



ACADEMIC
PRESS

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Magnetic Resonance 158 (2002) 52–59

JMR

Journal of
Magnetic Resonance

www.academicpress.com

Measurement of dipolar couplings in partially oriented molecules by local field NMR spectroscopy with low-power decoupling

Malgorzata Marjanska,¹ Franca Castiglione,^{1,2} Jamie D. Walls, and Alexander Pines*

Materials Sciences Division, Lawrence Berkeley National Laboratory, Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720-1460, USA

Received 28 January 2002; revised 25 June 2002

Abstract

Low-power phase-modulated Lee–Goldburg homonuclear decoupling was used to record PDLF spectra of fluorine-substituted benzene derivatives dissolved in nematic thermotropic liquid crystalline solvents. The low-power decoupling minimizes sample heating during RF irradiation while still achieving highly resolved PDLF spectra. The method is illustrated by recording spectra for 1,3-dichloro-4-fluoro-5-nitrobenzene, 1,3-dichloro-4-fluorobenzene, and 1,2-difluorobenzene dissolved in different nematic solvents. © 2002 Elsevier Science (USA). All rights reserved.

Keywords: Liquid crystalline solvents; NMR; Proton-detected local field; PDLF; Phase-modulated Lee–Goldburg; PMLG; Heteronuclear spin–spin couplings; Multiple pulse sequence

1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy of molecules dissolved in liquid-crystalline phases provides a powerful method for determining detailed structural and conformational information since the spectral parameters depend upon the internuclear distance and, for flexible molecules, on the conformational distribution [1–3]. There are many examples of such studies on relatively simple molecules [4,5]. However, the observed spectra are often complex and difficult to assign. This complexity arises from the existence of unaveraged intramolecular dipolar couplings, D_{ij} , the magnitudes of which typically exceed chemical shift differences, leading to second-order spectra. Also, the spectral complexity increases rapidly with the size of the molecular spin system or with decreasing molecular symmetry.

Various techniques have been designed to simplify the second-order spectra to facilitate analysis. One such

technique is proton-detected local field (PDLF) spectroscopy [6–9]. This technique, previously applied to study ^{13}C – ^1H dipolar couplings in nematic liquid crystals, simplifies the second-order spectra by removing the homonuclear couplings between protons. It yields high-resolution ^{13}C – ^1H couplings by detecting the dipolar local field produced by the ^{13}C spins at the site of each proton in the indirect dimension of the 2D experiment. In the presence of multiple-pulse homonuclear dipolar decoupling, each proton “sees” the local field of a single ^{13}C spin due to the low natural abundance (1.1%) of the ^{13}C nuclei. The ideal spectrum contains a maximum of N doublets for a ^{13}C nucleus coupled to N protons. The frequency splitting of each doublet is proportional to the strength of the heteronuclear ^{13}C – ^1H coupling. The accuracy to which the heteronuclear couplings can be obtained depends upon the efficiency of the homonuclear decoupling.

Many well-known homonuclear decoupling sequences designed for solid samples such as MREV-8 [10], BR-24 [11], BLEW-48 [12], Lee–Goldburg CW [13], and frequency-switched Lee–Goldburg (FSLG) [14,15] have been successfully implemented on a high-resolution spectrometer/probe configuration using low RF irradiation powers. These methods have been applied to

* Corresponding author. Fax: 510-486-5744.

E-mail address: pines@cchem.berkeley.edu (A. Pines).

¹ Both authors put equal amounts of work into this project.

² Present address: Biosearch Italia SpA, Via R. Lapetit 34, 21040 Gerenzano (Varese) Italy.

obtain ^{13}C separated local field spectra in liquid crystals under static and off-magic-angle spinning conditions [16]. The use of low RF power is of prime importance since high decoupling powers can introduce thermal gradients in thermotropic liquid crystalline samples [17]. Thermal gradients induce a distribution of order parameters which causes broadening of the spectral lines.

Recently Vinogradov et al. [18] proposed a new class of LG experiments based on continuous phase modulation of the pulses with constant RF field amplitude. Their method, phase-modulated Lee–Goldburg (PMLG), is equivalent to FSLG but performed only with phase modulations, capitalizing on the direct correlation between frequency and phase modulation. PMLG can be potentially less challenging to implement experimentally than FSLG since most commercial instruments can perform phase switches faster and with better accuracy than frequency switches. Up to now, this new method was applied only to the 2D NMR study of solid samples such as malonic acid, glycine, and monoethyl fumarate [18]. The experiments were performed on a solid state spectrometer using a 4-mm CRAMPS probe with a high-power decoupling field of 82 kHz.

In this paper, to our knowledge, the first PDLF spectra for a number of mono- and difluorinated molecules (1,2-dichloro-4-fluoro-5-nitrobenzene, 1,3-dichloro-4-fluorobenzene, 1,2-difluorobenzene) dissolved in nematic solvents studied with low-power PMLG decoupling using a liquid state probe/spectrometer configuration are presented. In the case of monofluorinated systems, the simple PDLF spectrum can be directly analyzed to yield the ^{19}F – ^1H dipolar couplings. For the difluoro compound, the effect of the ^{19}F – ^{19}F dipolar coupling complicates the analysis.

