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MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

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Phil. Trans. R. Soc. Lond. A 1982 **305**, 591-607
doi: 10.1098/rsta.1982.0052

Phil. Trans. R. Soc. Lond. A **305**, 591–607 (1982)
Printed in Great Britain

Analytical chemical applications of high-resolution nuclear magnetic resonance spectroscopy of solids

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The basis of the combined cross-polarization–magic-angle spinning (c.p.–m.a.s.) experiment, which yields high-resolution n.m.r. spectra of solid materials, is described and the general applicability of the technique, including its quantitative reliability, discussed.

Solid-state n.m.r. is in many ways complementary to X-ray diffraction, as shown by its application to amorphous systems in which diffraction methods cannot be used (for example resins, coals, glasses and surface-immobilized catalysts) and also by its application to crystalline materials where X-ray structural data are available but where, for various reasons, a fuller description of the structure may be obtained by n.m.r. Examples include zeolites and chemically exchanging solid systems. The technique also provides a bridge between the solid-state structures of conformationally mobile and charged species as determined by diffraction techniques and the structures of these species in solution. Quantitative reliability of the c.p.–m.a.s. technique has been evaluated for phenolic resins and coals.

1. INTRODUCTION

Despite the obvious academic and commercial importance of many solid materials, the interest of chemists in the solid state has been limited, as reflected, for example, in undergraduate curricula. This attitude has developed, to some extent at least, because of a lack of reliable analytical techniques capable of providing 'high-resolution' information for solid samples, i.e. information characteristic of specific atoms or functional groups in molecules that can be related to chemical structures and reactivities. High-resolution n.m.r. has been used for many years and has become the most powerful tool for the analysis of compounds of unknown structure in solution (Wehrli & Wirthlin 1980; Bovey 1972; Slonim & Lyubimov 1970; Pople *et al.* 1959; Breitmaier & Voelter 1974; Levy & Nelson 1972; Martin *et al.* 1980; Stothers 1972). Figure 1*a* shows the high-resolution proton n.m.r. spectrum of liquid ethanol, in which the

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chemical shift values of the signals are characteristic of the different types of nuclei present; their intensities are proportional to the numbers of such nuclei, while spin–spin couplings reflect the geometric relation between them. The chemical structure of the molecule can be deduced from this information.

Figure 1*b* shows the spectrum of frozen ethanol. It contains only a very broad, featureless absorption, being dominated by the direct dipole–dipole interactions between the nuclei. As a result, the information relating to the chemical and molecular structure present in the (very much smaller) chemical shifts and spin–spin couplings is lost. Although such spectra are useful for the study of molecular motion in the solid state, and the dipolar interactions average to zero for completely isotropic motion in solution, these studies are not of primary interest to chemists.

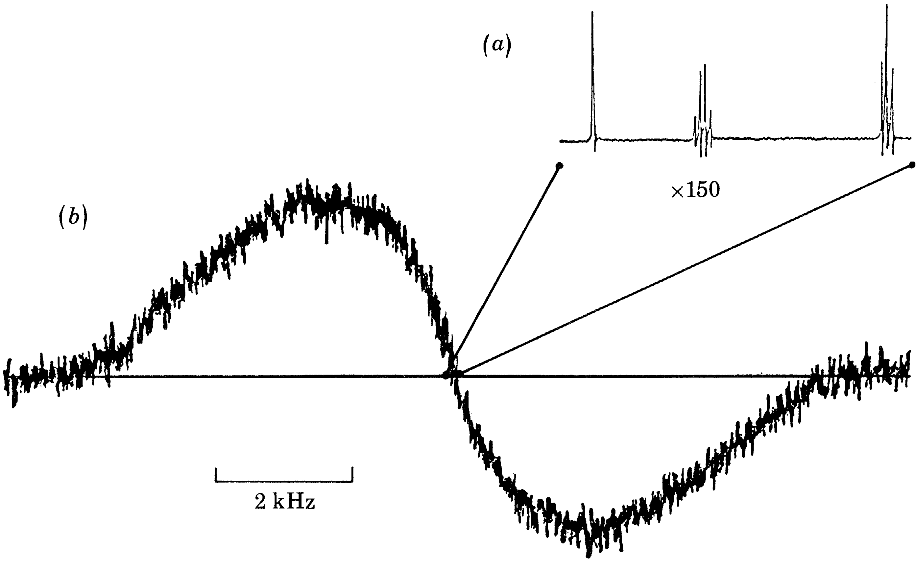


Figure 1. (*a*) Typical high-resolution proton n.m.r. of liquid ethanol showing chemical shift differences and spin–spin couplings between the nuclei. (*b*) Solid-state n.m.r. spectrum of solid frozen ethanol at 77 K presented as the first derivative. (At this temperature the structure is not completely rigid, with methyl group reorientation occurring fast on the n.m.r. timescale.) The lines connecting the two spectra indicate the difference in scale.

2. THE CROSS-POLARIZATION–MAGIC-ANGLE SPINNING EXPERIMENT

It is now possible to achieve resolution in solid-state experiments comparable with (but not as good as) that in solution, where the chemical shifts are characteristic of the magnetic (and therefore chemical and structural) environment of the nuclei observed if the correct choice of nucleus and experiment is made.

2.1. *Choice of nucleus*

The reasons why solid-state n.m.r. can cope with different nuclei are shown in scheme 1. For protons, n.m.r.-active nuclei are of both high natural abundance and high concentration. As can be seen from figure 1*b*, the problem is that the spectrum is completely dominated by the direct (H–H) dipole–dipole interactions, in comparison with which other interactions such as spin–spin couplings and chemical shifts are negligible. Although, in principle, these interactions can be removed by m.a.s., and by pulse techniques, in practice they are so large in comparison with the chemical shift range of protons that it is not normally possible to obtain analytically useful spectra.

^{1}H: example of an 'abundant' spin system

$$\mathscr{H}_{\text{(tot)}} = \mathscr{H}_{\text{(Zeeman)}} + \mathscr{H}_{\text{(H-H dipolar)}} + \mathscr{H}_{\text{(others)}}$$

^{13}C: example of a 'dilute' spin system

$$\mathscr{H}_{\text{(tot)}} = \mathscr{H}_{\text{(Zeeman)}} + \mathscr{H}_{\text{(H-C dipolar)}} + \mathscr{H}_{\text{(C-C dipolar)}} + \mathscr{H}_{\text{(shift anisotropy)}}$$

SCHEME 1

For ^{13}C, a 'magnetically dilute spin' present at only 1.1 % natural abundance, there are more interactions. However, certain important simplifications make high-resolution experiments possible. Thus (H–C dipole–dipole) interactions are large, but they are between different types of nuclei and can be removed by the application of a powerful decoupling field at ^{1}H frequency. The (C–C dipole–dipole) interactions may be ignored in view of the low abundance of the ^{13}C isotope. The largest of the remaining interactions is usually the chemical shift anisotropy. Before discussing this it should be noted that in practice many nuclei satisfy the 'dilute spin' requirement: even in the case of a 100 % abundant spin $\frac{1}{2}$ nucleus like ^{31}P, the (P–P dipole–dipole) term is still small as long as the concentration of phosphorus nuclei is not large and they are not in close proximity. In fact, in *most* chemical systems, all nuclei except ^{1}H or ^{19}F usually satisfy the 'dilute spin' requirement, which makes the technique very versatile.

