Journal of Magnetic Resonance 299 (2019) 28–32

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Combination of OPSY and PhD-PHIP results in enhanced sensitivity in PHIP

S. Bussandri, L. Buljubasich, R.H. Acosta

[a] Universidad Nacional de Córdoba, Facultad de Matemática, Astronomía, Física y Computación, Córdoba, Argentina
[b] CONICET, Instituto de Física Enrique Gaviola (IFEG), Córdoba, Argentina

ARTICLE INFO

Article history:
Received 31 October 2018
Revised 5 December 2018
Accepted 6 December 2018
Available online 7 December 2018

Keywords:
Parahydrogen
PHIP
PhD-PHIP
OPSY
SABRE
J-spectroscopy
Hyperpolarization
Pulse sequences
CPMG
Echo trains
NMR
J-coupling
Spin dynamics

ABSTRACT

Despite the large degree of polarization in PHIP experiments compared to the Boltzmann factor, the presence of a large amount of non-reacted molecules with thermal polarization is an important obstacle when dealing with very diluted samples. The feasibility of enhancing both sensitivity and resolution in a single experiment by combining two well established pulse sequences, OPSY and PHD-PHIP is presented. OPSY is used as a block for filtering the signals originated from thermally polarized protons. PhD-PHIP, on the other hand, is used as an acquisition block, increasing the resolution and further improving the sensitivity by preventing signal canceling in the presence of magnetic field inhomogeneities. Experiments in a complex sample with very low hyperpolarization levels are presented showing the excellent performance of the method.

1. Introduction

The increasing popularity of PHIP [1] over the last two decades rests on the relatively low hardware requirements compared with other hyperpolarization techniques, and it is reflected in its wide range of applications. The technique is vastly used in a number of applications within NMR [2]. In chemistry, it was demonstrated to be useful in the investigation of reaction kinetics [3–6] and catalysts design [7–9]. Very often, the hyperpolarization is transferred to other nuclei (either ^{1}H or ^{13}C) via specially designed pulse sequences [10–12] or by physical transport [13–15] for different purposes. For instance, in MRI, the hyperpolarized protons were used as a contrast agent either directly [16–18], or after the hyperpolarization transfer to heteronuclei (^{13}C) [19–21]. A particularly interesting feature of PHIP is the feasibility to create long-lived spin orders from the former parahydrogen protons [22–24].

Although the degree of polarization in PHIP is a few orders of magnitude larger than the Boltzmann factor, giving rise to the signal enhancement, the presence of a large amount of molecules that were not hydrogenated with parahydrogen protons sometimes represents an important obstacle. When the reactants are present in very-low concentration and/or the reaction efficiency is poor, the PHIP originated signals may become unobservable. In this regard, an alternative to the single pulse acquisition was introduced few years ago, aimed to filter out signals form thermally polarized protons and therefore clean up the PHIP spectra. The pulse sequence, known as OPSY (Only Parahydrogen SpectroscopY) exploits the particular spin state of former parahydrogen protons (and protons strongly interacting with them) to remove any contribution to the spectrum from thermally polarized ones [25,26]. This also improves the sensitivity, because the removal of major contributions from solvent signals or whatever source of interference prevents the receiver saturation, and better signal-to-noise ratio can be achieved by rising the receiver gain level.

Resolution is another important issue when dealing with PHIP. For instance, when the hydrogenation with pH_2 and detection are carried out at high magnetic field (Parahydrogen And Synthesis Allow Dramatically Enhanced Nuclear Alignement: PASADENA) the spin state at the end of the chemical reaction is dominated

E-mail address: lbulju@famaf.unc.edu.ar (L. Buljubasich)

https://doi.org/10.1016/j.jmr.2018.12.006
1090-7807/

by longitudinal two spin-order terms [27], which displays an anti-phase doublet in frequency domain, i.e. two peaks with opposite signs separated by the *J*-coupling constant (of a few Hz for protons). Any source of magnetic field inhomogeneity leading to broader NMR lines produces signal canceling [28]. When dealing with resonance lines of about 20 Hz of FWHM, an important fraction of hyperpolarization is lost. This imposes a serious limitation in the experimental setups. In previous publications, we presented a method to overcome this interference by means of a multipulse sequence which renders partial *J*-spectra practically independent of field inhomogeneities [29–34]. Additionally, our pulse sequence, denominated PhD-PHIP (for Parahydrogen Discriminated-PHIP) also separates the contribution from PHIP and thermally polarized spins, by shifting them to different regions of the spectral window. However, as thermally polarized signals are still acquired, the receiver gain must be carefully adjusted in order to prevent saturation of the receiver.

