JOURNAL OF MAGNETIC RESONANCE 41, 440–446 (1980)

Deuterium NMR in Solids with a Cylindrical Magic Angle Sample Spinner

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Received May 13, 1980

A cylindrical NMR sample spinner employing gas bearings is described. Its application to high-resolution deuterium NMR in solids by magic angle spinning is demonstrated. Resolution in the isotropic deuterium chemical shift spectra is extremely sensitive to the magic angle setting and fluctuations of the spinner axis. The cylindrical-gas bearing design provides the stability necessary for nearly complete removal of the deuterium quadrupole coupling. Typical high-resolution deuterium solid-state spectra are shown of some polycrystalline organic molecular solids.

INTRODUCTION

The use of magic angle sample rotation to obtain NMR spectra of ^{13}C in crystalline and amorphous solid materials has grown rapidly. Similarly the use of multiple-pulse line narrowing to obtain chemical shift information from ^{1}H in crystalline materials has been quite successful. However, the major drawback to this method is the overlapping of the chemical shift spectra in both polycrystalline and amorphous materials. This is a severe limitation even for small molecules when there are inequivalent protons. Ryan *et al.* (*1*) have demonstrated a solution to this problem by combining multiple-pulse and magic angle spinning techniques to obtain isotropic chemical shift spectra. It was also demonstrated recently that this problem can be circumvented by deuterium isotopic labeling and observation of ^{2}H isotropic chemical shift spectra by magic angle spinning combined with rotation synchronized data acquisition (*2*, *3*). Using this method the removal of quadrupole broadening was extremely sensitive to fluctuations in β, the angle the spinner axis makes with the direction of B_0. It thus appeared that the conical spinner design employed was not adequate since the spinner stability was the major factor limiting resolution. In this paper we describe a cylindrical sample spinner using gas bearings for extreme stability of the axis of rotation and present results of its application, showing the first well-resolved isotropic deuterium spectra.

CYLINDRICAL GAS-BEARING SAMPLE SPINNER

The complete high-speed turbine probe head is shown in Fig. 1. The basic design is that of a cylindrical turbine or spinner which rides in gas bearings and is packaged

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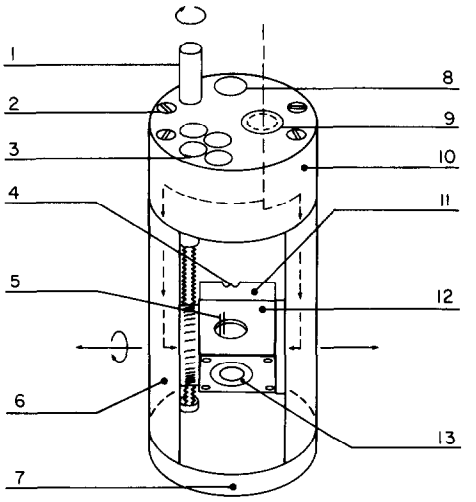

FIG. 1. Cylindrical gas-bearing type sample spinning probe head for superconducting magnet bore: (1) worm screw for cradle angle adjustment, (2) top plate-side plate machine screws, (3) holes for rigid copper coaxial cable, (4) inlet holes for fiber optic cables, (5) NMR coil leads, (6) side plate, (7) bottom plate, (8) hole for fiber optic cables, (9) spinner operating gas inlet holes for vacuum-jacket stainless-steel transfer line, (10) top plate, (11) stator end cover plate, (12) cradle, (13) stator.

to fit a wide-bore superconducting magnet. Spinners of similar design have been used by Schneider and Doskocilova *et al.* (*4*, *5*), by Balimann *et al.* (*6*), and in Tallinn (*7*, *8*).

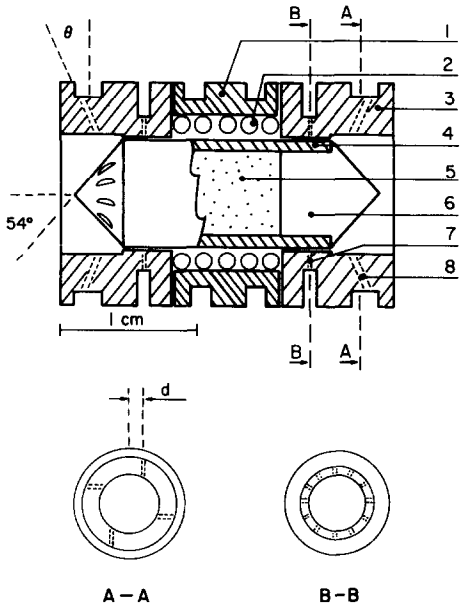

FIG. 2. Rotor and stator: (1) center coil section, (2) NMR coil, (3) drive and bearing section, (4) rotor tube, (5) sample chamber, (6) rotor cap, (7) gas bearing inlet hole, (8) turbine drive inlet hole.

