of β .

Expressing $\cos \theta_{ij}$ in terms of other angles of the system:

$$\cos \theta_{ij} = \cos \beta \cos \beta'_{ij} + \sin \beta \sin \beta'_{ij} \cos (\omega_r t + \phi_{oij}) \quad (3)$$

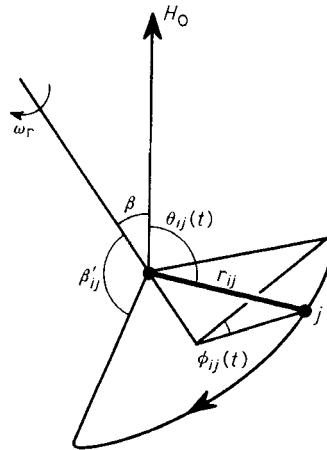


FIG. 2. Diagram illustrating the motion of a typical inter-nuclear vector \mathbf{r}_{ij} when a solid is rotated with angular velocity ω_r about an axis inclined at angle β to \mathbf{H}_0 .

we find after rearrangement that:

$$\mathcal{H}_D(t) = \sum_{i < j} \frac{1}{2} \gamma_i \gamma_j \hbar^2 r_{ij}^{-3} (\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{iz} I_{jz}) \left[\frac{1}{2} (3 \cos^2 \beta - 1) (3 \cos^2 \beta'_{ij} - 1) + \frac{3}{2} \sin 2\beta \sin 2\beta'_{ij} \cos(\omega_r t + \phi_{oij}) + \frac{3}{2} \sin^2 \beta \sin^2 \beta'_{ij} \cos 2(\omega_r t + \phi_{oij}) \right]. \quad (4)$$

We notice that the first term in the square bracket is constant, while the second and third terms are periodic with zero mean value. It is convenient to divide $\mathcal{H}_D(t)$ into two terms, its mean value $\overline{\mathcal{H}_D}$ and the remainder which is periodic with zero mean value:

$$\mathcal{H}_D(t) = \overline{\mathcal{H}_D} + (\mathcal{H}_D - \overline{\mathcal{H}_D}). \quad (5)$$

The first term on the right-hand-side is constant and gives a reduced dipolar interaction and the narrowed spectrum. The second term is periodic in ω_r and $2\omega_r$ and gives rise to rotational sidebands at multiples of ω_r . We note that in the special case of $\beta = \pi/2$ that since $\sin 2\beta = 0$, only even order sidebands contribute. We see therefore that:

$$\overline{\mathcal{H}_D} = \frac{1}{2} (3 \cos^2 \beta - 1) \sum_{i < j} \frac{1}{2} \gamma_i \gamma_j \hbar^2 r_{ij}^{-3} (\mathbf{I}_i \cdot \mathbf{I}_j - 3I_{iz} I_{jz}) (3 \cos^2 \beta'_{ij} - 1). \quad (6)$$

If we now compare Eqs. (1) and (6) we see that for polycrystalline and amorphous material the spectrum retains an identical shape, but is reduced in width by the scale factor:

$$F(\beta) = \frac{1}{2} (3 \cos^2 \beta - 1). \quad (7)$$

The second moment of the narrowed spectrum is reduced by $F^2(\beta)$. On the other hand, one can show that the second moment of the whole spectrum, including sidebands, is unchanged, expressing the expected invariance of the second moment of the whole spectrum (Andrew *et al.*, 1958a,b; Andrew and Newing, 1958; Andrew and Jenks, 1962).

We may note some particular values of $F(\beta)$:
for

$$\begin{aligned} \beta = 0 & & F(\beta) = 1 \\ \beta = \pi/2 & & F(\beta) = \frac{1}{2} \\ \beta = \cos^{-1} \frac{1}{\sqrt{3}} = 54^\circ 44' & & F(\beta) = 0. \end{aligned}$$

Thus rotation of the specimen about \mathbf{H}_o has no effect, rotation about an axis normal to \mathbf{H}_o halves the spectral width, while rotation about an axis making the *magic angle** of $54^\circ 44'$ should reduce the average dipolar broadening to zero.

These predictions were found to be borne out experimentally. The first experiments were made with ^{23}Na NMR in sodium chloride. A single crystal was used in order to avoid any significant quadrupolar broadening due to strains or other defects in this cubic crystal. The measured second moment from the static crystal agreed within experimental error with the value of 0.55 G^2 calculated from the theory of Van Vleck (1948). Rotating the crystal first about an axis perpendicular to \mathbf{H}_o ($\beta = \pi/2$), the spectrum was indeed halved in width with sidebands appearing at $2\omega_r$ (Andrew *et al.*, 1958a,b), as illustrated in Fig. 3. Then rotating the crystal using the magic angle ($\beta = 54^\circ 44'$), the central line did indeed narrow very sharply with spinning sidebands appearing at multiples of ω_r (Andrew *et al.*, 1959), as also

* It was at the AMPERE Congress in Pisa in 1960 where we presented some of our results that the late Professor C. J. Gorter of Leiden referred to the apparently 'magic' properties of this special angle, which led us to refer to it as the 'magic angle' thereafter.

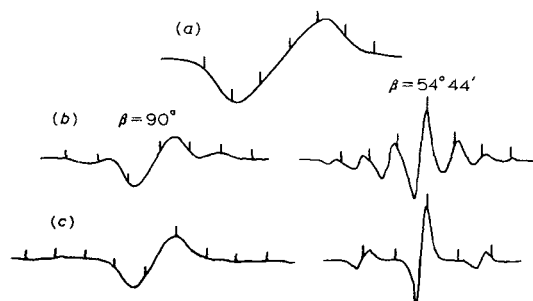


FIG. 3. The effect of rapid rotation of a solid on its dipolar-broadened NMR spectrum. ^{23}Na NMR derivative spectra of sodium chloride. (a) Static solid, (b), (c) recordings with the solid spinning at 800 and 1600 Hz respectively. The left hand pair of recordings were obtained with the rotation axis perpendicular to the magnetic field. The right hand pair were obtained with the rotation axis inclined at the magic angle of $54^\circ 44'$ to \mathbf{H}_0 (Andrew *et al.*, 1958a,b, 1959).

shown in Fig. 3. These spectra were obtained before the days of Fourier transform NMR spectrometers and appear as derivative spectra as was customary from wideline NMR spectrometers at that time. The variation of the width of the central spectrum followed the reduction factor $F(\beta)$, Eq. (7), quite well, as shown in Fig. 4. The residual linewidth at the magic angle was 200 Hz, largely determined by field inhomogeneity of the wideline spectrometer. Since those first experiments many workers have narrowed NMR lines from solids by this means and magic-angle linewidths as narrow as a few Hz have since been obtained using high-resolution magnets. Early verification of these ideas was independently made by Lowe (1959) using a crystal of calcium fluoride and a sample of polytetrafluoroethylene.

A good example of the removal of dipolar broadening by magic angle spinning is provided by the ^{27}Al spectrum of polycrystalline aluminium metal (Andrew, Hinshaw and

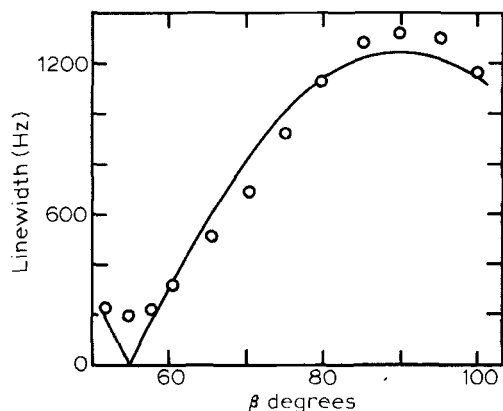


FIG. 4. Variation of the linewidth of ^{23}Na NMR spectrum of a rotating crystal of sodium chloride with the angle β . The full line is the theoretical curve given by (7); the circles are the experimental observations. (Andrew *et al.*, 1959).

Aluminium

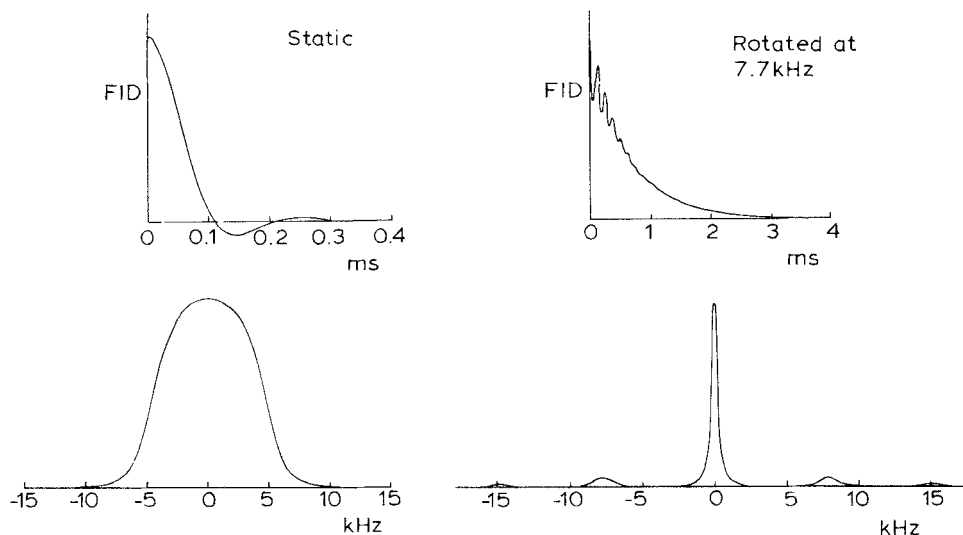


FIG. 5. ^{27}Al free induction decays and Fourier-transformed NMR spectra of polycrystalline aluminium. The left-hand diagrams refer to the static specimen; the right-hand diagrams refer to the specimen spinning about the magic axis at 7.7 kHz. Two rotation sidebands are seen on either side of the narrowed central line (Andrew *et al.*, 1973, 1974a).

