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J. P. Bayle^a; E. Lafontaine^a; J. Courtieu^a

^a Laboratoire de chimie organique structural, Btiment 410, Université Paris-Sud, Orsay Cedex, France

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Scalar coupling and frequency shift in liquid crystal solvents spinning at the magic angle

by J. P. BAYLE, E. LAFONTAINE and J. COURTIEU

Laboratoire de chimie organique structurale, Bâtiment 410, Université Paris-Sud,
91405 Orsay Cedex, France

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When a nuclear spin system dissolved in a liquid crystal is spun at the magic angle, it is shown that unusual N.M.R. spectral features are observed when the spinning frequency approaches the chemical shift difference between a pair of coupled nuclei. A detailed experimental analysis shows a strong enhancement of the sideband intensities as well as a resonance frequency shift analogous to a level anticrossing situation. The total frequency shift appears to be equal to the scalar spin-spin coupling between the nuclei concerned.

1. Introduction

We have shown [1] that when a nematic sample is spun at the magic angle, at a frequency between the director reorientation rate [2] and the inertial switching rate [3], the average magnetic torque vanishes. Consequently the director distributes itself isotropically over the entire sample. The N.M.R. spectra are then similar to those obtained with solid powders where we can see an isotropic spectrum flanked with spinning sidebands whose intensities depend normally on the dipolar couplings and the shielding anisotropies of the observed nuclei [1]. This has been shown by studying spin systems of equivalent nuclei such as A_2 or A_3 dissolved in a nematic medium.

In the present study we try to understand the spectral features encountered when more complex molecules are observed under the same experimental conditions. More specifically we study the amazing behaviour of spinning sidebands when the chemical shift difference $|v_i - v_j|$ between two coupled nuclei is a harmonic number of the sample spinning frequency.

2. Experimental

The experiments presented here have been performed on several polyfluorinated compounds dissolved in a nematic liquid crystal. As a typical example, the case of octafluorotoluene dissolved in 4-methoxy-benzylidene-(4'-*n*-butyl)aniline (MBBA) is described (see figure 1). The ^{19}F N.M.R. spectra were recorded on a WP 60 Bruker instrument working at 56.459 MHz. The magic angle probe used in the experiments was adapted for the rotation of liquid crystal samples as well as variable temperature control [4]. A 15 mm long and 5 mm outer diameter N.M.R. tube was filled with the sample under study and then inserted in a 10 mm cylinder rotor, the speed of which could be varied between 20 and 2000 Hz. At the top of the stator is mounted a goniometer which allowed the angle between the magnetic field and the rotation axis to be adjusted within an accuracy of $\pm 0.01^\circ$. The temperature of the air flow was constantly regulated throughout the experiment.

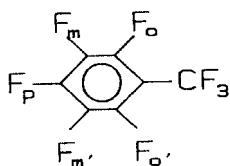


Figure 1. Labelling of the fluorine nuclei in octafluorotoluene.

3. Results

Figure 2(a) shows the spectrum obtained at a spinning frequency of 1680 Hz; it is quite easy to analyse. The strongest transition, at low field, is due to the CF_3 group taken as an arbitrary reference. The smallest signal, at -90.8 ppm, comes from the unique fluorine in the para position and the peaks at -85.0 and at -109.5 originate from the fluorines in the ortho and meta positions, respectively. It should be noted that the linewidth is such that it is not possible to observe the fine structure due to the

