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Carbon-13 Nuclear Magnetic Resonance of Polymers Spinning at the Magic Angle

Sir:

Cross polarization (CP) of carbons by protons is a practical way of obtaining high sensitivity natural abundance ^{13}C NMR spectra of solids.[1] In the Hartmann–Hahn version of the CP experiment,[1,2] polarization transfers from the protons to nearby carbons via static dipolar interactions in a time characterized by a spin-lock CP relaxation time in the rotating frame, T_{CH}.[3] In many cases T_{CH} is on the order of 100 μs.[1,4] After the CP transfer, the carbon free-induction decay can be observed while the protons are being dipolar decoupled. Although dipolar broadening has been removed by strong decoupling during data acquisition, chemical shift anisotropy may still severely complicate the ^{13}C spectrum. For sufficiently simple systems involving only a few chemically different types of carbons, resolved or partially resolved chemical shift anisotropy can be a useful source of information about the geometry and electronic structure of the solid.[1] But in many systems of interest to the chemist, overlapping anisotropies are not interpretable, and the ^{13}C spectrum of the solid becomes a poorly resolved and disappointing wide-line spectrum.

In this situation the information contained in the chemical shift anisotropies may be sacrificed for the improvement in resolution which can often be achieved by high-speed mechanical sample rotation at the magic angle.[5] By fashioning the solid into a rotor[4] (or placing the solid inside a hollow rotor) and aligning the axis of rotation of the rotor at 54.7 ± 1° relative to H_0, chemical shift anisotropic dispersions are averaged to their isotropic values by sample rotation of 2–3 kHz, spinning frequencies which are somewhat greater than the width of the dispersion.[4,5]

The question arises as to the practical limits to the achievable resolution and hence the complexity of chemical systems which can, in fact, be approached by CP ^{13}C NMR with spinning at the magic angle. We have investigated, at room temperature, over a dozen synthetic and natural macromolecular systems by magic-angle CP ^{13}C NMR and present here results on three such systems, illustrating what we feel are the present capabilities and limitations of the technique.

As shown in Figure 1, the magic-angle CP spectrum of solid polysulfone, an engineering plastic, is nearly as detailed as the standard FT spectrum of the polymer in solution. (The CP spectra were obtained by the single-contact Hartmann–Hahn procedure, using ^{1}H and ^{13}C rf fields of 8 and 32 G, respectively. The data for each CP spectrum were acquired from 500 sequence repetitions requiring a

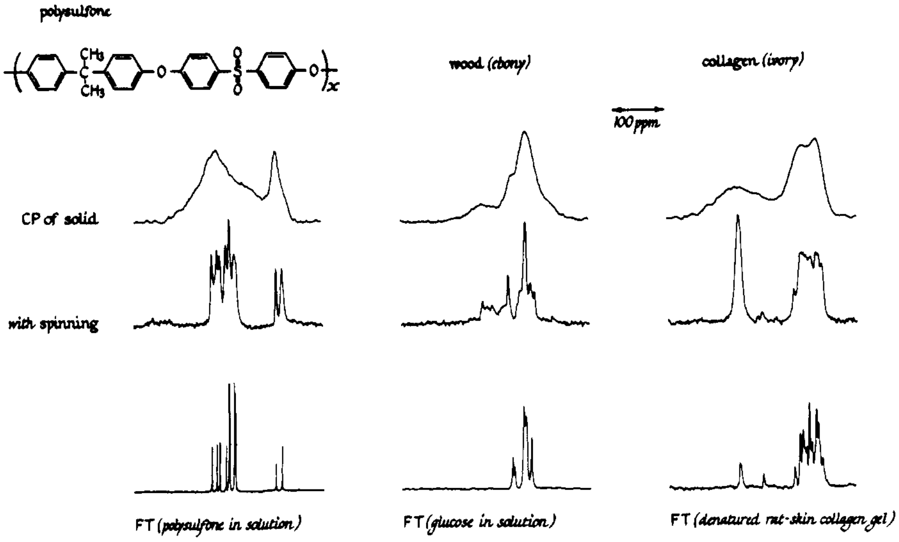

Figure 1. Dipolar-decoupled natural abundance ^{13}C NMR spectra of some solids obtained using single Hartmann–Hahn cross-polarization contacts of 1 ms duration. The cross-polarization spectra, obtained both with and without magic-angle spinning, are compared to some standard Fourier transform ^{13}C NMR spectra of various materials in solution. (The FT spectrum of the protein gel, bottom right, is not fully relaxed, and the intensity of the lowest field line has been discriminated against.) Each spectrum is 8 kHz wide (at 22.6 MHz). The magnetic field increases from left to right.

total of 8 min.) Note that we observe strong signals from the nonprotonated carbons in polysulfone. That is, in spite of reasonable fears to the contrary,[1,4] the 3-kHz magic-angle spinning does not eliminate, by motional averaging, the dipolar interactions required for transfer of magnetization from polarized nonbonded protons to nearby quaternary carbons.