Tiffen, 1973, 1974a). As illustrated in Fig. 5 the spectrum of the static material is almost 10 kHz broad. Magic angle spinning at 7.7 kHz reduced this width to about 400 Hz. This enabled the isotropic Knight shift to be measured with very much improved precision, yielding a value of 1640 ± 1 ppm relative to AlCl_3 solution at 298 K. A similar improvement in precision of measuring isotropic Knight shifts was obtained for ^{63}Cu and ^{65}Cu in polycrystalline copper metal (Andrew, Carolan and Randall, 1971a; Andrew 1973).

3. MAGIC ANGLE SPINNING AND ANISOTROPIC SHIFT INTERACTIONS

The electron shielding or chemical shift interaction of nuclei in non-metals may be written:

$$\mathcal{H}_s = \hbar \sum_i (\mathbf{I}_i \cdot \boldsymbol{\sigma}_i \cdot \mathbf{H}_0) \quad (8)$$

where $\boldsymbol{\sigma}_i$ is the chemical shift tensor of nucleus i . In metals the shift interaction (Knight shift) is conventionally defined with opposite sign:

$$\mathcal{H}_s = -\hbar \sum_i (\mathbf{I}_i \cdot \mathbf{K}_i \cdot \mathbf{H}_0) \quad (9)$$

where \mathbf{K}_i is the Knight shift tensor of nucleus i . Apart from this difference in sign, the behaviour of $\boldsymbol{\sigma}$ and \mathbf{K} is the same in what follows.

We note that $\boldsymbol{\sigma}$ and \mathbf{K} are second rank tensors, but unlike the dipolar interaction tensor which is a traceless, axially-symmetric second rank tensor, $\boldsymbol{\sigma}$ and \mathbf{K} are not traceless, are

not necessarily axially-symmetric, and may not even necessarily be symmetric (Buckingham and Malm, 1971). However any antisymmetric components have negligible effects on the spectrum (Haeberlen, 1976) and will be neglected.

Since the components of the shift tensor are in practice small compared with unity we need only retain σ_{izz} and rewrite (8) as:

$$\mathcal{H}_S = \hbar \sum_i \gamma_i \sigma_{izz} \mathbf{H}_o. \quad (10)$$

If the principal values of σ are σ_p ($p = 1, 2, 3$) and the direction cosines of its principal axes with respect to \mathbf{H}_o are λ_p , then dropping the suffix i for simplicity:

$$\sigma_{zz} = \sum_p \lambda_p^2 \sigma_p. \quad (11)$$

Since the isotropic average of each λ_p^2 is $\frac{1}{3}$, the average value of σ_{zz} in an ordinary isotropic fluid is

$$\sigma_{zz} = \frac{1}{3} \text{tr } \sigma = \sigma \quad (12)$$

where σ is the scalar chemical shift encountered in high-resolution NMR spectra of fluids.

When a rigid array of nuclei in a solid is rotated with angular velocity ω_r about an axis inclined at angle β to \mathbf{H}_o and at angles χ_p to the principal axes of σ we have (cf. Eq. (3))

$$\lambda_p = \cos \beta \cos \chi_p + \sin \beta \sin \chi_p \cos (\omega_r t + \psi_p). \quad (13)$$

From (10), (11) and (13) we see that a time-dependence is imposed on \mathcal{H}_S , and as with the dipolar interaction we may decompose \mathcal{H}_S into its mean value $\overline{\mathcal{H}_S}$ and terms periodic in ω_r which generate spinning sidebands. Substituting (13) into (11) and taking the time average we find that for each nucleus:

$$\overline{\sigma_{zz}} = \frac{1}{3} \sigma \sin^2 \beta + \frac{1}{2} (3 \cos^2 \beta - 1) \sum_p \sigma_p \cos^2 \chi_p. \quad (14)$$

Consequently when β is the magic angle $\cos^{-1} (1/\sqrt{3})$, we see that $\overline{\sigma_{zz}}$ reduces to the scalar isotropic value σ and the shift anisotropy is removed from the NMR spectrum for every nucleus in the specimen whatever the degree of anisotropy or asymmetry of its shift tensor and whatever the orientation of its principal axes. This result, demonstrating that magic angle spinning removes shift anisotropy, was first derived by Andrew and Wynn (1966) (see also Andrew, 1971).

The time-averaged shift given in (14) may be re-expressed in terms of the anisotropy parameter $\delta = \sigma_3 - \sigma$ and the asymmetry parameter $\eta = (\sigma_2 - \sigma_1)/\delta$ of each nucleus, introduced by Lippmaa, Alla and Tuherm (1976). Substituting these parameters in (14) and rearranging we get:

$$\overline{\sigma_{zz}} = \sigma + \frac{1}{2} (3 \cos^2 \beta - 1) \delta \left[\frac{1}{2} (3 \cos^2 \theta' - 1) + \frac{1}{2} \eta \sin^2 \theta' \cos 2\phi' \right] \quad (15)$$

where θ' and ϕ' are spherical polar angles which relate the specimen rotation axis to the principal axes of the shift tensor ($\cos \chi_1 = \sin \theta' \sin \phi'$, $\cos \chi_2 = \sin \theta' \cos \phi'$, $\cos \chi_3 = \cos \theta'$). Expressed in this form we see in a direct manner how the Legendre factor $\frac{1}{2}(3 \cos^2 \beta - 1)$ controls the shift anisotropy in the time-averaged Hamiltonian $\overline{\mathcal{H}_S}$ for every nucleus in the specimen.

An early clear experimental example of the removal of shift anisotropy by magic angle spinning is provided by cadmium, a metal with hexagonal crystal structure. The ^{111}Cd NMR spectra of a polycrystalline specimen of cadmium metal are shown in Fig. 6

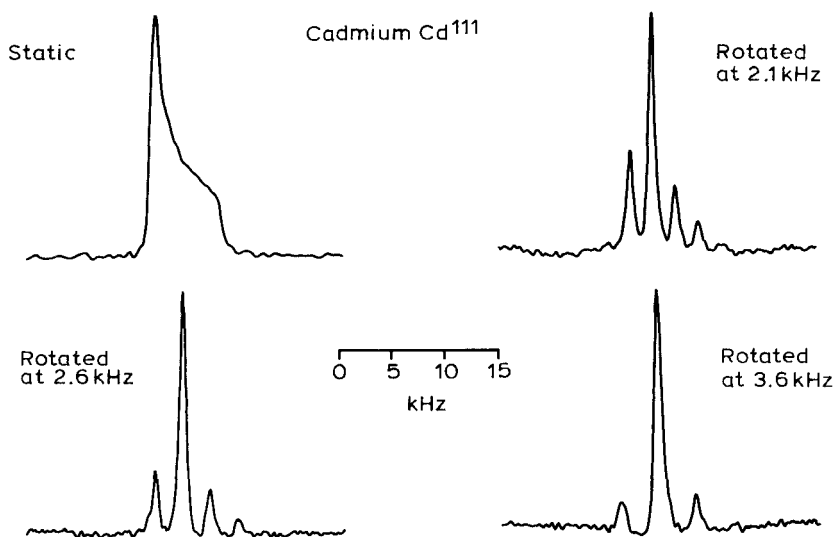


FIG. 6. The removal of shift anisotropy by magic angle spinning. ^{111}Cd NMR spectra of polycrystalline cadmium metal static and rotating about the magic axis at 2.1 kHz, 2.6 kHz, and 3.6 kHz (Andrew *et al.*, 1974a,b).

(Andrew *et al.*, 1974a,b). The spectrum for the static material shows the asymmetric profile characteristic of an axially-symmetric shift tensor. Dipolar broadening is small in this material on account of the low abundance (12 per cent) of both magnetic isotopes and their low magnetic moments (-0.6 nuclear magnetons); the Knight shift anisotropy is therefore the dominant source of NMR broadening in cadmium powder in a field of 1.4 T. Also shown in Fig. 6 are spectra for three spinning rates. It is seen that magic angle spinning removes the anisotropy and it enables the isotropic Knight shift to be obtained with precision (4321 ± 7 ppm for ^{111}Cd , 4324 ± 7 ppm for ^{113}Cd , relative to cadmium nitrate solution). It is believed that this was the first experimental demonstration of the removal of shift anisotropy by magic angle spinning.

We may notice a new feature in Fig. 6. Unlike the dipolar broadened spectra, where the rotation rate must be comparable with the linewidth to get substantial narrowing, here we see that the line breaks up almost immediately into an array of satellites each of narrow breadth. This was subsequently noticed for non-metals by Schaefer and Stejskal (1976) and by Lippmaa *et al.* (1976). The essential difference is that here, with shift anisotropy, the spectrum is inhomogeneously broadened. Each element of the spectrum of the static specimen arises from crystallites of a particular orientation, each with small intrinsic width. The situation is closely analogous to the NMR line from a liquid broadened by an inhomogeneous magnetic field; each volume element in the sample contributes its own portion of the spectrum. The intrinsic width of the spectrum may then be recovered from the decay of the spin-echo envelope (Hahn, 1950). Analogous rotational echoes have been observed by Maricq and Waugh (1977), and the decay envelope of such echoes gives the intrinsic width of each shifted spin packet.

In a subsequent paper Maricq and Waugh (1979) have discussed the behaviour of such rotational spin echoes in terms of average Hamiltonian theory (Haeberlen and Waugh, 1968) from which it is seen that the criterion for precise averaging with slow rotations is that the terms in the intrinsic Hamiltonian commute. If chemical shift interactions dominate, the terms do commute and the spectrum is inhomogeneous; if dipolar or

pseudo-dipolar terms are important the terms do not commute, the line is homogeneous, and higher rates of rotation are required to achieve effective narrowing of the spectrum. However, it should be added that even though slower rates of rotation narrow inhomogeneously broadened spectra, in the interests of good signal intensity it is of course still very desirable to spin the specimen at a rate fast compared with the static linewidth in order to make the sidebands unobservably weak and concentrate all the intensity onto the central line.



