

be as close as possible to the fast-spin limit. A method has also been introduced to reduce spectral congestion by eliminating sidebands.³⁹

Sample Effects. Even under ideal experimental CPMAS conditions, static and/or dynamic effects can limit resolution in particular samples. Amorphous materials, such as polymers²⁸ or matrices,¹³ may have a distribution of isotropic chemical shifts for a single carbon. This can contribute several parts per million of broadening. Furthermore, interference between coherent motion (e.g., spin locking or sample rotation) and molecular motion can conspire to degrade the resolution gained in the CPMAS technique.^{3a,28,40} Splittings due to solid state effects (see Figure 1d) or coupling to nuclei with quadrupole moments (e.g., ¹⁴N, ³⁵Cl) may complicate or broaden ¹³C spectra of solids,^{12,41} but can also lead to new structural information.⁴² Some of these, as well as other more subtle effects, have been considered in a recent comprehensive study.⁴³ The authors conclude that the resolution in ¹³C spectra of organic solids will generally not be as good as in liquids, and

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furthermore, that increasing the magnetic field may not help.

Conclusions

¹³C CPMAS spectroscopy in organic solids uses high power decoupling (spin locking) to remove proton dipolar broadening, magic angle spinning to eliminate broadening due to carbon chemical shift anisotropy, and coherently driven proton-carbon cross relaxation to enhance ¹³C sensitivity. The result is well-resolved ¹³C NMR spectra of organic solids.

The spectrum of the benzil derivative shown in Figure 1d dramatically illustrates the power of the CPMAS technique for structural studies in solids, purely from the viewpoint of resolution. Another major area that has been opened up through CPMAS is the study of molecular dynamics on a carbon-by-carbon level. Individual carbon T_1 ⁴⁴ or $T_{1\rho}$ measurements have already been used to study main chain and side group dynamics in polymers.^{28,45} In this respect, the power of CPMAS is substantially increased by variable temperature capability,^{2,46} especially for studies of dynamic processes at temperatures heretofore inaccessible by solution NMR. The following Account will report on the use of a CPMAS spectrometer with variable temperature capability to address a variety of structural and dynamical problems of chemical interest.

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Chemical Applications of Variable-Temperature CPMAS NMR Spectroscopy in Solids

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Introduction

Significant advances in the development of "high-resolution" nuclear magnetic resonance (NMR) tech-

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niques for the characterization of molecular properties of solids have occurred in the past decade.¹ From the viewpoint of chemical applications, the most promising of these developments is the cross-polarization (CP),² magic angle spinning (MAS),³ NMR experiment. Indeed, the intervening 6 years since Schaefer and Stejskal⁴ first reported high-resolution ¹³C spectra of polymers in the glassy state have witnessed the extension of this spectroscopy into a diversity of chemically interesting areas, e.g., natural as well as synthetic

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polymers,⁵ resins,^{6,7} model membranes,⁸ coals,⁹ surface-bonded species,¹⁰ organometallics, and other organic solids.¹¹ Although still a rapidly developing technique, these initial studies utilizing CPMAS ¹³C NMR spectroscopy have clearly established its potential as a highly diagnostic probe of physical and chemical properties in the solid state. In this Account we emphasize one emerging aspect of this technique—that of variable-temperature magic angle spinning (VT-MAS).

The Cross-Polarization, Magic Angle Spinning NMR Experiment

The CPMAS ¹³C NMR experiment has been described in detail in the accompanying Account¹² as well as elsewhere in the literature¹³ and is only briefly outlined here for completeness. The dominant source of broadening of ¹³C lines in solids is ¹³C–¹H heteronuclear dipolar interactions (ca. 10–40 kHz in magnitude), ¹³C–¹³C dipolar interactions being of relative unimportance by virtue of the rare spin character (1.1% natural abundance) of the ¹³C isotope. Removal of ¹³C–¹H dipolar broadening is accomplished by coherent averaging via strong irradiation (decoupling) at the proton resonance frequency and results in individual carbon resonances subject to residual broadening by chemical shift anisotropy. This added source of broadening derives from the directional dependence of the chemical shift associated with a spatial nonuniformity in magnetic shielding of the nucleus by the surrounding electrons. Thus, unlike in solution where an average chemical shift (i.e., one-third the sum of the principal elements of the shielding tensor) is observed due to rapid tumbling of the molecule, in the solid state the chemical shift for a given nucleus will depend on the molecular orientation with respect to the applied magnetic field. Removal of the broadening from this source is optimally accomplished by mechanically rotating the sample about an axis inclined at the magic angle (54.7°) relative to the

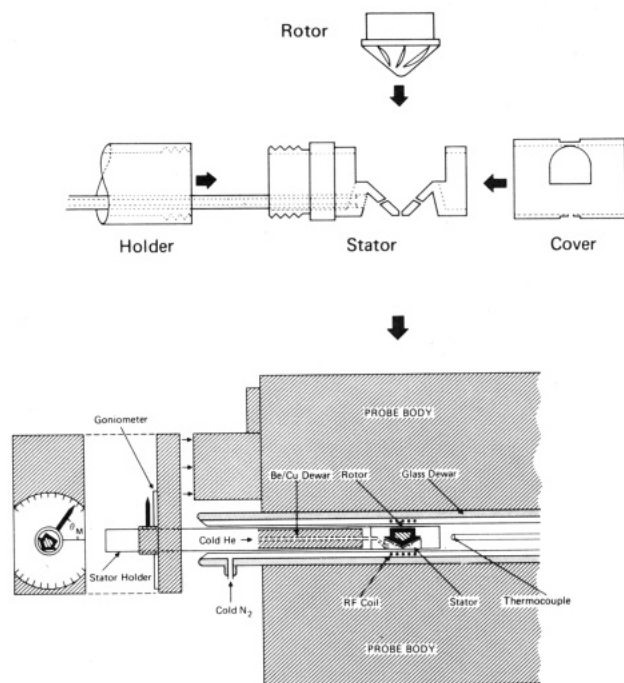


Figure 1. Schematic representation of the component parts of the spinning apparatus and their relationship to one another (see text); shown below is a schematic representation of the spinner assembly positioned in the variable-temperature probe.

applied magnetic field³ at a rate fast compared to the anisotropy expressed in frequency units.⁴ The result of MAS is coherent averaging of the shielding anisotropy; in combination with proton irradiation, this produces, in principle, a ¹³C spectrum in which each magnetically distinct carbon appears as a narrowed single resonance at a frequency characteristic of the isotropic chemical shift for the solid state.