2. Pulse sequence

2.1. PDLF pulse sequence

The pulse sequence shown in Fig. 1 was used to record the two-dimensional PDLF spectra. The ^1H magnetization was excited by a $\pi/2$ pulse and then immediately tilted by a magic angle pulse, θ_m , into a frame perpendicular to the effective field of the PMLG sequence, which appears along the magic angle. The multiple pulse train was applied during the evolution time t_1 to suppress the effects of the proton homonuclear couplings. During

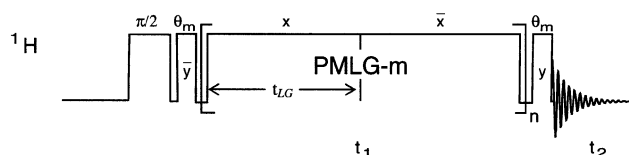


Fig. 1. Pulse sequence used for the 2D PDLF experiment.

that time the ^1H magnetization evolved only under the effect of the chemical shifts and ^{19}F – ^1H dipolar and scalar interactions. At the end of the evolution period, the magnetization was tilted back into the rotating frame by another magic angle pulse and acquired in the direct dimension, t_2 . The experiments were repeated for different values of t_1 so that a data set was acquired as a function of t_1 and t_2 . Two-dimensional Fourier transformation yielded spectra that display, in the indirect (F_1) dimension, ^{19}F – ^1H dipolar doublets and, in the direct (F_2) dimension, the normal ^1H spectrum.

2.2. PMLG decoupling scheme

The PMLG multiple-pulse sequence consists of a series of RF pulses with the phase sequentially varying from one pulse to another. In the following, we review the theoretical details of the PMLG sequence [18].

The total Hamiltonian, H_{tot} , describing a PMLG experiment can be divided into the time-dependent RF field term, $H_{\text{RF}}(t)$, and the spin Zeeman and coupling Hamiltonian, H ,

$$H_{\text{tot}} = H_{\text{RF}}(t) + H. \quad (1)$$

The general form of $H_{\text{RF}}(t)$ in the rotating frame for an LG unit of duration t_{LG} , where $(n-1)t_{\text{LG}} < t < nt_{\text{LG}}$ and $n = 1, 2, \dots$ can be written as

$$H_{\text{RF}}(t) = \omega_{\text{RF}} [I_x \cos(\omega_{\text{PMLG}}t + \theta_{\text{LG}}) + I_y \sin(\omega_{\text{PMLG}}t + \theta_{\text{LG}})], \quad (2)$$

where ω_{RF} is the RF field strength, ω_{PMLG} the phase modulation frequency, and θ_{LG} an arbitrary phase angle.

The spin Hamiltonian, H , for a system of N spins I and one spin S in the liquid crystalline solvent can be written

$$H = H_I^Z + H_S^Z + H_{\text{II}}^D + H_{\text{II}}^I + H_{\text{IS}}, \quad (3)$$

where H_I^Z and H_S^Z are the Zeeman interaction terms for spins of type I and S, respectively,

$$H_I^Z = - \sum_i v_i^I I_i^Z, \quad (4)$$

$$H_S^Z = -v^S S^Z. \quad (5)$$

I_i^Z and S^Z are the components of the nuclear spin angular momentum operators along the direction of the applied magnetic field and v^I is the chemical shift of spin I.

The third term in Eq. (3) represents the dipolar interactions among the I spins

$$H_{\text{II}}^D = \sum_{i < j} D_{ij}^{\text{II}} \left[2I_i^Z I_j^Z - \frac{1}{2} (I_i^+ I_j^- + I_i^- I_j^+) \right], \quad (6)$$

while the fourth term describes the much smaller indirect interactions among these spins

$$H_{\text{II}}^{\text{J}} = \sum_{i < j} J_{ij} I_i \cdot I_j \quad (7)$$

The H_{IS} term accounts for both the direct and indirect heteronuclear coupling terms

$$H_{\text{IS}} = - \sum_i T_{\text{IS}} I_i^Z S^Z, \quad (8)$$

where $T_{\text{IS}} = (2D_{\text{IS}} + J_{\text{IS}})$.

The zero-order average dipole–dipole Hamiltonian, \bar{H}_{II}^0 , is predicted to vanish during a LG irradiation unit with the following parameters:

$$|\omega_{\text{PMLG}}| = \sqrt{\frac{1}{2}} \omega_{\text{RF}}, \quad (9)$$

$$t_{\text{LG}} = \sqrt{\frac{2}{3}} \frac{2\pi}{\omega_{\text{RF}}}. \quad (10)$$

From Eq. (10), for a given RF field strength and number of pulses m , the duration of the individual pulses in a PMLG unit is t_{LG}/m . The angle through which the RF precesses in one unit of LG in the rotating frame is given by

$$\alpha_{\text{LG}} = |\omega_{\text{PMLG}}| t_{\text{LG}} = 207.8^\circ. \quad (11)$$

The precession of the RF field for $\omega_{\text{PMLG}} > 0$ is denoted as X and that for $\omega_{\text{PMLG}} < 0$ as \bar{X} . A full unit of PMLG, for symmetrization arguments, takes the form $X\bar{X}$ or $\bar{X}X$. Hence under one $X\bar{X}$ unit of the PMLG sequence, the RF field precesses from 0° to 207.8° during X and then to 180° , after a 180° flip, during \bar{X} . The increment in the phase angle of each pulse amounts to $\Delta\alpha = 207.8^\circ/m$ starting with $\Delta\alpha/2$ for X and $(\pi - (\Delta\alpha/2))$ for \bar{X} .