FIG. 7. ^{31}P NMR spectrum of polycrystalline phosphorus pentachloride with magic angle spinning. The two lines arise from the differently shielded PCl_4^+ and PCl_6^- ions of which the solid is composed. Markers at 1 kHz intervals (Andrew *et al.*, 1960a,b, 1966).

Chemically-shifted fine structures have been resolved in the ^{31}P NMR spectra of a number of polycrystalline phosphorus compounds using magic angle spinning (Andrew and Wynn, 1966; Kessemeyer and Norberg, 1967; Andrew *et al.*, 1976; Herzfeld *et al.*, 1980; Andrew *et al.*, 1981). In solid phosphorus pentachloride two well-resolved lines reduced to 10 Hz breadth by fast magic angle spinning were obtained from the differently shielded PCl_4^+ and PCl_6^- ions of which the solid is composed, and this enabled interesting cross-relaxation effects to be examined (Andrew *et al.*, 1960a,b, 1963, 1966; Burton *et al.*, 1980). The ^{31}P NMR spectrum of the rapidly rotated solid is shown in Fig. 7. This is an excellent example of a material which has a different molecular structure in the solid and liquid states. In CS_2 solution it has the molecular form PCl_5 giving a single resonance line. Taken with the measured shift for liquid PCl_5 , we have the following monotonic sequence of chemical shifts for the four phosphorus chlorides in ppm relative to 85 per cent orthophosphoric acid solution:

PCl_3	PCl_4^+	PCl_5	PCl_6^-
-215	-91	+80	+282

It is sometimes useful to spin the polycrystalline specimen about an axis making an intentional small deviation from the magic axis (Lippmaa *et al.*, 1976). This leads to an essentially high resolution solid-state NMR spectrum, but with fairly narrow lineshapes which retain the shift anisotropy though strongly scaled by the factor $F(\beta)$ of Eqs. (7) and (15). The shift anisotropy can then be recovered from the spectrum without it generating undesirable broadening.

4. MAGIC ANGLE SPINNING AND ANISOTROPIC INTERACTIONS

In the two previous sections we have shown from first principles that fast specimen rotation about an axis oriented at angle β to \mathbf{H}_0 introduces a factor $\frac{1}{2}(3 \cos^2 \beta - 1)$ into the time-averaged Hamiltonian representing the dipolar interaction and also into that representing the anisotropic shift interaction. In fact this is quite a general result. Similar calculations from first principles show that the same factor appears in the time-averaged Hamiltonian representing the anisotropic electron-coupled spin-spin interactions (Andrew

and Farnell, 1968) and in that representing the first-order electric quadrupole interaction (Cunningham and Day, 1966), and that magic angle spinning should therefore remove all these anisotropic interactions. Although all these cases were originally examined individually they may actually be treated in a common formalism which covers the effect of magic angle spinning on all symmetric second rank tensor interactions.

The various interactions may be written:

$$\text{Direct dipolar interaction } \mathcal{H}_D = \sum_{i < j} (\mathbf{I}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{I}_j) \quad (16)$$

$$\text{Indirect electron-coupled interaction } \mathcal{H}_J = h \sum_{i < j} (\mathbf{I}_i \cdot \mathbf{J}_{ij} \cdot \mathbf{I}_j) \quad (17)$$

$$\text{Electron shielding, non-metals } \mathcal{H}_S = h \sum_{i < j} \gamma_i (\mathbf{I}_i \cdot \boldsymbol{\sigma}_i \cdot \mathbf{H}_0) \quad (18)$$

$$\text{Electron shielding, metals } \mathcal{H}_S = -h \sum_i \gamma_i (\mathbf{I}_i \cdot \mathbf{K}_i \cdot \mathbf{H}_0) \quad (19)$$

$$\text{Electric quadrupolar interaction } \mathcal{H}_Q = \sum_i \frac{eQ_i}{6I_i(2I_i - 1)} (\mathbf{I}_i \cdot \mathbf{V}_i \cdot \mathbf{I}_i) \quad (20)$$

Equation (16) is an alternative expression of Eq (1), where \mathbf{D}_{ij} is the truncated dipolar interaction tensor between nuclei i and j . In (17) \mathbf{J}_{ij} is the electron-coupled spin-spin interaction tensor between nuclei i and j . In (20) eQ_i is the nuclear electric quadrupole moment of nucleus i and \mathbf{V}_i is the electric field gradient tensor at its site.

\mathbf{D}_{ij} , \mathbf{J}_{ij} , $\boldsymbol{\sigma}_i$, \mathbf{K}_i and \mathbf{V}_i are all second rank tensors. \mathbf{D}_{ij} is axially-symmetric and traceless; \mathbf{V}_i is symmetric and traceless; the other three are not restricted. We shall however continue to neglect any antisymmetric component of tensors $\boldsymbol{\sigma}_i$, \mathbf{K}_i and \mathbf{J}_{ij} , and we can render them all traceless by the simple expedient of subtracting their constant isotropic trace. Thus:

$$\mathbf{J} = J \mathbf{1} + \mathbf{J}^* \quad \text{where } J = \frac{1}{3} \text{tr } \mathbf{J} \quad (21)$$

$$\boldsymbol{\sigma} = \sigma \mathbf{1} + \boldsymbol{\sigma}^* \quad \text{where } \sigma = \frac{1}{3} \text{tr } \boldsymbol{\sigma} \quad (22)$$

$$\mathbf{K} = K \mathbf{1} + \mathbf{K}^* \quad \text{where } K = \frac{1}{3} \text{tr } \mathbf{K} \quad (23)$$

In these expressions $\mathbf{1}$ is the unit tensor, J , σ and K are the isotropic coupling constants and shifts encountered in isotropic liquids. The tensors \mathbf{J}^* , $\boldsymbol{\sigma}^*$, \mathbf{K}^* are all traceless symmetric tensors representing the anisotropic properties of these interactions.

These five second-rank tensor interactions represented by (16) to (23) all have a common structure and as Haeberlen (1976) has shown, they may be cast in a common form in terms of their irreducible tensor operators:

$$\mathcal{H}_\lambda = C^\lambda \sum_l \sum_{m=-l}^l (-1)^m R_{l,-m}^\lambda T_{l,m}^\lambda \quad (24)$$

in which C^λ are constants specific to each interaction, the terms $R_{l,-m}^\lambda$ are angular functions in coordinate space and the terms $T_{l,m}^\lambda$ are spin products. Since we are dealing with traceless symmetric second rank tensors the only terms $R_{l,-m}^\lambda$ in (24) which are non-zero are those with $l = 2$ and $m = 0, \pm 2$.

We now need to express the tensor components $R_{l,-m}^{\lambda}$ for each nucleus or pair of nuclei in the laboratory frame in terms of its components in a convenient crystal frame of reference rotating in the laboratory frame. Next these components in the crystal frame need to be expressed in terms of the invariant principal values of the tensor in its principal axis frame. These two transformations are readily accomplished using the Wigner rotation matrices $\mathcal{D}_{m'm}^{\lambda}(\alpha, \beta, \gamma)$, where α, β, γ are the Euler angles relating the frames of reference. The number of terms in this double transformation is severely limited since in calculating the spectra we are restricted to terms $T_{l,m}^{\lambda}$ in the Hamiltonian which are secular, $m = 0$. In the transformation from the crystal frame to the laboratory frame we are left with Wigner rotation matrices of the form $\mathcal{D}_{m'0}^{\lambda}(0, \beta, \omega_r t)$; as before β is the angle between the spinning axis and \mathbf{H}_0 . Noting that those Wigner matrices with factors $e^{\pm i\omega_r t}$, $e^{\pm 2i\omega_r t}$ average to zero under fast rotation, we find only one non-zero rotation matrix is left, namely

$$\mathcal{D}_{00}^2(0, \beta, \omega_r t) = \frac{1}{2}(3 \cos^2 \beta - 1). \quad (25)$$

Thus all terms in the time-averaged Hamiltonian $\overline{\mathcal{H}}_{\lambda}$, for all five traceless tensor interactions, contain this factor (25). When β is the magic angle $\cos^{-1}(1/\sqrt{3}) = 54^{\circ} 44'$, all these interactions therefore vanish from the spectrum under fast rotation.

5. MAGIC ANGLE SPINNING AND INDIRECT SPIN-SPIN INTERACTIONS

The removal of anisotropic broadening interactions by magic angle spinning frequently reveals fine structure previously obscured; a good example is the demonstration of spin multiplets in solids. In Fig. 8 the ^{19}F NMR spectrum of polycrystalline hexafluoroarsenate KAsF_6 is shown (Andrew *et al.*, 1967). The spectrum from the static material is about 15 kHz broad. Magic angle spinning at 5.5 kHz substantially removed the anisotropic sources of broadening (\mathbf{D} , \mathbf{J}^* , σ^*) and resolved a spin quartet, with an isotropic coupling constant J of 905 Hz. The quartet arises from the coupling of the ^{19}F nuclei with the 100 per cent abundant ^{75}As nucleus in the octahedral AsF_6^- ions in the solid. This was in fact the first spin multiplet to be resolved in the NMR spectrum of a solid by any method.

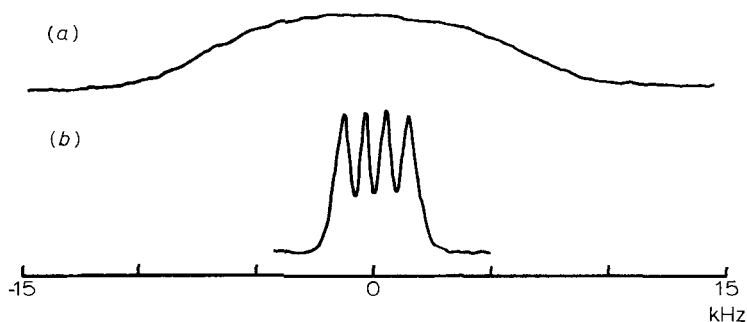


FIG. 8. A spin multiplet resolved in the solid state by magic angle spinning. ^{19}F NMR spectra of polycrystalline KAsF_6 . (a) Static specimen; (b) specimen spinning at 5.5 kHz displaying a quartet structure due to J coupling between ^{19}F and ^{75}As nuclei (Andrew *et al.*, 1967).