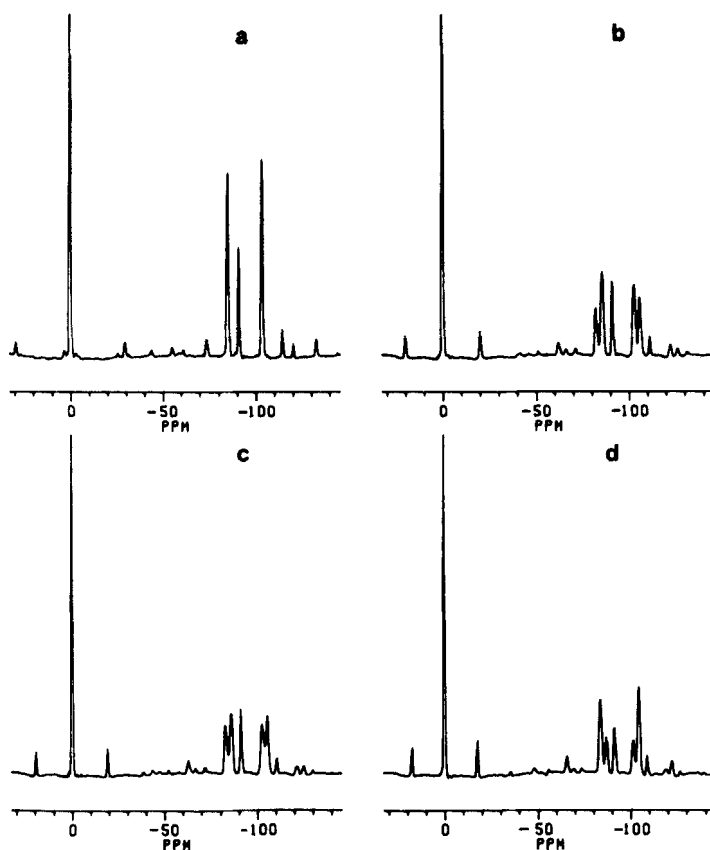


Figure 2. ^{19}F N.M.R. experimental spectra of octafluorotoluene dissolved in MBBA for various spinning speeds. (a) 1680 Hz, (b) 1139 Hz, (c) 1085 Hz, (d) 976 Hz. The assignment of the bands is from left to right $-\text{CF}_3$, ortho, para, meta. The sideband intensities are quite normal for high and low spinning speeds. At about 1085 Hz spinning speed, enhancement of spinning sideband is observed. An energy exchange occurs when the spinning speed is equal to the chemical shift difference between the two coupled fluorine (o, m).

isotropic part of the scalar couplings J_{FF} . Furthermore, each of these four lines, which we call in what follows the centrebands, are flanked with spinning sidebands of orders $1, 2, \dots, n$. These bands are symmetrically placed on each side of the centrebands at $\pm\omega_r, \pm 2\omega_r, \dots, \pm n\omega_r$. This is not surprising as we have shown that when a nematic sample is spun at the magic angle, the magnetic torque which tends to align the director along the magnetic field is, on the average, zero over the rotation. Consequently the director is distributed isotropically over the entire sample. The spectrum obtained is then comparable to that from a powder sample, but with all the anisotropic interactions partially averaged by the molecular motion in the director frame.

Spectra 2*b*, 2*c* and 2*d* show the curious behaviour of spinning sidebands when the rotation frequency is slightly higher (2*b*), equal (2*c*) and slightly smaller (2*d*) than the chemical shift difference between the ortho and meta fluorine nuclei. On these spectra, the following features can be noted:

- (a) as the first order sidebands approach the centrebands, they increase in intensity. This effect is a maximum when $\omega_r = \Delta\nu$;
- (b) the same effect is also observed for the second order sidebands when $2\omega_r = \Delta\nu$;
- (c) when the centreband frequency is plotted versus the spinning speed, a relative frequency shift of the former is observed.

This last effect is better shown in figure 3 where centreband frequencies of the ortho (O(0)), meta (M(0)) and para (P(0)) fluorines are plotted together with frequencies of the first order spinning sidebands (P(+1), O(+1) and M(-1)). It can be seen that the spinning sideband O(+1) does not go through the centreband M(0), but actually takes its place in a way which looks like a situation involving the anticrossing of energy levels [5]. The measured frequency shift between the extreme cases $|v_{F_0} - v_{F_m}| \ll \omega_r$ and $|v_{F_0} - v_{F_m}| \gg \omega_r$ is equal to 20 ± 1 Hz. This value exactly matches the scalar coupling constant $J_{o,m}$ [8] to within experimental precision. This equality between the frequency shift and the scalar coupling is observed for another pair (m, p) of coupled fluorines. For instance, the measured frequency shift of F_m and F_p (19 ± 1 Hz) is also found to equal $J_{m,p}$ (see figure 3).

We have studied the same phenomenon through a 2D experiment of the COSY type. The 2D spectrum obtained with ω_r much greater than $|v_{F_0} - v_{F_m}|$ is shown in figure 4(a). Under this condition, the four centrebands are found to lie on the diagonal, as expected. Furthermore, correlation peaks appearing between the different signals show that the different fluorines are coupled together. This is rather interesting as the 2D experiment allows us to see couplings between nuclei which otherwise are not resolved in the 1D spectrum. Finally the lateral bands appear at $\omega_0 + n\omega_r$ in both dimension, but not on the diagonal as we have already shown [6].