2.2. *Chemical shift anisotropy: magic-angle spinning* (*Andrew* 1971, 1976)

The origin of the line broadening caused by the chemical shift anisotropy is the orientation dependence of the chemical shift (figure 2). Thus, a solution containing a molecule with a C=O group will show a single absorption in the ^{13}C spectrum at a field or frequency value that we say is 'characteristic of the magnetic environment or shielding' of the C=O group. This, however, is the isotropic average value of all possible molecular orientations caused by the random thermal motion. In a single crystal, the signal will appear at a position that depends on the orientation of the C=O group to the magnetic field (figure 2*a*). For a polycrystalline material, all such orientations are present simultaneously. The resulting envelope of signals is called the 'shift anisotropy pattern'. It may be averaged to its isotropic value by 'magic-angle' spinning (m.a.s.), where the whole sample is spun about an axis inclined at a certain angle to the magnetic field. The anisotropy is modified by the term $(3\cos^{2}\theta - 1)$, where θ is the angle between the spinning axis and the magnetic field vector (figure 3). If $\theta = 54.74°$, then $(3\cos^{2}\theta - 1) = 0$ and the chemical shift anisotropy is averaged to the isotropic value. The net result of magic-angle spinning is thus the same as that of completely random motion. Spinning rates of 3–5 kHz are necessary, and various designs of spinning apparatus are available that fulfil this requirement and have different individual advantages.

2.3. *Cross-polarization*

In addition to magic-angle spinning, which yields the high-resolution component of the experiment, it is possible to increase the signal:noise ratio (S/N) of the dilute nucleus by using 'cross-polarization' (c.p.), a technique introduced by Pines, Gibby & Waugh (Gibby *et al.* 1972; Pines *et al.* 1972, 1973). In this, ^{1}H spins and the dilute spins are 'spin-locked' during a

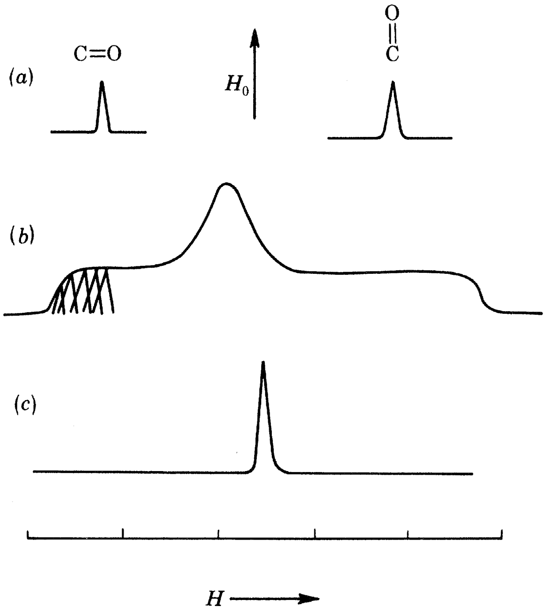


FIGURE 2. Schematic representations of the ^{13}C n.m.r. signal from a carbonyl group. (*a*) In a single crystal in two different orientations to the applied magnetic field H_0. (*b*) The envelope or 'shift anisotropy pattern' formed by the contributions from signals from all possible random orientations of the carbonyl group to the magnetic field. (*c*) The 'isotropic average' value found in solution where the shift anisotropy has been averaged by the fast and random molecular reorientations.

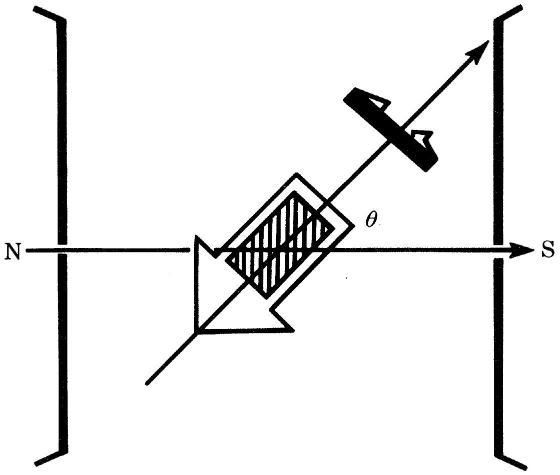


FIGURE 3. Schematic representation of the principle of m.a.s. showing the angle θ between the spinning axis and the magnetic field vector.

time T_c (figure 4) called the 'contact time' while the magnitudes of the spin locking fields are adjusted so that $H_H\gamma_H = H_C\gamma_C$ ('Hartman–Hahn condition'). As a result, the magnetization of the dilute spins is increased to a theoretical maximum factor of γ_H/γ_C, giving a corresponding increase in S/N. A further indirect gain is that the experiment now depends only on the ^{1}H relaxation parameters and can be repeated in a time T_r, determined *only* by the proton T_1 values, which are usually much shorter than those for carbon.

The combined c.p.–m.a.s. experiment, first performed by Schaefer & Stejskal (Schaefer &

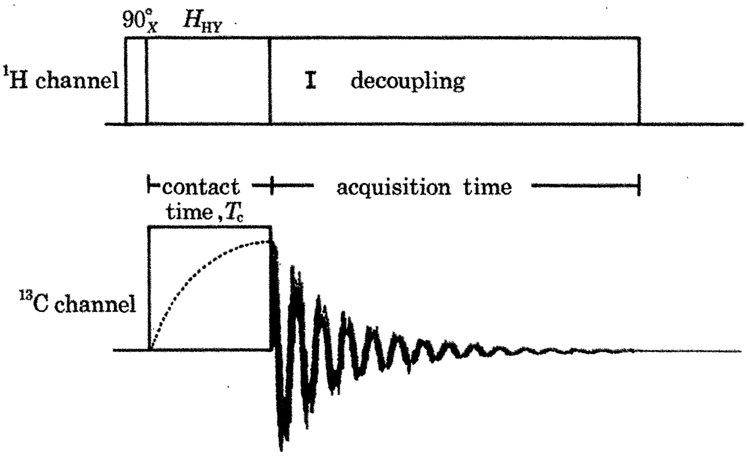


FIGURE 4. Schematic representation of the 'cross-polarization' pulse sequence for both ^{1}H and ^{13}C spin systems. T_c is the 'contact time' where both sets of spins are spin-locked with spin-locking fields H_H and H_C respectively so that the relationship $\gamma_H H_H = \gamma_C H_C$ is satisfied.

Stejskal 1976; Schaefer *et al.* 1977) yields spectra of moderate to good resolution for completely solid samples and has obvious importance in chemical analysis. It is applicable to many nuclei, including ^{13}C, ^{29}Si, ^{27}Al, ^{31}P, ^{11}B, ^{23}Na and ^{113}Cd. The success of these measurements is currently promoting a resurgence of interest in the chemistry of the solid state (Griffin 1977; Andrew 1981; Mehring 1976; Miknis *et al.* 1982; Fyfe *et al.* 1979; Hill *et al.* 1979; Lyerla *et al.* 1979; Lippmaa *et al.* 1978; Garroway *et al.* 1979; Sefcik *et al.* 1979; Bartuska *et al.* 1977).

3. APPLICATIONS

We wish to emphasize three general classes of important applications of solid-state n.m.r., illustrating them with examples of work done in our own laboratory. The technique is in many ways complementary to X-ray diffraction measurements; thus it can be applied to any solid system, but has particular advantages in cases where either diffraction techniques are powerless (*a*) or where they give incomplete information (*b*). It forms a 'bridge' between solution and the solid state (*c*).

(*a*) In amorphous, insoluble systems or where the scattering amplitudes of different atoms in the system are similar, c.p.–m.a.s. measurements yield critical information as neither diffraction nor high-resolution solution n.m.r. techniques are applicable.

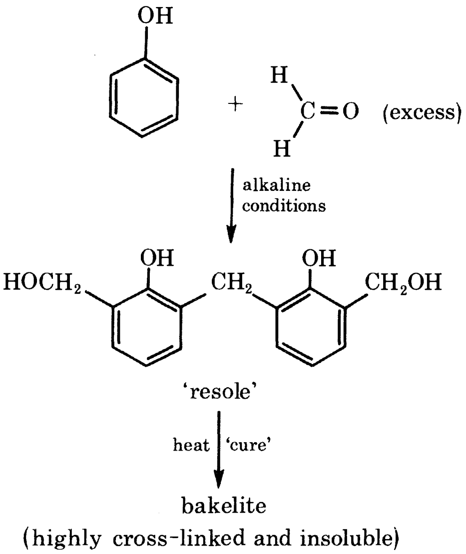
(*b*) In soluble crystalline materials where high-resolution n.m.r. is possible in solution and X-ray structures are available, c.p.–m.a.s. measurements can yield information on the dynamic structure. In some cases where the structural data are incomplete, for example in zeolites, such measurements provide additional information.