As explained in the foregoing Account, sensitivity enhancement is achieved in the solid-state experiment by rotating-frame transfer of polarization (cross polarization) between the protons and the carbons.² By this method, carbon magnetization can be enhanced up to fourfold above the Zeeman value; furthermore, additional S/N enhancement per unit time is achieved since the CP process can be recycled at the proton spin-lattice relaxation time, which is in general much shorter than the corresponding carbon time.

Variable-Temperature Magic Angle Spinning

A variable-temperature capability is an integral part of liquid-state NMR methodology and is also required for CPMAS ¹³C NMR in order to fully exploit the technique. The resolution afforded by the CPMAS experiment in conjunction with variable-temperature operation presents the potential for detailed insight into molecular structure, dynamics, and reactivity in the solid state, for example, the investigation, at the atomic level, of (1) molecular motions and mechanisms involving chemical exchange processes; (2) reactive chemical intermediates trapped and stabilized by the lattice and low temperature; (3) molecular dynamics in organic solids and polymers; (4) substances that are liquids or gases at ambient temperature; (5) substances that have inimical relaxation times at ambient temperature for cross polarization. We turn next to con-

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sideration of a variable-temperature spinner design conceived and implemented in our laboratory.¹⁴

VT-MAS Apparatus. Two main techniques have been used to produce the high spinning rates (kHz) required for MAS, one in which rotors are supported by a gas bearing^{3a,c} and the other in which rotors are supported by an axle assembly.^{3b} Each technique has its merits and drawbacks, and the design we have employed¹⁴ (Figure 1) represents a compromise between the two. The general philosophy behind the design is to provide for (1) ease of loading samples, including those sensitive to air, moisture, or ambient temperature, and (2) temperature variation. In using the apparatus, the sample is inserted into the stator cone, which is then sealed by the covering sleeve. The spinning gas is introduced through an inlet into the stator cone. When assembled, the apparatus has the cylindrical geometry of a standard NMR tube and can be easily inserted into a conventional design of probe having an insert around which the coil is wound (see Figure 1). For an electromagnet, the magic angle may be reached by inserting the holder vertically into the probe (with the rotor spinning around a horizontal axis) and rotating it until the correct angle is reached, or by inserting the holder horizontally into the probe (Figure 1) (with the rotor spinning around a vertical axis) and then rotating the holder until the correct angle is reached.¹⁴ The first arrangement in reaching the angle corresponds to a conventional rf-coil/ B_0 field geometry. In both arrangements, the exact angle chosen is reached by continuous adjustment of the rotation angle which is controlled by a goniometer head attached to the top or front of the probe body. When the full complement of rotational angles (0–90°) is available, ¹³C spectra can be obtained in which the chemical shift anisotropy is scaled by $(3 \cos^2 \theta - 1)/2$, where θ is the angle between the field and the spinning axis.¹⁵ This allows measurement of the individual elements of the shielding tensor in compounds with multiple carbon resonances.¹⁵

Temperature variation is achieved by preheating or precooling the gas used for spinning. The driving gas is transferred by a Be/Cu dewar (over which the spinning assembly fits) directly into the stator cup, resulting in spinning and heating or cooling. An important feature of the present design of VT-MAS apparatus is that it enables the rf coil to be isolated physically from the spinner and driving gas (see Figure 1). This in turn makes possible the use of helium (which undergoes electrical breakdown in direct contact with high rf fields) as propellant and thereby provides for fast spinning rates at relatively low gas pressures even down to liquid nitrogen temperature. Spinning rates up to 3.5 kHz are obtained as low as 77 K without problems of rotor stability.¹⁴ Although it is possible to spin with nitrogen gas at low temperature,¹⁶ it is difficult to achieve the spinning rates necessary to obtain spectra free of sidebands.¹² The CPMAS experiments may be performed down to 77 K by using assemblies fabricated from Kel-F or Delrin, while temperatures above am-

bient are accessible by using boron nitride or machinable glass. (Note: for study of hydrocarbon materials, Kel-F is used, while for study of fluorocarbon materials, Delrin is used. The use of spin temperature inversion¹² ensures that signals from a fluorocarbon (hydrocarbon) spinning apparatus will not interfere with the spectrum of a hydrocarbon (fluorocarbon) sample generated by ¹H–¹³C (¹⁹F–¹³C) cross polarization.)

Sensitivity and Variable-Temperature CP Experiments. Before detailing some chemical applications of VT-MAS, it is worthwhile to note the importance of temperature variation from the purely operational point of view. As discussed in the previous Account,¹² the presence of unfavorable relaxation times ($T_{1\rho}$, T_1) can conspire to make cross polarization inefficient at a given temperature. For example, poly(ethylene oxide), PEO, has a minimum in its proton $T_{1\rho}^H$ value at ambient temperature.¹⁷ This results in a very weak ¹³C signal via cross polarization since the proton order is destroyed before polarization transfer has proceeded to a significant degree.¹² However, a VT-MAS capability allows manipulation of relaxation parameters and thereby cross-polarization efficiency. In the case of PEO, ¹³C spectra in the bulk¹⁸ are readily obtained by CP at temperatures below –60 °C, where $T_{1\rho}^H$ is sufficiently long for polarization transfer to take place. Similarly, VT-MAS allows operation in temperature regions where effects of motional broadening (see later discussion) are minimized.

