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Two-dimensional N.M.R. in liquid crystal solvents spinning at various angles from the magnetic field

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It is shown that rotation near the magic angle, owing to the coherent reduction of all anisotropic interactions, provides a way to obtain first order spectra in liquid crystal solvents which can be analysed through all the classical two dimensional experiments.

1. Introduction

Two-dimensional N.M.R. in liquid crystal solvents has not developed as it has in isotropic liquids in the past few years. The main reason is that the partially averaged dipolar interactions are so large that only second order patterns can be obtained [1, 2]. They are almost impossible to analyse. Only Turner [1], Avent *et al.* [3] and Rukmani and Kumar [4] have found ways to perform subspectral analysis through symmetry filtering.

In this paper we would like to show that rotation near magic angle [5], owing to the coherent reduction of all anisotropic interactions, allows first order spectra to be obtained which can be analysed through all the classical two-dimensional experiments.

2. Experimental results

Figure 1 (a) shows the one-dimensional ^{19}F N.M.R. spectra of the chiral molecule of



dissolved in the Merck Licristal mixture of negative diamagnetic susceptibility anisotropy ZLI 2806. This spectrum has been obtained in the classical probe of our Bruker WP 60 electromagnet spectrometer, working at 56.4 MHz. In these conditions the director is perpendicular to the magnetic field. It is an ABC_3X -type spectrum which is almost impossible to calculate as the number of unknown ordering parameters is too large. Figure 1 (b) shows the spin echo two-dimensional spectrum for the same sample and the same relative position of the director and the magnetic field. Obvious second order patterns appear, making the spectra impossible to interpret.

Figure 2 (a) shows the two-dimensional spectrum of the same sample spinning at 96 Hz around an axis tilted at 63.9° from the magnetic field. The spectrum is now much simpler and of an ABX_3M type. The AB nature of the CF_2 group is due, of course, to the vicinity of the asymmetric carbon. This two-dimensional spin echo can be seen as a first order D -resolved spectrum where the residual dipolar couplings appear in dimension f_1 and the chemical shifts in dimension f_2 .

In figure 2 (b) a similar experiment is presented but for an angle of 58.4° , slightly closer to the magic angle. A new D -resolved spectrum is obtained where only the anisotropic interactions are modified.