3. Experimental

3.1. Sample preparation

The different solutes, 1,2-dichloro-4-fluoro-5-nitrobenzene, 1,3-dichloro-4-fluoro-benzene, and 1,2-difluorobenzene (Aldrich Chemical Company), and the liquid crystalline solvents, ZLI 1132 and ZLI 1695 (EM Industries), were used without further purification. ZLI 1132 has a positive anisotropy of the magnetic susceptibility, and the liquid crystal directors align uniformly parallel to the magnetic field. ZLI 1695 has a negative anisotropy, and the liquid crystal directors align uniformly in the plane perpendicular to the applied magnetic field. The oriented samples, contained in 5-mm tubes (Wilmad), were prepared by placing $\sim 10\%$ by weight of the solute either in ZLI 1132 or in ZLI 1695 liquid crystals.

3.2. NMR spectra

One- and two-dimensional PDLF ^1H spectra were recorded at 300.13 MHz with a Bruker DRX-300 spec-

trometer equipped with 5-mm HDCF liquid state probe. The two-dimensional PDLF spectra were recorded nonspinning with temperature controlled at 25°C , and the field-frequency lock was not used. A recycle delay of 10 s was used to avoid sample heating. The number of increments in t_1 was 512. The signals were accumulated into 2 K of computer memory, and 2 FIDs were summed up for each t_1 increment. The t_1 dimension was zero-filled to 1 K of data points, giving a final 2D matrix of 2 by 1 K before Fourier transformation. A line broadening of 1 Hz was applied in the direct dimension and 10 Hz in the indirect dimension, and spectra were obtained in the magnitude mode.

Experimentally, increasing the number of pulses in the PMLG unit results in better decoupling performance but leads to very short individual pulses in the PMLG unit. Modern commercial high-resolution spectrometers allow phases to be preset during the previous pulse but require a time of $3\ \mu\text{s}$, implying that the length of the individual pulses in PMLG unit cannot be shorter than $3\ \mu\text{s}$. With this constraint in mind, we have chosen for all the experiments the number of individual pulses, m , to be either 6, making $\Delta\alpha = 34.63^\circ$, or 10, making $\Delta\alpha = 20.78^\circ$. For $m = 6$, RF field strengths of 17 and 20 kHz were used, making the individual pulse lengths 8 and $6.8\ \mu\text{s}$, respectively, and requiring the use of 12 pulses for either an $X\bar{X}$ or $\bar{X}X$ LG unit. For $m = 10$, an RF field strength of 23 kHz was used, making the individual pulse lengths $3.5\ \mu\text{s}$ and requiring the use of 20 pulses for either an $X\bar{X}$ or $\bar{X}X$ LG unit. The $X\bar{X}$ units, with stroboscopic sampling, were used, where each unit had duration of 96, 81.6, and $70\ \mu\text{s}$ for the 17-, 20-, and 23-kHz fields, respectively. A scaling factor of $(\sqrt{3})^{-1}$ for chemical shifts and heteronuclear couplings is characteristic of this decoupling scheme. In all PDLF spectra a zero peak is observed, which is consistent with the observations of Vinogradov et al. [18].

4. Results and discussion

In order to demonstrate the utility of the PDLF sequence in determining the ^{19}F – ^1H couplings, to test the performance of the PMLG decoupling scheme, and to look at characteristics of fluorine as a spreading parameter, experiments were performed on a difluoro compound and on a number of monofluorinated molecules with increasing proton spin system complexity.

4.1. 1,2-Dichloro-4-fluoro-5-nitrobenzene

The initial testing of the pulse sequence was performed on a simple molecule, 1,2-dichloro-4-fluoro-5-nitrobenzene. This molecule has three magnetically active nuclei: two protons and one fluorine. The chemical shift difference between protons obtained from

isotropic solution is small, 0.726 ppm. The ^1H 1D spectrum of the solute in ZLI 1132 liquid crystals shown in Fig. 2A is first order and the dipolar couplings between all magnetically active nuclei can be read off directly. The 1D spectrum demonstrates that the two protons become more easily distinguishable due to the difference in fluorine dipolar coupling. The peaks around zero belong to the proton farther away from fluorine, whereas the peaks around ± 1500 Hz belong to the proton closer to fluorine. The PDLF spectrum becomes even simpler since homonuclear couplings are removed, as shown in Fig. 2B. The imperfections of observed intensities could arise due to errors in the pulse sequence such as phase, the existence of higher order terms, and differences in offset. The two pairs of peaks in the PDLF spectrum arise from the two different ^{19}F - ^1H couplings in this molecule. The heteronuclear couplings can simply be read off the spectrum, taking into consideration the PMLG scaling factor of 0.58. Note that for all PDLF spectra the frequency scale is not corrected for the scaling factor of the decoupling sequence. These couplings are reported in Table 1 together with couplings that were obtained from the ^1H 1D spectrum.