Chemical Rate Processes in the Solid State

Motional Effects in the Solid State. One of the important applications of NMR spectroscopy is that chemical rate processes with lifetimes of ca. 10^{-10} – 10^{-6} s can be studied directly by observing line shape changes as a function of temperature. An important situation arises when the solid state induces magnetic inequivalence in a pair or pairs of carbon atoms that are equivalent in solution due to rapid molecular reorientation. If molecular motion, which renders these atoms equivalent, occurs in the solid state at higher temperature, coalescence of the signals will be observed. Such a situation has been found by Garroway and co-workers⁶ who investigated a piperidine-cured epoxy based on a resin from the diglycidyl ether of bisphenol A. Over the temperature range 150–350 K, the resonances for the C-3, C-3' carbons were observed to be distinct and then undergo coalescence as motional averaging occurred (Figure 2). An important feature of spectral sensitivity to the occurrence of molecular motions is that motions will be detected which occur at rates comparable to the frequency separation of the signals (ca. 100 Hz in this case). In contrast to the epoxy, the inequivalence of the C-3, C-3' ring carbons in poly(*p*-hydroxybenzoic acid)¹⁹ is unaffected over the temperature range –155–80 °C. The 80 °C spectrum allows a minimum barrier to motional averaging of greater than 17 kcal/mol to be estimated. It is probable that VT-MAS measurements on samples whose spectra show reduced symmetry due

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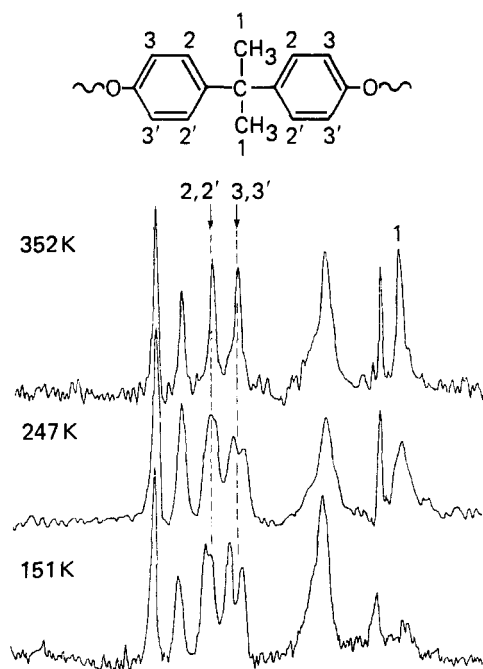
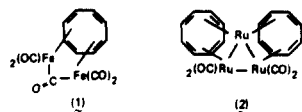


Figure 2. CPMAS spectra recorded at the temperatures indicated of a cured epoxy based on a resin from the diglycidyl ether of bisphenol A and containing the residue shown in the figure.⁶

to solid-state effects will provide incisive information regarding low frequency motions in complex systems.

Chemical Exchange in the Solid State. As in solution NMR experiments, the CPMAS experiments are very sensitive to the situation where the motion of all or part of a molecule is accompanied by a chemical exchange process. Because the experiment yields the isotropic chemical shift values for individual carbon resonances, the only process (apart from accidental degeneracy), that can give a single signal from magnetically inequivalent carbons in a molecule, is a chemical exchange process which interconverts them—exactly the situation that exists for such processes in solution. Proton NMR of solids can detect the occurrence of molecular motion; however, the resolution is not sufficient to discern whether the motion involves a chemical exchange process or not. The spectrum of the organometallic²⁰ complex pentacarbonyl(cyclo-octatetraene)diiron (1) shows only a single signal for the



eight protons in the room temperature solution NMR spectrum.²¹ This indicates that although localized bonding of the iron atoms to the ring is expected, the points of bonding are continually changing due to a chemical exchange process involving the mutual re-orientation of the ring and the $\text{Fe}_2(\text{CO})_5$ moiety, which results in a single average environment for each of the ring carbon and hydrogen atoms. Such complexes are termed fluxional organometallics.²⁰ The ^{13}C CPMAS spectrum of 1 shows the same averaging of the ring carbon signals (Figure 3a). This averaging, which is