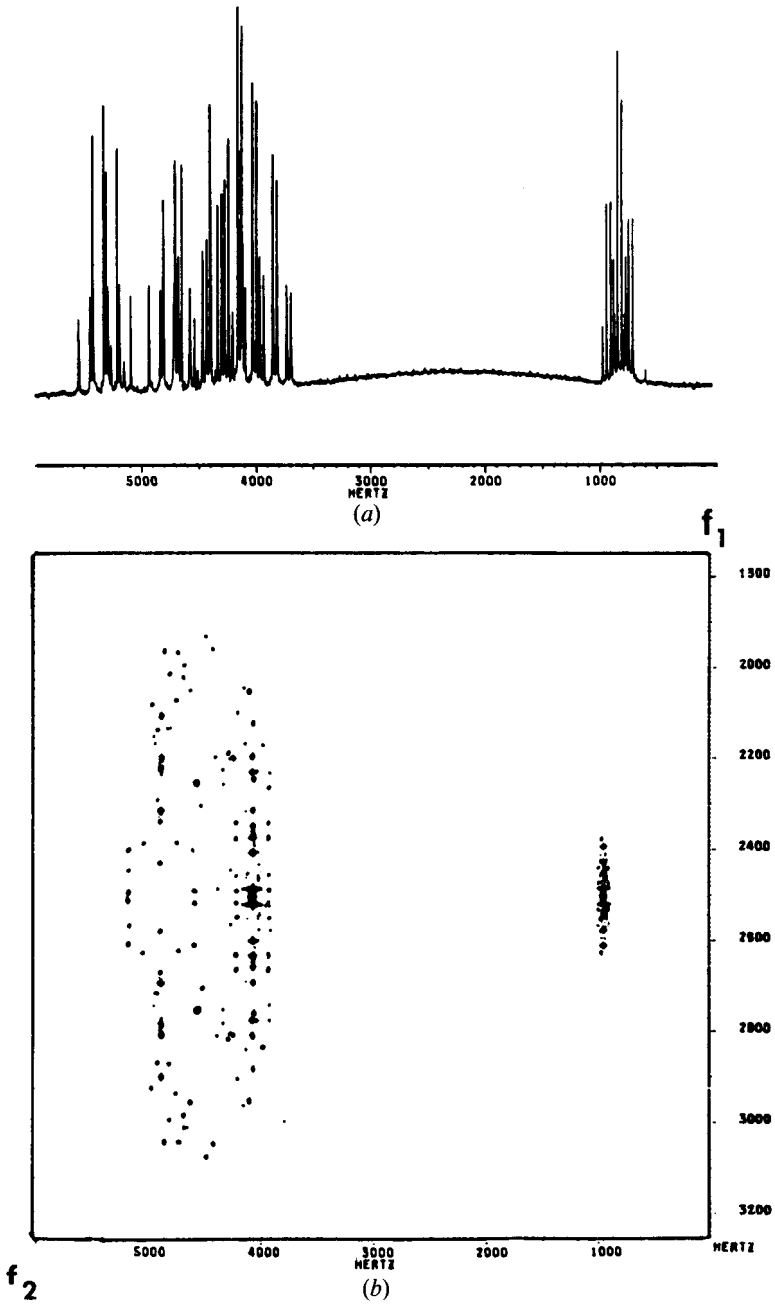


Figure 1. (a) One-dimensional ^{19}F spectrum of $\text{CF}_3\text{-CFBr-CF}_2\text{Br}$ dissolved in a nematic liquid crystal. (b) Two-dimensional spin echo ^{19}F spectrum of the same sample. Note the strong second order effects.

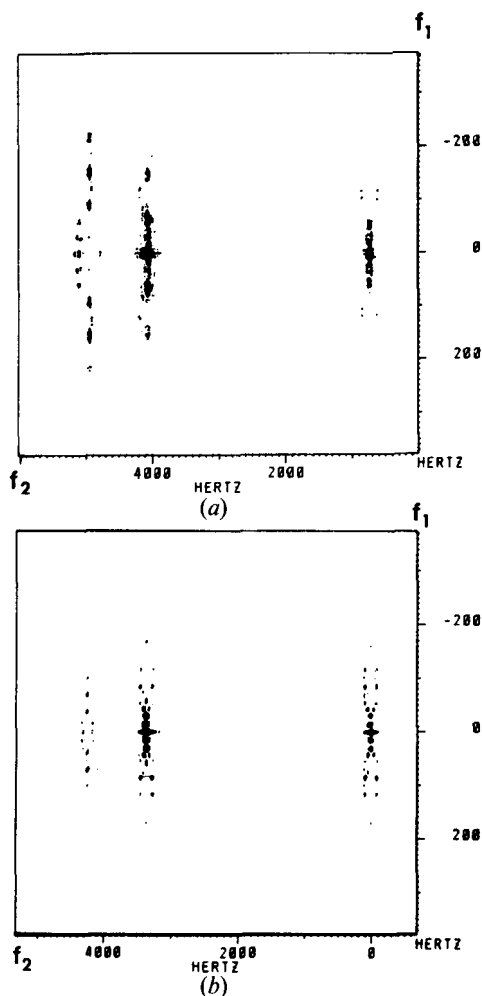


Figure 2. Two-dimensional spin echo ^{19}F of the same sample spinning around an axis tilted at (a) 63.9° and (b) 58.4° from the magnetic field. Note the coherent reduction of the dipolar interactions which allows the first order analysis of D -resolved spectra.

3. Discussion

The above experiments obviously show that combining two-dimensional N.M.R. and rotation near the magic angle provides a new tool for the analysis of the spectra of small molecules in liquid crystal solvents, which should push again the limit of the molecular size and symmetry that can be handled by this otherwise very precise method of topological investigation. The detailed analysis of the above spectra is presently under study in the laboratory, but some interesting features have already appeared.