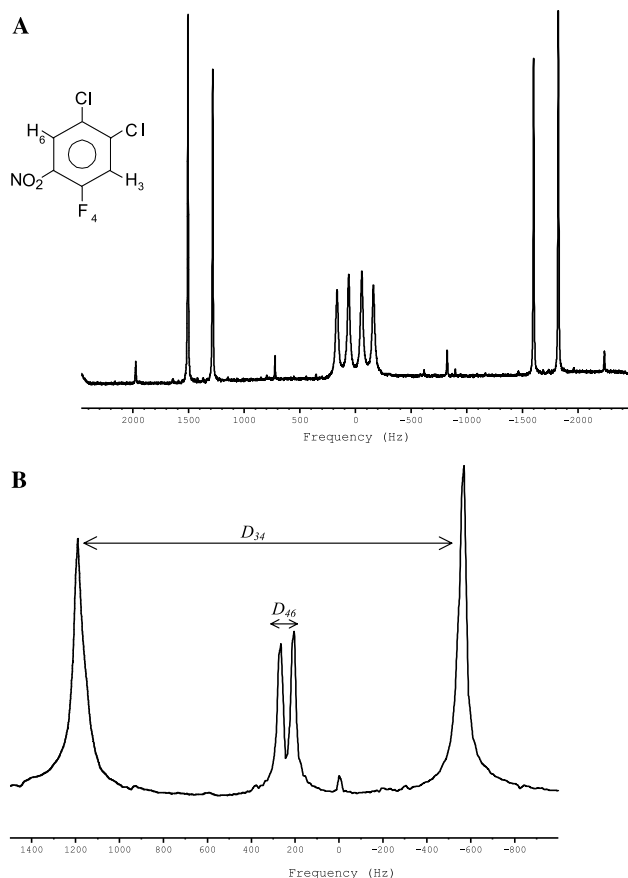


Fig. 2. (A) 300.13-MHz 1D ^1H spectrum and (B) projection in the indirect dimension of 2D PDLF experiment obtained under 17-kHz decoupling with PMLG-6 of a sample of 1,2-dichloro-4-fluoro-5-nitrobenzene dissolved in nematic solvent ZLI 1132.

Table 1
Heteronuclear couplings obtained from the ^1H 1D spectrum and PDLF spectrum of 1,2-dichloro-4-fluoro-5-nitrobenzene dissolved in ZLI 1132

i, j	Couplings from 1D spectrum in Hz	Couplings from PDLF spectrum in Hz
3, 4	1546.0	1514.7
4, 6	52.1	52.1

4.2. 1,3-Dichloro-4-fluorobenzene

1,3-Dichloro-4-fluorobenzene has four magnetically active nuclei: three protons and one fluorine. As in the previous sample fluorine acts as a label. 1D and PDLF ^1H spectra were recorded for the solute placed in ZLI 1132 and in ZLI 1695. Six lines are expected in the

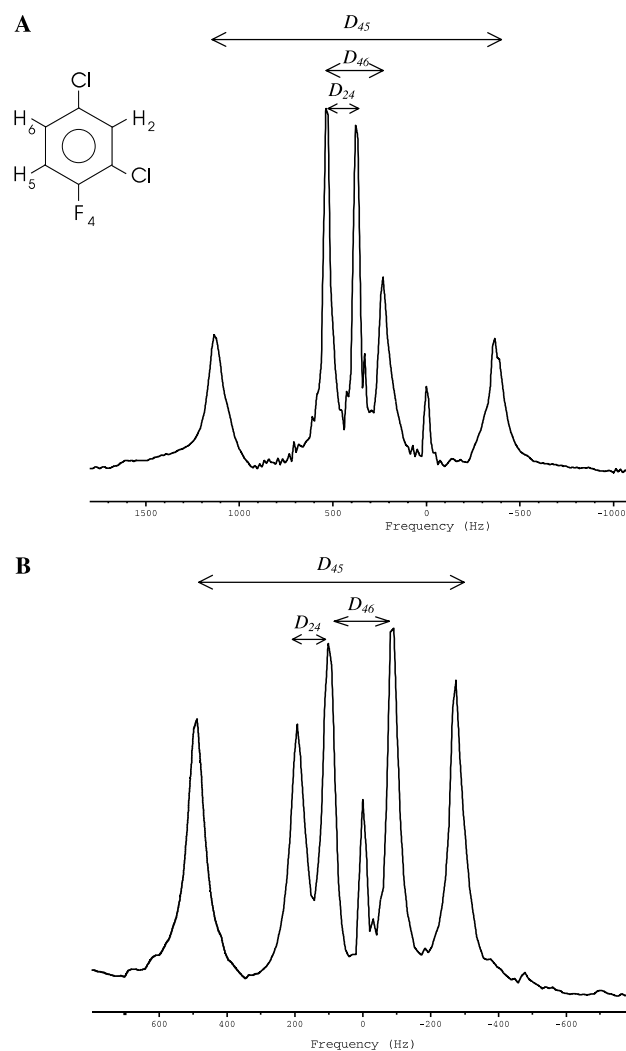


Fig. 3. Projection in the indirect dimension of 2D PDLF spectrum of a sample of 1,3-dichloro-4-fluorobenzene dissolved (A) in the nematic solvent ZLI 1132 obtained under a 23-kHz decoupling field with PMLG-10 and (B) in the nematic solvent ZLI 1695 under a 17-kHz decoupling field with PMLG-6.

