

EXPERIMENTAL RESULTS ON DEUTERIUM NMR IN THE SOLID STATE BY MAGIC ANGLE SAMPLE SPINNING

J.L. ACKERMAN*, R. ECKMAN and A. PINES

*Department of Chemistry, University of California, Lawrence Berkeley Laboratory,
Berkeley, California 94720, USA*

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Magic angle sample spinning has been applied to remove the first order quadrupole broadening in NMR spectra of deuterium in the solid state. The free induction decay of the rotating sample consists of a series of spatially-induced echoes which were sampled in synchronism with the rotation to produce an isotropic decay. A minute adjustment of the axis of rotation with respect to the laboratory field direction was necessary since the spectra were narrowed by about three orders of magnitude. The resulting spectra exhibit resolved, isotropic, chemically shifted lines and indicate the feasibility of high resolution deuterium NMR in solids.

1. Introduction

The difficulty in attempting NMR on spin-1 deuterium is the enormous broadening of the powder spectrum by the anisotropy of the nuclear electric quadrupole interaction. The well known theoretical lineshape for the case of high magnetic field and axially symmetric electric field gradient, illustrated in fig. 1, consists of overlapping powder patterns for each quadrupole satellite [1]. Such a spectrum allows immediate measurement of the quadrupole anisotropy parameter

$$\nu_Q = \frac{1}{h} \frac{3e^2qQ}{4I(2I-1)} = \frac{1}{h} \frac{3}{4} e^2qQ,$$

where h is Planck's constant, $I = 1$ for deuterium, eq is the electric field gradient, and Q is the electric quadrupole moment. However, it does not allow observation of chemical shift information. This problem was solved by the introduction of double-quantum Fourier transform NMR (DQFTNMR) [2] which permits measurement of the anisotropic chemical shift powder pattern spectrum. The current problem is the extraction of the isotropic chemical shift spectrum when there

exists many chemically or crystallographically inequivalent deuterium sites. In this case, the powder spectra usually overlap and the analysis can be difficult or impossible. Solving this problem is an important step in the direction of high resolution deuterium labeling studies.

It has been demonstrated that sample rotation about an axis inclined at $\beta = \arccos 3^{-1/2}$ to the external magnetic field, the "magic axis", can be used to remove the broadening due to the anisotropy of the chemical shift in spectra of powders [3-7]. When the frequency of rotation is less than the powder chemical shift anisotropic linewidth, the free induction decay (fid) after a single pulse consists of a series of spatially

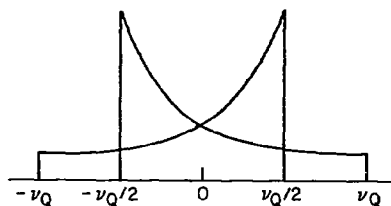


Fig. 1. Theoretical powder absorption lineshape for spin-1 deuterium in an axially symmetric electric field gradient in high magnetic field. The overlapping patterns arise from the orientation dependence of the frequencies of the two quadrupole satellites. Zero frequency is the nuclear Larmor frequency.

* Present address: Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, USA.

induced echoes. The separation between echoes is the period of sample rotation and the fid may be sampled in synchronism with the rotation [6] to produce a "high resolution", isotropic decay. If the frequency of rotation can be made to exceed the anisotropic linewidth, the echoes merge to form the isotropic decay and the high resolution spectrum is available directly.

These statements also apply to the first order (truncated) quadrupole broadening in high magnetic field for nuclei with $I > 1/2$. Thus we have two approaches to high resolution deuterium NMR in powders, i.e. DQFTNMR with magic angle spinning and magic angle spinning with synchronous sampling. In this paper we present the first examples of the application of magic angle spinning to deuterium in solids where the static powder linewidth can be over 255 kHz and synchronous sampling of the fid is mandatory [8,9]. It also requires minute adjustment of the axis of rotation with respect to the laboratory field direction since the broadest deuterium spectra were narrowed by about three orders of magnitude. We believe that this work strongly complements measurement of the chemical shift anisotropy by double-quantum spec-

troscopy and that together they provide a useful tool for the study of deuterium in solids.

2. Experimental

The powder samples were rotated with a turbine of the Henriot-Huguenard type first used by Andrew [10] (see fig. 2). The probe head pieces and rotors were made from Delrin and Kel-F polymers. Stable spinning frequencies between one and four kHz could be maintained with Delrin, limited mainly by the large rotor diameter. Kel-F would not rotate faster than about 1.7 kHz. The powders were simply tamped into the rotor chamber with plaster plugs formed over them if necessary. Measurement of the spinning frequency and synchronization of the data acquisition were accomplished with a digital tachometer employing a lamp, phototransistor, and optical fiber cables which monitored reflected light from the rotor surface.