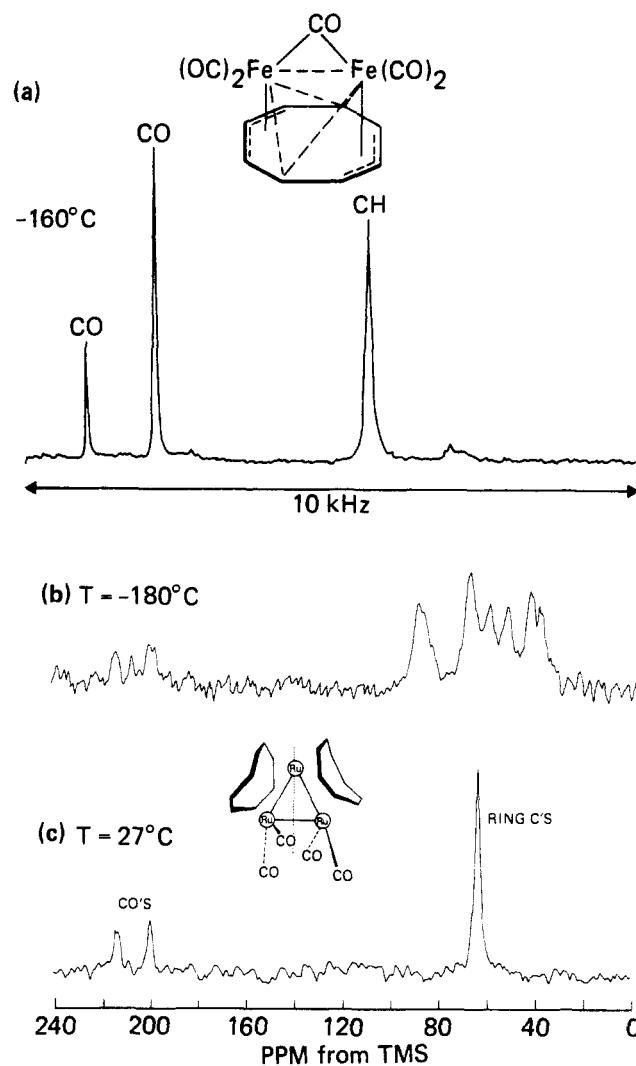


Figure 3. (a) CPMAS spectrum of 1 at -160°C with CP contact time of 1-ms and 2-s repeat time; (b) CPMAS spectrum of (2) at -180°C with CP contact time of 5 ms and a repeat time of 1 s; (c) CPMAS spectrum of (2) at 27°C with conditions the same as (b).

not detected by X-ray diffraction techniques unless disorder is introduced by the dynamic process, persists down to at least -160°C in the solid state (proton NMR relaxation measurements on the solid yield an activation barrier of 2.0 kcal/mol).²²

In some cases, the exchange process may be frozen out, yielding separate signals from each of the magnetically inequivalent carbons in the molecule. For tetracarbonylbis(cyclooctatetraene)triruthenium (2), the room temperature ^{13}C CPMAS spectrum again shows a single resonance for all the ring carbons; however, this degeneracy is lost at low temperature (Figure 3b).²³ Proton relaxation studies of the solid indicate that the energy barrier is 5.5 kcal/mol and that the motion of the ring has ceased by ca. -120°C .²² From a series of VT-MAS spectra at intermediate temperatures, it may be possible to obtain information on the mechanism of the solid-state exchange process.

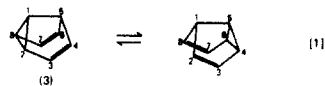
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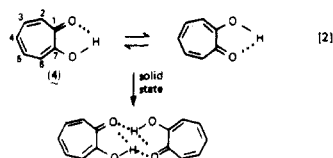
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Not all exchange processes that occur in solution²⁴ also occur in the solid state, even for the case where little change in geometry is involved. For example, semibullvalene (**3**) exhibits fluxional behavior in solution due to the degenerate Cope rearrangement shown in eq 1. The exchange proceeds with ease down to low

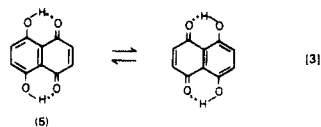


temperatures in solution with an activation barrier of ca. 5.5 kcal/mol.²⁴ In contrast CPMAS spectra of the solid at temperatures as high as $-110\text{ }^{\circ}\text{C}$ (mp ca. $-90\text{ }^{\circ}\text{C}$) show no evidence for exchange, indicating a minimum suppression in rate of a thousandfold.²⁵ These data clearly demonstrate that the results from measurements of chemical exchange processes in solids must be interpreted in terms of factors reflecting solid state as well as intrinsic electronic barriers. Tropolone (**4**) undergoes a tautomeric exchange in solution that cannot be frozen out even at very low temperatures, giving a four-line spectrum where the exchange has averaged the pairs of signals C-1,7, C-2,6, and C-3,5.²⁶



In the CPMAS spectrum of the solid at ambient temperature, seven lines are observed^{27a} due to the formation, in the crystallization, of a dimer.^{27b} If either inter- or intramolecular exchange occurs, it is at a rate greatly reduced relative to that in solution.^{27c}

Even where chemical exchange does occur in the solid state, the crystal lattice will play a contributing and perhaps dominant role. Thus, the room temperature spectrum of naphthazarin (**5**) shows only three signals



due to the intramolecular exchange process (Figure 4a);²⁸ in this regard it is similar to the situation in solution. However, in solution the equilibrium cannot be frozen out, whereas in the solid state a "static" spectrum is obtained at $-160\text{ }^{\circ}\text{C}$ (Figure 4). At intermediate temperatures, the broadening and coalescence of the low-temperature spectrum and the eventual formation of the high-temperature spectrum (the expected behavior for simple exchange averaging) are not observed. Instead, the spectra obtained are the superposition of

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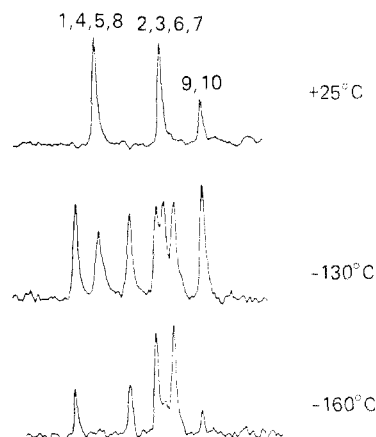
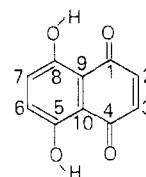
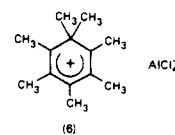


Figure 4. CPMAS spectrum of solid Naphthazarin B recorded at the temperatures indicated, a CP time of 1 ms, and a repeat time of 1 s.

the two limiting spectra in differing proportions depending on the temperature. It is thought that the spectra reflect the occurrence of a second-order phase transition in the solid state between a low-temperature phase where exchange is not possible²⁸ and a high-temperature phase where exchange is possible. Because of the very low activation barrier, the high-temperature phase, at formation, immediately yields the fast exchange limit spectrum. The proportion of the two phases in the spectra provide a quantitative measure of the progress of the phase transition.

