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Improved heteronuclear dipolar decoupling sequences for liquid-crystal NMR

Rajendra Singh Thakur [a], Narayanan D. Kurur [b,*], P.K. Madhu [a,*]

[a] Department of Chemical Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400 005, India
[b] Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110 016, India

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Abstract

Recently we introduced a radiofrequency pulse scheme for heteronuclear dipolar decoupling in solid-state nuclear magnetic resonance under magic-angle spinning [R.S. Thakur, N.D. Kurur, P.K. Madhu, Swept-frequency two-pulse phase modulation for heteronuclear dipolar decoupling in solid-state NMR, Chem. Phys. Lett. 426 (2006) 459–463]. Variants of this sequence, swept-frequency TPPM, employing frequency modulation of different types have been further tested to improve the efficiency of heteronuclear dipolar decoupling. Among these, certain sequences that were found to perform well at lower spinning speeds are demonstrated here on a liquid-crystal sample of MBBA for application in static samples. The new sequences are compared with the standard TPPM and SPINAL schemes and are shown to perform better than them. These modulated schemes perform well at low decoupler radiofrequency power levels and are easy to implement on standard spectrometers.

Keywords: Liquid-crystal NMR; Heteronuclear dipolar decoupling; TPPM; SPINAL; Swept-frequency TPPM

1. Introduction

The liquid-crystal phase is characterised by partial or complete alignment of the molecules along a certain direction. It is associated with certain kind of molecules owing to their structure and such structures constitute a large number of biologically important systems. For example, cell membranes, which are essentially lipid bilayers, are more similar to the liquid-crystal phase than to the liquid or the solid phase. Probing these structures along with their dynamics can yield a great amount of novel information. However, such compounds have various levels of structural organisation with each level having its own relevance. Nuclear magnetic resonance (NMR) can be a candidate of choice for such studies as it can reveal various levels of hierarchy in the structure of such systems, as in the case of proteins. However, being a partially aligned phase, resonances in the NMR spectrum are normally broad because of the incomplete averaging of dipolar couplings. This affects the observation of both ^{1}H and ^{13}C nuclear spins on account of homonuclear and heteronuclear dipolar couplings. Unravelling information from ^{13}C spectra requires efficient heteronuclear dipolar decoupling at lower radiofrequency (RF) powers as RF heating can be deleterious to such systems [1–3]. Details of the use of NMR experiments, especially ^{13}C NMR, to the study of liquid crystals can be found in recent reviews [2,4].

Several heteronuclear dipolar decoupling sequences have been suggested for the study of liquid crystals. These include the conventional continuous-wave (CW) method [5], two-pulse phase modulation (TPPM) [6], two of its variants, namely, small phase angle rapid cycling (SPARC) [7] and small phase incremental alternation (SPINAL) [8], and the DROOPY sequences [9]. Interestingly, the SPINAL method [8], originally conceived for static liquid

* Corresponding authors. Fax: +91 22 2280 4610 (P.K. Madhu).
E-mail addresses: nkurur@chemistry.iitd.ernet.in (N.D. Kurur), madhu@tifr.res.in (P.K. Madhu).

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crystals, has become routine in magic-angle spinning (MAS) experiments in solid-state NMR.

The SPARC scheme reported by Fung et al. [7] was an improvement over TPPM [6] and SPINAL [8], again from the group of Fung, was an improvement over SPARC. Whilst SPARC relies on rapid phase cycling, SPINAL, in addition, involves phase increments. Such methods generate frequency modulations and an intuitive understanding of the efficiency of such sequences may be obtained on the basis of the Fourier picture of the corresponding RF schemes [8]. Recently, we proposed an alternative heteronuclear dipolar decoupling scheme in which the pulse durations in the standard TPPM scheme were modulated [10]. This was shown to generate a normal distribution of Fourier components compared to SPINAL. The sequence, called SW_f-TPPM, was shown to be robust with respect to various experimental parameters in comparison with both TPPM and SPINAL [11]. Subsequently, we have investigated various other RF modulated schemes for heteronuclear dipolar decoupling arrived at mainly on the basis of the distribution of Fourier components. A detailed report on the design of these schemes is currently under preparation.

In addition to SW_f-TPPM, we here concentrate on two new RF modulated pulse schemes which were found to perform better at lower spinning frequencies for MAS experiments in solid-state NMR. We report in this manuscript the results of applying these sequences for heteronuclear dipolar decoupling in a liquid crystal. These sequences are compared with both TPPM and SPINAL over which they give an improvement in sensitivity and resolution. We also revisit the routinely used SPINAL-64 sequence and find that a systematic optimisation of the initial phase angle leads to considerable improvement in its performance. The new RF modulated schemes are easy to design and implement on modern NMR spectrometers.

2. Experimental

All experiments were performed on a Bruker AV500 MHz spectrometer equipped with a double-resonance BBI probe. The experiments were performed on a liquid-crystal sample of MBBA maintained at 22 °C. The gas flow rate was appropriately regulated (in excess of 11 l/min) to keep the temperature steady. In addition, recycle delays of 40 s were used for a decoupling RF power of 30 kHz and 30 s for power levels of 25 and 20 kHz. The acquisition time was 30 ms for the RF power level of 30 kHz and 40 ms for power levels of 25 and 20 kHz and were chosen to avoid RF heating. For these acquisition times some spectra had truncation artefacts, especially at higher decoupling powers. The values chosen closely follow suggestions of Fung [2].

3. Sequence design, results and discussions

We here compare five decoupling sequences, namely, TPPM, SPINAL, and three modulated TPPM sequences, in which the frequencies are swept, notated as SW_f-TPPM, SW_f^{tan}-TPPM, and SW_f^{inv}-TPPM.