The probe employed a single, double-tuned coil for deuterium detection with continuous high power proton decoupling [11], fixed in space just outside the sample chamber (fig. 2). The spectrometer was of home-built design with quadrature phase-sensitive detection, 200 W transmitter, and widebore Bruker superconducting solenoid operating at 182 MHz for ^1H and 28 MHz for ^2D . Maximum deuterium pulse amplitudes of 32 G or $\nu_1 = 21$ kHz were used. Spectra were obtained by application of a single pulse off-resonance with respect to the isotropic chemical shifts followed by phase-sensitive detection of the free induction decay with proton decoupling for the partially deuterated samples. The spectrometer audio bandpass filters were set almost to the width of the static quadrupole powder spectrum to pass the higher frequency components of the rotational echoes. Recycle times of up to 2 min were used due to long spin-lattice relaxation times in the solids. All spectra were taken at room temperature.

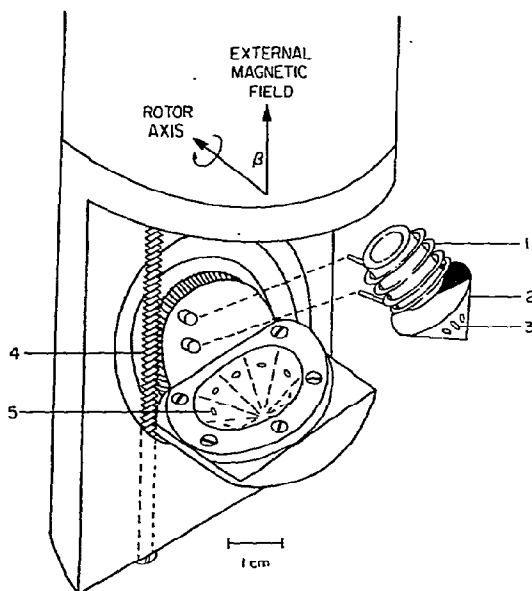


Fig. 2. NMR sample spinning probe head: (1) NMR coil, (2) rotor, (3) air drive flute, (4) rotor axis angle (β) adjust screw, (5) rotor air drive air outlet.

3. Results and discussion

In fig. 3 are shown the on resonance fid's of per-deutero-hexamethyl-benzene- d_{18} ($\text{hmb-}d_{18}$) rotating at 4.0 kHz. The upper fid consists of a series of rotational echoes and the lower fid is obtained by sampling the peaks of these echoes. Fids of the $\text{hmb-}d_{18}$ under

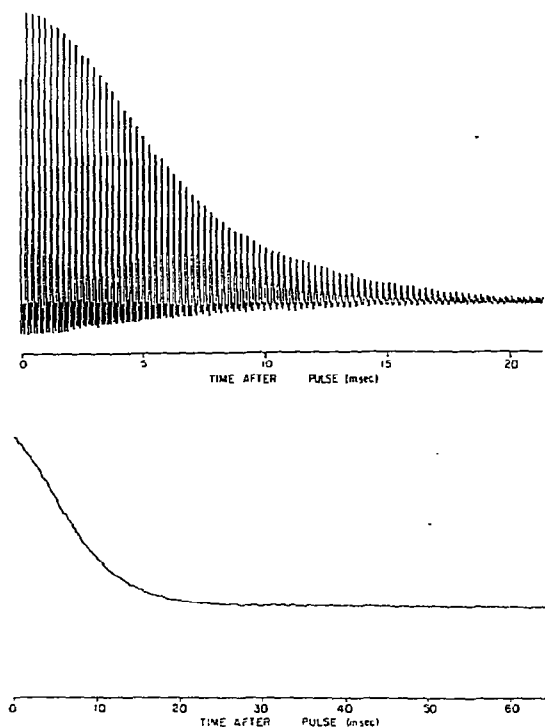


Fig. 3. On resonance free induction decays of hmb- d_{18} rotating at 4.0 kHz: (top) rotational echoes without synchronous sampling, (bottom) isotropic decay produced by synchronous sampling.