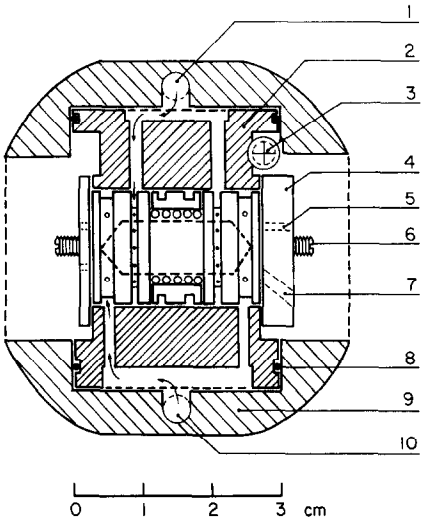

FIG. 3. Cross section of probe head along spinner axis: (1) gas bearing gas inlet hole, (2) cradle, (3) worm screw for cradle angle adjustment, (4) stator end cover plate, (5) gas exit hole, (6) rotor end stop screw, (7) fiber optic cable inlet hole, (8) o-ring, (9) side plate, (10) turbine drive gas inlet hole.

All parts except screws were machined from Delrin polymer. Compressed air, nitrogen, and helium were used as operating gases flowing through channels in the top plate and side plates and into each end of the cradle. The magic angle, β, is adjusted by rotating the cradle with a worm screw. The worm is driven by a reducing gear and pinion on top of the probe outside the magnet so that an increment of 0.003° in β was possible. An access hole was provided on top of the cradle for the leads to the NMR coil and for operating gas escape from the center stator section. The ends of the stator were enclosed by cover plates with exit holes to allow free escape of operating gas. Temperature of the spinner can be readily controlled by the temperature of the operating gas. The high-temperature limit is due to the melting of probe components and the low-temperature limit is due mainly to the low-temperature limit of the input operating gas. Operation down to about 175 K is routine and lower temperatures can be obtained with little alteration. Measurement of the spinning frequency and synchronization of the data acquisition were accomplished by monitoring reflected light from the rotor end with a fiber optic system.

A cross section of rotor and stator is shown in Fig. 2. Sample spinners were reusable and machined from Delrin and Kel-F polymers. Glass was also used as a material for rotor tubes. A minimum wall thickness of about 0.6 mm for polymer tubes 8 mm in diameter was necessary for handling. The spinner caps must fit tightly into the tube. Flutes in the caps were cut some 0.4 mm deep such that they present a flat face to the drive gas stream and are right and left handed. The 12 bearing holes were set at equal intervals and normal to the stator axis. Placement of the NMR coil just outside the rotor in the stator center section clearly provides an excellent filling factor. The spinners generally rotated at speeds up to a few

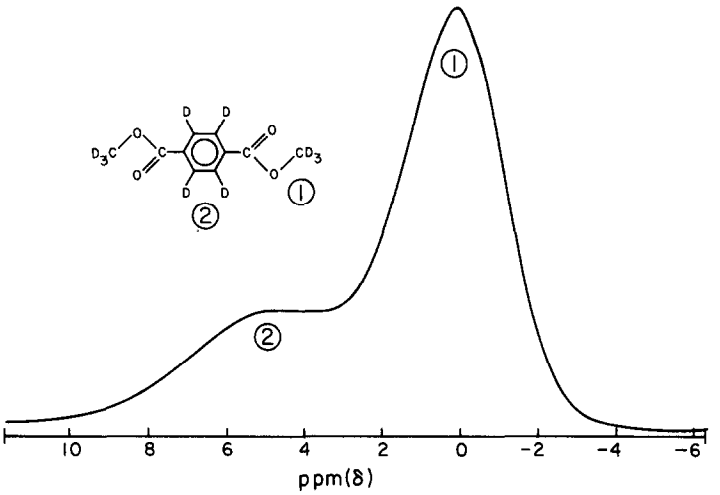

FIG. 4. Isotropic chemical shift spectrum of polycrystalline perdeuterated dimethylterephthalate-d_{10} rotating at 3.53 kHz, taken with conical spinner described previously. Resonances from methyl and aromatic deuterons were not resolved due to rotor instability. Average 64 shots.