(*c*) Since the n.m.r. experiment can be performed in both solid and solution phases, it can act as a bridge between solid-state structures, determined by X-ray diffraction, and structures in solution.

3.1. *Systems with limited diffraction data*

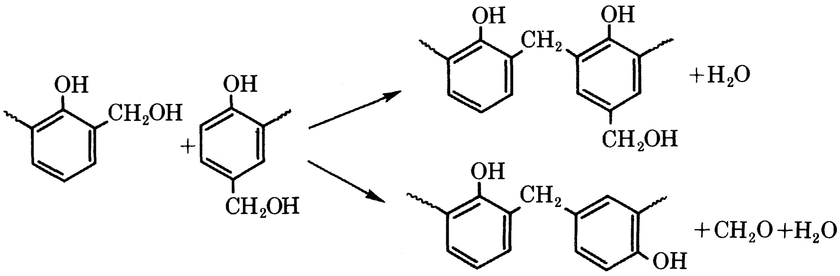
3.1.1. *Polymeric resins*

Scheme 2 shows the reaction between phenol and formaldehyde leading to oligomers with characteristic $-CH_2OH$ (methylol) and $-CH_2-$ (methylene) groups, the latter bridging different phenol moieties. The products are viscous liquids, which on heating (usually in a mould) form a hard, cross-linked material (Bakelite) (Gillis & Oesper 1964; Whitehouse *et al.* 1967). This is completely insoluble and although it was the very first completely synthetic polymer ever made, the details of its structure and the nature of the curing process are largely unknown owing to the insolubility and amorphous nature of the cured resin.



Scheme 2. Formation of phenolic resins.

Figure 5 shows the ^{13}C c.p.–m.a.s. spectra of a solid, cured resin (Fyfe *et al.* 1980): figure 5*a* is the spectrum of a stationary sample (c.p. only) and figure 5*b* that from the combined c.p.–m.a.s. experiment. The assignment of the high-field signals to the formaldehyde-derived groupings as indicated in the figure is confirmed by the use of 5 % enriched $^{13}CH_2O$ in the preparation (figure 5*c*). Under the appropriate conditions, quantitatively reliable spectra may be obtained and the nature of the curing process investigated. This involves the conversion of $-CH_2OH$ to $-CH_2-$ groups by the two possible reactions shown in scheme 3. The conversions are shown in figure 6 (Fyfe *et al.* 1982*d*).



Scheme 3. Curing reactions of phenolic resins.

3.1.2. *Surface-attached species*

The various advantages of surface-immobilized reagents bonded to glass, polymers and other substrates, such as ease of separation, high reagent concentration and possible stereochemical control of reactions, have made these species a field of intense activity (Hartley & Vezey 1977; Collman & Hegedus 1980). Unfortunately, when the reagents are immobilized, they have

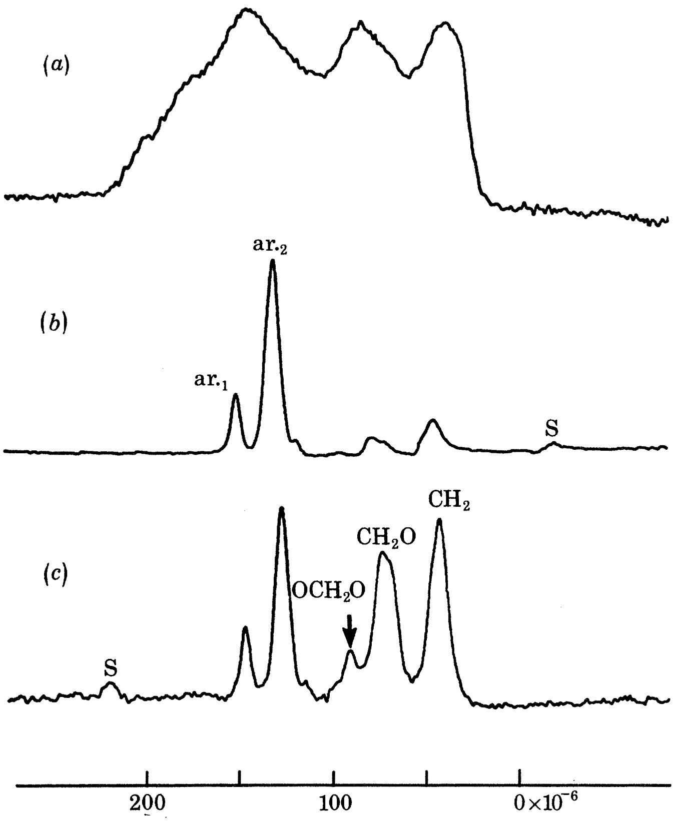


FIGURE 5. Solid-state ^{13}C n.m.r. spectra measured at 22.6 MHz in a solid cured phenolic resin by using decoupling and matching radiofrequency fields of 40 kHz. (*a*) Static sample, 1 ms cross-polarization time, 2 s recycle time, 3000 f.i.ds. (*b*) Magic angle spinning at 3.6 kHz, 1 ms cross-polarization time, 2 s recycle time, 2000 f.i.ds. (*c*) Conditions as in (*b*) except that 500 f.i.ds were averaged and the sample was prepared by using formaldehyde ^{13}C enriched to *ca.* 5%. The small peaks marked S denote spinning side bands. The chemical shifts are relative to TMS.

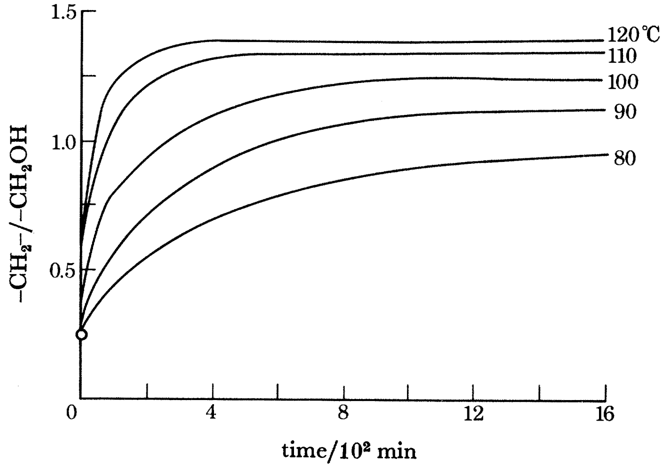


FIGURE 6. The curing process of solid phenolic resins as monitored by the ratio of methylene ($-CH_2-$) to methylol ($-CH_2OH$) peaks (see scheme 3) as a function of time of curing and curing temperature. The sample was cured as a thin film between plates to ensure accurate temperature control. The spectra were obtained from powdered samples.

n.m.r. properties characteristic of solid materials, and cannot be characterized by conventional high-resolution n.m.r. techniques. C.p.–m.a.s. experiments may, however, be used to characterize them. This is illustrated in figure 7, showing the ^{31}P c.p.–m.a.s. spectra of the phosphine ligands in a series of transition-metal catalysts, including one that is immobilized on a glass surface (Bemi *et al.* 1982*a*, *b*). As can be seen from the top spectrum of the crystalline catalyst, the ^{31}P nucleus acts as a very sensitive probe of the structure of *cis*-$PtCl_2(PPh_2CH_3)_2$. The central signal is split into two peaks (at $\delta = -2.1$ and $\delta = +1.6 \times 10^{-6}$ from external 85 % H_3PO_4), indicating that either the molecular plane of symmetry is lost in the solid or that there are two non-equivalent molecules in the unit cell. The spectrum also shows splittings of the central resonances $^1J(^{195}Pt, ^{31}P)$, of 3466 and 3759 Hz respectively due to scalar coupling with the ^{195}Pt nucleus (abundance 33 %), the magnitude of which indicates that the two phosphine ligands are attached to the central Pt atom in a *cis* arrangement. The centre spectrum is of very similar material, in which the triphenylphosphine ligands have been replaced with ligands with terminal trialkoxysilyl groups suitable for covalent attachment of the complex onto a glass