the same condition, but 0.4 kHz off resonance, are shown in fig. 4. The first isotropic solid state spectrum of an equal deuterium mole mixture of hmb- d_{18} and 20%-deutero-ferrocene- d_{10} is shown in fig. 5. The top spectrum is the non-spinning case and consists of the overlapping powder patterns of the two components. The inner peaks are the singularities of the hmb- d_{18} pattern and the outer peaks are those of the ferrocene pattern. From these we can immediately measure ν_Q (hmb- d_{18}) = 14 kHz and ν_Q (ferrocene- d_{10}) = 73 kHz. The shoulders of the hmb- d_{18} pattern are just visible, but those of the ferrocene pattern are not. The middle spectrum shows the distribution of the total powder spectrum into a set of spinning sidebands when the sample is rotated at 4.0 kHz. The sidebands are separated by that frequency and their envelope approximates the non-spinning pattern since the frequency of rotation, ν_r , is much less than ν_Q . Sampling in synchronism with the rotation effectively folds in

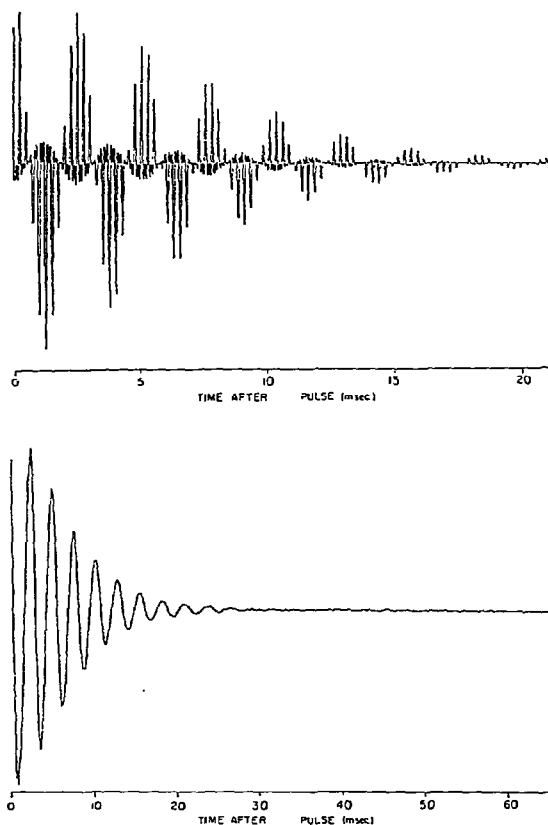


Fig. 4. 0.4 kHz off resonance free induction decays of hmb- d_{18} rotating at 4.0 kHz: (top) rotational echoes without synchronous sampling, (bottom) isotropic decay produced by synchronous sampling.

the sideband spectrum in such a way as to produce the lower spectrum; the isotropic chemical shift spectrum [6,12].

The isotropic chemical shift spectra of the perdeuterated dimethyl and diethylesters of terephthalic acid are shown in figs. 6 and 7, respectively. In both cases the narrower, more intense line arises from the $-CD_3$ position and the broader and less intense lines from the rigid $-CD_2$ and $-\phi D_4$ positions. Approximate absorption line integrals show that these latter positions contributed only about half of their expected intensity relative to the $-CD_3$ positions. This intensity loss is also evident in fig. 8, the spectrum of succinic acid monomethyl ester, deuterated as shown. The $-CDH$ and $-CD_3$ lines overlap and only a very small line is observed for the $-OD$ position.