TPPM, notated as $R_\phi R_{-\phi}$, is a sequence of 180° pulses, where R denotes the pulse flip angle with phase ϕ. Experimentally both R and ϕ need to be optimised. SPINAL-8 is obtained from the basic TPPM block by varying the values of ϕ and has the form $Q \equiv R_\phi R_{-\phi}$, $R_{\phi+5}R_{-\phi-5}$, $R_{\phi+10}R_{-\phi-10}$, $R_{\phi+5}R_{-\phi-5}$. SPINAL-64 is of the form $Q\bar{Q}\bar{Q}Q\bar{Q}QQ\bar{Q}$ with each Q representing SPINAL-8. In the original report ϕ was set to 10° (referred to here as SPINAL-$64_{\phi=10}$) leaving only R to be optimised [8]. We found that allowing ϕ to vary improved the decoupling efficiency of SPINAL-64. We observed that $\phi = 15°$ (referred to here as SPINAL-$64_{\phi=15}$) gave better performance than $\phi = 10°$ for the sample under study. Increasing ϕ beyond 15° was detrimental to the decoupling efficiency.

The design of the swept-TPPM schemes was based on modulating the values of pulse duration (as against ϕ for SPINAL) with respect to a central pulse pair whose duration τ_ϕ could be comparable to the optimum TPPM pulse R. All such schemes can be represented by specifying the pulse widths (τ) of each TPPM pair as phase ϕ is constant. The form of SW_f-TPPM approximates a tangential sweep as three linear segments leading to a sequence of the form [10]: $\{[0.78\tau_\phi 0.78\tau_{-\phi}]$ $[0.86\tau_\phi 0.86\tau_{-\phi}]$ $[0.94\tau_\phi 0.94\tau_{-\phi}]$ $[0.96\tau_\phi 0.96\tau_{-\phi}]$ $[0.98\tau_\phi 0.98\tau_{-\phi}]$ $[\tau_\phi \tau_{-\phi}]$ $[1.02\tau_\phi 1.02\tau_{-\phi}]$ $[1.04\tau_\phi 1.04\tau_{-\phi}]$ $[1.06\tau_\phi 1.06\tau_{-\phi}]$ $[1.14\tau_\phi 1.14\tau_{-\phi}]$ $[1.22\tau_\phi 1.22\tau_{-\phi}]\}$. Here, τ_ϕ and ϕ need to be optimised. The numbers multiplying τ determine the profile of the frequency modulation which we notate as f_i.

SW_f^{tan}-TPPM is a pure tangential sweep where the pulse durations were calculated analytically resulting in a sequence of larger sweep width and of a form: $\{[0.65\tau_\phi 0.65\tau_{-\phi}]$ $[0.75\tau_\phi 0.75\tau_{-\phi}]$ $[0.85\tau_\phi 0.85\tau_{-\phi}]$ $[0.90\tau_\phi 0.90\tau_{-\phi}]$ $[0.94\tau_\phi 0.94\tau_{-\phi}]$ $[0.96\tau_\phi 0.96\tau_{-\phi}]$ $[0.98\tau_\phi 0.98\tau_{-\phi}]$ $[\tau_\phi \tau_{-\phi}]$ $[1.02\tau_\phi 1.02\tau_{-\phi}]$ $[1.04\tau_\phi 1.04\tau_{-\phi}]$ $[1.06\tau_\phi 1.06\tau_{-\phi}]$ $[1.10\tau_\phi 1.10\tau_{-\phi}]$ $[1.15\tau_\phi 1.15\tau_{-\phi}]$ $[1.25\tau_\phi 1.25\tau_{-\phi}]$ $[1.35\tau_\phi 1.35\tau_{-\phi}]\}$.

SW_f^{inv}-TPPM was constructed by taking the inverse of the pulse durations that formed a linearly swept SW_f-TPPM sequence where the initial pulse duration was set to $0.5\tau_\phi$ and the final pulse duration was $1.5\tau_\phi$ with each pulse pair incremented by $0.1\tau_\phi$ comprising of again 11 pulse pairs. This mimics, to some extent, the design of the swept fast-amplitude modulated (SW-FAM($1/\tau$)) sequence demonstrated recently for the sensitivity enhancement of static half-integer spin quadrupolar nuclei [13], that resulted in a large sweep width. The sequence so constructed has the form: $\{[0.67\tau_\phi 0.67\tau_{-\phi}]$ $[0.71\tau_\phi 0.71\tau_{-\phi}]$ $[0.77\tau_\phi 0.77\tau_{-\phi}]$ $[0.83\tau_\phi 0.83\tau_{-\phi}]$ $[0.91\tau_\phi 0.91\tau_{-\phi}]$ $[\tau_\phi \tau_{-\phi}]$ $[1.11\tau_\phi 1.11\tau_{-\phi}]$ $[1.25\tau_\phi 1.25\tau_{-\phi}]$ $[1.43\tau_\phi 1.43\tau_{-\phi}]$ $[1.67\tau_\phi 1.67\tau_{-\phi}]$ $[2.00\tau_\phi 2.00\tau_{-\phi}]\}$.

Fig. 1 shows a spectrum of MBBA acquired with $SPINAL_{\phi=10}$, $SPINAL_{\phi=15}$, SW_f-TPPM, SW_f^{tan}-TPPM, and SW_f^{inv}-TPPM decoupling schemes applied on-resonance at an RF power level of 25 kHz. The phase values of the modulated sequences were 35°, 35°, and 45° for