The spectra in figures 4(b) and 4(c) were obtained under the same conditions but with a spinning speed near to the chemical shift difference between the meta and ortho fluorines. The results here are very interesting as a new spectrum now appears on the diagonal. Both ortho and meta fluorine signals are split as would be expected from a strongly coupled AB system. The corresponding correlation peaks show also a split fine structure. Note especially the structure of the correlation peaks between the CF₃ group and the ortho and meta fluorines; these appear to be doubled as if it were an ABX₃ spin system.

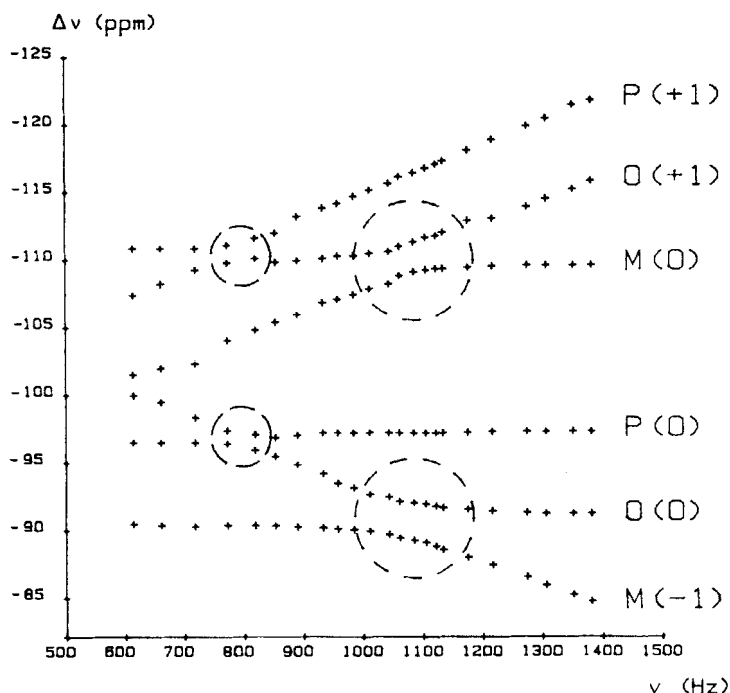


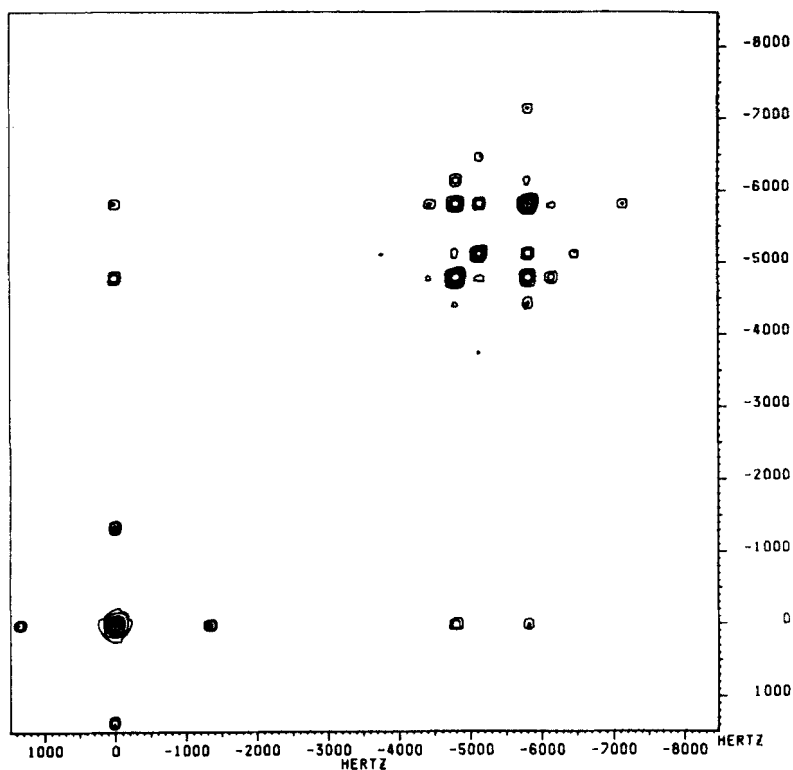
Figure 3. ^{19}F chemical shift versus the spinning speed for the aromatic fluorine alone. For clarity, only six bands are represented: three centrebands O(0), M(0), P(0) and three first order spinning sidebands O(+1), M(-1), P(+1). Two level crossings are observed and are displayed in the circles. The first is around ν_r of 1085 Hz between isotropic bands and the first order spinning sideband for the o, m coupled system. The frequency shift of 20 ± 1 Hz observed between the two centrebands before and after the level crossing matches exactly the coupling constant, $J_{o,m}$, of 20.5 Hz [8]. The second is around ν_r of 866 Hz for the m, p system. As can be clearly seen in the figure, the interaction between energy levels is more important between the o, m system than for the m, p system. In fact the dipolar interaction modulated by the molecular motion around its symmetry axis is less for the pair (m, p) than for the pair (o, m). This fact leads to a less effective interaction between the energy levels. In the same manner, the frequency difference between the two centrebands is equal to 19 ± 1 Hz and matches the coupling constant $J_{m,p}$ (19.1 Hz).