In this article we present the strategy of filtering the thermally polarized signals by the use of OPSY, while acquiring a specific spectral window with the high resolution provided by PhD-PHIP. This method will be extremely useful in situations in which the reacting molecules are very diluted, the resulting spectra is very complex and/or the magnetic field is inhomogeneous.

2. Theoretical background

In this section we give a short discussion of the principles behind the pulse sequences to be used along the article. A more detailed treatment of OPSY can be found in Ref. [26] whereas a comprehensive description of PhD-PHIP is available in Refs. [29,33,34].

2.1. OPSY

The OPSY sequence used in this work is schematically shown in Fig. 1. It consists of two hard r.f. pulses, $(\pi/2)_y$, and two evolution periods of duration τ in the presence of magnetic field gradients with different polarity and intensities. A free induction decay is acquired after the second pulsed field gradient.

The key of the sequence's performance is the behaviour of the different multiple quantum coherences during τ, due to the particular ratio between the field gradient strengths, $+g$ and $-2g$. In what follows we assume the density operator belonging to thermally polarized spins as,

$$\rho^{\mathrm{th}}(0) \propto \sum_j I_j^z.$$

The PHIP experiment is performed with the PASADENA protocol, where the chemical reaction and signal acquisition both occur

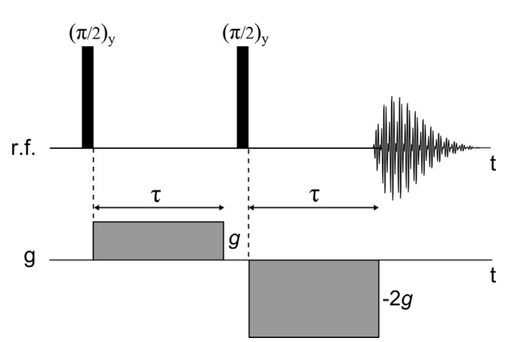

Fig. 1. OPSY-*d* pulse sequence, where the r.f. phases and gradient scheme is visualized.

at high field, and the density operator right after the hydrogenation is dominated of a linear combination of longitudinal two spin order and polarization differences between the spins involved in the secular spin Hamiltonian $\mathcal{H}$[35],

$$\rho^{\mathrm{pH}}(0) = \sum_{j<k} \alpha_{jk}\left(I_j^z - I_k^z\right) + \sum_{j<k} \beta_{jk} I_j^z I_k^z.$$

As the polarization differences behave similarly to ρ^{th}, we will focus our attention on the bilinear terms, denoted here as $\rho^{\mathrm{pH}}_{\mathrm{bi}}$, to understand the dynamics behind the filtering process achieved with OPSY.

After the first $(\pi/2)_y$ pulse, the thermally polarized spins produce single-quantum coherence terms ($\mathrm{SQ_{th}}$),

$$\rho^{\mathrm{th}}(0+) \propto \sum_j \left(I_j^+ + I_j^-\right),$$

whereas the bilinear part of the hyperpolarized spins generate a linear combination of zero- and double-quantum coherences ($\mathrm{ZQ^{pH}}$ and $\mathrm{DQ^{pH}}$),

$$\rho^{\mathrm{pH}}_{\mathrm{bi}}(0+) \propto \sum_{j<k} \beta_{jk}\left(I_j^+ I_k^+ + I_j^+ I_k^- + I_j^- I_k^+ + I_j^- I_k^-\right).$$

During the first evolution period the coherences evolve under the secular spin Hamiltonian superimposed to the interaction with the field gradient, which we will assume, with no loss of generality, oriented along the *z*-axis of the rotating frame (the same as B_0). The evolution under the field gradient adds a phase factor to the spin operators, which in turn, depends on the coherence order. A given *n*-coherence order evolves *n*-times compared to a SQ order. In the case of ZQ coherences, the gradient field has null global effect and therefore, only the evolution with the spin Hamiltonian is preserved.