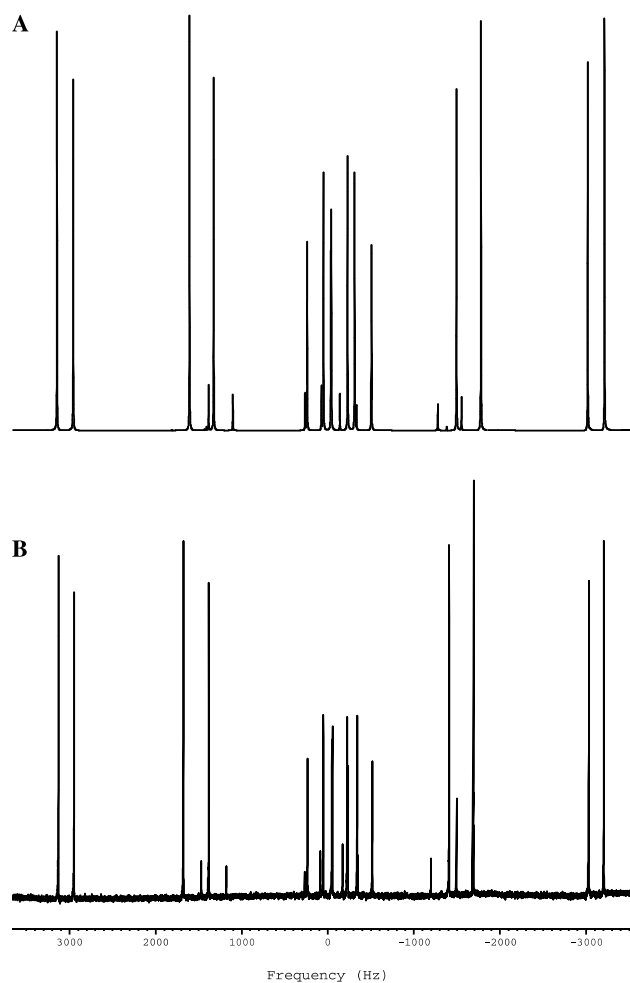


Fig. 4. (A) 300.13-MHz ^1H spectrum simulated using the NMR-SIM program and (B) experimental spectrum of a sample of 1,3-dichloro-4-fluorobenzene dissolved in the nematic solvent ZLI 1132, recorded at 25 °C.

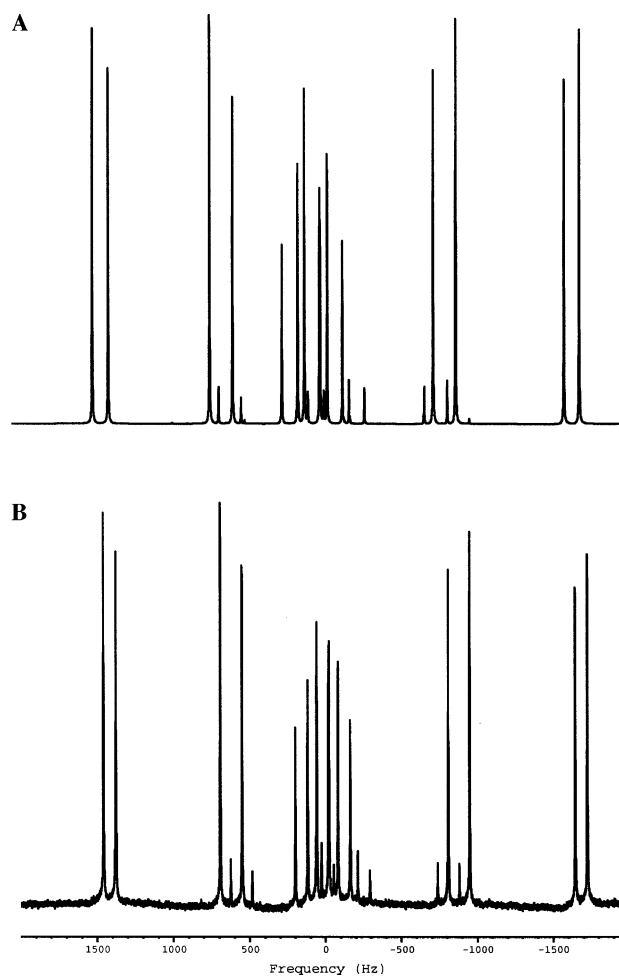


Fig. 5. (A) 300.13-MHz ^1H spectrum simulated using the NMR-SIM program and (B) experimental spectrum of a sample of 1,3-dichloro-4-fluorobenzene dissolved in the nematic solvent ZLI 1695, recorded at 25 °C.

Table 2

Spectral parameters of 1,3-dichloro-4-fluorobenzene dissolved in ZLI 1132 and in ZLI 1695 obtained by analysis of the ^1H 1D spectra and from PDLF spectra

Solvent	^1H chemical shifts in Hz		Scalar and dipolar couplings in Hz			From PDLF in Hz	
	i	ν_i^H	i, j	$(J_{ij})^a$	D_{ij}	D_{ij}	
ZLI 1132	2	0.0	2,4	6.3	141.0	136	
	5	120.0	2,5	0.0	83.5		
	6	27.0	2,6	2.6	157.5		
			4,5	8.6	1260.0		1288
			4,6	4.1	279.0		258
			5,6	8.7	1440.0		
ZLI 1695	2	0.0	2,4	6.3	76.5	81	
	5	-169.0	2,5	0.0	45.0		
	6	-128.1	2,6	2.6	135.5		
			4,5	8.6	657.5		657
			4,6	4.1	164.5		159
			5,6	8.7	702.5		

^a Taken from the analysis of 1,2-difluorobenzene in isotropic solution and kept fixed.