4. Discussion

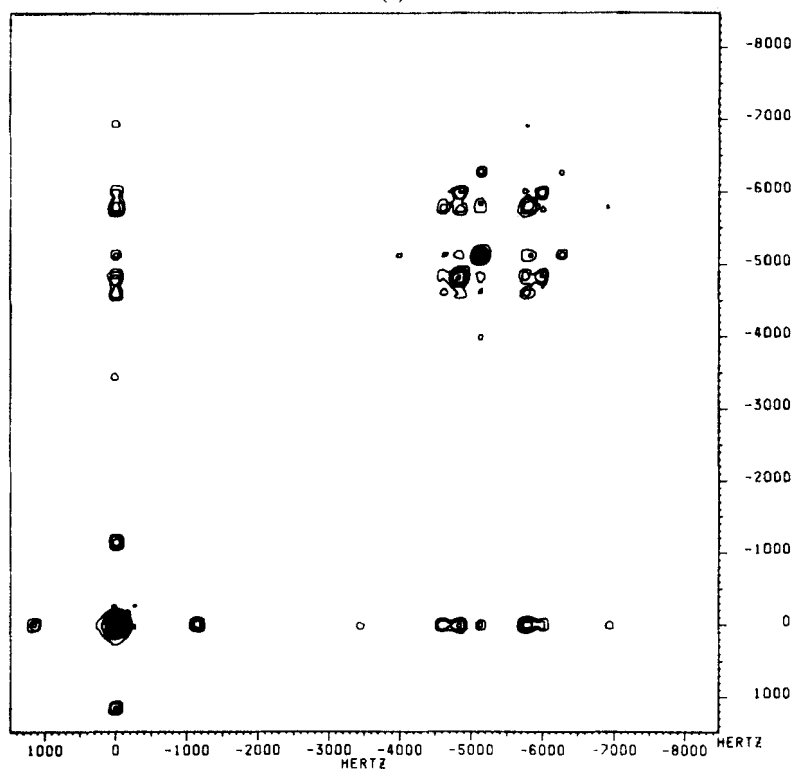
To some extent this behaviour has been reported by Raleigh *et al.* [7] while studying the ^{13}C spectrum of doubly labelled glycine rotating at the magic angle. But the relatively poor resolution intrinsic to the particular spin system studied did not give them the opportunity to observe all of the experimental details noted here. The latter show that the effect cannot be analysed simply as line broadening due to spin diffusion through cross-relaxation processes. Rather, it should be interpreted as a real second order perturbation.

Following [5] and [7], we write the hamiltonian between the spin 1/2 nuclei i and j coupled through dipolar and scalar interactions as

$$\mathcal{H} = \delta_i I_{zi} + \delta_j I_{zj} + (J_{ij} + 2D_{ij}) I_{zi} I_{zj} + 1/2(J_{ij} - D_{ij})(I_i^+ I_j^- + I_i^- I_j^+).$$