This can be expressed as:

$$\rho^{\mathrm{th}}(\tau) \propto \sum_j \left(I_j^+ e^{(-i\mathcal{H}\tau + i\phi_g\tau)} + I_j^- e^{(-i\mathcal{H}\tau - i\phi_g\tau)}\right),$$

and

$$\rho^{\mathrm{pH}}_{\mathrm{bi}}(\tau) \propto \sum_{j,k} \left\{ \begin{array}{l} I_j^+ I_k^+ e^{(-i\mathcal{H}\tau + i2\phi_g\tau)} \\ + \left(I_j^- I_k^+ + I_j^+ I_k^-\right) e^{(-i\mathcal{H}\tau)} \\ + I_j^- I_k^- e^{(-i\mathcal{H}\tau - i2\phi_g\tau)} \end{array} \right\},$$

where $\phi_g = \gamma g z$.

The second $\pi/2$ pulse transforms the $\mathrm{SQ^{th}}$ terms into a linear combination of longitudinal magnetization and $\mathrm{SQ^{th}}$. A subsequent evolution in the presence of a gradient with intensity $-2g$ will strongly dephase the $\mathrm{SQ^{th}}$ terms, resulting in no net signal at the beginning of the acquisition ($t = 2\tau$). In contrast, the density operator $\rho^{\mathrm{pH}}(\tau+)$ is composed by a linear combination of longitudinal two spin-order terms, $\mathrm{ZQ^{pH}}$, $\mathrm{SQ^{pH}}$ and $\mathrm{DQ^{pH}}$, with different phases accumulated during the first evolution. This can be written in compact form as,

$$\rho^{\mathrm{pH}}_{\mathrm{bi}}(\tau) \propto \sum_{j,k} \left\{ \begin{array}{l} I_j^z I_k^z + \mathrm{ZQ^{pH}} \\ + \mathrm{SQ^{pH}} + \mathrm{DQ^{pH}} \end{array} \right\} \times \sum_{m=-1}^{+1} e^{(-i\mathcal{H}\tau + i2m\phi_g\tau)}.$$

The potentially observable operator terms are related to:

(i) $\mathrm{SQ^{pH}} \times e^{(-i\mathcal{H}\tau + i2\phi_g\tau)}$,
(ii) $\mathrm{SQ^{pH}} \times e^{(-i\mathcal{H}\tau)}$,
(iii) $\mathrm{SQ^{pH}} \times e^{(-i\mathcal{H}\tau - i2\phi_g\tau)}$.

In the next free evolution period, for a sufficiently strong field gradient and relatively short τ (compared to a characteristic time of the quantum dynamics driven by the molecular Hamiltonian), the evolution under the *J*-coupling Hamiltonian can be safely ignored in the cases (i) and (iii). In all cases, on the other hand, after τ (i.e. at $t = 2\tau$), the evolutions with the chemical shift Hamiltonian are refocused. Moreover, term (i) is refocused after an evolution with a pulse gradient of duration τ and intensity $-2g$, whereas term (iii) requires a gradient intensity $+2g$. Term (ii), however, still displays the *J*-coupling evolution.

These differences give rise to the main two variants of the sequence, denominated by the authors as OPSY-*d* and OPSY-*z*, respectively [26]. The exact calculations show that a signal acquired with OPSY-*d* has half the intensity of a signal acquired with OPSY-*z*. However, as in the period with no field gradient the evolution with the *J*-coupling Hamiltonian cannot be disregarded, the filtering effect is not optimum. Experimentally, the OPSY-*d* pulse sequence is very efficient in removing the signal originated from thermally polarized spins. On the other hand, for eddy current considerations, the $(+g, -2g)$ gradient configuration represents the best alternative. As a result, the whole sequence acts as a filter for thermal polarization, and at the acquisition time only polarization coming from PHIP will contribute to the signal. In a recent publication [36] the authors examined up to nine different pulse sequences based on the same principles, and concluded that OPSY-*d* is the best choice. Consequently, we have adopted this scheme for our experiments.