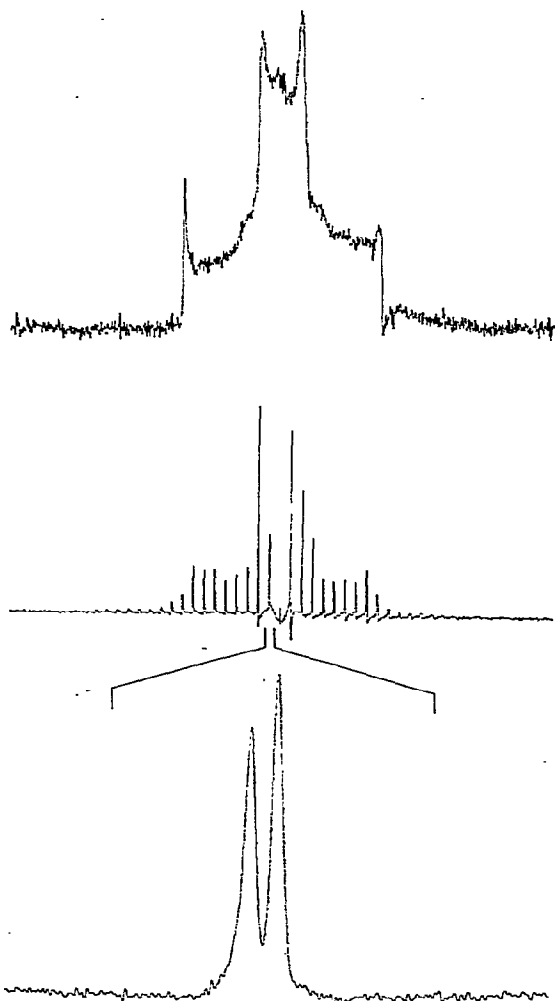


Fig. 5. Solid state deuterium spectra of an equal deuterium mole mixture of perdeutero-hexamethylbenzene- d_{18} and 20%-deutero-ferrocene- d_{10} : (top) non-spinning quadrupole powder pattern; total width of trace 200 kHz. The inner peaks are the singularities of the hmb- d_{18} pattern and the outer peaks are the singularities of the ferrocene- d_{10} pattern. (middle) Rotational sideband spectrum from Fourier transform of rotational echo fid (see fig. 3, top) with sample spinning at 4.0 kHz; total width of trace 200 kHz. Envelope of sidebands approximates non-spinning lineshape above when $\nu_r \ll \nu_Q$. (bottom) Isotropic chemical shift spectrum from Fourier transform of synchronously sampled fid (see fig. 3, bottom); total width of trace 2 kHz. Ferrocene- d_{10} is the downfield peak.

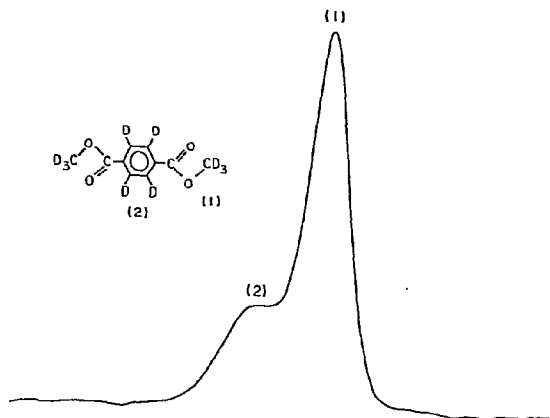


Fig. 6. Solid state isotropic chemical shift spectrum of perdeutero-terephthalic acid dimethyl ester, 1 kHz trace width.

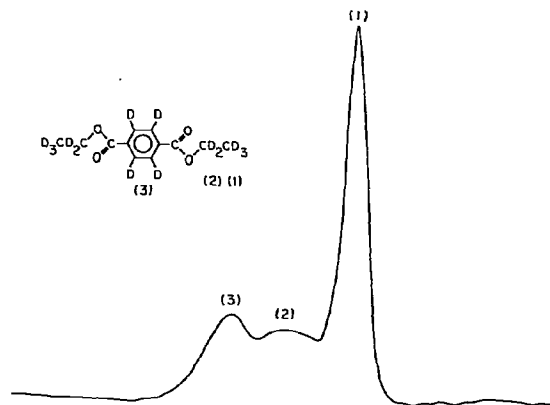


Fig. 7. Solid state isotropic chemical shift spectrum of perdeutero-terephthalic acid diethyl ester, 1 kHz trace width.

Two important observations must be discussed: (1) the rigid molecular positions which retain the full anisotropic quadrupole coupling range contribute much less relative intensity than expected, (2) the absorption linewidths are from 1.5 to 3.5 ppm at half maximum height. The first observation is in part the result of applying a pulse for which $\nu_1 \ll \nu_Q$. Under this condition, the pulse does not excite equally over the spectrum. For the rigid positions, $\nu_Q \approx 130$ kHz and ν_1 of at least 100 kHz or 155 G would be required to produce more uniform excitation.

The second observation is the result of two effects.

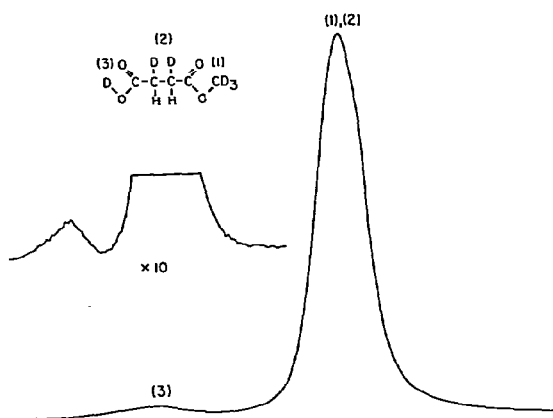


Fig. 8. Solid state isotropic chemical shift spectrum of selectively deuterated succinic acid monomethyl ester, 1 kHz trace width.