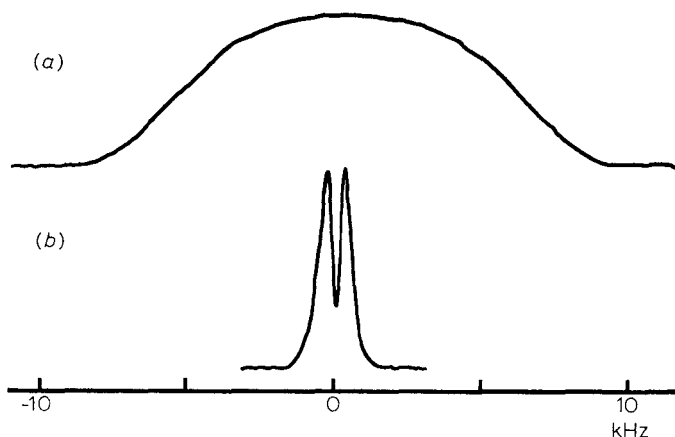


FIG. 9. A spin doublet resolved in the solid state by magic angle spinning. ^{19}F NMR spectra of polycrystalline KPF_6 . (a) Static specimen; (b) specimen spinning at 8 kHz revealing a doublet due to J coupling between ^{19}F and ^{31}P nuclei (Andrew *et al.*, 1970).

Another example is given in Fig. 9 which shows the ^{19}F spectrum of polycrystalline KPF_6 , both static and with magic angle spinning at 8 kHz (Andrew *et al.*, 1970). Again the spectrum of the static material is about 15 kHz wide; with spinning a doublet is resolved which arises from indirect ^{19}F - ^{31}P spin-spin coupling in the PF_6^- ions ($J = 743$ Hz). Similarly in polycrystalline KSbF_6 a ^{19}F - ^{121}Sb sextet and a ^{19}F - ^{123}Sb octet have also been resolved (Andrew *et al.*, 1970).

Electron-coupled nuclear spin interactions are also encountered in metals and in particular are manifested in the narrowed spectra of copper. As shown in Fig. 10 magic angle spinning substantially reduces the ^{63}Cu and ^{65}Cu linewidths, but for spinning frequencies above 3 kHz a constant limiting linewidth is reached which is evidently due to a rotationally invariant interaction (Andrew *et al.*, 1971b; Andrew, 1973). By comparing the second moments of the residual lines and finding them to be in the inverse ratio of the abundances of the two copper isotopes, it was shown that these residual breadths were due to the Ruderman-Kittel electron-coupled nuclear interactions. A value of $J = 230 \pm 10$ Hz was extracted for the nearest-neighbour coupling constants in reasonable agreement with theory, and consistent with the value for silver (Andrew and Hinshaw, 1973).

6. MAGIC ANGLE SPINNING AND NUCLEAR QUADRUPOLE INTERACTIONS

It was shown in Section 4 that fast magic angle spinning should also average the quadrupolar Hamiltonian \mathcal{H}_Q to a small value. This is not such an easy interaction to put to an experimental test since quadrupolar interactions in non-cubic environments tend to be large. Even if they are less than the Zeeman interaction, first-order perturbation theory is often not a sufficient approximation and second-order contributions need careful consideration as discussed by Maricq and Waugh (1979). On the other hand the smaller quadrupole couplings found in nominally cubic environments may be hard to distinguish from comparable dipolar interactions (Cunningham and Day, 1966).

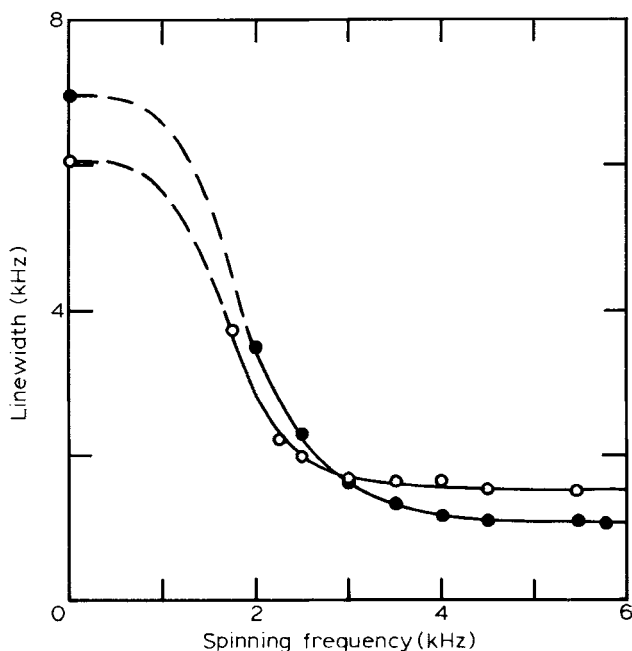


FIG. 10. NMR linewidths for copper metal as a function of spinning frequency. ● ^{63}Cu ; ○ ^{65}Cu (Andrew *et al.*, 1971b). The rotationally invariant linewidths at spinning frequencies over 4 kHz arise from the Ruderman–Kittel interaction.

However, an unequivocal test was carried out by Tzalmona and Andrew (1974) using two polycrystalline non-cubic caesium salts, Cs_2SO_4 and Cs_2CO_3 . The caesium nucleus ^{133}Cs , which has 100 per cent abundance and spin $7/2$, has an unusually small electric quadrupole moment, $-3 \times 10^{-27} \text{ cm}^2$. Consequently the quadrupole broadening in these salts was of order 10^3 Hz and the first order theory suffices to describe it. Moreover since the nearest-neighbour separation of the caesium atoms is about 0.4 nm, and there are no other abundant magnetic nuclei in these solids, the dipolar contribution to the linewidth is an order of magnitude smaller than the quadrupolar contribution. The results are summarized in Table 1. It is seen that magic angle spinning does substantially narrow the quadrupolar broadened lines in both solids.

TABLE 1. Magic angle spinning and quadrupole interactions

Solid compound	Linewidth (Hz)		Linewidth ratio
	Static	Rotating (3 kHz)	
Cs_2SO_4	1060	60	18
Cs_2CO_3	1270	180	7

More recently a very striking demonstration of the removal of quadrupolar broadening has been provided with ^2D NMR in polycrystalline specimens (Ackerman, Eckman and Pines, 1979). The quadrupolar-broadened spectra are of the order of 100 kHz broad. Since the spectra are inhomogeneously broadened, magic angle spinning generates a train of rotational echoes of the type discussed in section 3. By synchronously sampling the echo

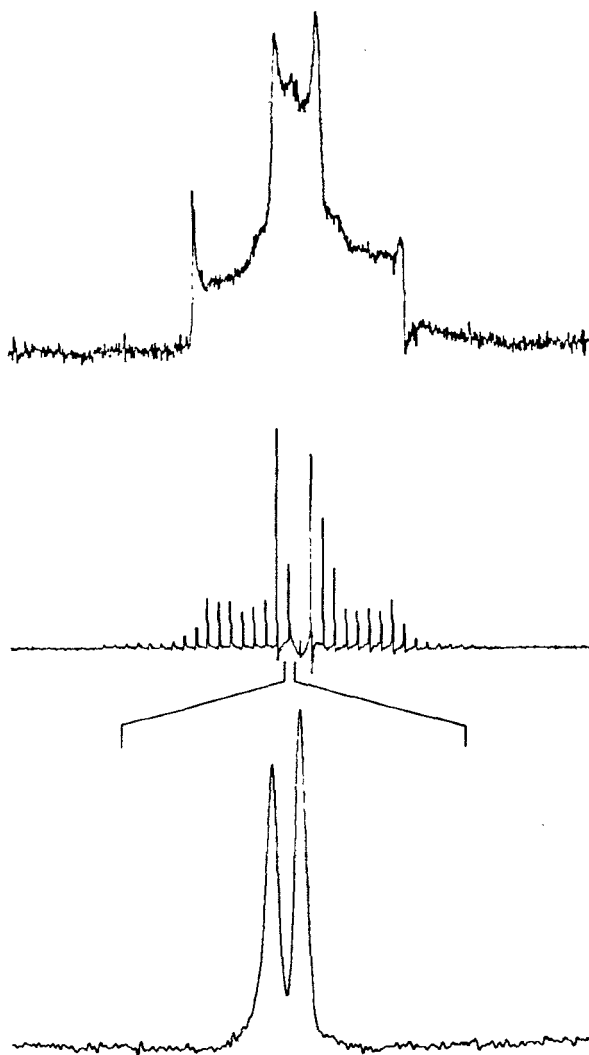


FIG. 11. Removal of quadrupole broadening by magic angle spinning in the ^2D NMR spectra of a polycrystalline mixture of perdeutero-hexamethylbenzene and deuterio-ferrocene (Ackerman *et al.*, 1979). Top: Static polycrystalline specimen; width of trace 200 kHz. Middle: With magic angle spinning at 4 kHz; width of trace 200 kHz. Bottom: Isotropic shift spectrum by FT of synchronously sampled FID; width of trace 2 kHz.

envelope and Fourier transforming, a ^2D spectrum is obtained with the first-order quadrupolar broadening removed. A modest rotation rate of a few kHz sufficed to secure a narrowing by three orders of magnitude. Fig. 11 shows the static spectrum for a mixture of perdeutero-hexamethylbenzene- d_{18} and 20 per cent deuterioferrocene- d_{10} . The upper recording shows the quadrupolar-broadened spectrum of the static solid mixture on a trace 200 kHz wide. The middle trace shows the spectrum, including rotational sidebands, for magic angle spinning at 4 kHz. The bottom recording on a trace expanded to 2 kHz width shows the FT echo-envelope spectrum with quadrupole broadening removed, enabling the

small isotropic ^2D chemical shift difference of the two components to be resolved. The residual breadth of order 2 ppm is thought to arise from second-order quadrupolar interactions and from instability in the adjustment to the magic angle.

