

High-Resolution ^{13}C Nuclear Magnetic Resonance Spectra of Frozen Liquids Using Magic Angle Spinning

C. A. Fyfe,*† J. R. Lyerla, and C. S. Yannoni*

Contribution from the IBM Research Laboratory, San Jose, California 95193.

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Abstract: The first variable-temperature isotropic high-resolution NMR spectra of solids (frozen liquids) are reported. Magic angle spinning, combined with cross-polarization and dipolar decoupling, were employed to obtain low-temperature ^{13}C NMR spectra of benzene and *tert*-butyl acetate. The preliminary results clearly demonstrate the value of variable-temperature magic angle spinning high-resolution NMR methods for the study of organic solids.

Recently, it was demonstrated¹ that ^{13}C NMR spectra of solids in which the resonance line widths approach those of liquids can be obtained by combining resolution and sensitivity enhancement (strong heteronuclear decoupling and ^{13}C - ^1H cross-polarization²) techniques with rapid sample rotation about an axis which makes an angle of 54.7° (the "magic" angle) with the external dc magnetic field. Magic angle spinning was originally designed³ to eliminate homonuclear dipolar broadening in the NMR spectra of abundant nuclei (e.g., ^1H , ^{19}F , ^{31}P) in solids, and met with limited success. More recently, however, the technique has been applied with great success to ^{13}C , a rare nucleus, in which conventional decoupling methods can be used to eliminate the line broadening effects of nearby protons, and the spinning is used to eliminate frequency dispersion due to ^{13}C chemical shift anisotropy.⁴ Well-resolved ^{13}C spectra for several polymers in the glassy state were obtained initially,¹ followed by similar work on a small number of other materials. All the materials studied to date, however, have been solid at room temperature. The ability to vary the temperature in this kind of experiment is important for several reasons: (1) many interesting materials are liquid at room temperature; (2) for many solids, the ^{13}C - ^1H cross-polarization scheme used for sensitivity enhancement does not work efficiently at room temperature² (glassy polymers work fortuitously well at room temperature; and (3) variable temperature studies are necessary to fully exploit individual-carbon relaxation time studies.⁵ In this note, the utility of the variable temperature magic angle spinning experiment is demonstrated for frozen room-temperature liquids.

Experimental Section

The basic NMR spectrometer is a Nicolet TT-14 with operating frequencies of 15.087 and 60.0 MHz for ^{13}C and ^1H , respectively. The spectrometer was modified for cross-polarization and high power (dipolar) decoupling by adding external gating circuitry and radio frequency amplifiers, and by rerouting some of the timing logic. A probe was built to withstand the high-voltage and heating effects of the large radio frequency fields used in the experiment. Liquids were loaded into a Kel-F rotor (volume 60 μL), frozen, and placed in the stator assembly, which fits in a tube with an inside diameter of 10.2 mm.⁶ The spinner driving gas (He) was precooled by flow through a heat exchanger immersed in liquid nitrogen in much the same fashion as samples are normally cooled in NMR experiments. Since it is desirable to have the freedom of changing temperature without affecting the spinning rate, warm and cold gases were mixed to achieve variable temperature. Spinning rates between 3 and 5 kHz were used. Temperatures were measured with a thermocouple placed in the exit gas flow.

Results

^{13}C spectra of solid benzene at -40°C obtained with and without magic angle spinning are shown in Figure 1. The

cross-polarization (CP) conditions² employed were $(\gamma_{\text{C}}/2\pi)H_{1\text{C}} = (\gamma_{\text{H}}/2\pi)H_{1\text{H}} \approx 28$ kHz, and a CP time of 10 ms; only one cross-polarization contact was made per proton polarization. The spectrum of a static sample (Figure 1a) was obtained by Fourier transformation of the accumulated carbon FID from 4475 experiment repetitions (0.8 s between repetition); the magic angle spectrum (Figure 1b) was obtained in only 448 repetitions. The static spectrum is consistent with an axially symmetric carbon chemical shift tensor; for benzene at -40°C , this symmetry is induced on the NMR time scale (\sim fractions of a millisecond) by rapid reorientation of the ring about the sixfold axis. The spectral spread is 2700 Hz (180 ppm).⁷ The ^{13}C spectrum of benzene with magic angle spinning, shown in Figure 1b, consists of a single symmetrical resonance at the frequency of the isotropic (liquid) chemical shift, with a full width at half maximum intensity of 20 Hz.