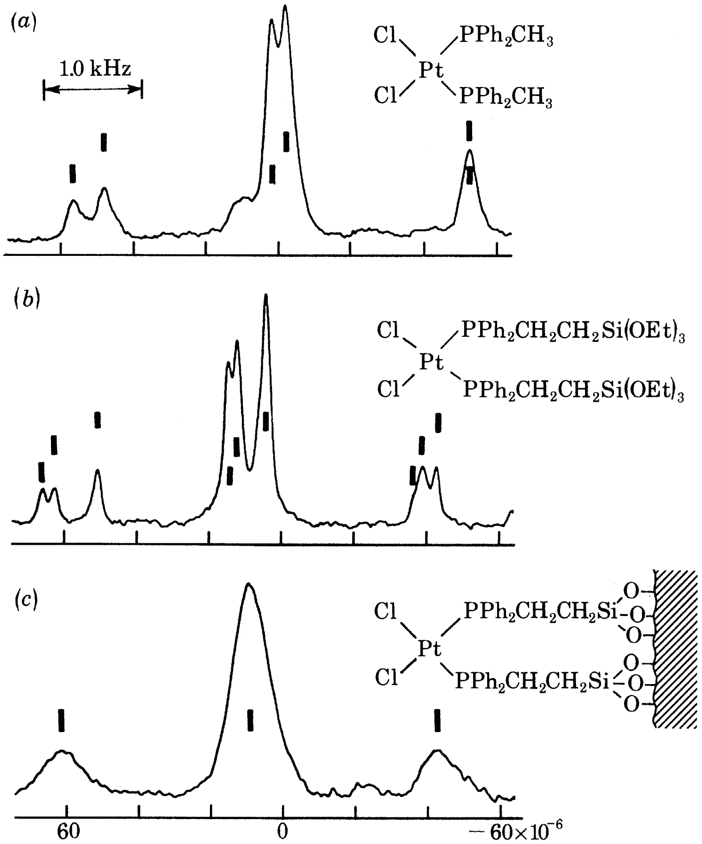


FIGURE 7. (*a*) ^{31}P c.p.–m.a.s. spectrum of solid complex *cis*-$[PtCl_2(PPh_2CH_3)_2]$ (250 mg) recorded at 36.442 MHz by using matching and decoupling fields of approximately 1 mT, spinning at 3 kHz in a Delrin rotor; 3000 scans were accumulated with a 1 s recycle time and a 1 ms single c.p. contact. The f.i.d. was transformed with a 15 Hz line broadening and the spectrum is referenced to 85 % external H_3PO_4(aq). (*b*) ^{31}P c.p.–m.a.s. spectrum of solid complex *cis*-$[PtCl_2(PPh_2CH_2CH_2SiOEt_3)_2]$, recorded as described above except that 6000 scans were accumulated. (*c*) ^{31}P c.p.–m.a.s. spectrum of *cis*-$[PtCl_2(PPh_2CH_2CH_2SiOEt_3)_2]$, covalently immobilized on glass beads (Porasil B, 125–250 $m^2\ g^{-1}$) after 14000 scans, transformed with a line broadening of 40 Hz.

surface. It is not possible to interpret unambiguously the multiplicity of the central peak without structural data, but the $^1J(^{195}\mathrm{Pt}, ^{31}\mathrm{P})$ couplings again indicate the *cis* geometry. The bottom spectrum is of the surface-immobilized species and indicates that a single pure compound of the geometry indicated is obtained and that the surface environment is disordered with no single preferred orientation. Similar experiments can be used to characterize immobilized polymer supports (Clark *et al.* 1982).

3.2. *Studies of crystalline systems with X-ray determined structures*

In some cases the X-ray diffraction data yield limited structural data even for crystalline materials, owing to the nature of the atoms or the molecules. In others, high-resolution c.p.–m.a.s. spectra can provide additional information to that obtained by X-ray diffraction. For example, molecular motions in the solid state are not detected by X-ray diffraction unless they introduce disorder into the crystal lattice (Fyfe 1979). In addition, these motions may also involve chemical exchange processes in which bond breaking and bond formation occur (Campbell *et al.* 1972, 1976*a*, *b*; Cottrell *et al.* 1972). In these different areas, the n.m.r. experiments supplement the information provided by the crystal and molecular structures determined by X-ray diffraction, as illustrated below.

3.2.1. *Multinuclear solid-state studies of zeolites*

Zeolites are crystalline compounds made up of frameworks of corner-sharing $\mathrm{SiO_4^{4-}}$ and $\mathrm{AlO_4^{5-}}$ tetrahedra (Barrer 1978; Breck 1974). Diffraction data are often limited because many zeolites are microcrystalline and also because the X-ray scattering amplitudes of the Si and Al atoms are almost identical. Thus, while the overall structure may be determined, the detailed placement of the Si and Al atoms generally cannot. It has been shown by Lippmaa *et al.* (1978, 1981) that the $^{29}\mathrm{Si}$ spectra are sensitive to the nature of atoms attached to the oxygen atoms of the $\mathrm{SiO_4^{4-}}$ tetrahedron, separate signals being observed for Si[4Al], Si[3Al,1Si], Si[2Al,2Si], Si[1Al,3Si] and Si[4Si]. It is interesting that no abundant spins are present in zeolites, which makes high-power decoupling unnecessary and cross-polarization impossible. We have shown that excellent spectra of these materials can be obtained at very high magnetic fields by using a conventional high-resolution spectrometer (Bruker Spectrospin/Oxford Instruments WH-400 high-resolution spectrometer with a narrow bore superconducting magnet), as shown in figure 8 for the zeolite analcite (Fyfe *et al.* 1982). The resolution is sufficient for accurate deconvolution of the spectra, which enables one to deduce the details of the distribution of the Si and Al atoms in the framework. Further, the technique may be used to monitor the progress of chemical modification as illustrated in figure 9 which shows the effect of dealumination of a Y-type zeolite by the action of $\mathrm{SiCl_4}$ vapour at elevated temperatures in which Si atoms replace the Al atoms in the lattice, yielding a highly siliceous material with the zeolite-Y structure (Klinowski *et al.* 1981). We have shown that it is possible to obtain spectra at these very high magnetic fields from $^{29}\mathrm{Si}$, $^{27}\mathrm{Al}$, $^{11}\mathrm{B}$, $^{23}\mathrm{Na}$ and other nuclei under high-resolution conditions from zeolites, borosilicate glasses (Fyfe *et al.* 1982*a*), and layer silicates. It appears that a more complete description of the structures of these important materials will emerge from the combined results on a variety of nuclei. In the case of quadrupolar nuclei of non-integral spins, the $(m = \frac{1}{2} \leftrightarrow m = -\frac{1}{2})$ transition is independent of the quadrupolar interaction to first order and is subject only to the second-order quadrupolar interactions. These are inversely proportional to the magnetic field strength and m.a.s. spectra of superior quality are obtained by working

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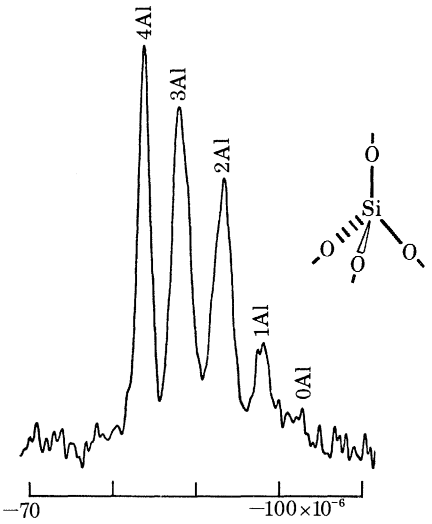


Figure 8. ^{29}Si m.a.s. n.m.r. spectrum of the zeolite analcite recorded at 79.8 MHz (proton frequency 400 MHz) with respect to external TMS. Resonances characteristic of the five possible Si/Al orderings of the attached groups to the SiO_4 tetrahedron (inset) can be seen. 5 s delay and 20 Hz line broadening.