3.1. Spinning side bands

In these rotation experiments we have noted elsewhere [6] that spinning side bands become important when the angle approaches the magic angle, sometimes making the spectra difficult to analyse when the reduction factor is close to 0. It seems important to note that in the above experiments, i.e. two-dimensional spin echo followed by the

classical cosmetics, tilt and symmetrization, the spinning side bands are rejected out of the main signal on the column of the right chemical shift. They appear at their own chemical shift in the f_2 domain and at integer values of the spinning frequency in the f_1 domain. This allows the observation of a signal free from those artefacts on the column corresponding to the chemical shift of a nucleus as can be seen on the extended displays of figures 3 and 4.

3.2. Selective decoupling through rotation

When rotation near the magic angle allows a first order spectrum in an oriented medium to be achieved, the splittings that can be directly measured on a spectrum is the quantity $2RD_{ij} + J_{ij}$, where R is the reduction factor $(3\cos^2 a - 1)/2$, D_{ij} the residual dipolar coupling between nuclei i and j when the angle a between the director and the magnetic field is null, and J_{ij} the isotropic spin-spin coupling constant. It is then obvious that a very interesting situation arises when a is adjusted such that $(2RD_{ij} + J_{ij}) = 0$. In such an eventuality it produces an effective decoupling between nuclei i and j through rotation. This effect can be observed in figures 4(b) and 4(c). In these spectra the fluorine F_2 resonating at high field intensity is a triplet. The position of this nucleus between a CF_3 and a CF_2 is such that they should appear as a triplet of quartet as can be seen in figure 3(c). Obviously in figure 4(c) there is no splitting of F_2 due to the CF_3 group:

$$2RD_{12} + J_{12} = 0 \quad \text{when } a = 58.4^\circ,$$

$$\text{i.e. } R = -0.088.$$

This allows us to conclude that D_{12} and J_{12} have the same sign and to calculate $D_{12} = 102$ Hz since the absolute value of J_{12} can be measured on the isotropic spectrum as 9 Hz.

This method of selective decoupling can be of wide application and is totally general. If D and J have opposite signs a $\Delta\chi > 0$ liquid crystal must be used as $R > 0$ when $0^\circ < a < \theta_m$ and if D and J have the same sign a $\Delta\chi < 0$ liquid crystal must be used as $R < 0$ when $\theta_m < a < 90^\circ$.

In this way, varying the dipolar couplings through angle adjustment is also interesting when analysing a deceptively simple AB spectrum, as is the case here on the low field part of figures 3 and 4, because the chemical shift difference between the two fluorines of the CF_2 group is small compared to the difference ($J_{34} - D_{34}$). In such a case the frequency difference between the components of the F_3 and F_4 multiplets is known to be related to the coupling terms through

$$\Delta\nu = \sqrt{[(\Delta\delta)^2 + (J - RD)] \pm (2RD + J)}.$$

It is obvious here again that varying R allows us to reach two interesting cases which help the evaluation of the dipolar coupling and the chemical shift difference, assuming that the scalar coupling is known from isotropic measurement:

$$\text{if } J - RD = 0$$

then

$$\Delta\nu = |\Delta\delta| + 3J;$$

if

$$2RD + J = 0$$

then

$$\Delta\nu = \sqrt{[(\Delta\delta)^2 + (3J/2)^2]}.$$

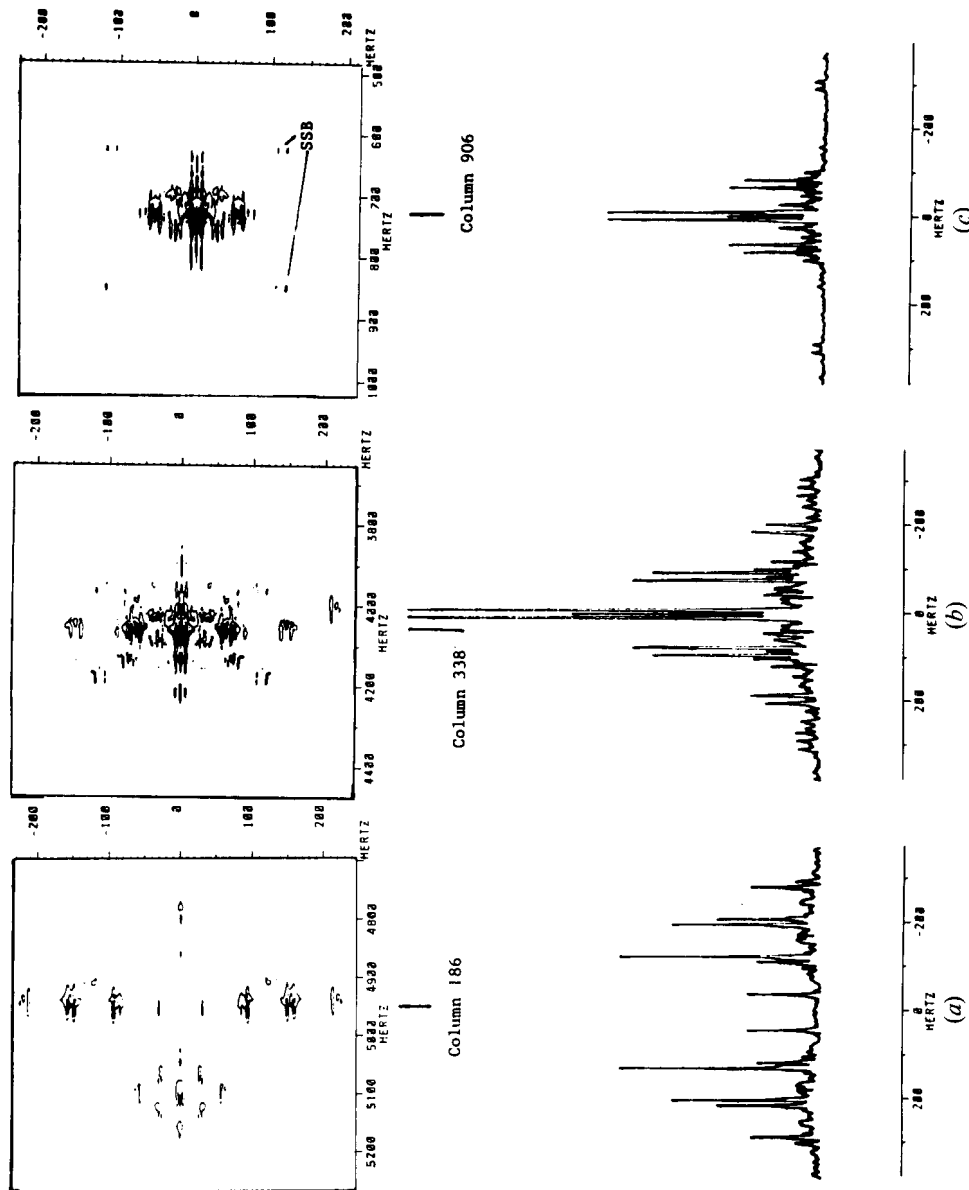


Figure 3. Extended displays (top) and plot of the columns (bottom) centred at the chemical shifts of the (a) CF_2 , (b) CF , and (c) CF groups.