hundred Hz on bearing gas alone. A difference of 0.05 mm between stator gas bearing inside diameter (i.d.) and the rotor outside diameter (o.d.) worked best. A gas exit hole about 1 mm in diameter in the center stator section or equivalent space about the coil leads for gas exit was necessary for stable operation. The four drive gas holes on either end were arranged so that the stream contacts the flat face of the flute at 60 to 65% of the distance from point to outer edge of the rotor cap. This was the most critical dimension and was adjusted using the values of θ and d (see Fig. 2), which were 14° and 2.30 mm, respectively, for the 8-mm-o.d. rotors. The bearing holes were 0.33 mm in diameter and the drive gas holes 0.41 mm in diameter; however, these dimensions were not critical.

The separate paths for the bearing and drive gas are shown in Fig. 3, a horizontal cross section along the cradle axis. Also shown are the stator end cover plates. The thicker cover plate served to hold two fiber optic cables near the rotor face. Polished brass machine screws in both cover plates acted as end stops for the spinner. To operate at high speed, one end screw was adjusted to center the spinner in the stator. Then with the operating gas on, the other end screw was tightened against the spinner and backed off just until a stable condition occurred with no vibration. Total rotor end clearance was usually about 0.2 mm. Further adjustment of end screws after a sample change was often not necessary. When spinners did not readily reach high-speed stability, they were usually brought to a stable condition by lowering the bearing input pressure to near zero. A sudden stabilizing usually occurred followed by a rapid increase in spinning frequency, after which the input pressures were adjusted to final value. Change of sample required lifting the probe from the magnet bore and removing the thin cover plate. Due to the extreme sensitivity of deuterium magic angle spinning to the angle β, a readjustment of β was necessary after each sample change.

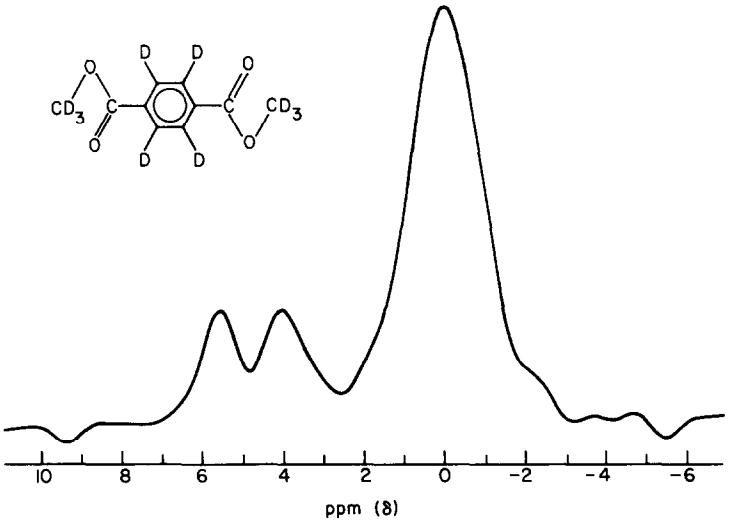

FIG. 5. Isotropic chemical shift spectrum of polycrystalline perdeuterated dimethylterephthalate-d_{10} rotating at 1.19 kHz, taken with cylindrical-gas bearing type spinner. Downfield aromatic doublet is resolved from methyl resonance. Splitting of 1.5 ppm occurs in aromatic peak due to inequivalence of 2,5 and 3,6 ring positions in the solid state. Average 100 shots.

With input drive pressures of up to 1.0 kg/cm^2 (15 psi) and bearing pressure of up to 0.6 kg/cm^2 (8 psi) spinning frequencies of up to about 2 kHz were achieved. Drive pressures up to 2.1 kg/cm^2 (30 psi) produced frequencies up to about 3 kHz, with helium the most efficient drive gas. The frequency stability could typically be maintained to $\pm 0.5\%$. Stability of the "magic" angle β, was $\leq 0.001°$. However, a change in input pressure altered β by several millidegrees. The use of rotor end stop screws, which are essentially friction thrust bearings, was the major factor limiting rotor stability.