Reactive Intermediates

In the case of reactive chemical intermediates, the CPMAS technique promises to be a very powerful tool, especially for the investigation of species where solution NMR studies leave doubt as to the detailed molecular structure or where the species of interest are unstable in solution. We have shown that it is possible to obtain VT-MAS spectra of relatively stable carbonium ions in the solid state.²⁹ As an example, spectra of heptamethylbenzenium tetrachloroaluminate (**6**) as a func-



tion of temperature are shown in Figure 5. The ambient temperature spectrum clearly shows that the ring carbons, C-2 and -6, and C-3 and -5, appear as "doublets" in the solid state spectrum, although these resonances are magnetically equivalent in solution. There are similar, but smaller, inequivalences induced in the corresponding methyl carbon signals. Doubling

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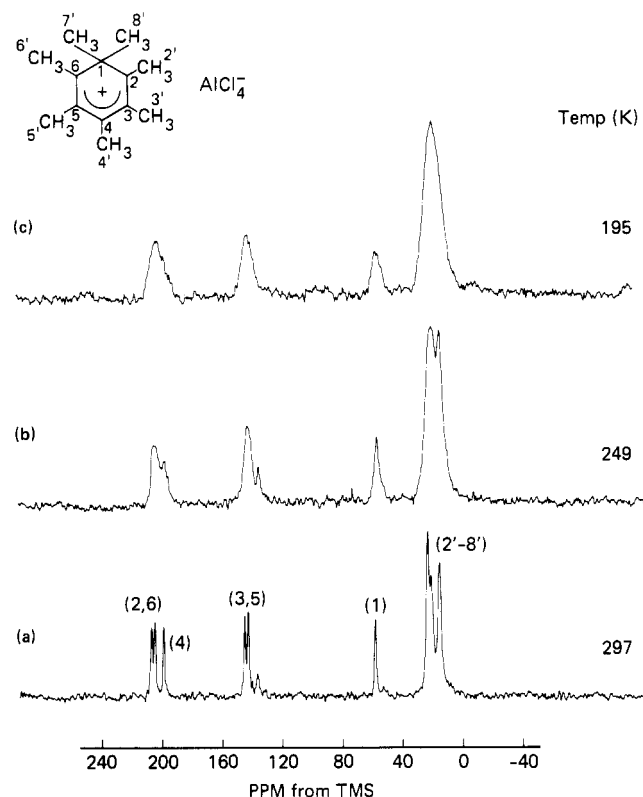


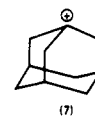
Figure 5. CPMAS ^{13}C spectra of heptamethylbenzenium tetrachloroaluminate at the temperatures indicated. The spectra were obtained with a CP time of 1.5 ms and an experiment repetition time of 2.0 s.

of signals in solid-state spectra could arise if there were two inequivalent lattice sites in the unit cell, but this should affect *all* of the lines in the spectrum. The fact that the signals from C-2 and -6 and C-3 and -5 are affected in the present instance, but those from C-1 or C-4 are not clearly indicates that this is not the mechanism. Instead, the effect arises because the molecular plane of symmetry through C-1 and C-4 has been lost due to the molecule occupying a site in the lattice which does not possess this symmetry element (i.e., site symmetry is lower than molecular symmetry). Consideration of the crystal structure of this complex indicates that this is indeed the case, although it should be noted the structure was refined on the assumption that the plane existed.³⁰ A similar situation is found for the ClO_4^- salt while the SbCl_6^- and BF_4^- salts give rise to ^{13}C spectra that indicate site symmetry is equal to or greater than the molecular symmetry.²⁹

The low-temperature spectra of **6** display an added complication for solid systems that does not occur in solution: possible dipolar broadening of the carbon resonances by the counterions if they contain halogen atoms that have a nucleus with an electric quadrupole moment (spin $> 1/2$). In the case of Cl or Br, the broadening depends strongly on the quadrupolar relaxation process and will be expected to be more important at low temperatures where motions of the counterion will be frozen out. The spectrum of **6** at 249 K (Figure 5b) shows incipient broadening while that at 195 K (Figure 5c) shows the full effect of C-Cl dipolar

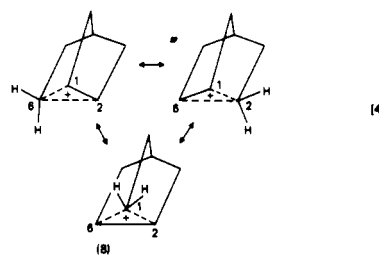
interactions originating from the chlorine nuclei in the AlCl_4^- . The broadening is not removed by MAS.³¹ At ambient temperatures (Figure 5a) a self-decoupling³² is observed due to the short Cl T_1 arising from the motion of the AlCl_4^- ion, but at low temperatures as the motion of the ion is slowed down, the relaxation is less efficient and C-Cl dipolar broadening becomes manifest. Similar effects have been observed in the VT-MAS ^{13}C spectra of poly(trifluorochloroethylene).³³

For a series of carbonium ions, representative of localized and delocalized charge types, it has been observed that the charge density/chemical shift relationships found in solution³⁴ transfer very well to the solid.²⁹ The CPMAS spectra may thus be used for diagnostic purposes as is illustrated by the case of the attempted preparation of the adamantyl carbonium ion (**7**) from the action of fluoroantimonic acid on 1-fluoro-, 1-chloro-, and 1-bromoadamantane. In the case of the



