

# An Accurate and Simple Method for Setting the Magic Angle for Solid State NMR Studies

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**Use of the deuterium NMR spectrum of a deuterated solute dissolved in the nematic phase of a liquid crystal is suggested for setting the magic angle in solid state NMR. The use of the method as a convenient and accurate means of setting the angle is demonstrated.** © 2000 Academic Press

**Key Words:** solid state NMR; magic angle spinning; oriented molecule; deuterium NMR.

Ever since the discovery that magic angle spinning (MAS) can average out anisotropies of interactions in the solid state (1, 2), the method has found enormous applications in a great variety of fields spanning several areas of physics, chemistry, and structural biology. In this method, the sample packed in a rotor spins within a stator assembly about an axis making the magic angle of  $54.7^\circ$  with the magnetic field. This averages out the anisotropic part of interactions, which are represented by a second rank tensor (3). The importance of setting this angle accurately is well recognized (4). An inaccurate setting of the angle can have deleterious effect on either or all of the following parameters namely (1) line-width, (2) line position, and (3) signal to noise ratio. Therefore, several methods have been suggested to set the axis of the spinner accurately at the magic angle (5–7). Of these, the method most commonly used is the monitoring of the  $^{79}\text{Br}$  signal from KBr, which, broadened by a large quadrupole interaction, breaks into a number of sidebands for magic angle spinning (5). Correspondingly, the time domain signal gives rise to a number of rotational echoes (8). The procedure generally adopted and also suggested in solid state probe manuals is to visually monitor the FID and change the orientation of the stator with respect to the magnetic field to obtain a maximum number of rotational echoes. The adjustment of the angle of the stator, which is usually not easily accessible is achieved, say, by means of a long rod connected to the stator assembly inside the probe in the magnet. Manipulating the other accessible end of the rod helps to locate the magic angle. This end of the rod is also calibrated with a vernier or other such suitable arrangement for readjustment if required at a later time. This procedure suffers from two

drawbacks. The appearance of the rotational echoes is fairly sensitive to the angle the rotor axis makes with the magnetic field and starts only when this angle is fairly close to the magic angle. When the angle is slightly away from the optimum position, there are no rotational echoes and the direction in which the stator is to be turned is based on experience or trial and error since angles other than the magic angle cannot be estimated from the FID by any simple procedure. The vernier scale provided is not dependable due to backlash and other mechanical characteristics, and it provides only a crude idea of the angle. The second difficulty with the method is that even when the rotational echoes appear, the procedure of maximizing their number is somewhat tedious and subjective since the rotational echoes do not directly provide an estimate of how close the stator axis is to the magic angle. The number of rotational echoes seen also depends on the spinning speed; more echoes are observed for higher spinning speeds and could thus provide a misleading indication of the exact magic angle. Every laboratory has optimized on some conditions for each probe and this information is passed on to other workers using the system. Though this method seems to be working reasonably well, it would be helpful to have an alternate method which gives an accurate quantitative spectroscopic estimate of the angle of the spinning axis at any setting. It will also be helpful if the method provides an easy and quick means of reaching the correct setting. Such a method will then help in setting the magic angle rapidly and accurately.

We propose here the use of the deuterium NMR spectrum of a deuterated solute molecule dissolved in any standard nematic liquid crystal. This method is in fact already in use for setting any angle for the rotor axis in experiments such as variable angle spinning (9). However, this method has remained in use mainly within groups which are interested in the study of liquid crystals and polymers and for estimating parameters such as chemical shift anisotropies. In this paper, we suggest the use of this method for magic angle setting and demonstrate its advantages. A variant of this method using  $^{13}\text{C}$  NMR has been suggested earlier by us (7); however, the method has certain drawbacks and therefore has not found wide acceptance. The present method overcomes those drawbacks and also gives the

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visual advantage of the KBr method for rapid setting of the angle.

The method is based on the fact that for a liquid crystal with a positive diamagnetic susceptibility anisotropy spinning in a magnetic field, the director orients parallel to the spinning axis when the spinning axis makes an angle  $\theta$  less than the magic angle  $\theta_m$  (10). For  $\theta$  greater than  $\theta_m$ , the director orients in a plane perpendicular to the spinning axis and also rotates at the spinning speed  $\omega_r$ . Exactly at  $\theta = \theta_m$ , the director experiences no orienting force and is distributed randomly. Therefore, the deuterium NMR spectrum of a molecule such as benzene-d<sub>6</sub>, dissolved in a liquid crystal such as trans-*p*-pentyl-4-cyanophenyl cyclohexane (ZLI-1114) reveals the following characteristics for various values of  $\theta$ .