7. MACROSCOPIC AND MICROSCOPIC MOTIONS

If an NMR spectrum is already partially narrowed by molecular motion within a solid it is of practical interest to enquire whether magic angle spinning will remove the remaining breadth. This situation has been examined by Andrew and Jasinski (1971), and two different situations may be distinguished. The first may be called 'fast restricted motion' and the second 'slow or moderate isotropic motion'.

In the first category of fast restricted motion, molecules or groups in the solid may for example reorient rapidly and randomly about one defined molecular axis leading to a reduced plateau value of the second moment. In such a case when the solid specimen is rotated about the magic axis the average interaction Hamiltonian must be found by taking the time average over both macroscopic and microscopic motions, and it is found that the anisotropic interactions all average to zero. This conclusion is borne out by experiment, for example with polytetrafluoroethylene (Lowe, 1959; Andrew, 1970). The ^{19}F NMR spectrum at room temperature is already narrowed to about 30 per cent of its low-temperature rigid-structure width, and magic angle spinning removes the remaining breadth associated with other degrees of molecular freedom. In such cases the microscopic molecular motion makes the task of macroscopic narrowing easier, since the rate of rotation need only be comparable with the already reduced linewidth.

In the second situation substantial spectral narrowing has been achieved by *isotropic* molecular rotation and diffusion. All degrees of freedom of the molecules have been mobilized, but the rate of motion, though fast enough to narrow the spectrum substantially, is not fast enough to give the really sharp lines characteristic of mobile liquids. Let us consider some typical orders of magnitude. Suppose we have a solid whose rigid-lattice NMR linewidth is 10^4 Hz. Internal isotropic motion with correlation frequency 10^6 Hz would narrow the spectrum to an observed width of 10^2 Hz. In this situation macroscopic spinning at 10^2 Hz will have no effect on the residual linewidth, nor even spinning at 10^4 Hz. The frequency of magic angle spinning will have to be greater than that of the internal motion, 10^6 Hz in our example, to produce further narrowing of the line, and such a fast rotation rate is impossible to achieve. With this class of material internal microscopic molecular motion is a hindrance and not a help in securing very narrow lines. It should be noted that this limitation to the achievement of high-resolution NMR spectra in solids applies equally to other methods of line narrowing in solids (Haeberlen and Waugh, 1968).

There are intermediate situations between these two extreme types of behaviour, and this enables information to be obtained about internal motions present; in particular it has been used in studies of molecular motions in polymers (Schneider, Pivcova and Doskocilová, 1972; Pivcova *et al.*, 1974; Schaefer, Stejskal and Buchdahl, 1977).

If the internal motions in solids are slow they do not inhibit the narrowing of the spectral lines by magic angle spinning, and a careful evaluation of the residual width enables the correlation time of such slow motions to be determined in favourable cases, as a function of temperature (Suwelack, Rothwell and Waugh, 1980).

8. FACTORS AFFECTING RESOLUTION

There are a large number of factors which determine the ultimate width of the NMR lines narrowed by magic angle spinning. A discussion of many of these has been given

previously by Andrew (1971) and aspects which particularly relate to magic angle spinning when used in combination with ^{13}C cross-polarization NMR spectroscopy have been analyzed by Garroway *et al.* (1981).

We first catalogue the more important sources of residual line broadening encountered in magic angle spinning, and then discuss some of them in more detail. The list is given in Table 2.

TABLE 2. Factors affecting resolution in magic angle spinning

A. Instrumental factors
(i) inhomogeneity of the laboratory magnetic field H_0
(ii) imperfect adjustment to the magic angle
(iii) angular instability
(iv) insufficiently fast spinning
(v) bulk susceptibility effects.
B. Residual interactions
(i) residual dipolar and pseudo-dipolar interactions
(ii) chemical shift distributions
(iii) intermolecular J couplings
(iv) Ruderman–Kittel interactions
(v) antisymmetric tensor interactions
(vi) quadrupole effects
(vii) higher order multipole effects
C. Motional and relaxation effects
(i) spin-lattice relaxation
(ii) cross-relaxation
(iii) slow internal motions

A(i) Inhomogeneity of the laboratory magnetic field H_0 . This is always an important factor in high-resolution NMR spectroscopy of all kinds. Clearly the most uniform magnetic field possible should always be employed. Specimen rotation itself removes residual inhomogeneities in planes normal to the rotation axis.

A(ii) Imperfect adjustment to the magic angle. This assumes greater importance the greater the degree of narrowing achieved. If the angle β deviates from the magic value $54^\circ 44'$ by a small angle ε , the residual linewidth will be $\sqrt{2\varepsilon}$ of the original width, as one sees directly from the reduction factor of Eqs (7) and (25) (Andrew, 1971). For a reduction of 100 times, ε must therefore be less than half a degree; for a reduction of 1000 times ε must be less than $2.5'$.

A(iii) Angular instability. It follows from A(ii) that the spinner axis must remain in adjustment and must not wander, wobble, precess or nutate significantly from its correct orientation.

A(iv) Insufficiently fast spinning. In general the faster the specimen is spun the narrower the lines become provided there is no rotationally-invariant residual broadening. Theory suggests the lines should narrow in proportion to ω_r^{-2} , though experiment bears this out only approximately (Kessemeier and Norberg, 1967; Clough and Gray, 1962).

A(v) Bulk susceptibility effects. For an ellipsoidal sample of homogeneous material with isotropic magnetic susceptibility placed in a uniform magnetic field, the field within the sample is also uniform. For a liquid sample such a state of affairs may be closely

approximated. For a polycrystalline sample of irregular particles, of possibly anisotropic susceptibility, and with voids in between, the approximation is less good. Garroway *et al.* (1981) report that magic angle spinning should remove bulk susceptibility broadening in a powder of arbitrarily shaped particles provided the susceptibilities of the particles are small and isotropic; on the other hand the effects of anisotropic susceptibilities are not removed by magic angle spinning. Effects of voids can be reduced by compaction.

B(i) Residual dipolar and pseudo-dipolar interactions. This is related to A(iv). There is also some evidence that the dipolar interaction between two like nuclei with different orientations of shift tensor may not be completely averaged out (Veeman, 1980). It will be of interest to examine this feature further.

B(ii) Chemical shift distributions. This item reflects a fundamental difference between the solid and liquid states. There can be a small distribution of isotropic shifts throughout the specimen for nominally equivalent nuclei arising from small variations of environment and physical defects. In solution any similar small variations of shift would be removed by dynamic averaging by the molecules; in solids the molecules remain in their particular environment. Such distributions generate a residual linewidth proportional to H_0 .

B(iii) Intermolecular J couplings. This item also reflects the fundamental difference between the solid and liquid states. Since in the solid state molecules continue to have the same environment, there is the possibility of static intermolecular J couplings; in the liquid state molecular motion removes their effect. A distribution of small J couplings would generate a field-independent residual linewidth.

B(iv) Ruderman–Kittel interactions. This applies to conductors and was discussed in Section 5.

B(v) Antisymmetric tensor interactions. The J tensor is not necessarily symmetric, but we have so far neglected any antisymmetric component of this interaction on the ground that its effect on the NMR spectrum should be small. Nevertheless when very narrow lines are achieved the contribution of these components should be remembered since magic angle spinning does not remove them (Andrew and Farnell, 1968).

B(vi) Quadrupole effects. In addition to residual quadrupole interactions discussed in Section 6 another interesting effect has been noted in ^{13}C high-resolution NMR in solids. When the ^{13}C atom is bonded to ^{14}N ($I = 1$) it is observed that the dipolar coupling between the two nuclei is not entirely removed by magic angle spinning, often leaving an asymmetric doublet. An example is shown in Fig. 12 (Groombridge *et al.*, 1980). The relatively strong quadrupole interaction of ^{14}N with the electric field gradient at its site competes with the Zeeman interaction for the alignment of the ^{14}N spins and modifies the angular dependence of its dipolar coupling with other spins. A detailed theory of this has been given by Kundla and Alla (1978) and by Opella *et al.* (1981). With ^{15}N ($I = \frac{1}{2}$) this source of broadening is absent in the ^{13}C spectra, thus confirming the correct identification of its origin. Although limiting the resolution obtainable with ^{13}C nuclei bonded to nitrogen this interaction does assist in the assignment of such lines in the spectrum.

B(vii) Multipole effects. Nuclei with $I \geq \frac{3}{2}$ may have a magnetic octupole moment and in several cases nuclear magnetic octupole interactions have been established. Nuclei with $I \geq 2$ may have an electric hexadecapole moment, and in general a nucleus with $I = n/2$

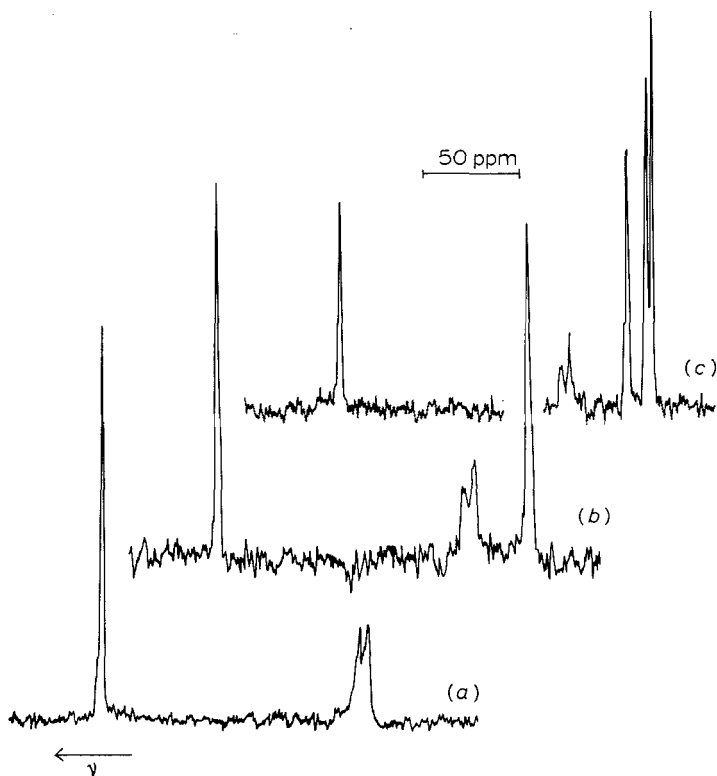


FIG. 12. ^{13}C NMR spectra of three polycrystalline amino acids obtained at 22.6 MHz by a combination of cross-polarization and magic angle spinning. (Groombridge *et al.*, 1980). (a) Glycine, (b) L-alanine, (c) L-valine. The carbon atoms bonded to nitrogen display a characteristic doublet arising from ^{14}N quadrupole interactions.

may have a 2^n moment (magnetic for n odd, electric for n even). Such interactions have not been significant in solids beyond $n = 2$. Nevertheless it may be pointed out that higher-order multipole interactions involve tensor products of higher rank whose transformations involve higher order spherical harmonics, and $54^\circ 44'$ will not be the appropriate magic rotation angle to average them to zero.