1-fluoroadamantane, the CPMAS spectra indicate that the product formed is always the carbonium ion. For 1-chloroadamantane the carbonium ion is the main product while 1-bromoadamantane reproducibly yields mainly another species.³⁵

In principle, reactive intermediates may be prepared at very low temperatures and studied at these (and lower) temperatures in the solid state without the limitations imposed by the requirements of solution NMR. As an example of the application of these techniques, Figure 6 displays spectra of the 2-norbornyl cation from 129 to 200 K.³⁶ The carbonium ion was prepared by high vacuum codeposition³⁷ of ^{13}C -enriched norbornyl chloride and antimony pentafluoride vapor onto a liquid nitrogen cooled surface. The sample was transferred at temperatures near -150°C to the spinner as a solid material and spectra were recorded. The spectral changes are due to the 6,2,1-hydride shift (eq 4) and a



line-shape analysis yielded an activation energy of 6.1 ± 0.5 kcal/mol, in agreement with a solution ^1H NMR study.³⁸ Nevertheless, the exchange rates in the solid

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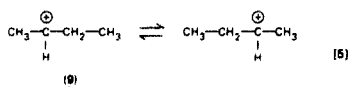
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state are a factor of 3 to 4 slower than in solution (see Figure 6), which indicates a solid-state effect that is relatively small compared with the results found for the Cope rearrangement in semibullvalene.²⁵ The first study of this kind actually was made on the much less stable *sec*-butyl cation, for which the low-temperature procedure described above was even more crucial.³⁹ Spectra obtained at temperatures down to 83 K indicate that if the structure of the *sec*-butyl cation possesses a positive charge localized on a single carbon, that an upper limit of 2.4 kcal/mol can be placed on the barrier to the hydride shift (eq 5).



Relaxation Measurements in the Solid State

One of the principal advantages of CPMAS experiments is that the resolution allows relaxation data to be obtained on each carbon of the molecule in the solid state. If a sufficient number of unique resonances exists, the results can, in principle, be interpreted in terms of rigid body and local motions (e.g., methyl rotation, segmental modes in polymers, etc.).^{4,5} This presents a distinct advantage over the more common proton relaxation measurements where efficient spin diffusion¹² usually results in averaging of relaxation behavior over the ensemble of protons to yield a single relaxation time for all protons, making interpretation of the data in terms of localized motions difficult.

There are a large number of relaxation parameters of interest for the study of organic solids and polymers, and these include the ¹³C and ¹H spin-lattice relaxation times (T_{1C} and T_{1H}), the spin-spin relaxation time (T_2), the nuclear Overhauser enhancement (NOE), the proton and carbon rotating-frame relaxation times ($T_{1\rho}^H$ and $T_{1\rho}^C$), the C-H cross-relaxation time (T_{CH}), and the proton relaxation time in the dipolar state (T_{1D}).⁵ Not all of these parameters provide information in a direct manner; nonetheless, the inferred information is important in characterizing motional frequencies and amplitudes in solids. The initial studies of carbon relaxation in solids have emphasized T_1 and $T_{1\rho}$ measurements, which provide information on molecular motions in the MHz and kHz frequency ranges, respectively. Again, Schaefer and Stejskal have carried out the pioneering work in their investigations of glassy polymers.^{4,5} In particular, they stress the utility of $T_{1\rho}$ measurements for probing the dynamic heterogeneity of the glassy state and as a potential source of insight into the mechanical and other physical properties of polymers at the molecular level. Garroway and co-workers⁶ reported the first VT MAS $T_{1\rho}$ results in their study of epoxy resins, and together with VanderHart,⁴⁰ have detailed the complications in extracting information on molecular motion from $T_{1\rho}$ experiments.

Spin-Lattice Relaxation in Poly(propylene). Relaxation measurements over a range of temperatures are fundamental to characterization of molecular dynamics in gas, liquid, or solid state. Thus, variable-

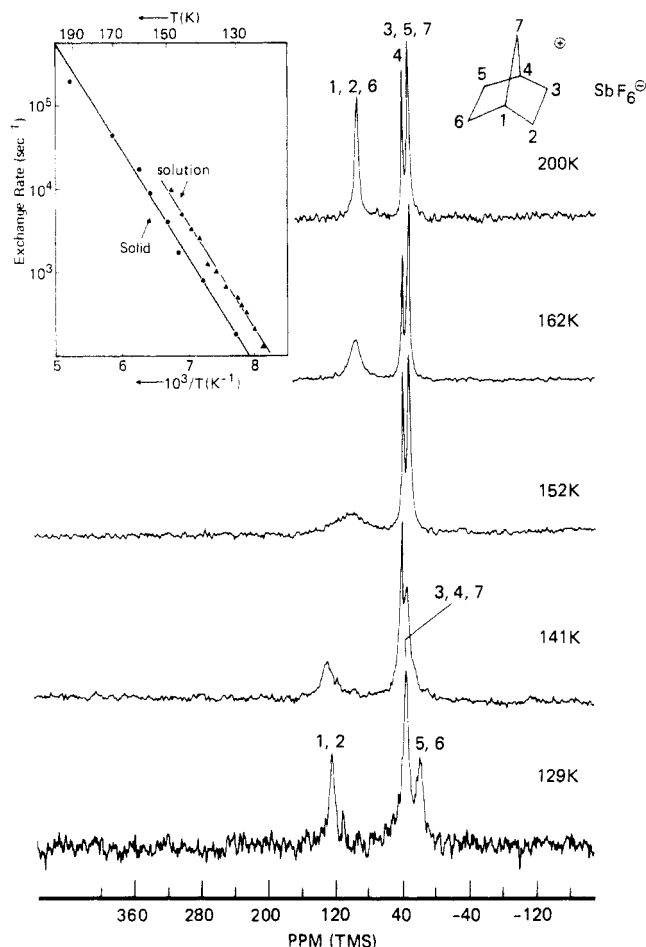
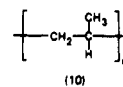