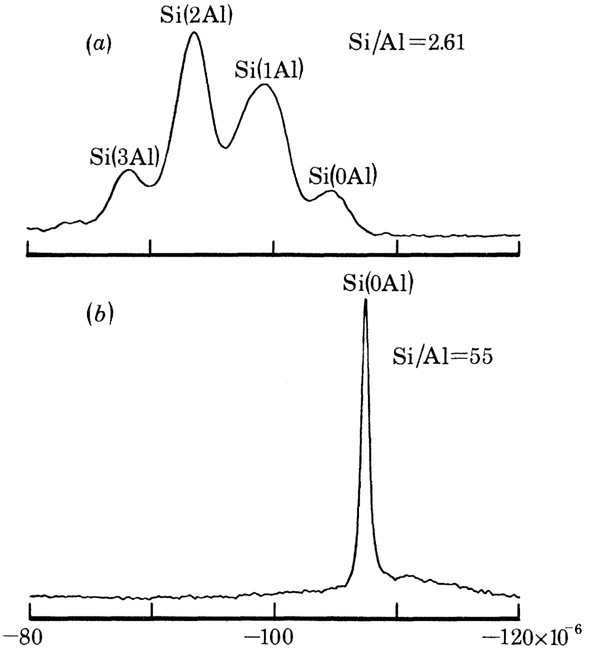


Figure 9. ^{29}Si m.a.s. n.m.r. spectra at 79.8 MHz: (*a*) parent NaY zeolite; (*b*) after treatment with $SiCl_4$. Chemical shifts are relative to TMS.

at the highest possible field strength where the quadrupolar interactions are minimized and the chemical shift dispersion maximized. This is illustrated in figure 10 for the ^{27}Al spectrum of the zeolite Y sample whose ^{29}Si spectrum is shown in figure 9.

3.2.2. *Chemical exchange processes*

A simple spinning apparatus capable of routine variable-temperature operation and its application to the investigation of molecular motions and chemical exchange processes has been

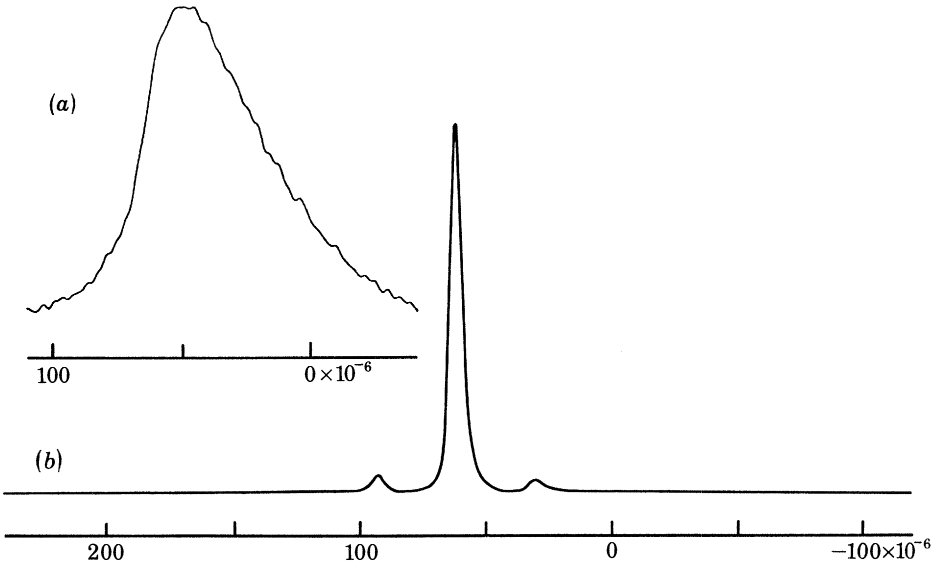


FIGURE 10. ^{27}Al m.a.s. n.m.r. spectra of NaY zeolite recorded at (*a*) 23.5 MHz (proton frequency 90 MHz) and (*b*) 104.2 MHz (proton frequency 400 MHz). The chemical shifts are reported relative to external $Al(H_2O)_6^{3+}$ in aqueous solution.

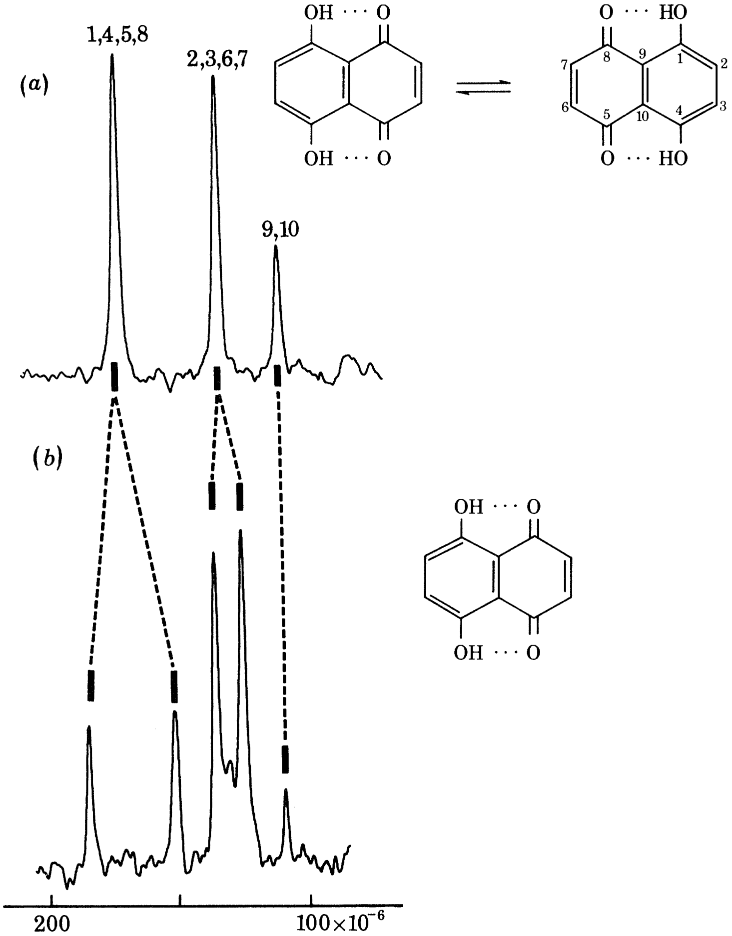
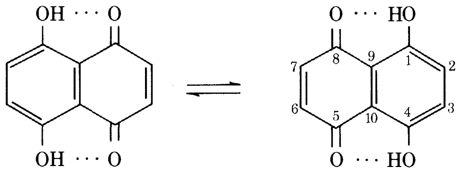
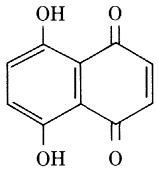


FIGURE 11. ^{13}C n.m.r. spectra at 22.6 MHz of solid naphthazarin B, obtained by using c.p.–m.a.s. techniques (600 scans, 30 Hz line broadening, cross-polarization time 1 ms, recycle time 3 s): (*a*) 25 °C; (*b*) −160 °C. Chemical shifts are relative to TMS.

described (Fyfe *et al.* 1982*c*). Here we present an example from our recent work that illustrates the general characteristics of such measurements and emphasizes the differences that may occur between solution and solid-state behaviour. Figure 11 shows the room-temperature and low-temperature solid-state ^{13}C c.p.–m.a.s. spectra of naphthazarin B (**1**) (Shiau *et al.* 1980). Various attempts to determine the molecular structure by diffraction techniques have led to centrosymmetric structures such as **2**, whereas the n.m.r. spectra clearly indicate the occurrence of the tautomeric chemical exchange process as indicated in scheme 4.