2.2. PhD-PHIP

Notwithstanding the sensitivity enhancement achieved with OPSY, the spectral resolution is the same as in the single pulse experiment. The antiphase signals are particularly sensitive to the magnetic field inhomogeneities, and any source of line broadening leads to loss of signal, in contrast to in-phase lines, where the extra broadening only decreases resolution [28]. In previous contributions we have introduced a technique known as PhD-PHIP, where the signal is acquired at the top of the echoes in a train of N_E π pulses with phases relative to the excitation pulse following the scheme: $x - (yy\bar{y}\bar{y})_{N_E/4}$, with a digital filter centred at the desired multiplet in the spectrum [29,30,32,34]. The result is a partial *J*-spectrum with the spectral window determined by the echo time t_E. In addition to the line narrowing due to the differences between T_2 and T_2^*, the differences in the dynamics during the train of refocusing pulses produces a clear separation of thermally an hyperpolarized originated signals in the spectral window. The overall behaviour is schematized in Fig. 2.

When the hyperpolarized signals are superimposed with thermally polarized ones (Fig. 2a), the partial *J*-spectrum will display the antiphase signals in the middle of the spectral window, whereas all the signals originated from thermally polarized spins with NMR frequencies within the digital filter (rectangle with dashed lines in the figure) will fall at the borders. Fig. 2b shows the situation when no thermal signal is present within the filter region in the spectrum: a clean partial *J*-spectrum of the selected multiplet is obtained.

At first sight, it would seem as if the method filters out the signals from thermally polarized spins falling out of the filter's window. However, when the signal is acquired with a digital filter, all the frequencies are recorded in the receiver before the filtering process is performed [37]. This is a severe limitation on PhD-PHIP experiments, where the resolution enhancement carries with it a sensitivity enhancement by preventing the peak canceling, but the receiver gain level is still limited by all thermally polarized spins within the sample.

2.3. OPSY + PhD-PHIP

It seems quite natural to combine both sequences in order to filter thermally polarized signals with OPSY, and to perform high resolution acquisition with PhD-PHIP. The pulse sequence is presented in Fig. 3, where a train of refocusing pulses is placed at the end of OPSY-*d*, right after a free evolution time of duration $t_E/2$. Therefore, OPSY-*d* plays the role of the exciting $\pi/4$ pulse in the original PhD-PHIP.

3. Results and discussion

Fig. 4 shows the results obtained with the hyperpolarized 1-hexene. The molecule with the former parahydrogen proptons labeled as H_A^* and H_B^* is depicted in the top panel. The spectrum acquired with a single $\pi/4$ r.f. pulse is shown in Fig. 4a. The presence of a large amount of non-reacted molecules is evident, where only a small degree of reaction is observed between 4.5 and 6.5 ppm.

When the same experiment is detected out with OPSY (Fig. 4b) only the characteristic doublets originated from PHIP are present. An increase in the receiver gain will turn out in a receiver saturation, which basically consists of a convolution of the acquired signal with a step function, leading to presence of a modulation of each resonance line with a sinc function, as shown in Fig. 4c. However, the signal acquired with OPSY-*d* for the same receiver gain appears undistorted, Fig. 4d, with an increase in the signal-to-noise ratio.

As previously stated, acquisition with PhD-PHIP is limited by the presence of thermally polarized signals. In order to see the effect of these signals on the acquisition with the selected digital filter centred at H_A^* (see the molecule in Fig. 4), a spectrum was acquired without hydrogenation without pH_2. As there is no signal in the acquired frequency range, one would expect the presence of white noise, however, Fig. 5a shows that a large amount of signal appears in the center of the frequency window, which comes from

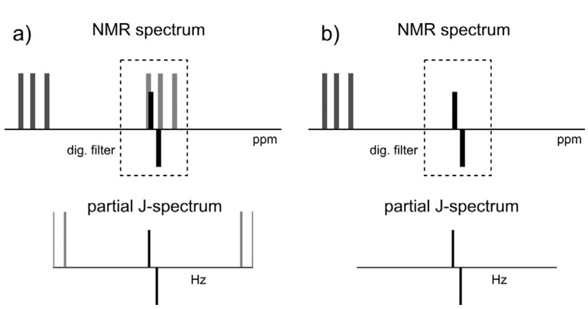

Fig. 2. Scheme of the PhD-PHIP performance in the presence (a) or absence (b) of thermal signals falling within the digital filter window.