Figure 6. ¹³C CPMAS solid-state NMR spectra of the 2-norbornyl cation showing line-shape changes due to the 6,2,1-hydride shift.³⁶ Cross polarization was achieved by using 1–5 ms contact time, and 1- or 2-s delay between scans. Decoupling field strengths during acquisition time were 18 mT (77 kHz) and 15 mT (60 kHz) for ¹H and ¹⁹F, respectively. The inset shows the rates in the solid compared with those determined by ¹H solution NMR.³⁸

temperature spinning is critical for solid-state investigations. Recently, we have obtained the first extended VT-MAS ¹³C T_1 and $T_{1\rho}$ data on a solid. The material selected was a 90% isotactic, 70% crystalline sample of poly(propylene) (PP, 10), which has been studied¹⁸



over a temperature range of 77–297 K. The high degree of stereoregularity and high crystallinity of the polymer provide a more homogeneous local environment than in a glass where distributions of relaxation times are commonly observed,^{4,5} owing to site heterogeneity. Additionally, each carbon of the PP repeat unit is readily resolved and thus, in principle, allows observation of side-group (methyl) motion distinct from backbone motion in the polymer. T_1 measurements at 15.08 MHz were made by using a pulse sequence developed by Torchia⁴¹ that allows CP enhancement of the signals. The $T_{1\rho}$ measurements were made at 58 kHz by using the methodology of Schaefer et al.⁴ The two sets of data for the crystalline component of the polymer are reported in Figure 7.

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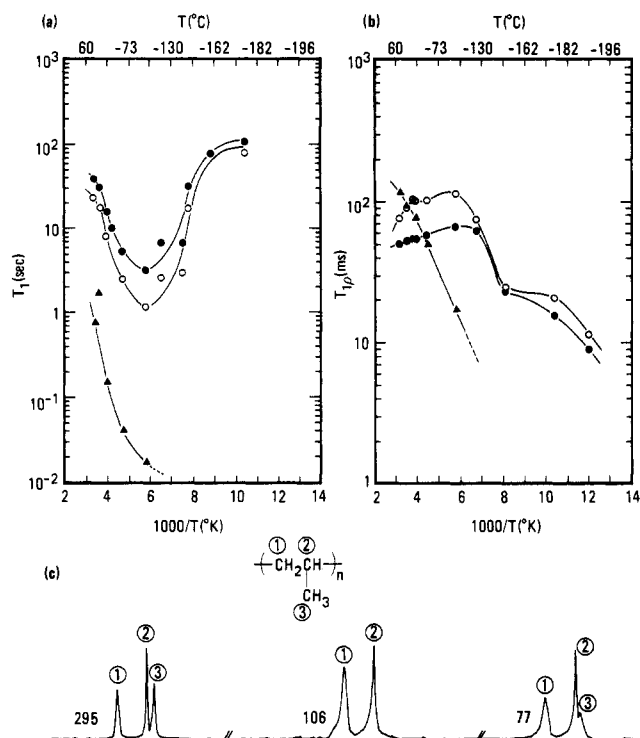


Figure 7. ^{13}C relaxation times for the methyl, methylene, and methine carbons of PP as a function of temperature: (a) spin-lattice relaxation times at 15 MHz; (b) rotating-frame relaxation times ($T_{1\rho}$) at 58 kHz. Legend: methyl, triangles; methylene, filled circles; methine, open circles; (c) ^{13}C spectra of PP at three temperatures: 297, 133, 77 K.

Several qualitative characteristics of the PP relaxation data are immediately apparent: (1) the methyl relaxation is followed over only a portion of the temperature range; (2) the CH and CH_2 carbon T_1 's are one to two orders of magnitude longer than the CH_3 T_1 ; (3) the CH and CH_2 carbons have a T_1 minimum at ca. 163 K; (4) the CH carbon has a shorter T_1 than the CH_2 carbon over the entire temperature range, but the situation is reversed for the $T_{1\rho}$ data; (5) over a portion of the temperature range, the CH and CH_2 carbon $T_{1\rho}$'s are little affected by temperature. In the following discussion, we will demonstrate that these observations are consistent with relaxation behavior dominated by dipolar interactions between carbons and methyl protons modulated by methyl group rotation. This result has implications for the interpretation of individual carbon relaxation behavior in all methyl-containing compounds. Assuming a C-H heteronuclear dipolar relaxation mechanism, the shorter T_1 observed for the methine carbon relative to methylene (despite there being two direct C-H interactions for the methylene carbon) is explained by dominance of the relaxation behavior by dipolar interactions with methyl protons. Apparently backbone motions are characterized by such small amplitudes and low frequencies that contributions from the direct C-H interactions to spectral density in the MHz region of the frequency spectrum are minor relative to that from the side group. The r^{-6} distance dependence of dipolar relaxation then accounts for the long T_1 values of CH and CH_2 carbons relative to the methyl carbon as well as the shorter T_1 for methine carbon relative to the methylene. The fact that the observed T_1 minimum for CH and CH_2 carbons is close

to that reported for a proton T_1 minimum (at 30 MHz)⁴² in PP assigned to methyl reorientation provides unequivocal support for the dominance of the T_1 relaxation by methyl protons.