(i) For  $\theta < \theta_m$ : A doublet whose separation  $\Delta\nu$  given by

$$\Delta\nu = k(3 \cos^2\theta - 1)/2 \quad [1]$$

is observed, where  $k$  is the separation between the deuterium doublet for a static sample.

(ii) For  $\theta > \theta_m$ : A centerband and sidebands which are all doublets with separations

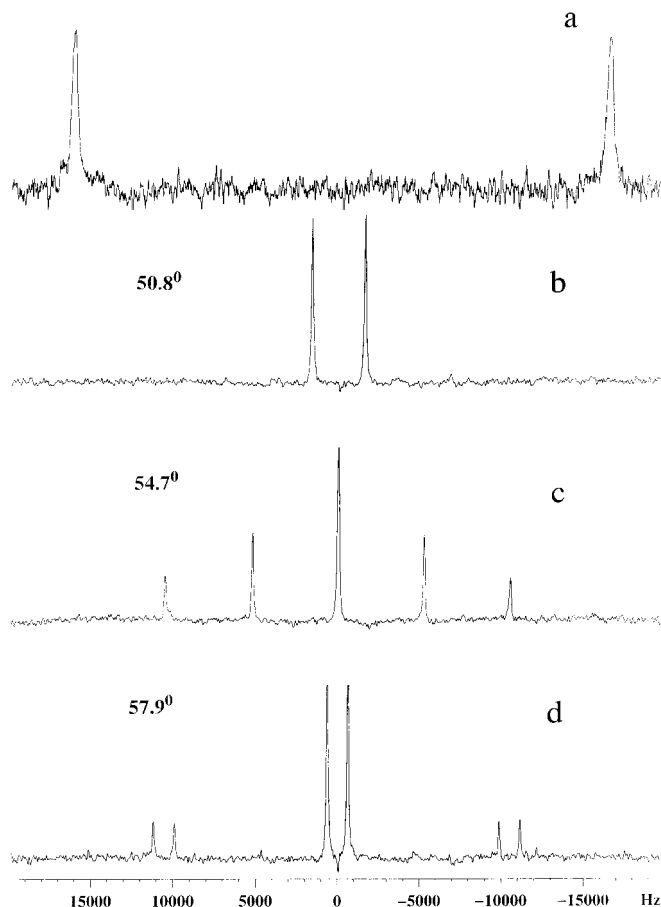
$$\Delta\nu = -k(3 \cos^2\theta - 1)/4 \quad [2]$$

are observed. The sidebands are at twice the rotation frequency.

(iii) For  $\theta = \theta_m$ : The doublets collapse to singlets and sidebands spaced at  $\omega_r$  with the envelope encompassing the Pake powder pattern are observed.

These features are very characteristic of the value of  $\theta$  in relation to  $\theta_m$  as shown in Fig. 1, and the examination of the spectrum gives an immediate qualitative visual indication of the orientation of the spinning axis. A quantitative estimate of the same can also be obtained by using Eqs. [1] and [2]. For setting the magic angle, the direction in which the spinning axis is to be turned becomes immediately obvious. The magic angle orientation is easily achieved by monitoring the frequency domain spectrum and watching the doublets collapse into singlets. Further fine tuning may be achieved by reducing the width of the center band.

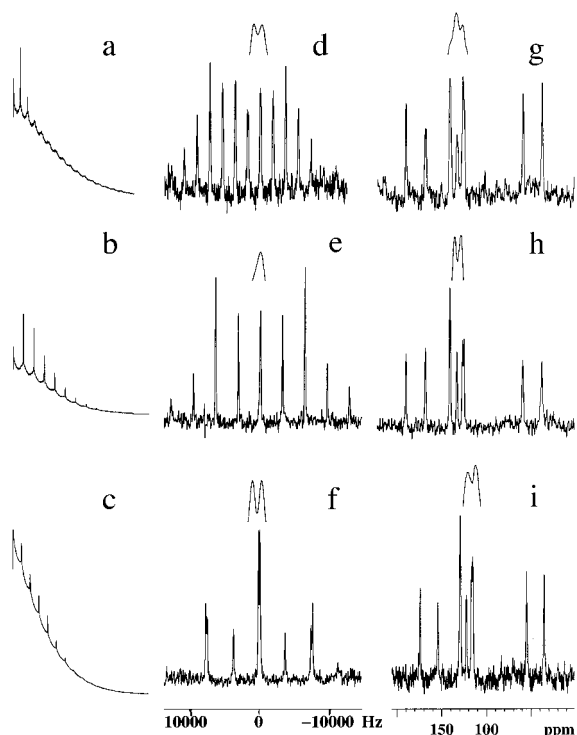
The advantages of the method are illustrated in the following examples. NMR spectra of <sup>79</sup>Br in potassium bromide, <sup>2</sup>H in benzene-d<sub>6</sub> dissolved in the liquid crystal ZLI-1114, and <sup>13</sup>C in tyrosine recorded at three different angles of the stator assembly close to the magic angle are shown in Fig. 2. Figures 2a, 2b, and 2c are <sup>79</sup>Br FID's. Figures 2a and 2b were recorded at a spinning speed of 1.2 kHz. Figure 2c was recorded at a spinning speed of 2.1 kHz. Though Figs. 2b and 2c correspond to slightly different settings, an eye judgment of angle using these FID's likely indicate that they correspond to the same angle, as the number of rotational echoes are nearly the same. On the