First, the absorption linewidth in the isotropic spectrum should have an inhomogeneous contribution from the anisotropy of the quadrupole coupling taken to second order as a perturbation on the Zeeman energy. This interaction does not average to zero under magic angle spinning since it has a different angular dependence. Its contribution to the linewidth is on the order of $4 \times 10^{-2} \nu_Q^2/\nu_0$ or about 1 ppm for the rigid positions. Second, the axis of sample spinning was not exactly "magic" and could sometimes be seen to wobble with the unaided eye. Thus the quadrupole broadening is not completely removed even in first order. In fact, the fid varied significantly from shot to shot and in fig. 9 is shown the spectrum of the diethyl-ester of terephthalic acid obtained by visually selecting those shots with long decays for averaging. Clearly, rotor instability was the major factor in linewidth and resolution obtained and must be improved to employ signal averaging. Since the spectra were narrowed by the factor $\frac{1}{2}(3 \cos^2\beta - 1)$, a deviation of a few hundredths of a degree from $\beta = \arccos 3^{-1/2}$ gives broadening of hundreds of Hz and makes chemical shifts unobservable. Even lesser deviations cause enough broadening of the lines from rigid positions (those with large ν_Q) to create an apparent intensity loss as cited in the first observation.

Summarized in table 1 are the measured isotropic chemical shifts using hmb- d_{18} as internal standard

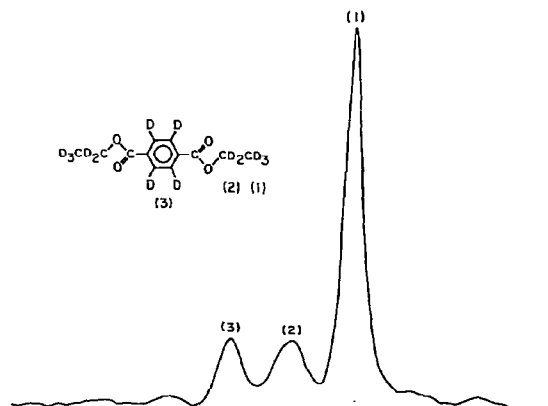


Fig. 9. Isotropic spectrum of perdeutero-terephthalic acid diethyl ester produced by visually selecting shots with long decays for signal average, 1 kHz trace width. The selection procedure partially compensates for rotor instability and shows that the instability is a dominant factor in resolution obtained.

and for comparison, the corresponding values for protons in liquid. The solid values are significantly downfield from the liquid values due to a downfield shift of the solid absorption line position from second order quadrupole effects. This shift depends on the ratio ν_Q^2/ν_0 and is negligible for the standard hmb- d_{18} which has the unusually small value $\nu_Q = 14$ kHz due to rapid molecular motions in the solid. The second order quadrupole effects will be discussed in more detail in a forthcoming paper.

4. Summary

Relatively slow magic angle sample rotation has been applied to remove the first order quadrupole broadening from spectra of deuterium in powders. Perdeuterated and selectively and partially deuterated samples have been used. Stability and control of the axis of rotation is crucial since the spectra were narrowed by about three orders of magnitude. Resolution of lines from isotropically shifted positions in a molecule has been demonstrated and a downfield shift due to second order quadrupole effects has been observed. The availability of these isotropic chemical shift spectra is an attractive alternative to the study of protons in solids when this becomes difficult and for isotopic labeling studies. Experiments to combine sample rota-

Table 1
Isotropic solid state ^2D chemical shifts and corresponding values for ^1H in liquid (ppm δ)

Compound	Position	^2D solid ^{a)}	^1H liquid
ferrocene		3.1	1.9 ^{b)}
terephthalic acid	(1)	2.4	1.7 ^{c)}
dimethylester ($\text{D}_3\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{CD}_3$)	(2)	7.5	5.8
	(2) (1)		
terephthalic acid	(1)	0.0	-0.8 ^{d)}
diethyl ester	(2)	4.4	2.2
($\text{D}_3\text{CD}_2\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{CD}_2\text{CD}_3$)	(3)	8.3	5.9
	(3) (2) (1)		
succinic acid	(1)	1.7 ^{e)}	0.5 ^{c)}
monomethyl ester	(2)	1.7	0.4
(DOOCCDHCDHCOOCD_3)	(3)	13.8 (?)	-
	(3) (2) (1)		

a) Internal reference solid perdeutero-hexamethylbenzene- d_{18} . Uncertainty in solid values ± 0.4 ppm.

b) In CCl_4 with internal reference protonated hexamethylbenzene.

c) Referenced to protonated hexamethylbenzene [13].

d) In CHCl_3 with internal reference protonated hexamethylbenzene.

e) Externally referenced to solid perdeutero-hexamethylbenzene- d_{18} .

tion with double-quantum FTNMR and to reduce second order quadrupole effects are in progress.

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