PDLF spectra, one doublet for each of the protons with the splitting proportional to its coupling with the fluorine nucleus. The PDLF spectra of the ZLI 1132 sample and ZLI 1695 sample (Fig. 3) show five lines with two lines appearing to overlap. The 2D contour plot (not shown) helps in determining which lines arise from the same proton. The heteronuclear couplings thus obtained were used as starting values for the simulation of 1D ^1H spectra (Figs. 4 and 5), and the final spectral parameters are reported in Table 2. The analysis was performed using the NMR-SIM program build into the Bruker XWIN-NMR. The comparison of the two sets of parameters shows good agreement between the PDLF and the 1D D_{ij} values. The small differences arise from the lower resolution of the 2D experiments.

4.3. 1,2-Difluorobenzene

1,2-Difluorobenzene has six magnetically active nuclei: two fluorines and four protons. Some of the nuclei are equivalent, so there are three unique nuclei. The ^1H and PDLF spectra of the solute in ZLI 1132 are shown in Fig. 6. The observed PDLF spectrum of this molecule

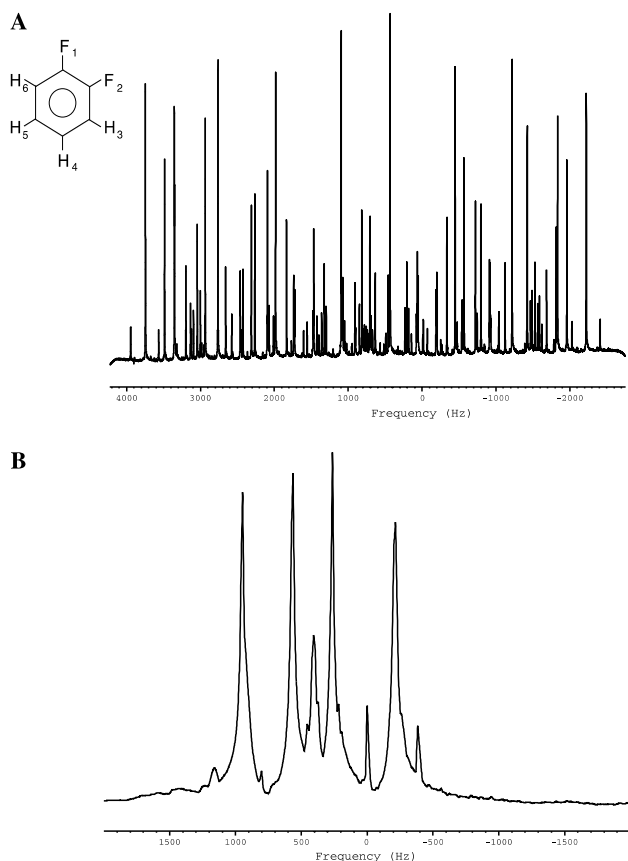


Fig. 6. (A) 300.13-MHz ^1H spectrum and (B) projection in the indirect dimension of 2D PDLF experiment obtained 400 Hz off resonance under 20-kHz decoupling with PMLG-6 of a sample of 1,2-difluorobenzene dissolved in the nematic solvent ZLI 1132, recorded at 25 °C.

is more complicated than the spectra of monofluorinated systems due to the strong (547 Hz) ^{19}F – ^{19}F dipole–dipole coupling. Under these circumstances, the heteronuclear couplings cannot be directly read off from the PDLF spectrum.

We have investigated the influence of the strength of the ^{19}F – ^{19}F dipolar coupling on the PDLF spectrum by