**FIG. 1.** <sup>2</sup>H NMR spectrum of benzene-d<sub>6</sub> dissolved in ZLI-1114 recorded at 46.44 MHz using a Bruker DSX-300 FTNMR spectrometer and a DOTY 5-mm variable angle probe at room temperature. (a) Static spectrum (b), (c), (d) spectra of the sample spinning at 5200 Hz about an axis making angles 50.8°, 54.7°, and 57.9°, respectively, with respect to the magnetic field.

other hand, Figs. 2d, 2e, and 2f, which are the <sup>2</sup>H NMR spectra of benzene-d<sub>6</sub> dissolved in liquid crystal ZLI-1114 and recorded at the same settings of the stator corresponding to Figs. 2a, 2b, and 2c, respectively, clearly bring out the difference in the three settings. The insets show the center bands for these three settings. The collapse of the doublets (Figs. 2d and 2f) to a singlet (Fig. 2e) indicates that the setting corresponding to Fig. 2e is nearest to the magic angle.

The estimation of the angles corresponding to Figs. 2d and 2f can be made by using Eqs. [1] or [2], depending on whether the corresponding angle is lesser or greater than the magic angle. The latter information is easily obtained since the corresponding spectra look like those in Fig. 1 if the spinning speed is increased or if the angle is changed in the same direction slightly (11). Thus, from the doublet splittings of 156 and 190 Hz in Figs. 2d and 2f, respectively, the corresponding angles were estimated to be 54.5° and 55.2°, respectively. The frequency separation between the collapsed doublets of Fig. 2e has been obtained by deconvolution which indicates that the



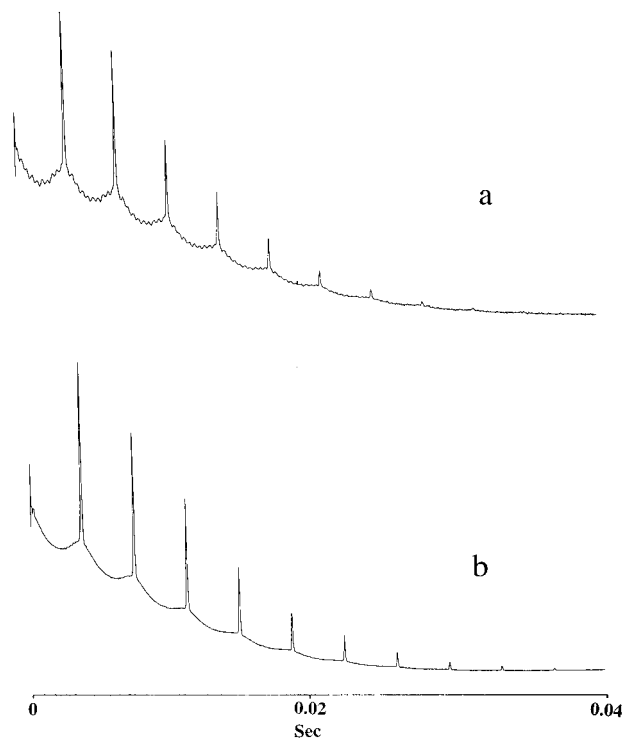
**FIG. 2.** (a), (b), (c) <sup>79</sup>Br FID signals of KBr at three different orientations of the stator with respect to the magnetic field. FIDs (a) and (b) were recorded at a spinning speed of 1.2 kHz, and FID (c) was recorded at the spinning speed of 2.1 kHz. (d), (e), (f) <sup>2</sup>H NMR spectra of benzene-d<sub>6</sub> in ZLI-1114 recorded at the same setting of the stator as (a), (b), and (c), respectively, the spinning speeds being 2.1, 3.2, and 3.7, kHz, respectively. The insets show an expanded plot of the center band in each case. From the frequency separation between the doublet of the center band and using Eqs. [1] and [2], the angles of the stator corresponding to spectra (d), (e), and (f) were obtained as 54.5°, magic angle, and 55.2°, respectively. (g), (h), (i) <sup>13</sup>C spectra of tyrosine spinning at 8000 Hz at the same setting of the stator as (a), (b), and (c), respectively. The insets show expanded plots of the peaks at 115 ppm.

