

## DEUTERIUM DOUBLE-QUANTUM NMR WITH MAGIC ANGLE SPINNING

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Received 2 June 1980

The combination of double-quantum NMR with magic angle spinning is demonstrated for deuterium in solids. Under magic angle spinning the single-quantum resonance lines are extremely sensitive to spinner angle adjustment and stability while the double-quantum lines are not. This provides an additional approach to high resolution.

### 1. Introduction

It was recently demonstrated that high-resolution deuterium NMR in solids may be accomplished by magic angle sample spinning even when the rotation frequency,  $\omega_r/2\pi \approx 1$  kHz, is much less than the quadrupole coupling,  $\omega_Q/2\pi = \frac{3}{4}e^2qQ/h \approx 130$  kHz [1-4]. The sample rotation removes the broadening of spectra of amorphous and polycrystalline samples due to the anisotropic quadrupole and chemical-shift interactions. Isotropic chemical-shift spectra can be obtained by sampling the free induction decay (FID) synchronously with the sample rotation [5]. This results in a narrowing of the deuterium powder spectra by a factor of  $1/2(3\cos^2\theta - 1)$ , where  $\theta$  is the angle between the spinner axis and the direction of laboratory magnetic field,  $B_0$ . Practically, this yields a narrowing of about three orders of magnitude. Thus an extremely stable sample spinner is required, which is described elsewhere [4], having angular fluctuations smaller than a few millidegrees. However, it was recently shown that by detecting the deuterium double-quantum transitions the anisotropic chemical-shift spectra can be obtained since the double-quantum absorption lines are free of large first-order quadrupolar broadening [6-10]. A novel possibility, which we demonstrate here, is to combine magic angle spinning with double-quantum NMR in an alternative approach to high resolution in solids. In removing the quadrupole coupling via the detection of double-quantum transitions the spinner requirements become much less stringent since it has only to remove the smaller chemical-

shift anisotropy as in the case of high-resolution magic angle  $^{13}\text{C}$  NMR.

### 2. Double-quantum Fourier transform NMR in rotating solids

The "forbidden" deuterium ( $I = 1$ ) double-quantum transitions ( $\Delta m = 2$ ) are independent of the quadrupole coupling to first order. Thus the double-quantum spectrum for polycrystalline and amorphous solids usually consists of overlapping chemical-shift powder patterns. By rotating the sample about the magic angle and sampling the double-quantum FID in multiples of spinner cycles,  $\tau_r = 2\pi/\omega_r$ , the remaining chemical-shift anisotropy is also removed. Since the range of the chemical shift is over two orders of magnitude smaller than the quadrupole splittings, it is expected that the width of double-quantum resonance lines is considerably less sensitive to deviations of the spinner axis from the magic angle,  $\theta_m = \tan^{-1}2^{1/2} = 54.74^\circ$ . Also, the chemical shift of the double-quantum line is just twice that of the single-quantum line.

Double-quantum coherence is prepared by two strong pulses near resonance separated by a short delay as in fig. 1. After evolution for some number of spinner cycles,  $t_1 = n\tau_r$ , a detection pulse creates single-quantum signal (FID) which appears as a train of rotational echoes since the sample is rotating about the magic angle. A series of such FIDs for increasing values of  $n = 1, 2, 3, \dots$  are collected. The decay of the first rotational echo in

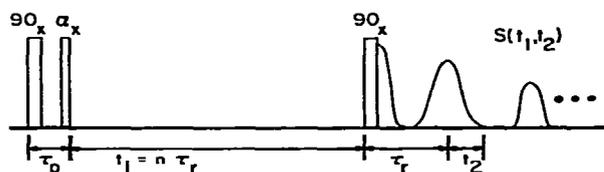


Fig. 1. Pulse sequence for observation of deuterium isotropic chemical-shift spectrum in solids by double-quantum NMR with magic angle spinning. Double-quantum coherence is prepared by a pair of strong pulses and evolves during time  $t_1$  which is an integral multiple of sample spinner cycles. A third detection pulse transfers double-quantum to observable single-quantum coherence which appears as a train of rotational echoes. The decay of the first echo ( $t_2$  domain) is Fourier transformed and the double-quantum FID is obtained as a cross section through those spectra as  $n = 1, 2, 3, \dots$  ( $t_1$  domain). Proton decoupling is applied except during the deuterium rf pulses.

each of these FIDs is Fourier transformed to give a single-quantum quadrupole powder pattern spectrum. The double-quantum FID is obtained as a cross section through these spectra in the second or  $t_1$  time domain. This procedure avoids receiver ring-down after the detection pulse and phase cancellation of double-quantum coherence which occurs in a cross section through the rotational echoes. Fourier transformation of the double-quantum FID then gives the frequency spectrum of the  $t_1$  domain (2D spectrum). For the three-level spin-1 deuterium system this spectrum exhibits any single- and double-quantum coherence which existed after evolution time  $t_1$ . In the present work,  $\alpha$  was set to a value less than  $90^\circ$  (fig 1) in order to allow simultaneous generation of single- and double-quantum lines in the 2D spectrum

### 3. Experimental

The pulse sequence of fig. 1 was applied to a polycrystalline sample of 28% randomly deuterated ferrocene- $d_{10}$  rotating at 1.11 kHz. Spectra were taken at room temperature on a homebuilt spectrometer operating at  $\omega_L/2\pi(2D) = 28$  MHz. The ferrocene quadrupole coupling constant was  $\omega_Q/2\pi = 73$  kHz. High-power proton decoupling was applied at all times except during the deuterium rf pulses.