Scheme 4. Napthazarin B tautomeric exchange process.



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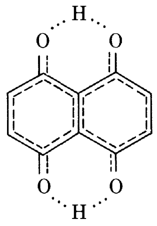

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In the crystalline material at room temperature, the exchange is fast on the n.m.r. timescale, giving the molecule an additional apparent plane of symmetry in which the sets of carbon atoms (1, 4, 5, 8) and (2, 3, 6, 7) are equivalent. The room-temperature ^{13}C spectrum contains only three lines (figure 11). The exchange process, which is also present in solution but which cannot be frozen out in the liquid phase, is frozen out in the solid state at 160 K (figure 11). If only a simple exchange process were taking place, a gradual broadening, coalescence and sharpening of the resonances of carbons (1, 4, 5, 8) and (2, 3, 6, 7) would be expected with increasing temperature, the signal from carbons (9, 10) being unaffected by the exchange. Yet this is not observed: the spectra at intermediate temperatures are a superposition of the limiting low-temperature and high-temperature spectra (figure 12) (Fyfe *et al.*, unpublished results). It is thought that these changes reflect the occurrence of a second-order phase transition that sets the exchange process into operation. At low temperatures, the molecules are in a phase where the exchange cannot occur; as the temperature is increased, more molecules enter the high-temperature phase, where not only can the exchange take place but the energy barrier is sufficiently low for their n.m.r. behaviour to be in the 'fast exchange' limit. Thus as well as detecting the occurrence of the exchange process, n.m.r. monitors the progress of the phase transition.

3.3. *A bridge between solution and solid-state structures: reactive intermediates*

A potential problem with solid-state molecular structures is that they may differ from those in solution owing to packing interactions with the surrounding molecules in the crystal lattice. This can be expected to be of particular importance with charged species and conformationally mobile molecules. With stable carbonium ions such as the heptamethylbenzenium

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ion, where the structures are well known, it has been demonstrated that there is little change in the spectra between the solid state and solution and therefore that the charge density – shift relations measured by solution n.m.r. studies may be used in the solid-state investigations (Fyfe *et al.* 1979*a*). For molecules of unknown structure, the solid-state spectra may be used to bridge the gap between a solid-state structure determined by diffraction techniques and that in solution. An example of such a study on the structure of the 2-hydroxyhomotropylium ion is

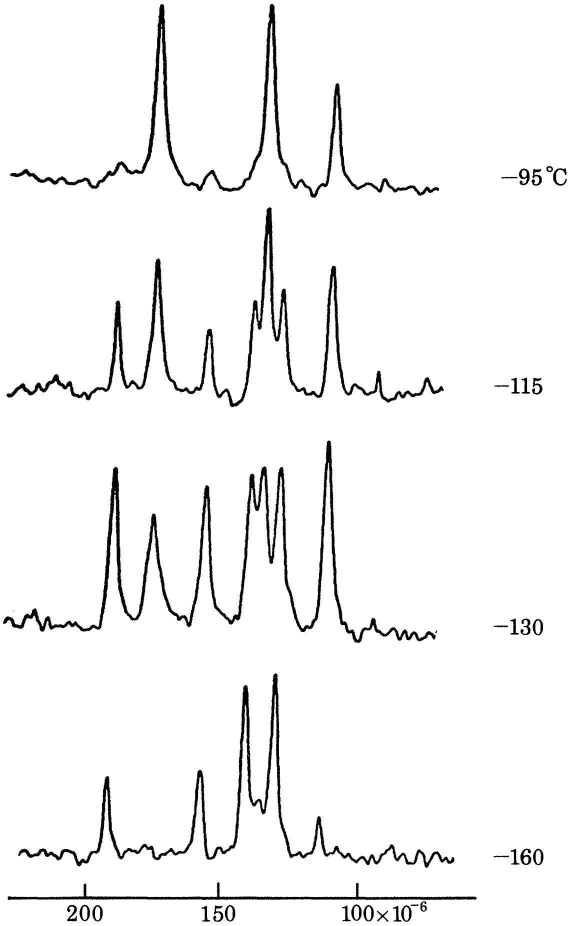


FIGURE 12. ^{13}C n.m.r. spectra at 22.6 MHz of solid naphthazarin B at the temperatures indicated. Chemical shifts are relative to TMS. The spectra were all recorded under conditions similar to those of figure 11.

shown in figure 13 (Fyfe *et al.* 1982*e*). The argument here is whether delocalization of the positive charge takes place around the whole of the tropylium moiety as indicated for the homotropylium ion (**3**) or whether it exists in the more localized form (**4**) where there is no bonding between C 1 and C 7. The structure shown in the inset in figure 13 is that determined by X-ray diffraction and clearly demonstrates bonding between C 1 and C 7. The equivalence of the solution and solid-state spectra indicates that this structure is also present in solution. The comparison between the two states is *only* possible by n.m.r. and it is to be expected that many solution–solid-state n.m.r. studies of this general type will be carried out in the future.

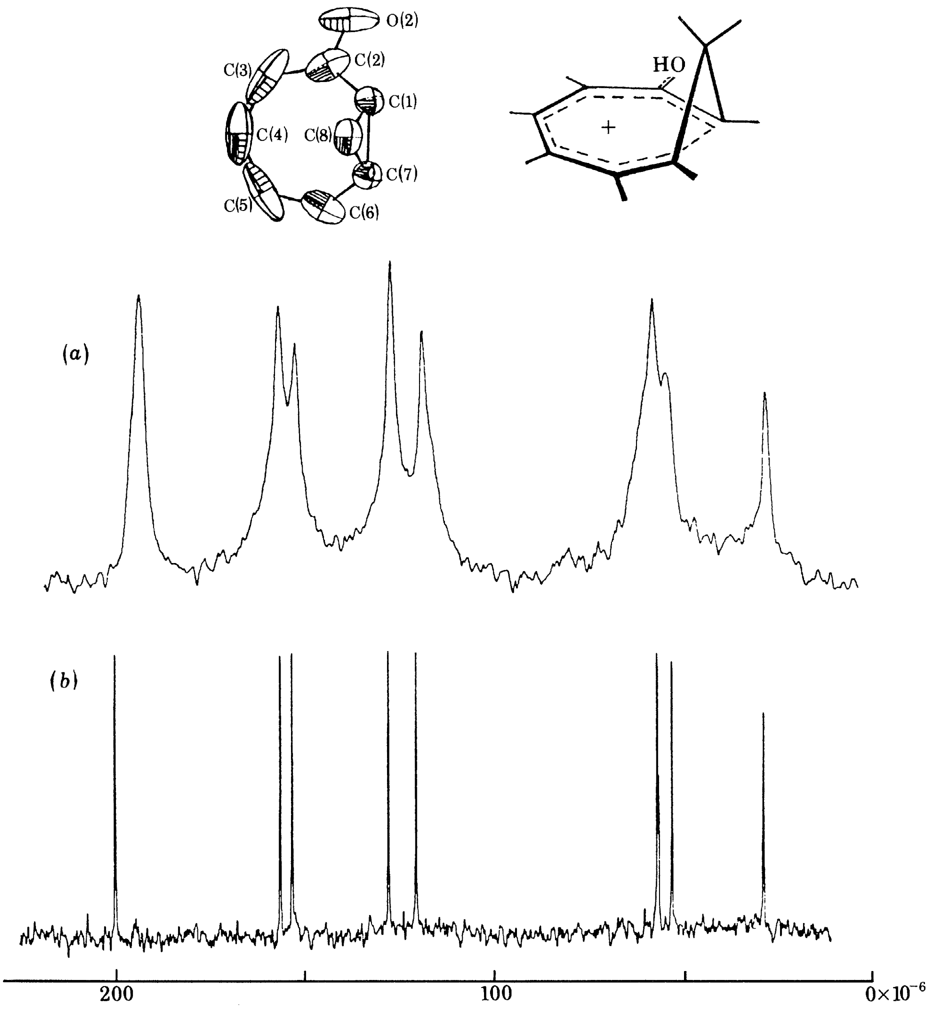
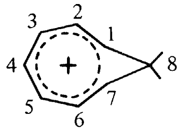


FIGURE 13. (*a*) The ^{13}C c.p.–m.a.s. solid-state spectrum of the 2-hydroxyhomotropylium ion at 22.6 MHz. (*b*) The ^{13}C solution spectrum obtained at 100 MHz. The X-ray determined solid-state structure of the ion is shown with a diagram of its molecular structure above the spectra. Chemical shifts are relative to TMS.