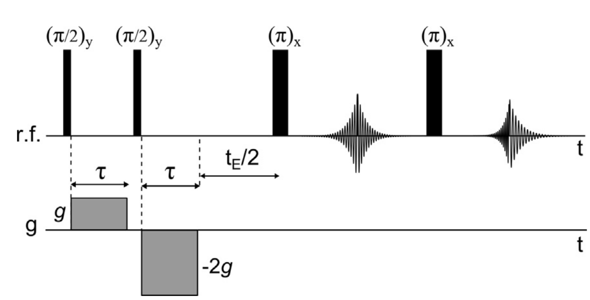

Fig. 3. Pulse sequence obtained implementing OPSY-*d* as a filter and PhD-PHIP as acquisition block.

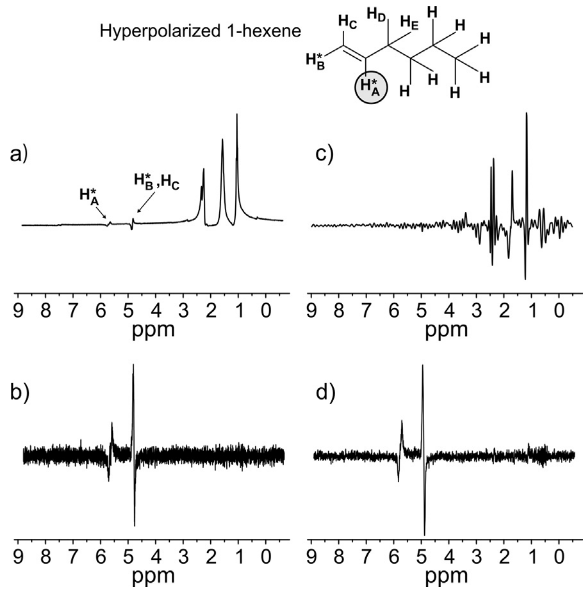

Fig. 4. Top panel: hyperpolarized 1-hexene, with the former parahydrogen protons labeled as H_A^* and H_B^*. (a) NMR spectrum aquired with a single $\pi/4$ pulse, and (b) with OPSY-*d* to filter out the thermal contributions. (c) Same experiment as in (a) with the receiver gain raised over the saturation level. (d) No distortion and an improved signal-to-noise ratio is observed using OPSY-*d* with the same receiver gain level.

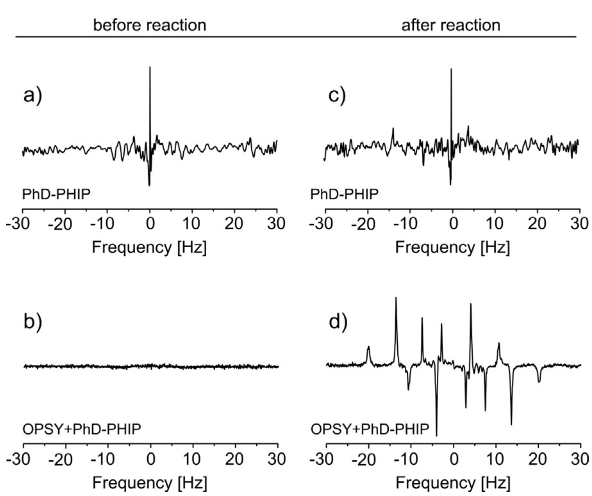

Fig. 5. (a) Partial *J*-spectrum with the digital filter centred at the H_A^* before hydrogenation with pH_2 and the receiver gain set over the saturation limit. (b) Result of OPSY + PhD-PHIP without reaction. (c) and (d) show the corresponding experiments after the hydrogenation. The sharp NMR lines in d) have a FWHM of ~ 0.3 Hz.

clipped thermal signals acquired during the pulse train. Under the same conditions, the application of OPSY + PhD-PHIP provides a clean white noise, as expected (Fig. 5b). When hydrogenation with pH_2 is carried out and detection is carried out with high receiver gain level (same situation as in Fig. 4c), PhD-PHIP provides a spectrum the is highly distorted as shown in Fig. 5c. In fact, there in no much difference in the saturated spectra with or without PHIP, as the reaction were set to very low levels. However, under this situation, the application of OPSY + PhD-PHIP renders a very clean partial *J*-spectrum as seen in Fig. 5d, where the linewidth is about 0.3 Hz. As previously stated, this high resolution is given due to the fact that relaxation produces a line broadening proportional to $1/T_2$ rather than by $1/T_2^*$ during data acquisition.