This result is understandable qualitatively in view of the results of some *single* resonance experiments on solid polymers.[6] The undecoupled ^{13}C NMR spectra of the quaternary carbons of amorphous polymers such as polysulfone invariably have room-temperature dipolar line widths of 3–4 kHz, which narrow by only a factor of 2–4 under 3-kHz magic-angle spinning.[6] This narrowing is far less than that observed for combination spinning and dipolar decoupling experiments. Part of the failure of spinning to narrow more completely the undecoupled line is due to the spinning speed being somewhat less than the dipolar line width, while part is due to dipolar interactions arising from segmental motions of the polymer having correlation frequencies on the order of 10 kHz.[6] (Broadening due to the latter is not removed by spinning at 3 kHz, but is removed by resonant dipolar decoupling at 30 kHz.) In either situation, substantial spectral density associated with $^{1}H-^{13}C$ dipolar interactions remains at zero frequency[7,8] under magic-angle spinning at 3 kHz. This is consistent with the observation that the spin-lock T_{CH}'s for quaternary carbons in amorphous polymers (which are on the order of 300 μs at room temperature) increase by less than a factor of about 2 under spinning conditions. Of course, there is virtually no effect of spinning on protonated carbon T_{CH}'s because the 3-kHz spinning frequency is so much less than the dipolar line width.

Regardless of the details of the spin dynamics, the fact remains that for a wide variety of macromolecular systems near room temperature, efficient $^{1}H-^{13}C$ CP transfers do indeed occur under magic-angle spinning conditions. In the case of polysulfone, with individual lines resolved for all types of carbons, a variety of ^{13}C relaxation experiments can be performed and interpreted unambiguously in terms of the motions of the polymer in the solid state.[6] In addition, for many synthetic polymer systems, the magic-angle CP ^{13}C NMR spectra are well enough resolved not only to simplify relaxation experiments but also to begin to identify details such as rotational and configurational isomerism in the main chain.[6] In short, we are convinced that spinning will prove to be invaluable in the study of the chemistry and physics of synthetic polymers in the solid state.

Also shown in Figure 1 are the CP ^{13}C NMR spectra of a dense wood under nonspinning and spinning conditions, compared to a standard FT spectrum of a solution of glucose (with lines artificially broadened somewhat for display purposes). Wood is a complicated blend of celluloses, hemicelluloses, and lignin. We attempt no detailed analysis of the spectra here, except to note that the resolution of the magic-angle CP spectrum of wood is adequate to identify lines associated with each of the three major components. In addition, we find that the spectra are of high enough quality to distinguish, semiquantitatively, between the overall composition of different woods such as maple and pine. While the quality of the CP spectra of wood is comparable to that of the plastic, the chemical complexity of wood itself hampers realizing truly high resolution. For example, the lowest field lines in the wood spectrum (due entirely to lignin) are relatively poorly resolved and for most practical purposes must be considered as a resonance band, rather than as a collection of identifiable lines. The 50-Hz resolution presently achieved by spinning is simply not quite good enough to obtain high resolution in highly complex systems. (However, we feel that as much as a fivefold improvement in resolution may be obtained by order of magnitude increases in the decoupling power and in the accuracy of positioning of the rotor axis, together with a 50% increase in the spinning frequency, all of which should have only modest effects on CP transfer rates.)

The existing limitation on resolution is further illustrated by the third system displayed in Figure 1, ivory, the organic component of which is the protein collagen. Clearly, magic-angle spinning produces a dramatic improvement in the resolution of the CP spectrum of the solid, allowing the chemical shifts of some half-dozen or so lines to be immediately identified. If one happens to be interested in the particular residues whose resonances are fortuitously resolved, then obviously spinning is a great advantage. Unfortunately, the vast majority of resonances fall into one of two poorly resolved bands. While the kind of resolution presently obtainable may be, therefore, disappointing for use in some chemical structure studies, spinning is, nevertheless, still useful in simplifying the interpretation of T_1 or $T_{1\rho}$ experiments[6] by reducing the dispersion of relaxation times across an individual resonance line normally observed in the solid state.[1]

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Temporal Fluctuations in the Emission from Irradiated Acetone Solutions

Sir:

Systems of chemical reactions which display temporal or spatial oscillations have aroused considerable interest, although the number of homogeneous chemical systems known to display such phenomena is quite small.[1-5] We therefore consider it important to report the observation of temporal fluctuations in the photochemical formation of biacetyl from acetone in fluid solution.

Solutions of Fisher Certified acetone or Matheson Coleman and Bell spectroquality acetone were made up in Matheson Coleman and Bell spectroquality acetonitrile. The concentrations of acetone ranged from 0.07 to 0.27 M. The solutions, in quartz tubes, were degassed by six freeze-thaw cycles on a vacuum line. Uncorrected emission spectra were obtained on a Hitachi Perkin-Elmer MPF-2A fluorescence spectrophotometer, using 310-nm excitation and 10 nm wide excitation slits. Solutions were studied in the temperature range from 20 to 40 °C. The incident photon flux was approximately 6×10^{13} photons/s as determined by potassium ferrioxalate actinometry. At this photon flux no significant temperature gradient should develop around the irradiated portion of a solution.

Nondegassed solutions of acetone gave unstructured emission spectra, as shown in Figure 1, curve a, with peak maxima at roughly 395 nm. Degassed solutions yielded enhanced emission with peak maxima at roughly 410 nm.