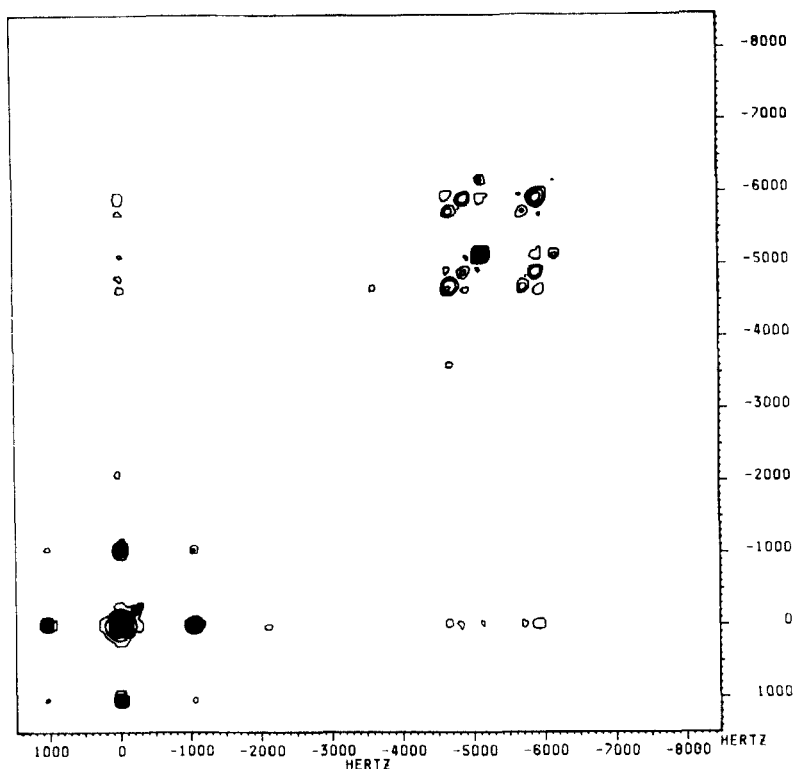


(a)



(b)

Figure 4.



(c)

Figure 4. ^{19}F COSY spectra of octafluorobenzene for different spinning frequencies. (a) $V_r = 1580$ Hz, note the correlation peaks between all of the fluorines. (b) $V_r = 1115$ Hz, note the splitting of the transitions along the diagonal and the splitting of the correlation peaks between CF_3 and the o and m fluorines. (c) $V_r = 1000$ Hz, the same remarks as for (b) apply but with different intensities.

In a liquid crystal spinning at the magic angle, the situation is quite complex as different parts of \mathcal{H} become time dependent;

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}(t).$$

If we neglect the chemical shift anisotropy, these hamiltonians may be expressed as

$$\mathcal{H}^0 = \delta_i I_{zi} + \delta_j I_{zj} + J_{ij} I_z^i I_z^j + 1/2 J_{ij} (I_i^+ I_j^- + I_i^- I_j^+)$$

and

$$\mathcal{H}(t) = 2D_{ij}(t) I_z^i I_z^j - D_{ij}(t) 1/2 (I_i^+ I_j^- + I_i^- I_j^+).$$

The dipolar terms $D_{ij}(t)$ oscillate at ω_r and $2\omega_r$. If $\omega_r \gg D_{ij}$ and $|v_i - v_j|$ the average of the time dependent hamiltonian vanishes and so we obtain a classical high resolution spectrum, where the second order perturbation proportional to J_{ij} can be neglected. It is not true if $\omega_r \approx D_{ij}$, and this leads to the appearance of a set of spinning sidebands. As long as $\omega_r \gg |v_i - v_j|$, the flip-flop term will still oscillate and

will therefore be averaged out. However, when the special condition $|v_i - v_j| = n\omega$, is met where n is an integer, the flip-flop term becomes time dependent and will no longer vanish. This leads to a second order perturbation which gives rise to a pattern which can be analysed, in some sense, as an AB spin system whose coupling is dependent on the scalar and the partially averaged dipolar couplings. It seems to use that the true AB nature of the spectra obtained when $|v_i - v_j| = n\omega$, is perfectly perceptible in the COSY 2D spectra where two new transitions appear on the diagonal and where correlation peaks show a new coupling.

It should be noted that we did not observe any line broadening in our experiments and that the line broadening described in the experiment on doubly labeled glycine could also be considered as two overlapping transitions. Of course, the flip-flop term generates a new relaxation pathway generally known as spin diffusion, but its order of magnitude still depends on other parameters such as molecular motion and dipolar interactions. In liquid crystal solvents, this relaxation pathway does not give rise to an appreciable line broadening.

5. Conclusion

The arguments given here are evidently very simple and a more rigorous analysis of the total time evolution operators should be made. But we think that it is unnecessary as the effects described do not seem to us to be the right way to measure chemical shifts, spin-spin couplings or other interactions. The main interest of this study is to be able to understand, when studying complex molecules in liquid crystal media spinning at the magic angle, that a *quasi* infinity of different spectra may be obtained when there is a large spread of chemical shifts. Changing the spinning speed will produce different frequency shifts, also several multiplet structures will occur which are just totally impossible to analyse if the experimentalist is not aware of the unusual behaviour which we have described. We have shown that when the chemical shift difference between the two coupled nuclei is a harmonic number of the spinning frequency, a second order perturbation transforms the spin system in such a way that the latter produces a second order spectrum which evolves very rapidly with the spinning frequency. The main features are the enhancement of the rotation spinning sidebands together with a frequency shift of the zero order transitions. This frequency shift appears to be equal to the scalar coupling between the nuclei studied.

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