C(i) Spin-lattice relaxation. Nuclear spin-lattice relaxation is always a source of spectral broadening contributing a width of order $(\pi T_1)^{-1}$, where T_1 is the nuclear spin-lattice relaxation time.

C(ii) Cross-relaxation. If the spinning rate is exactly equal to the frequency separation between two chemically-shifted lines mutual spin exchanges can take place between the two systems of nuclei. This promotes spin-lattice relaxation and also generates a resonant rotational line-broadening, which amounted to 50 Hz in solid phosphorus pentachloride (Andrew *et al.*, 1963, 1966).

C(iii) Slow internal motions. This was discussed in Section 7.

9. MAGIC ANGLE SPINNING AND MULTIPLE PULSE NMR

It was mentioned in Section 1 that the combination of magic angle spinning and multiple pulse NMR enables more highly resolved spectra to be obtained than either technique can achieve separately. This is particularly the case for proton NMR spectra from polycrystalline and amorphous solids. For static samples the dipolar-broadened spectrum can be 30 to 100 kHz wide and spinners do not rotate fast enough to narrow homogeneously broadened spectra of this width. On the other hand multiple pulse sequences can substantially narrow such spectra. They do not however remove all sources of broadening, and it is worth noting the principal differences between the effects of the two methods.

Whereas magic angle spinning removes all anisotropic sources of broadening which can be represented by symmetric second rank tensor interactions (*see* Section 4), provided the specimen is spun fast enough, multiple pulse NMR does not remove broadening due to heteronuclear interactions, both direct dipolar **D** and indirect **J***, nor does it remove broadening due to anisotropic chemical shifts in polycrystalline materials. The hetero-

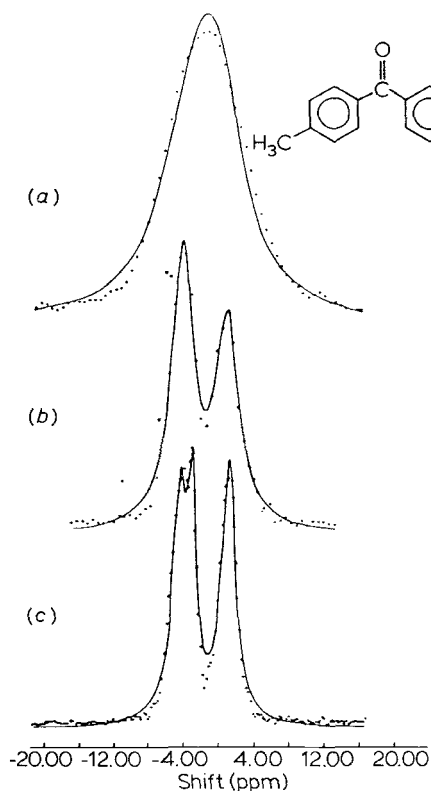


FIG. 13. Combined magic angle spinning and multiple pulse irradiation. (Ryan *et al.*, 1980; Gerstein, 1981). Proton NMR spectra of polycrystalline 4,4'-dimethylbenzophenone at 55 MHz. (a) Using MREV8 multipulse sequence alone; (b) using MREV8 multipulse sequence together with magic angle spinning; and (c) using BR24 multipulse sequence together with magic angle spinning.

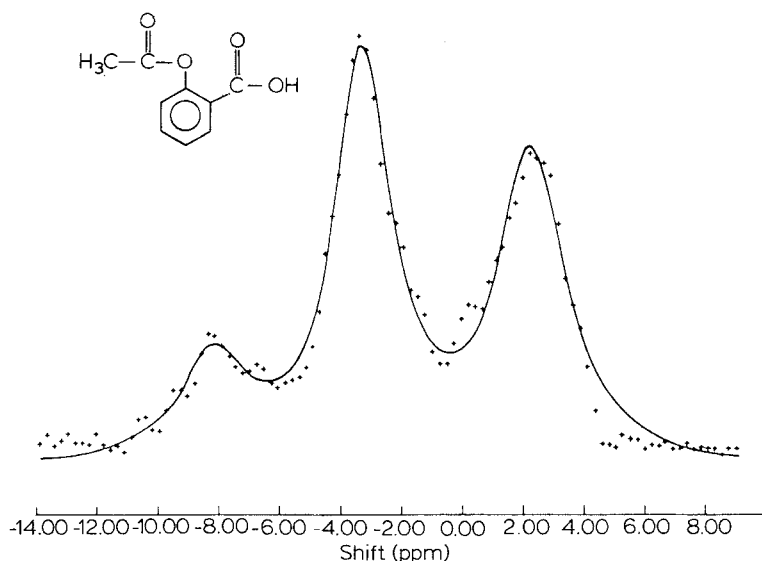


FIG. 14. Combined magic angle spinning and multiple pulse irradiation (Ryan *et al.*, 1980; Gerstein, 1981). Proton NMR spectrum of polycrystalline acetylsalicylic acid (aspirin) at 55 MHz.

nuclear interactions can in principle be removed by spin decoupling, but there still remains the broadening due to chemical shift anisotropy. For protons this may typically be 5 to 10 ppm, equivalent to a few kHz depending on the operating NMR frequency. It is clear therefore that magic angle spinning can remove the residual sources of anisotropic broadening that multiple pulse irradiation cannot remove.

An example is shown in Fig. 13 of proton NMR spectra at 55 MHz of polycrystalline 4,4'-dimethylbenzophenone (Ryan *et al.*, 1980; Gerstein, 1981). The top spectrum is obtained using a multiple eight-pulse cycle alone, reducing the spectrum to a single broad line about 550 Hz wide, with no indication of chemical shift structure. The middle spectrum shows the effect of adding magic angle spinning, which enables two peaks from aromatic and aliphatic protons to be resolved, with separation 5 ppm. The bottom spectrum was obtained using a 32-pulse cycle together with magic angle spinning, so enabling further splitting to be resolved.

A second example in Fig. 14 shows the proton NMR spectrum at 55 MHz of polycrystalline acetylsalicylic acid (aspirin) obtained by the combination of magic angle spinning and a 32-pulse sequence (Ryan *et al.*, 1980; Gerstein, 1981). Clear resolution is achieved of the hydroxyl, aromatic and methyl protons.

10. MAGIC ANGLE SPINNING AND CROSS-POLARIZATION NMR

Highly resolved ^{13}C NMR spectra may be obtained from solid specimens using magic angle spinning in combination with cross-polarization double-resonance methods (Pines *et al.*, 1972). This very fruitful combination of techniques was pioneered by Schaefer and Stejskal (1976), Lippmaa *et al.* (1976) and others. The double resonance procedure decouples the strong proton heteronuclear dipolar interactions and heteronuclear J couplings, and by using the Hartmann-Hahn condition provides enhancement of the weak

^{13}C NMR signal by proton polarization transfer. Consequently the residual spectral width of several kHz arises mainly from the anisotropic ^{13}C chemical shifts in polycrystalline and amorphous specimens, and the weak homonuclear dipolar interactions of the 1 per cent abundant ^{13}C nuclei; both of these interactions are readily removed by magic angle spinning.

The spectra shown in Fig. 15, taken from the paper by Schaefer and Stejskal (1976) show how magic angle spinning dramatically improves the resolution of the ^{13}C NMR spectra in solid polysulphone, in ebony and in ivory (collagen). The series of ^{13}C spectra of polycrystalline adamantane shown in Fig. 16 (Stejskal *et al.*, 1977) is instructive. The top trace shows the basic ^{13}C FT spectrum which is just over 1 kHz wide. The second spectrum shows the effect of magic angle spinning alone at a rotation rate of 2.2 kHz, which resolves the methine and methylene carbon nuclei in the adamantane molecules. The third spectrum shows that heteronuclear dipolar decoupling alone also enables the two carbon nuclei to be resolved. In both these two spectra the resolution is incomplete and the lines have a residual breadth of about 100 Hz. However when both magic angle spinning *and* dipolar decoupling are applied (bottom recording) the two lines narrow sharply with a residual width of 3 Hz. Spectra recorded more recently of solid adamantane show the linewidths reduced to less than 1 Hz.

In the last few years a very large number of applications have been made of this combination of magic angle spinning and cross-polarization to obtain solid state NMR spectra of ^{13}C , ^{15}N , ^{29}Si , ^{31}P in a wide variety of compounds in the solid state. An example of ^{13}C spectra in solid amino acids was shown in Fig. 12 (Groombridge *et al.*, 1980). In Fig. 17 ^{13}C spectra of a cyclic peptide (Opella *et al.*, 1981) both in polycrystalline form and in solution are shown; comparison shows that there are essentially no changes in isotropic chemical shift between the solid and liquid states. Opella *et al.* (1981) have also used magic angle spinning to obtain high resolution NMR spectra from viruses.