A comparison of performances can be qualitatively observed in Fig. 6, where the partial *J*-spectrum of the multiplet corresponding to proton H_A^* acquired with OPSY + PhD-PHIP plotted together with the portion of the spectrum acquired with OPSY-*d*. It is clear that the noise level with OPSY + PhD-PHIP is lower than the one in OPSY-*d*, which is a benefit of the use of a sharper digital filter. Finally we must clarify that these plots correspond to samples with an extremely low degree of reaction especially prepared for demonstrative purposes.

It is worth noticing that neither OPSY nor PhD-PHIP sequences decrease their performance in non-weak coupled systems. However, the chemical reaction involved in PHIP experiments suffers in these kinds of systems because most of the singlet state is untouched. Therefore, the amount of hyperpolarization available after the reaction is even less than in the cases of weakly coupled spin systems. Due to this inconvenient, the combination of both sequences, OPSY-PhD-PHIP, represents a remarkable improvement in non-weak coupled systems, when sensitivity enhancement is targeted (see Electronic Supporting Information for further details).

In addition, despite the experiments and theoretical treatment given until here are focused in the context of PHIP, this pulse sequence will also improve the sensitivity and spectral resolution in any case in which the NMR signal is dominated by a linear combination of longitudinal two-spin orders, as it is for instance, in SABRE experiments [38,26].

4. Experimental details

4.1. NMR experiments

The experiments were conducted at a magnetic field strength of 7 T with a Bruker Avance II console, equipped with an imaging probe with a 10 mm birdcage coil and 3D gradient coils with a maximum gradient of 1.5 T/m. The r.f. power was set such that $\omega_{rf}/2\pi = 12.5$ kHz, corresponding to pulses with durations of 14.5 µs and 29 µs for $\pi/2$ and π pulses respectively. All the samples were prepared with approximately half the length of the NMR birdcage coil, to maintain the effects of r.f. inhomogeneities to minimum. The magnetic field gradients were aligned with the

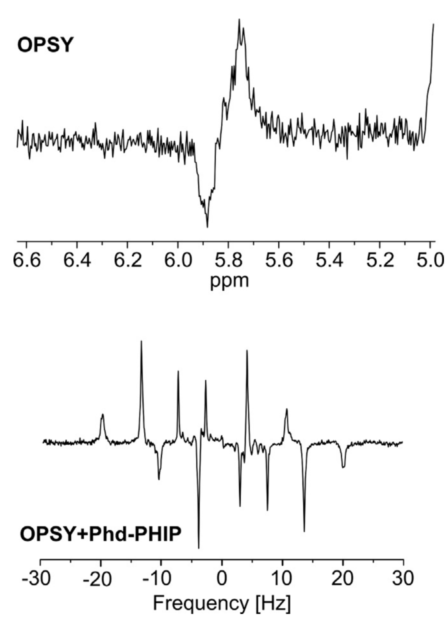

Fig. 6. Experimental results obtained in Figs. 3d and 5d shown together to highlight the sensitivity and resolution improvement obtained by OPSY + PhD-PHIP compared to OPSY.

direction of the external magnetic field (i.e. z-direction of the rotating frame), with duration $\tau = 1$ ms, and strength g = 50 mT/m, applied in the scheme of OPSY-d, $(+g, -2g)$. Concerning the PhD-PHIP block, the echo time was set to $t_E = 8$ ms and 2048 pulses were used, with the phases following the scheme $y - (xx\bar{x}\bar{x})_{N_e/4}$, rotated $\pi/2$ respect to the experiments with only PhD-PHIP, to be compatible with the phases of OSY-d. The digital filter width to 500 Hz, centred at 5.8 ppm, to select the multiplet corresponding to H_A^*. All the experiments were performed in a single scan.