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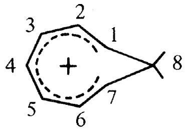

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4. QUANTITATIVE ASPECTS OF THE EXPERIMENT

An obviously important aspect of any analytical technique is its quantitative reliability. As indicated in §2.3, cross-polarization brings very substantial gains in S/N, and most solid-state studies have used this technique. However, this gain in sensitivity is made at the expense of the more quantitative aspects of the experiment. In general, the magnetization of the dilute nucleus observed grows with a characteristic time constant $T_{\text{C–H}}$ that is different for different nuclei and decays at a rate determined usually by $T_{1\rho(\text{H})}$, which affects all carbon nuclei equally, or

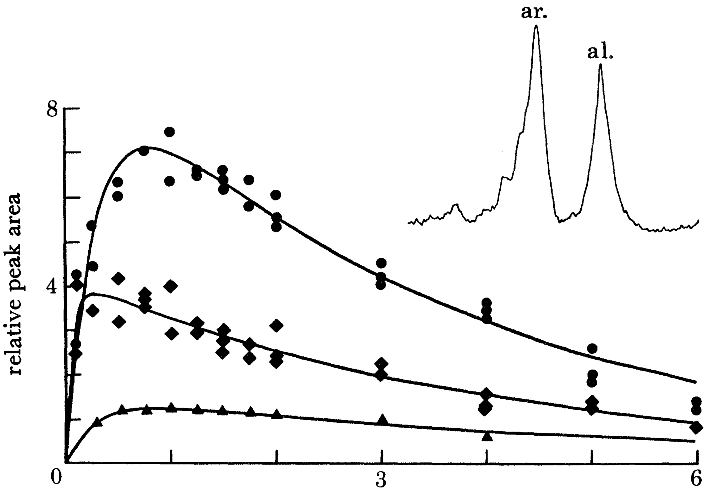

FIGURE 14. The dependence of the ^{13}C magnetization of the aromatic (ar.) and aliphatic (al.) resonances of lignite A coal sample from Estevan, Saskatchewan, on the contact time. The solid curves are from theoretical fits to the data in each case. ●, aromatic carbons; ◆, aliphatic carbons; ▲, non-protonated aromatic carbons. A typical spectrum (0.75 ms contact time, 1 s delay, 2000 scans) is shown inset above the curves.

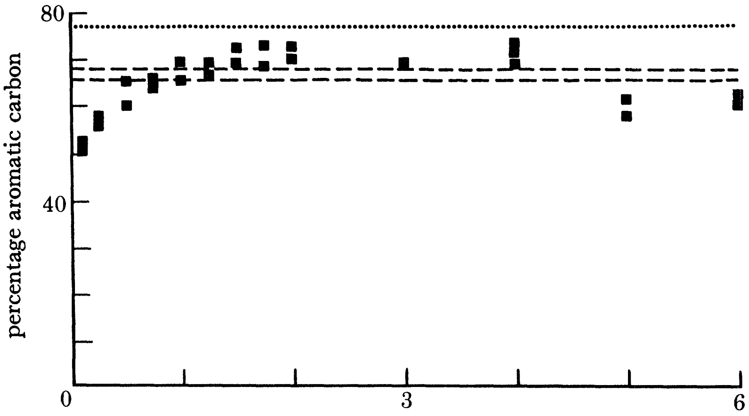

FIGURE 15. Percentage aromatic carbon as a function of contact time for lignite A. The dashed lines represent the range of values from fitting the magnetization curves of figure 14. The dotted line indicates the value obtained from a simple 90° pulse sequence with a long delay time.

may discriminate between different carbon nuclei. All the c.p. spectra described above (with the exception of figure 6) are thus semi-quantitative at best, with unknown discrimination among the chemically different nuclei detected. Using a procedure that is quite general in nature we have investigated in detail two cases where quantitative information is essential: phenolic resins (Fyfe *et al.* 1982*d*) and coals and related materials (Dudley & Fyfe 1982). C.p.-m.a.s. spectra have been used by a number of authors for the chemical analysis of coal samples (Van der Hart *et al.* 1976; Bartuska *et al.* 1977; Retcofsky *et al.* 1978; Zilm *et al.* 1979; Maciel *et al.* 1979*a*, *b*; Wemmer *et al.* 1981). In general, there is sufficient resolution to distinguish between aromatic and aliphatic carbon atoms (figure 14 inset), with further fine structure observable in some cases. The signal intensities show different dependences on the contact time (figure 14) and this is reflected in the apparent ratio of aromatic to aliphatic carbons (figure 15). The *absolute* intensities of the different carbon signals may be found by determining the spin–lattice relaxation times of the carbon nuclei and then recording the spectrum, by using a simple single-pulse technique with a repeat time five times the longest carbon T_1 value to ensure complete remagnetization between pulses. Such a procedure is much more time-consuming than the c.p. sequence but yields quantitatively reliable spectra that may be used as benchmark values for the c.p. data. This is shown in figure 15, together with the results from an alternate procedure of fitting the magnetization behaviours of figure 14 to an analytical expression representing the net effect of the growth and decay processes. As can be seen, quantitatively reliable, high-resolution spectra may be obtained by either procedure. They may also be used to calibrate the c.p. measurements by choosing the appropriate contact time for the system which (for whatever reasons) gives the same value as the quantitative experiment; this may be useful for quality control applications.

5. CONCLUSIONS

The combined c.p.–m.a.s. n.m.r. experiment is applicable to many nuclei and yields spectra of moderate resolution from solid samples. The technique is complementary to X-ray diffraction measurements and can be used on microcrystalline and amorphous materials where diffraction measurements are not possible. It can provide additional information on, for example, chemical exchange processes and the relation between solid-state and solution structures in materials where diffraction information is available. In its simple form the technique is semi-quantitative but can be made completely quantitative with further work.

We acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada for operating funds (C. A. F., R. C., H. C. C., J. S. H., R. E. L., C. I. L., A. R. and R. E. W.) and the Science and Engineering Research Council (J. M. T.). The high-field spectra were obtained at the South Western Ontario NMR Centre funded by a Major Installation Grant from N.S.E.R.C.