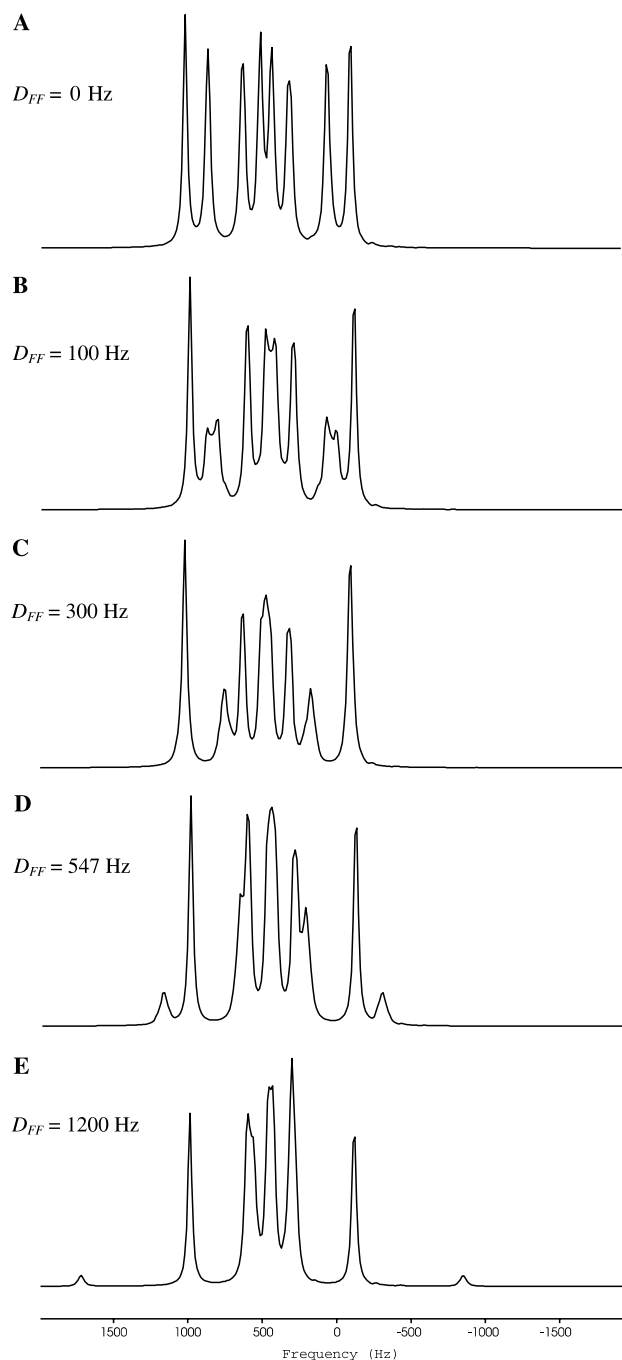


Fig. 7. Simulated spectra that show the influence of the ^{19}F – ^{19}F dipolar coupling on the PDLF spectra under PMLG of a sample 1,2-difluorobenzene dissolved in the nematic solvent ZLI 1132. (A) $D_{\text{FF}} = 0$ Hz, (B) $D_{\text{FF}} = 100$ Hz, (C) $D_{\text{FF}} = 300$ Hz, (D) $D_{\text{FF}} = 547$ Hz, (E) $D_{\text{FF}} = 1200$ Hz.

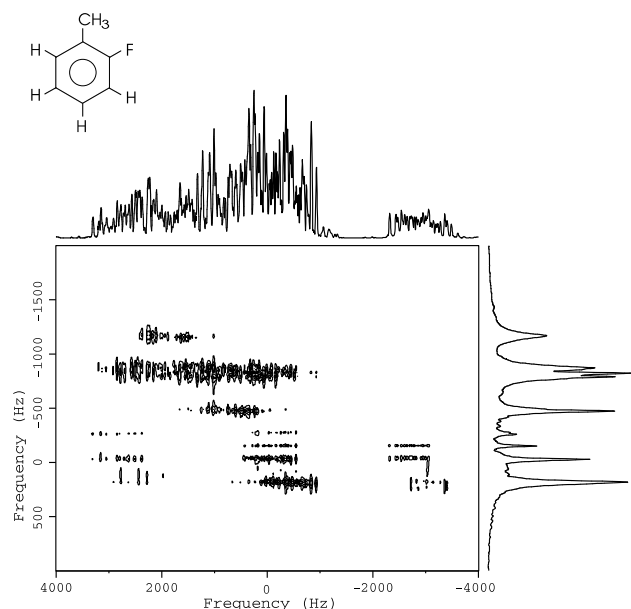


Fig. 8. Contour plot of the 2D PDLF experiment performed on a sample of 2-fluorotoluene dissolved in the nematic solvent ZLI 1695. The top projection shows the completely coupled ^1H spectrum and the right projection shows the PDLF spectrum obtained under 17-kHz decoupling with PMLG-6.

performing simulations using MATLAB (MathWorks) of the PDLF spectrum using the ^{19}F – ^1H parameters from [19] and changing the ^{19}F – ^{19}F coupling. The results presented in Fig. 7 show that for $D_{\text{FF}} = 0$ the PDLF spectrum consists of four doublets, one for each of the protons coupled with two fluorines, as expected for isolated fluorines. As the D_{FF} value increases, the spectrum shows more complicated features, and the heteronuclear couplings cannot be simply read off from the spectrum.

4.4. 2-Fluorotoluene

The usefulness of the technique for structural analysis can be seen in more complicated systems. The spectra displayed in Fig. 8 show that even for a large system such as 2-fluorotoluene, dissolved in ZLI 1695 liquid crystals, where seven protons are present and where the 1D ^1H spectrum is very complicated, the PDLF spectrum is simplified and can be interpreted. This spectrum is the subject of further analysis.

5. Conclusions

In conclusion, the PDLF sequence using PMLG decoupling applied with a high-resolution/low-power probe setup is successful in producing a first order spectrum for the monofluorinated samples. In the absence of proton homonuclear dipolar couplings, the heteronuclear coupling can be used as an additional

label in order to distinguish between protons and can be used as a basis for selective excitation [20]. Besides being a source of addressability in molecules, the heteronuclear dipolar coupling can potentially provide gates in quantum computing in liquid crystalline samples faster than those in liquid samples. This is due to the fact that the heteronuclear dipolar couplings are typically much greater in magnitude than the J couplings and are not limited by bond connectivities [21–23]. In the case of multifluorinated samples, we have shown that in the limit of strong ^{19}F – ^{19}F dipolar coupling the PDLF spectra are still complicated. The limit in which the fluorines are completely isolated from each other can be obtained by performing homonuclear decoupling on both proton and fluorine nuclei, and work is currently underway.