The interpretation of the carbon $T_{1\rho}$ data is complicated by the fact that spin-spin processes as well as rotating-frame spin-lattice processes can contribute to the relaxation,⁴⁰ only the latter provide direct information on molecular motion. Both types of relaxation show a dependence on the number of directly bonded protons and thus could explain the shorter $T_{1\rho}$ for the CH_2 carbon relative to the CH carbon between 160 K and ambient temperature. However, the relative insensitivity of the $T_{1\rho}$'s to temperature suggests that spin-spin processes dominate the relaxation above 160 K.⁴³ Below 160 K, the $T_{1\rho}$'s of both carbons decrease by roughly an order of magnitude, but also tend toward equality, indicating that spin-lattice processes are becoming competitive with the spin-spin process in relaxing the carbon magnetization. This result, as well as the report by McBrierty et al.⁴² of a proton $T_{1\rho}$ minimum in PP at 93 K that reflects methyl group reorientation at kHz frequencies, makes it apparent that the methyl protons are responsible for these spin-lattice contributions to the CH and CH_2 $T_{1\rho}$'s. The fact that no clear minimum is observed in the data is perhaps due to the interplay of the spin-spin and spin-lattice processes.

The domination of both spin-lattice relaxation times for CH and CH_2 carbons in PP by methyl reorientation is clearly disappointing since the potential for information on backbone motion due to the high resolution in the CPMAS experiment is not realized. The implication is that it may not be possible to observe backbone motion in crystalline materials having rapidly reorienting side groups without resorting to deuterium substitution of the side groups.

The relaxation data on the methyl carbon in PP could only be measured down to ca. 130 K, since below this temperature severe line broadening ensues (as is illustrated in Figure 7). The broadening arises as the reorientation rate of the methyl group about the C_3 axis becomes comparable to the frequency of the coherent motion impressed by the proton decoupling field. Rothwell and Waugh⁴⁴ have developed the theory for T_2 (the inverse of the ^{13}C line width) for an interplay between stochastic and coherent motions. For such a system, the profile of line width vs. temperature shows a maximum where the correlation time for molecular motion, τ_C , is equal to the modulation period of the decoupling, $(\omega_1)^{-1}$. In the "short correlation" limit ($\omega_1\tau_C \ll 1$) (high temperature), the line width is reduced by the rapid motional averaging, while in the "long correlation" limit ($\omega_1\tau_C \gg 1$) (low temperature), the line width is reduced by efficient decoupling of C-H dipolar interactions. The spectra of PP in Figure 7 are consistent with the progression of the methyl resonance

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(43) If spin-spin effects dominate the rotating-frame relaxation and the carbon cross relaxation to the proton dipolar reservoir is less efficient than the corresponding proton spin-lattice relaxation, $T_{1\rho}$, then the observed $T_{1\rho}$ for the CH carbon will be about twice that of the CH_2 carbon based on the approximate twofold difference in the second moments (due to protons) for the two types of carbons.⁴⁰ This is roughly the result observed in the data displayed in Figure 7.

(44) W. P. Rothwell and J. S. Waugh, *J. Chem. Phys.*, **74**, 2721 (1981).

through the line-width regions as the temperature is lowered. The reappearance (or narrowing) of the methyl resonance at 77 K indicates the "long correlation" regime has been reached.⁴⁵ The methyl carbons in cured epoxy resins show a similar broadening as illustrated in Figure 2. In addition, this type of line-width effect has been reported in poly(tetrafluoroethylene)³³ at the onset of the rapid molecular reorientation about the chain axis which accompanies the 19 °C phase transition.

Although line-width contributions arising from motional effects can cause resolution problems in the solid-state experiments, line-width data as a function of temperature can provide a ready measure of rotational barriers. Using this type of analysis, Rothwell and Waugh⁴⁴ have determined the methyl rotational barrier in hexamethylethane, the hexad rotational barrier in hexamethylbenzene, and the rotational barrier in β -phase adamantane.

A similar broadening of resonance lines can occur when the molecular motion is comparable to the co-

(45) The authors thank Dr. Volker Macho, IBM San Jose, for obtaining the 77-K spectrum.

herent motion introduced into the spin system by magic-angle spinning. Waugh et al.^{46,47} have carried out line-width vs. temperature studies at different spinning rates on decamethylferrocene and hexamethylbenzene and have determined the barrier to the five-site jump process in the former and studied the 116 K phase transition in the latter. The importance of this type of experiment is that, in the limit of very slow spinning rates, detection of motional frequencies of a few hertz are possible.

Conclusions

The provision for VT-MAS extends the range of applications of CPMAS NMR to a broad spectrum of chemical areas including reactive species, unstable systems, and mechanisms of molecular reorientation. The initial results of variable-temperature CPMAS ¹³C NMR studies have demonstrated considerable potential for elucidating structure and dynamics in the solid state.

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Mössbauer Effect Studies of Intercalation Compounds

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Intercalation compounds¹ are formed from solids of low dimensionality in which there exists a large anisotropy in the chemical bonding forces. Such solids are characterized by layers of atoms held together by van der Waals type bonds. These layers can be pried apart by chemical means to effect the insertion of a "guest" species into the "host" lattice. The guest species may be either electron donors (alkali metals, alkaline earths, or rare earths), electron acceptors (AsF₅, SbF₅), or organic and inorganic molecules that can form weak bonds with the host matrix. Intercalation invariably results in significant modifications in the interlayer distance and can bring about pronounced changes in the properties of the host matrix, including changes in the electrical conductivity by many orders of magnitude,² an increase (or decrease) in the superconducting transition temperature of the matrix,³ the specific heat and related properties of the solid,⁴ the optical⁵ and magnetic⁶ properties of the layered material, and the structural properties of the system,^{4,7} inter alia.

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Because of the range of chemical and physical properties influenced by intercalation, a large number of physicochemical techniques have been used to elucidate the intercalation process. Recently nuclear γ -ray resonance spectroscopy (the Mössbauer effect)⁸ has joined this list, and a great deal of new information has been

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