4.2. Sample preparation

Samples were prepared under controlled nitrogen atmosphere. The mixture consisted in a solution of 0.443 g of acetone-d_6, 0.015 g of 1-hexyne and 0.010 g of catalyst (Rhodium complex: CAS 79255-71-3). All components were acquired from Sigma Aldrich.

Parahydrogen was prepared by putting hydrogen in contact with activated charcoal at liquid nitrogen temperature during 30 min. The enriched parahydrogen gas was stored in stainless steel cylinders (Swagelok, Germany) at $\sim$4 bars. Plastic 4 mm OD tubing was used for the transfer lines to the sample placed at the magnet's bore. pH_2 was delivered to the sample by bubbling during 15 s followed by a 5 s waiting period in which it is ensured that no bubbles remain in the NMR detection volume.

5. Conclusions

In this article we dealt with the problem of improving sensitivity and resolution during the acquisition of PHIP hyperpolarized signals in very dilute samples. We demonstrated the feasibility of enhancing both in a single experiment by combining two well established pulse sequences. OPSY provides spectra that are free of the contribution of thermally polarized signals, so that the receiver gain can be set to maximize the signal to noise ratio. PhD-PHIP on the other hand also filters thermally polarized signals and additionally increases the resolution by acquisition of partial J-spectra. However, acquisition is carried out in the presence of thermally polarized signals, so the receiver gain is limited. A combination of both sequences exploits the benefits of both worlds. The new pulse sequence is of straightforward implementation and not extra hardware is required. The experiments in a complex sample with very low hyperpolarization level showed and excellent performance of the method. The quality of the results allows to envisage the implementation in still lower concentrations and a variety of experimental setups where the B_0 homogeneity is perturbed by the presence of devices and or sensors in the proximity of the coil's sensitive volume.

Acknowledgements

We would like to acknowledge the financial support from CONICET (PIP-11112201301007460O), SeCyT-UNC and ANPCYT (PICT-2014-1295).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jmr.2018.12.006.