A set of spectra were taken with  $\theta$  adjusted to the

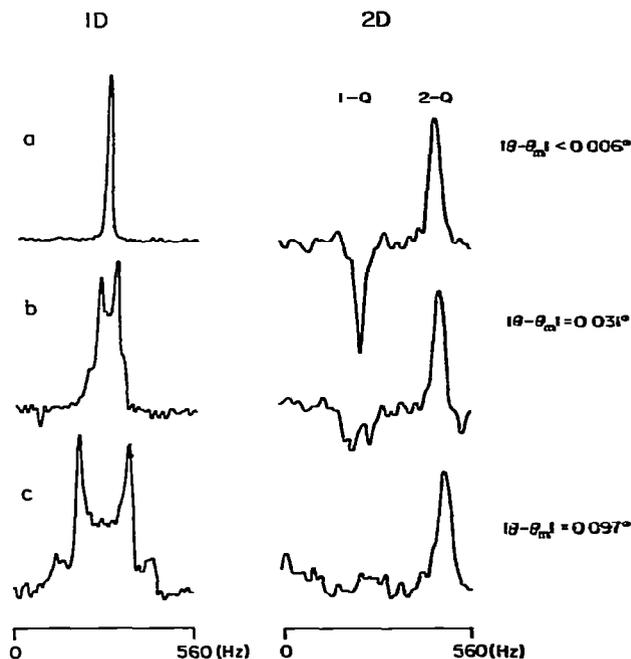


Fig. 2. One-dimensional (1D) and two-dimensional (2D) deuterium solid state spectra of polycrystalline 28% randomly deuterated ferrocene- $d_{10}$  rotating at 1.11 kHz. The 1D spectra show the narrowing of the ferrocene ( $\omega_Q/2\pi = 73$  kHz) quadrupole powder pattern by the spinning as  $\theta$  approaches the magic angle. The 2D spectra exhibit the single-quantum (1-Q) and double-quantum (2-Q) lines and illustrate the fact that the 2-Q chemical shift is double that of the 1-Q. As  $\theta$  deviates from the magic setting, the 1-Q line splits into the quadrupole powder pattern and is lost in the noise while the 2-Q line remains sharp.

optimal narrowing setting and at successive deviations from that setting. Each set consisted of the usual single-quantum spectrum from the FID after a single pulse (one-dimensional or 1D) and the two-dimensional or 2D spectrum as described above. The results are shown in fig. 2.

### 4. Results and discussion

The 1D spectra show the narrowing of the quadrupole powder pattern to a sharp line as the angle  $\theta$  becomes magic. The 2D spectra exhibit single-quantum (1-Q) and double-quantum (2-Q) lines and the chemical shift of the 2-Q is just twice that of the 1-Q. While the

1-Q linewidth depends strongly on the adjustment of  $\theta$ , the 2-Q linewidth is insensitive to it. For small deviations of  $\theta$  from the optimal setting the 1-Q line broadens and falls into the noise while the 2-Q linewidth does not change.

In fig. 2a the width of the 1-Q line is 20 Hz. The width of the 2-Q line is about twice this value. Two reasons for this effect are.

(1) Static field inhomogeneity and susceptibility anisotropies over the sample have exactly double their effect for double-quantum transitions since all chemical shifts are doubled.

(2) The second-order quadrupole perturbation shifts only the highest and the lowest of the three deuterium energy levels, leading to a broadening and shift of the deuterium resonance in a spinning sample [2], which are exactly twice in size for the double-quantum transition relative to the single-quantum transitions at exact be concluded that the width of deuterium double-quantum lines in magic angle spinning solids are expected to be somewhat smaller than twice the linewidth of the corresponding single-quantum transitions at exact magic angle, since the lifetime of the double-quantum coherence can be greater than one-half the single-quantum  $T_2$ , and in fact greater than the single-quantum  $T_2$  [11,12]. Thus the expected resolution in a double-quantum spectrum is always better than in a single-quantum spectrum.

On the basis of these results, we feel that the combination of double-quantum NMR with magic angle spinning offers the possibility for high resolution without unusually stringent spinner requirements, especially in complicated molecules with several inequivalent deuterium positions

### Acknowledgement

We are indebted to Sidney Wolfe for preparation of sample materials. R.E. is grateful to D. Weitekamp, J. Murdoch, and J.L. Ackerman for helpful discussions. L.M. acknowledges a Swiss National Science Foundation Scholarship. This work was supported by the Division of Fossil Energy, Office of Assistant Secretary for Energy Technology, U.S. Department of Energy under contract No. W-7405-ENG-48.

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