^{13}C NMR spectra of solid *tert*-butyl acetate (mp -50°C) which illustrate the potential of variable temperature capability for studying dynamics in solids are shown in Figures 2 and 3. The cross-polarization conditions are the same as for benzene, except that a CP time of 2 ms was used, with 1.0 s between accumulations. The spectrum of a static sample (8352 runs, 10 ms CP time) at -100°C is shown in Figure 2a. Owing to overlap of broad anisotropic resonances from several inequivalent carbons, the spectrum is difficult to analyze. A spectrum of the same sample using magic angle spinning is shown in Figure 2b; well-resolved resonances are obtained for each chemically distinct carbon. For comparison, the liquid spectrum taken in methanol- d_4 at -100°C is shown in Figure 2c. The two spectra are identical except in the methyl region. Based on spectra of the compound in the solid state taken at several temperatures (Figure 3), we assign the sharp upfield component to the acetate methyl carbon and the broad downfield shoulder to the *tert*-butyl methyl carbons. As is evident from Figure 3, both the shape and position of this resonance vary with temperature, with the position of the line at higher temperature approaching that for the *tert*-butyl methyl carbons found in solution. This suggests the possibility of solid state effects on the motion of the *tert*-butyl methyl groups, e.g., hindered rotation. The origins of these spectral variations are under investigation.

Conclusions

The results presented here greatly broaden the scope and applicability of high-resolution NMR experiments in solids in several ways: (1) liquids can now be frozen and studied; (2) solids, for which the cross-polarization scheme does not work at room temperature, may be successfully studied at other temperatures—for example, in many cases the best temperature may be near the proton T_1 minimum, which can occur at temperatures far from ambient; and (3) variable temperature studies, such as relaxation measurements,⁵ can now be made on both solids and frozen liquids. We have already obtained

† On sabbatical leave. Permanent address: Department of Chemistry, University of Guelph, Guelph, Ontario, Canada.

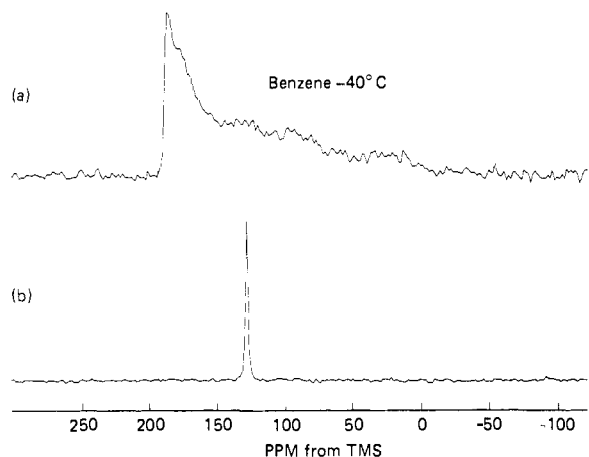


Figure 1. ^{13}C NMR spectra of solid benzene, obtained at -40°C : (a) stationary sample; (b) same sample but with magic angle spinning.

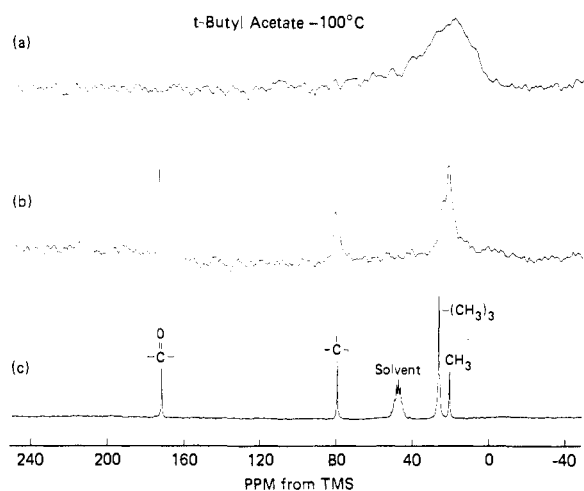


Figure 2. ^{13}C NMR spectra of *tert*-butyl acetate at -100°C : (a) stationary solid; (b) same sample but with magic angle spinning; (c) liquid sample (CD_3OD solvent).

a number of new results on fluxional molecules, charge transfer complexes, and polymers using this technique⁸ and have used the equipment to obtain spectra at temperatures down to 77 K.

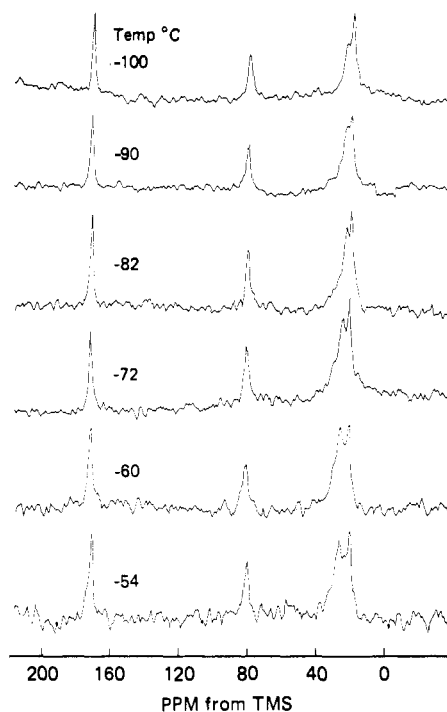


Figure 3. ^{13}C NMR spectra of *tert*-butyl acetate obtained using magic angle spinning over a range of temperatures. Between 1000 and 1500 transients were accumulated for a given spectrum.

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References and Notes

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