References

[1] C.R. Bowers, D.P. Weitekamp, Phys. Rev. Lett. 57 (1986) 2645–2648.
[2] R.A. Green, R.W. Adams, S.B. Duckett, R.E. Mewis, D.C. Williamson, G.G. Green, Prog. Nucl. Magn. Reson. Spectrosc. 67 (2012) 1–48.
[3] T.C. Eisenschmid, R.U. Kirss, P.P. Deutsch, S.I. Hommeltoft, R. Eisenberg, J. Bargon, R.G. Lawler, A.L. Balch, J. Am. Chem. Soc. 109 (1987) 8089–8091.
[4] J. Natterer, O. Schedletzky, J. Barkemeyer, J. Bargon, S.J. Glaser, J. Magn. Reson. 133 (1998) 92–97.
[5] P. Hübler, R. Giernoth, G. Kümmerle, J. Bargon, J. Am. Chem. Soc. 121 (1999) 5311–5318.
[6] E.W. Zhao, H. Zheng, K. Ludden, Y. Xin, H.E. Hagelin-Weaver, C.R. Bowers, ACS Catal. 6 (2016) 974–978.
[7] I.V. Koptyug, K.V. Kovtunov, S.R. Burt, M.S. Anwar, C. Hilty, S.-I. Han, A. Pines, R. Z. Sagdeev, J. Am. Chem. Soc. 129 (2007) 5580–5586.
[8] R. Zhou, E.W. Zhao, W. Cheng, L.M. Neal, H. Zheng, R.E. Quiñones, H.E. Hagelin-Weaver, C.R. Bowers, J. Am. Chem. Soc. 137 (2015) 1938–1946.
[9] K.V. Kovtunov, D.A. Barskiy, O.G. Salnikov, D.B. Burueva, A.K. Khudorozhkov, A. V. Bukhtiyarov, I.P. Prosvirin, E.Y. Gerasimov, V.I. Bukhtiyarov, I.V. Koptyug, ChemCatChem 7 (2015) 2581–2584.
[10] S.B. Duckett, C.L. Newell, R. Eisenberg, J. Am. Chem. Soc. 115 (1993) 1156–1157.
[11] M. Haake, J. Natterer, J. Bargon, J. Am. Chem. Soc. 118 (1996) 8688–8691.
[12] H. Sengstschmid, R. Freeman, J. Barkemeyer, J. Bargon, J. Magn. Reson. Ser. A 120 (1996) 249–257.
[13] K.L. Ivanov, A.V. Yurkovskaya, H.-M. Vieth, J. Chem. Phys. 128 (2008), 154701–154701-13.
[14] S.E. Korchak, K.L. Ivanov, A.V. Yurkovskaya, H.-M. Vieth, Phys. Chem. Chem. Phys. 11 (2009) 11146.
[15] L. Buljubasich, M. Franzoni, H. Spiess, K. Münnemann, J. Magn. Reson. 219 (2012) 33–40.
[16] L.-S. Bouchard, K. Kovtunov, S. Burt, M. Anwar, I. Koptyug, R. Sagdeev, A. Pines, Angew. Chem. 119 (2007) 4142–4146.
[17] L.-S. Bouchard, S.R. Burt, M.S. Anwar, K.V. Kovtunov, I.V. Koptyug, A. Pines, Science 319 (2008) 442–445.
[18] J.F. Dechent, L. Buljubasich, L.M. Schreiber, H.W. Spiess, K. Münnemann, Phys. Chem. Chem. Phys. 14 (2012) 2346.
[19] M. Goldman, H. Johannesson, Comp. Rend. Phys. 6 (2005) 575–581.
[20] M. Goldman, H. Johannesson, O. Axelsson, M. Karlsson, Magn. Reson. Imag. 23 (2005) 153–157.
[21] F. Reineri, A. Viale, G. Giovenzana, D. Santelia, W. Dastru, R. Gobetto, S. Aime, J. Am. Chem. Soc. 130 (2008) 15047–15053.
[22] D. Canet, S. Bouguet-Bonnet, C. Aroulanda, F. Reineri, J. Am. Chem. Soc. 129 (2007) 1445–1449.
[23] E. Vinogradov, A.K. Grant, J. Magn. Reson. 194 (2008) 46–57.
[24] M.B. Franzoni, L. Buljubasich, H.W. Spiess, K. Münnemann, J. Am. Chem. Soc. 134 (2012) 10393–10396.
[25] J.A. Aguilar, P.I.P. Elliott, J. López-Serrano, R.W. Adams, S.B. Duckett, Chem. Commun. (2007) 1183.
[26] J.A. Aguilar, R.W. Adams, S.B. Duckett, G.G. Green, R. Kandiah, J. Magn. Reson. 208 (2011) 49–57.
[27] C. Bowers, D. Weitekamp, JACS 109 (1987) 5541–5542.
[28] L. Buljubasich, I. Prina, M. Franzoni, K. Münnemann, H. Spiess, R. Acosta, J. Magn. Reson. 230 (2013) 155–159.
[29] I. Prina, L. Buljubasich, R.H. Acosta, J. Phys. Chem. Lett. 4 (2013) 3924–3928.
[30] L. Buljubasich, I. Prina, M. Franzoni, R. Acosta, Micropor. Mesopor. Mater., 1016.
[31] D. Graafen, S. Ebert, O. Neudert, L. Buljubasich, M.B. Franzoni, J.F. Dechent, K. Münnemann, in: Annual Reports on NMR Spectroscopy, volume 82, Elsevier, 2014, pp. 167–215.
[32] I. Prina, L. Buljubasich, R. Acosta, J. Magn. Reson. 251 (2015) 1–7.
[33] R.H. Acosta, I. Prina, L. Buljubasich, in: K. Jackowski, M. Jaszunski (Eds.), New Developments in NMR, Royal Society of Chemistry, Cambridge, 2016, pp. 304–335.
[34] S. Bussandri, I. Prina, R. Acosta, L. Buljubasich, J. Magn. Reson. 289 (2018) 55–62.
[35] L. Buljubasich, M.B. Franzoni, K. Münnemann, Top. Curr. Chem. 338 (2013) 33–74.
[36] A.N. Pravdivtsev, F. Sönnichsen, J.-B. Hövener, J. Magn. Reson. (2018).
[37] D. Moskau, Concepts Magn. Reson. 15 (2002) 164–176.
[38] R.W. Adams, S.B. Duckett, R.A. Green, D.C. Williamson, G.G.R. Green, J. Chem. Phys. 131 (2009) 194505.