corresponding angle lies within 0.05° of the magic angle. These estimates are based on the quadrupolar splitting of 33.8 kHz observed for the static sample and a linewidth of 110 Hz obtained for spectra recorded with spinning and shown in Figs. 2d, 2e, and 2f. However, with a linewidth of 40 Hz under spinning that could be easily achieved for this sample, simulation indicates that doublets with a separation of 10 Hz can be seen as distinct peaks and a doublet separation of 5 Hz can be distinguished from the linewidth. This means that the stator angle could be set to within an accuracy of 0.01° by this method. In summary, monitoring the <sup>2</sup>H spectrum of a deuterated solute dissolved in a suitable liquid crystal spinning in the magnetic field and observing the collapse of the center band from a doublet into a singlet provides a sensitive and accurate means of setting the magic angle quickly. The <sup>13</sup>C NMR spectra of tyrosine (Figs. 2g to 2i) recorded at the same three angles mentioned before also reveal important features, which emphasize the need to set the angle as accurately as possible. For example, the two peaks at 115 ppm (inset in Figs. 2g to 2i)

are best resolved in Fig. 2h, which corresponds to the magic angle. Also, the linewidths and signal to noise ratios for the tallest peak at 130 ppm are 201, 130, and 158 Hz and 6.4, 11.1, and 7.3 corresponding to Figs. 2g, 2h, and 2i, respectively. Thus, the spectrum in Fig. 2h has an S/N higher by 50% compared to those of Figs. 2g and 2i. It is possible to further fine tune the angle by reducing the linewidth of the center band at the magic angle; the result of such an exercise is shown in Fig. 3, where the <sup>79</sup>Br time domain signal of KBr is compared for the cases when (1) the angle is set directly using KBr (Fig. 3a) and (2) when the angle is first set with the liquid crystal sample and subsequently the <sup>79</sup>Br FID is recorded (Fig. 3b). It is seen in Fig. 3b that the rotational echoes are observed for a longer time. It is therefore concluded that the liquid crystal method provides an easy, accurate, and alternate method for setting the magic angle. The preparation of the sample for this purpose is also straightforward as described at the end and can be preserved as a standard sample for use as and when required.

We had earlier suggested the use of the proton-coupled <sup>13</sup>C NMR spectrum of a solute such as CHCl<sub>3</sub> for such a purpose (7). The difficulties that are associated with the method for routine use are:

- (i) It does not give a easy visual idea of the angle and hence the direction in which the stator assembly is to be turned to get to the magic angle requires some calculations.



**FIG. 3.** <sup>79</sup>Br FID's of KBr (a) obtained directly and (b) obtained after setting the magic angle using the method described in this paper.

(ii) Background signal from the liquid crystal could be a hindrance.

The spectra in the present experiments have been recorded on a Bruker DSX-300 FTNMR spectrometer using a Doty 5-mm variable angle probe. A 5 wt% solution of benzene- $d_6$  in ZLI-1114 (E-Merck, Germany) was prepared. Approximately 40 mg of this sample was filled in a Doty teflon ceiling cell (volume 100  $\mu$ l), which was inserted into a Doty 5-mm thin-walled  $ZrO_2$  rotor. The Bruker MAS pneumatic unit was used for sample spinning. The deuterium NMR spectra at room temperature were recorded at 46.44 MHz using a  $90^\circ$  pulse of width 5  $\mu$ s with a 1-s delay between pulses. Typically, 128 scans were used to obtain the spectra shown in Fig. 1. However, much fewer scans are required to quickly reach the angle close to the magic angle. Spinning rates of 1 kHz are sufficient to orient the liquid crystal director parallel or perpendicular to the spinning axis depending on the orientation of the spinning axis with respect to the magnetic field as described elsewhere in the text.  $^{79}Br$  spectra of KBr at 79.13 MHz and  $^{13}C$  spectra of tyrosine at 75.47 MHz were obtained by using standard one-pulse and Hartmann–Hahn cross polarization sequences, respectively.

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