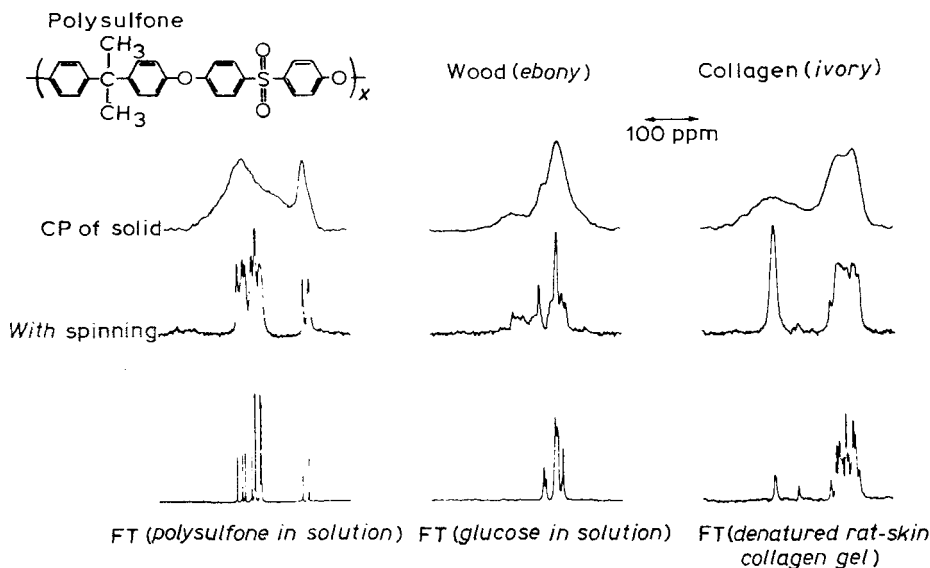


FIG. 15. Combined cross-polarization and magic angle spinning (Schaefer and Stejskal, 1976). ^{13}C NMR spectra at 22.6 MHz of solid polysulphone, ebony and ivory (collagen). Top recordings: without magic angle spinning. Middle recordings: with magic angle spinning. Bottom recordings: solution spectra.

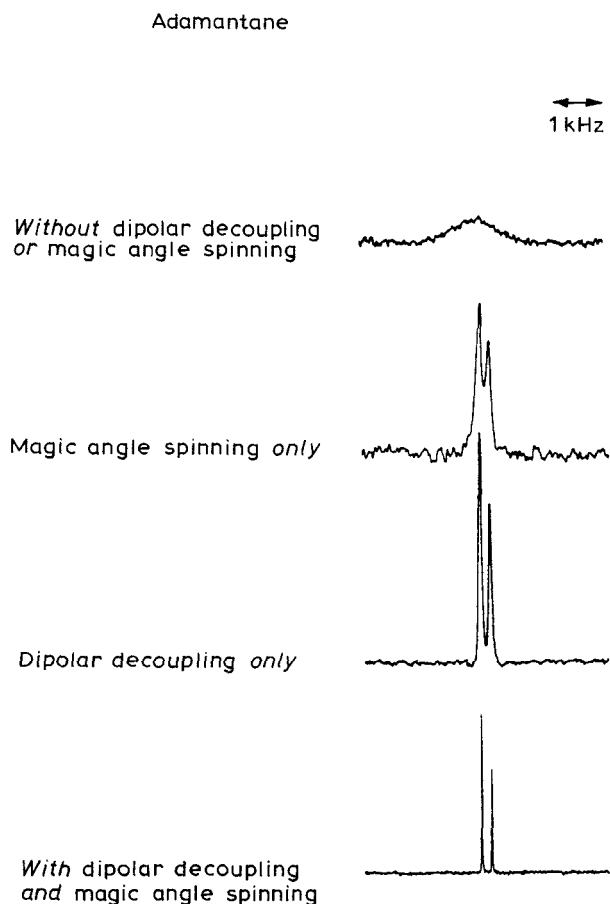


FIG. 16. Combined cross-polarization and magic angle spinning. (Stejskal and Schaefer, 1977). ^{13}C NMR spectra at 22.6 MHz of polycrystalline adamantane under different conditions of operation as indicated.

A final example in this section, shows in Fig. 18 a most interesting ^{13}C spectrum of polycrystalline lysozyme (Jardetzky and Wade-Jardetzky, 1980). The top recording shows the ^{13}C spectrum of this solid protein, the middle spectrum shows that of the same protein in aqueous solution, while the bottom diagram shows a superimposition of the two spectra after the solution spectrum had been appropriately convoluted to give both the same residual linewidths. The spectra from solid and liquid are very similar, so supporting the view that the conformation of the lysozyme molecule in solution is closely similar to that determined by X-ray crystallography in the solid state.

11. MAGIC ANGLE SPINNING AND DOUBLE QUANTUM NMR

As we saw in Section 6 ^2D NMR spectra in polycrystalline solids are of the order of 100 kHz wide and may be narrowed by three orders of magnitude by magic angle spinning. However, the task is easier in double-quantum NMR spectroscopy since the $\Delta m = 2$ transitions for

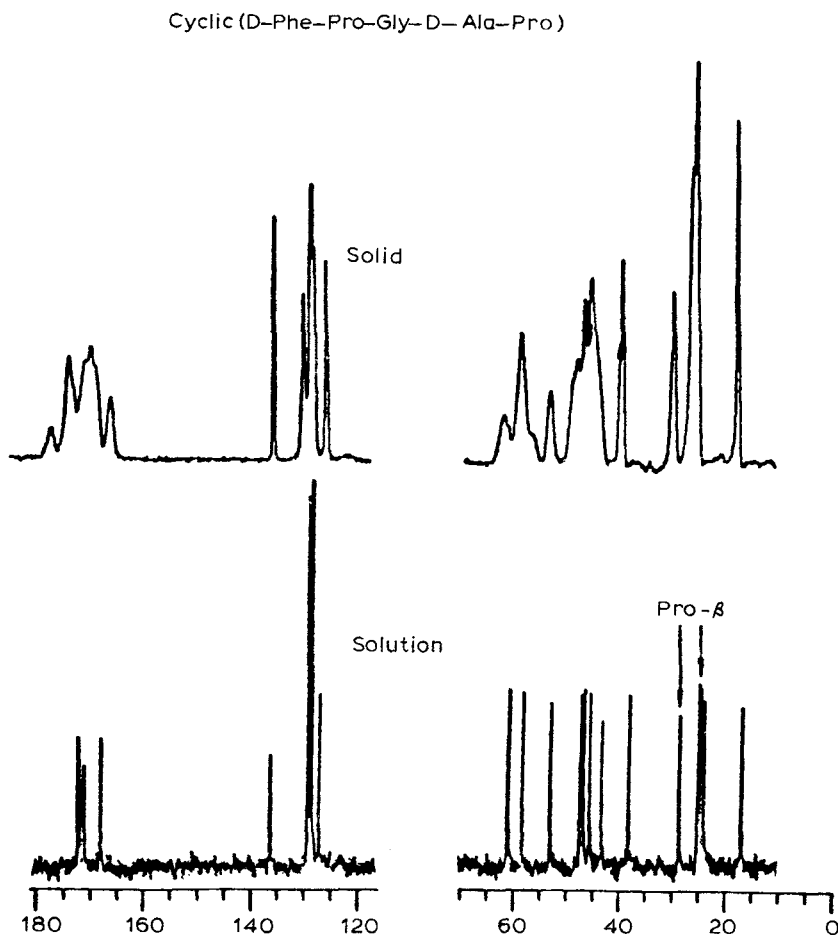


FIG. 17. Combined cross-polarization and magic angle spinning (Opella *et al.*, 1981). ^{13}C NMR spectra at 38 MHz of the cyclic pentapeptide (D-Phe-Pro-Gly-D-Ala-Pro). Top: polycrystalline sample. Bottom: sample dissolved in CDCl_3 .

nuclei with $I = 1$ are independent of quadrupole broadening in first order, and therefore have a much narrower intrinsic width of order 1 kHz, mainly arising from chemical shift anisotropy. Magic angle spinning therefore easily removes the spectral broadening and yields narrow lines.

This has been demonstrated by Eckman, Müller and Pines (1980b) for the ^2D double quantum NMR spectrum of deuterated ferrocene at 28 MHz. The resonance line was reduced to about 40 Hz width, with a rotation rate of 1.1 kHz. Moreover adjustment of the spinner to the magic angle is much less crucial. To remove the large quadrupole broadening encountered in single quantum ^2D spectra, the spinner had to be adjusted within $1'$ of the magic value $54^\circ 44'$, and had to remain stable within that adjustment. On the other hand to remove the smaller chemical shift broadening encountered in double quantum ^2D spectra the requirement on adjustment and stability of the spinner is more than an order of magnitude less severe.