REFERENCES (Fyfe *et al.*)

Andrew, E. R. 1971 *Prog. nucl. magn. Reson. Spectrosc.* **8**, 1.
Andrew, E. R. 1981 *Int. Rev. phys. Chem.* **1**, 175.
Barrer, R. M. 1978 *Zeolites and clay minerals as sorbents and molecular sieves.* New York: Academic Press.
Bartuska, V. J., Maciel, G. E., Schaefer, J. & Stejskal, E. O. 1977 *Fuel* **56**, 354.
Bemi, L., Clark, H. C., Davies, J. A., Fyfe, C. A. & Wasylishen, R. E. 1982*a* *J. organometall. Chem.* **224**, C5.
Bemi, L., Clark, H. C., Davies, J. A., Drexler, D., Fyfe, C. A. & Wasylishen, R. E. 1982*b* *J. Am. chem. Soc.* **104**, 438.
Bovey, F. A. 1972 *High-resolution NMR of macromolecules.* New York: Academic Press.
Breck, D. W. 1974 *Zeolite molecular sieves.* New York: John Wiley & Sons.
Breitmaier, E. & Voelter, W. 1974 ^{13}C *NMR spectroscopy.* Germany: Verlag Chemie.
Campbell, A. J., Fyfe, C. A. & Maslowsky, E. Jr 1972 *J. Am. chem. Soc.* **94**, 2690.
Campbell, A. J., Cottrell, C. E., Fyfe, C. A. & Jeffrey, K. R. 1976*a* *Inorg. Chem.* **15**, 1321.
Campbell, A. J., Cottrell, C. E., Fyfe, C. A. & Jeffrey, K. R. 1976*b* *Inorg. Chem.* **15**, 1326.
Clark, H. C., Davies, J. A., Fyfe, C. A., Hayes, P. J. & Wasylishen, R. E. 1982 (In preparation.)
Collman, J. P. & Hegedus, L. S. 1980 In *Principles and applications of organotransition metal chemistry*, p. 130. California: University Science Books.
Cottrell, C. E., Fyfe, C. A. & Senoff, C. V. 1972 *J. organometall. Chem.* **43**, 203.
Dudley, R. L. & Fyfe, C. A. 1982 *Fuel.* (In the press.)
Fyfe, C. A. 1979 *Molec. Cryst. liq. Cryst.* **52**, 1.
Fyfe, C. A., Bruck, D., Lyerla, J. R. & Yannoni, C. S. 1979*a* *J. Am. chem. Soc.* **101**, 4770.
Fyfe, C. A., Lyerla, J. R. & Yannoni, C. S. 1979*b* *J. Am. chem. Soc.* **101**, 1351.
Fyfe, C. A., Rudin, A. & Tchir, W. 1980 *Macromolecules* **13**, 1320.

Fyfe, C. A., Gobbi, G. C. & Hartman, J. S. 1982*a* (In preparation.)
Fyfe, C. A., Gobbi, G. C., Hartman, J. S., Lenkinski, R. E., O'Brien, J. H., Beange, E. R. & Smith, M. A. R. 1982*b* *J. magn. Reson.* **47**, 168.
Fyfe, C. A., Lyerla, J. R. & Yannoni, C. S. 1982*c* *Acct. chem. Res.* (In the press.)
Fyfe, C. A., Rudin, A. & Tchir, W. 1982*d* (In preparation.)
Fyfe, C. A., Wasylishen, R. E., Childs, R. & Lock, C. L. 1982*e* *J. Am. chem. Soc.* (In the press.)
Garroway, A. N., Moniz, W. B. & Resing, H. A. 1979 *Am. chem. Soc. Symp. Ser.*, no. 103, p. 67.
Gibby, M. G., Pines, A. & Waugh, J. S. 1972 *Chem. Phys. Lett.* **16**, 296.
Gillis, J. & Oesper, R. E. 1964 *J. chem. Educ.* **41**, 224.
Griffin, R. G. 1977 *Analyt. Chem.* **49**, 951A.
Hartley, F. R. & Vezey, P. N. 1977 *Adv. organometall. Chem.* **15**, 189.
Hill, H. D. W., Zens, A. P. & Jacobus, J. 1979 *J. Am. chem. Soc.* **101**, 7090.
Klinowski, J., Thomas, J. M., Audier, M., Vasudevan, S., Fyfe, C. A. & Hartman, J. S. 1981 *J. chem. Soc. chem. Commun.*, p. 570.
Levy, G. C. & Nelson, G. L. 1972 ^{13}C *NMR for organic chemists*. New York: Wiley-Interscience.
Lippmaa, E., Alla, M. A., Pehk, T. J. & Engelhardt, G. 1978*a* *J. Am. chem. Soc.* **100**, 1931.
Lippmaa, E., Mägi, M., Samoson, A. & Engelhardt, G. 1978*b* *J. Am. chem. Soc.* **100**, 1929.
Lippmaa, E., Mägi, M., Samoson, A., Tarmak, M. & Engelhardt, G. 1981 *J. Am. chem. Soc.* **103**, 4992.
Lyerla, J. R., Yannoni, C. S., Bruck, D. & Fyfe, C. A. 1979 *J. Am. chem. Soc.* **101**, 4770.
Maciel, G. E., Bartuska, V. J. & Miknis, F. P. 1979*a* *Fuel* **58**, 155.
Maciel, G. E., Bartuska, V. J. & Miknis, F. P. 1979*b* *Fuel* **58**, 391.
Martin, M. L., Delpuech, J.-J. & Martin, G. J. 1980 *Practical NMR spectroscopy*. London: Heyden.
Mehring, M. 1976 *N.M.R. – basic principles and progress*, vol. 11. New York: Springer.
Miknis, F. P., Bartuska, V. J. & Maciel, G. E. 1982 *Am. Lab.* (In the press.)
Pines, A., Gibby, M. G. & Waugh, J. S. 1972 *Chem. Phys. Lett.* **15**, 273.
Pines, A., Gibby, M. G. & Waugh, J. S. 1973 *J. Chem. Phys.* **59**, 569.
Pople, J. A., Schneider, W. G. & Bernstein, H. J. 1959 *High-resolution nuclear magnetic resonance*. New York: McGraw-Hill.
Retcofsky, H. L. & Vanderhart, D. L. 1978 *Fuel* **57**, 421.
Schaefer, J. & Stejskal, E. O. 1976 *J. Am. chem. Soc.* **98**, 1031.
Schaefer, J., Stejskal, E. O. & Buchdahl, R. 1977 *Macromolecules* **10**, 384.
Sefcik, M. D., Stejskal, E. O., McKay, R. A. & Schaefer, J. 1979 *Macromolecules* **12**, 423.
Shiau, W.-I., Duesler, E. N., Paul, I. C., Curtin, D. Y., Blann, W. G. & Fyfe, C. A. 1980 *J. Am. chem. Soc.* **102**, 4546.
Slonim, I. Ya. & Lyubimov, A. N. 1970 *The NMR of polymers*. New York: Plenum Press.
Stothers, J. B. 1972 ^{13}C *NMR spectroscopy*. New York: Academic Press.
Vanderhart, D. L. & Retcofsky, H. C. 1976 *Fuel* **55**, 202.
Wehrli, F. W. & Wirthlin, T. 1980 *Interpretation of carbon-13 NMR spectra*. London: Heyden.
Wemmer, D. E., Pines, A. & Whitehurst, D. D. 1981 *Phil. Trans. R. Soc. Lond.* A **300**, 15.
Whitehouse, A. A. K., Pritchett, E. G. K. & Barnett, G. 1967 *Phenolic resins*. London: Iliffe.
Zilm, K. W., Pogmire, R. J., Grant, D. M., Wood, R. E. & Wiser, W. H. 1979 *Fuel* **58**, 11.

Discussion

J. E. Page (127 *Northumberland Road, Harrow, U.K.*). I congratulate Professor Fyfe on his interesting paper. I have two questions. Has his group studied the solid-state n.m.r. spectra of polymorphic compounds and attempted to correlate such spectra with X-ray structural data? Could he comment, further, on the quantitative reliability of n.m.r. spectra of solid organic compounds?

C. A. Fyfe. On the first point, small spectral differences may be observed between polymorphs if they are very crystalline. Further, different crystalline forms may show quite different physical behaviour, which may be detected by solid-state n.m.r. For example, the polymorphic forms A and C of naphthazarin show quite different dynamic behaviour from that of naphthazarin B, which we have discussed. On the second point, a simple m.a.s. experiment, as with the ^{29}Si and ^{27}Al spectra, which we have discussed, can easily be made quantitatively reliable by a choice of delay time, which is $5 \times T_1$ for the slowest relaxing nucleus. The c.p.–m.a.s. experiments are more difficult and care should be taken to calibrate these, as discussed for the coal spectra, if quantitatively reliable spectra are desired.