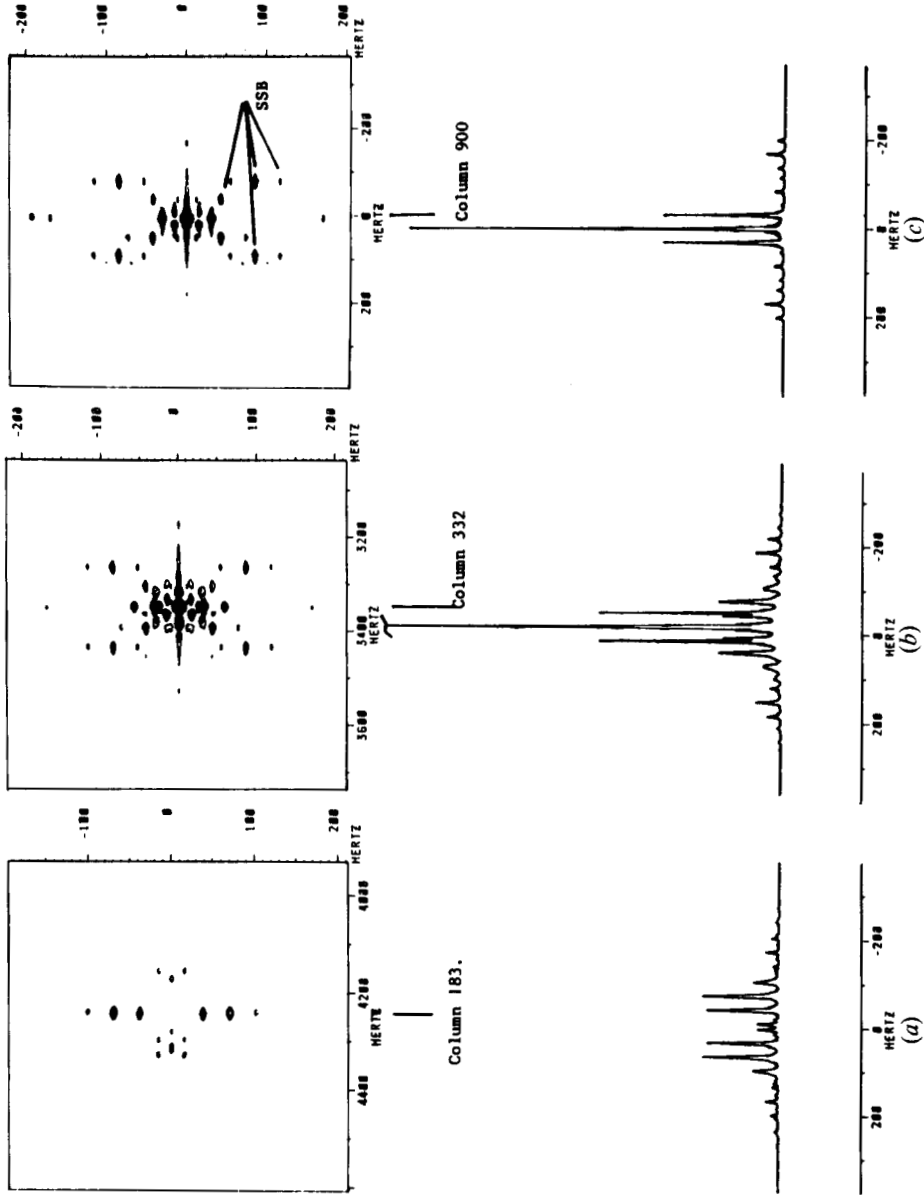


Figure 4. Extended displays (top) of figure 2 (b) and plot of the columns (bottom) centred at the chemical shifts of the fluorine nuclei. Note the two-dimensional structure of the spinning side bands (SSB) and the selective decoupling achieved through rotation between (b) the trifluoromethyl group and (c) the fluorine resonating at high field.

This last situation is illustrated in figure 3 (a) using $J_{34} = +181$ Hz and 100 Hz as the chemical shift difference.

The analysis of these particular situations, with the help of computer simulation, allowed us to analyse the spectra in figures 3 and 4. The results are expressed in the table. We believe this is the first example of the spectral analysis of a chiral molecule in an anisotropic solvent.

Splittings measured on the columns of the D -resolved spectra presented in figures 3 and 4, giving the best fit between experimental and calculated spectra. Assuming the J s from the isotropic spectrum allows the D s to be calculated.

	Angle	
	58.4°	63.9°
$3D_{11}$	60	145
$2D_{12} + J_{12}$	0	12.5
$2D_{14} + J_{14}$	30	64
$2D_{15} + J_{15}$	30	64
$2D_{23} + J_{23}$	30	55
$2D_{24} + J_{24}$	30	55
$2D_{34} + J_{34}$	100	374

4. Conclusions

We have shown that variable angle rotation experiments allows two-dimensional N.M.R. experiments to be carried out in liquid crystal solvents that can be analysed in first order. A convenient choice of the angle can provide selective decoupling through rotation and is of interest in analysing deceptively simple spectra. We are developing this work into the COSY, NOESY and other classical two-dimensional experiments with a special emphasis on the correlation N.M.R. among spin systems of the A_n type.

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