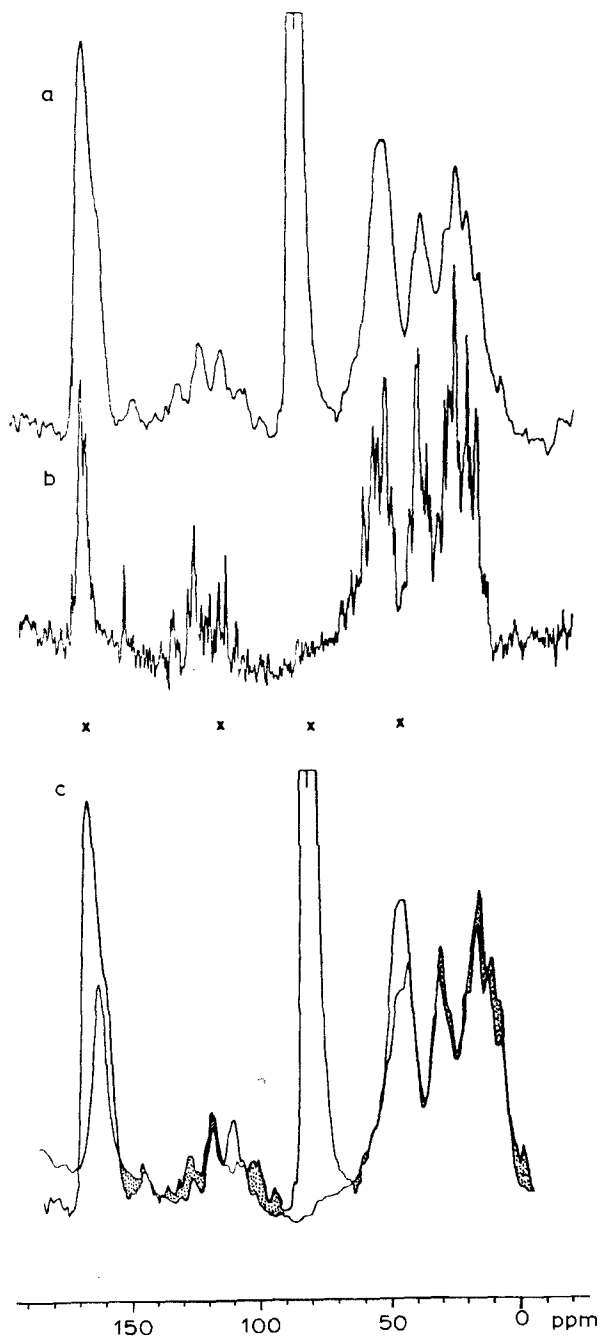


FIG. 18. Combined cross-polarization and magic angle spinning (Jardetzky and Wade-Jardetzky, 1980). ^{13}C NMR spectra at 35 MHz of lysozyme at 25°C. (a) Polycrystalline specimen. (b) Aqueous solution spectrum. (c) Broadened aqueous solution spectrum superimposed on solid state spectrum. There are additional peaks in the solid state spectrum at X from the rotor material and from spinning sidebands.

It may therefore be expected that the spectral narrowing achieved by magic angle spinning in double quantum NMR will provide another approach to high resolution NMR spectroscopy in solids.

12. SPINNERS

A variety of spinner configurations have been used by various workers. A type which we have used for many years (Andrew *et al.*, 1958, 1969) is illustrated in Fig. 19, and illustrates many features common to all spinners. It is based on a type introduced by Henriot and Huguenard (1925, 1927) and developed by Beams (1930, 1937) and was recognized as convenient for NMR work since it was compact and having a gas bearing was capable of very high frequencies of rotation. It was necessary for our purposes to make the rotors of non-metallic materials for use in a magnetic field, to incorporate a specimen chamber into the rotor and to adapt the system for use in an NMR spectrometer probe.

The turbine is driven by compressed gas which emerges through inclined jets machined in the stator and impinges on the conical underside of the rotor which is provided with a set of flutes. The rotor is thus supported on a gas bearing and rotates with little frictional resistance. The specimen chamber is on top of the rotor and is an integral part of the rotor construction; it spins freely within the radiofrequency coil of the NMR spectrometer, with a good filling factor. The rotors spin with very constant speed about an axis inclined at any angle to the vertical, even upside down. Magic angle spinners of this general type are now found in several commercial NMR spectrometers.

In Fig. 20 the variation of rotation rate with air pressure is shown for a family of such spinners with rotor diameters of 13, 19 and 25 mm. At high pressures the rate of rotation tends towards a limiting value when the peripheral velocity of the rotor approaches the velocity of sound in air. In pursuit of higher rotation rates we have used helium as the propelling gas since its velocity of sound is 2.7 times higher than that of air. The remarkable increase of rotation rate attained using helium gas is illustrated in Fig. 21 for a

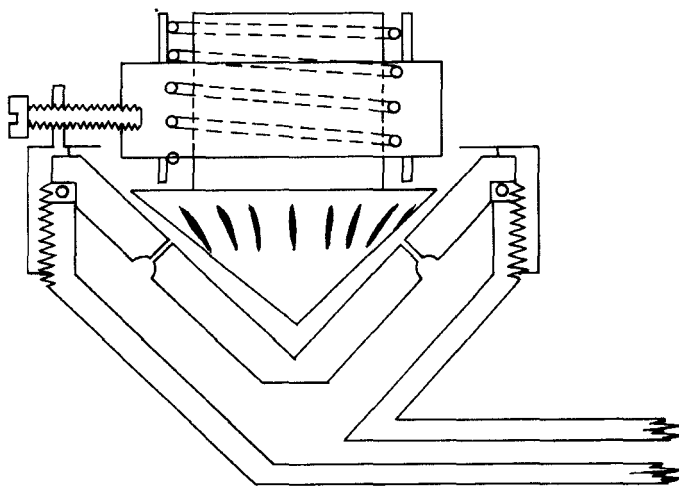


FIG. 19. Turbine assembly for magic angle spinning (Andrew *et al.*, 1969).

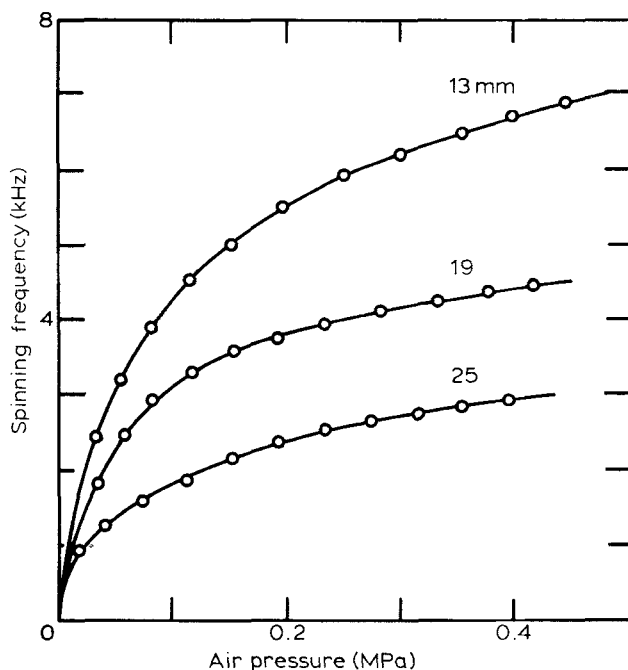


FIG. 20. Variation of spinning frequency with air pressure for turbines of the type shown in Fig. 19, using nylon rotors of diameter 13, 19, 25 mm (Andrew *et al.*, 1969).

19 mm diameter rotor. The highest frequency of rotation we achieved with a spinner of this type was 13 kHz.

At a rotation frequency of 10 kHz (600 000 revolutions per minute) the peripheral velocity of a 19 mm rotor is $6 \times 10^4 \text{ cm s}^{-1}$ (2000 km h⁻¹), and the peripheral acceleration is $4 \times 10^6 \text{ g}$. The rotors must therefore be made of strong material. Nylon was the strongest homogeneous material used; for the highest rotation frequencies glass-fibre and carbon-fibre reinforced materials were used.

The ideal magic angle spinner will rotate at high speeds with great stability for long periods of time. The specimen within the rotor must occupy the RF coil with high filling factor. The ideal spinner assembly should contain no nuclei of the species whose resonance is being recorded. It should be possible to change specimens rapidly as in high resolution NMR of liquids, and without having to dismantle the probe assembly in order to do so. There should be reliable precise fine adjustment to the magic angle. It should moreover be possible to vary the temperature of the specimen over a wide range.

Naturally all these desirable attributes are not easy to realize simultaneously. Some rotor systems concentrate on optimization of a particular aspect such as very high rotation frequency, or excellent stability, or ready interchangeability of specimen. The recent resurgence of interest in magic angle spinning has stimulated improvements in design. A reading list on the topic of spinners includes Andrew *et al.* (1958a), Lowe (1959), Schnabel (1965), Andrew and Wynn (1966), Cunningham and Day (1966), Kessemeier and Norberg (1967), Andrew *et al.* (1969), Andrew (1971), Babka *et al.* (1971), Zilm, Alderman and Grant, (1978), Lippmaa *et al.* (1979), Fyfe, Mossbrugger and Yannoni,

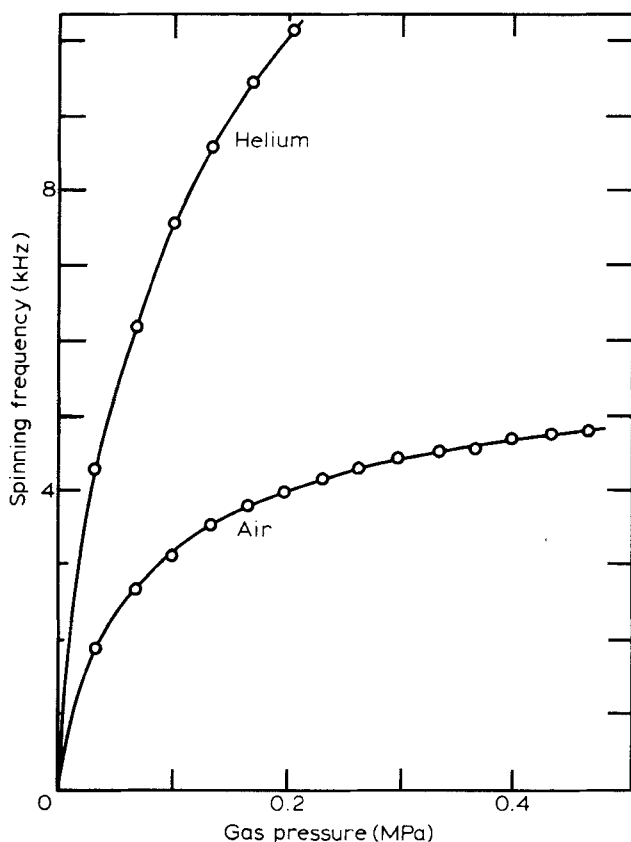


FIG. 21. Comparison of spinning frequencies for a turbine of the type shown in Fig. 19 with a nylon rotor 19 mm diameter, when driven by air and by helium (Andrew *et al.*, 1969).

(1979), Balimann *et al.* (1980), Opella *et al.* (1980), Schneider *et al.* (1980), Eckman *et al.* (1980), van Dijk *et al.* (1980) and Bartuska and Maciel (1981).

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