EXPERIMENTAL

The NMR was performed on a home-built spectrometer with superconducting solenoid operating at $\omega_L/2\pi(^2H) = 28$ MHz and $\omega_L/2\pi(^1H) = 182$ MHz. The probe rf design was that of Cross *et al.* (*9*) with a double-tuned coil. Isotropic solid-state chemical shift spectra were obtained by application of a single pulse followed by sampling of the fid once per rotor cycle at the peaks of rotational echoes (synchronous sampling). Results presented here were obtained at room temperature.

In Fig. 4 is reproduced the isotropic chemical shift spectrum of 98% deuterodimethylterephthalate-d_{10} taken with a conical spinner described previously (*2*). The downfield peak due to aromatic deuterons ($-\phi D_4$) was not resolved from the upfield line due to methyl deuterons ($-CD_3$). The methyl linewidth was 3.2 ppm. The same spectrum taken with the cylindrical spinner is shown in Fig. 5. A narrowing of lines was evident and a splitting of 1.5 ppm in the aromatic peak appeared which was attributed to the inequivalence in the solid state of the 2,5 and 3,6 ring positions. The methyl linewidth was 2.1 ppm and the aromatic linewidths were

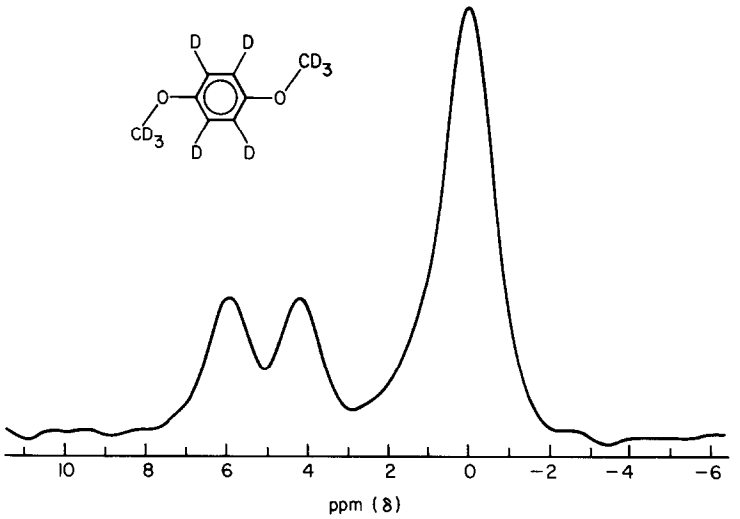

FIG. 6. Isotropic chemical shift spectrum of polycrystalline perdeuterated *para*-dimethoxybenzene-d_{10} rotating at 1.12 kHz, taken with cylindrical-gas bearing type spinner. Splitting of 1.7 ppm occurs in aromatic peak due to inequivalence of 2,5 and 3,6 ring positions in the solid state. Average 10 shots.

equal valued at 1.4 ppm. The isotropic spectrum of 98% deutero-*para*-dimethoxybenzene-d_{10}, shown in Fig. 6, exhibited the same features. The aromatic splitting between 2,5 and 3,6 positions was 1.7 ppm and the widths of aromatic and methyl lines were both 1.6 ppm. This solid-state chemical shift splitting in the aromatic line has also been observed in the carbon-13 spectra of these and other compounds by proton-enhanced high-resolution magic angle spinning (*3*, *8*).

In all spectra the intensity of aromatic lines relative to methyl lines was low because scans were obtained at a rate faster than the aromatic T_1 and slower than the methyl T_1 (*10*). Also, some aromatic signal is lost relative to methyl due to the broad spectral width of aromatic quadrupole splittings in the powder and the high Q factor of the probe.

CONCLUSION

The cylindrical sample rotor with gas bearings, a feature which is being incorporated into new designs of conical rotors, provides the stability necessary for deuterium NMR in solids by magic angle spinning. The axial stability is well within tolerance for nearly complete removal of first-order quadrupole couplings. The cylindrical spinner can be made large for its relative stability and will operate to very low frequencies. The coil filling factor approaches that of the usual stationary sample NMR. These characteristics provide relatively good sensitivity for deuterium and allow signal averaging to be used, which brings the technique into the regime of high-resolution work. Major contributions to linewidths in the isotropic spectra were variation in the diamagnetic susceptibility in the powder and residual quadrupole broadening not removed by magic angle spinning (*2*, *3*).

ACKNOWLEDGMENTS

We are indebted to Sidney Wolfe for synthesis of sample compounds and Carl Gaskins for high-quality machine work. This work was supported by the Division of Fossil Energy, Office of Assistant Secretary for Energy Technology, U.S. Department of Energy, under Contract W-7405-Eng-48.

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