Acknowledgments

The authors thank Dr. J. Granwehr for comments about the paper. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the US Department of Energy under Contract DE-AC03-76SF00098.

References

- [1] J.W. Emsley, J.C. Lindon, *NMR Spectroscopy Using Liquid Crystal Solvents*, Pergamon, Oxford, 1975.
- [2] R.Y. Dong, *Nuclear Magnetic Resonance of Liquid Crystals*, Springer, New York, 1996.
- [3] J.W. Emsley, Liquid crystals: General considerations, in: D.M. Grant, R.K. Harris (Eds.), *Encyclopedia of NMR*, Wiley, Chichester, 1996, pp. 2781–2788.
- [4] G. Celebre, G. de Luca, M. Longeri, D. Catalano, M. Lumetti, J.W. Emsley, An investigation of the conformations of 4-chloroethylbenzene as a solute in a nematic liquid crystalline solvent, *Mol. Phys.* 85 (1995) 221.
- [5] E.K. Foord, J. Cole, M.J. Crawford, J.W. Emsley, G. Celebre, M. Longeri, J.C. Lindon, An NMR study of the conformational flexibility of phenyl acetate dissolved in a nematic liquid crystalline solvent, *Liq. Cryst.* 18 (1995) 615.
- [6] K. Schmidt-Rohr, D. Nanz, L. Emsley, A. Pines, NMR measurement of resolved heteronuclear dipole couplings in liquid crystals and lipids, *J. Phys. Chem.* 98 (1994) 6668.
- [7] M. Hong, K. Schmidt-Rohr, A. Pines, NMR measurement of signs and magnitudes of C–H dipolar couplings in lecithin, *J. Am. Chem. Soc.* 117 (1995) 3310.
- [8] M. Hong, A. Pines, S. Caldarelli, Measurement and assignment of long-range C–H dipolar couplings in liquid crystals by two-dimensional NMR spectroscopy, *J. Phys. Chem.* 100 (1996) 14815.
- [9] S. Caldarelli, M. Hong, L. Emsley, A. Pines, Measurement of carbon–proton dipolar couplings in liquid crystals by local dipolar field NMR spectroscopy, *J. Phys. Chem.* 100 (1996) 18696.
- [10] W.K. Rhim, D.D. Elleman, R.W. Vaughan, Enhanced resolution for solid state NMR, *J. Chem. Phys.* 58 (1973) 1772–1773.
- [11] D.P. Burum, W.K. Rhim, Analysis of multiple pulse NMR in solids, *J. Chem. Phys.* 71 (1979) 944–956.

- [12] D.P. Burum, N. Linder, R.R. Ernst, Low-power multipulse line narrowing in solid-state NMR, *J. Magn. Reson.* 44 (1981) 173–188.
- [13] M. Lee, W. Goldburg, Nuclear-magnetic-resonance line narrowing by a rotating RF field, *Phys. Rev.* 140 (1965) 1261–1271.
- [14] M. Mehring, J.S. Waugh, Magic-angle NMR experiments in solids, *Phys. Rev. B* 5 (1972) 3459–3471.
- [15] M.H. Levitt, A.C. Kolbert, A. Bielecki, D.J. Ruben, High-resolution ^1H NMR in solids with frequency-switched multiple-pulse sequences, *Solid State NMR* 2 (1993) 151–163.
- [16] B.M. Fung, K. Ermolaev, Y. Yu, ^{13}C NMR of liquid crystals with different proton homonuclear dipolar decoupling methods, *J. Magn. Reson.* 138 (1999) 28–35.
- [17] B.M. Fung, The effect of radiofrequency heating in carbon-13 NMR studies of liquid crystals, *J. Magn. Reson.* 86 (1990) 160.
- [18] E. Vinogradov, P.K. Madhu, S. Vega, High-resolution proton solid-state NMR spectroscopy by phase-modulated Lee-Goldburg experiment, *Chem. Phys. Lett.* 314 (1999) 443–450.
- [19] F. Castiglione, G. Celebre, B. Luca, M. Longeri, The use of heteronuclear multiple quantum spectra in the automatic analysis of NMR spectra of samples dissolved in liquid crystalline phases, *Liq. Cryst.* 28 (2001) 1403–1413.
- [20] J.D. Walls, M. Marjanska, D. Sakellariou, F. Castiglione, A. Pines, Selective excitation in dipole coupled systems, *Chem. Phys. Lett.* 357 (2002) 241–248.
- [21] C.S. Yannoni, M.H. Sherwood, D.C. Miller, I.L. Chuang, L.M.K. Vandersypen, M.G. Kubinec, Nuclear magnetic resonance quantum computing using liquid crystal solvents, *Appl. Phys. Lett.* 75 (1999) 3563–3565.
- [22] M. Marjanska, I.L. Chuang, M.G. Kubinec, Demonstration of quantum logic gates in liquid crystal nuclear magnetic resonance, *J. Chem. Phys.* 112 (2000) 5095–5099.
- [23] T.S. Mahesh, N. Sinha, K.V. Ramanathan, A. Kumar, Ensemble quantum-information processing by NMR: Implementation of gates and the creation of pseudopure states using dipolar coupled spins as qubits, *Phys. Rev. A* 65 (2002) 022312.