Simultaneous multi-slice excitation in spatial encoded NMR experiments

Laura Castañar, Pau Nolis, Albert Virgili, and Teodor Parella

Servei de RMN and Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, Barcelona (Spain)

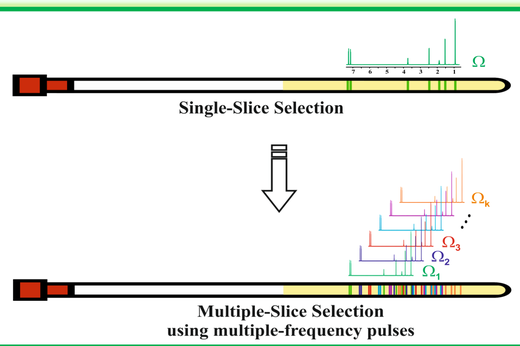
Laura.castanar@uab.cat

Universitat Autònoma de Barcelona

Introduction

Recently, it has appeared a growing interest in spatially localized NMR spectroscopic techniques. Several high-resolution NMR methods applying spatial frequency encoded excitation into the NMR tube have been proposed for obtaining specific information from a particular slice as, for instance, to obtain broadband homodecoupled ^{1}H spectra using the Zangger-Sterk (ZS) method[1].

The most serious drawback of spatially encoded NMR experiments is their reduced sensitivity because the observed signal only arises from a discrete slice of the sample. In this work, we exploit the sensitivity benefits of applying a multiple-frequency modulated pulse to excite simultaneously different slices in a single NMR experiment. Our proposal is based on the careful setting of multiple offsets to avoid the excitation of mutually J-coupled protons into the same slice which would produce distorted multiplets due to J_{HH} evolution[2].



Methodology

NMR Pulse Sequences

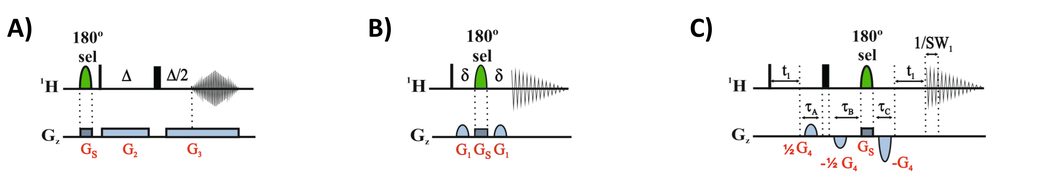


Figure 1: Pulse sequences of the A) 1D z-profile image, B) 1D spatially-encoded single pulsed-field gradient echo (se-SPFGE) and C) ^{1}H pure-shift experiments. Spatial frequency encoding is achieved by simultaneous application of a spatial-encoding gradient (G_s) and a frequency-selective 180º ^{1}H pulse. The G_s gradient is adjusted to cover a spectral width of k*SW_{1H} (k≥1). G_1 gradients act as defocusing/refocusing coherence elements. The duration of G_3 gradient is two times G_2. The delays τ_a, τ_b and τ_c are automatically calculated so that $\tau_a + \tau_c = \tau_b$; $\tau_a = \tau_c$; $\tau_a = 1/4*SW_1$.

Experimental Part

Evaluation of effectiveness of multiple-frequency pulses

We have used two basic experiments (Fig. 1A-B) to evaluate the effectiveness of multiple-frequency pulses in slice-selective spectra: 1D z-profile image (Fig. 2A-F) and se-SPFGE experiments (Fig. 2G-L) to visualize the frequency excitation achieved along the z dimension and the experimental effects on the NMR spectrum, respectively.

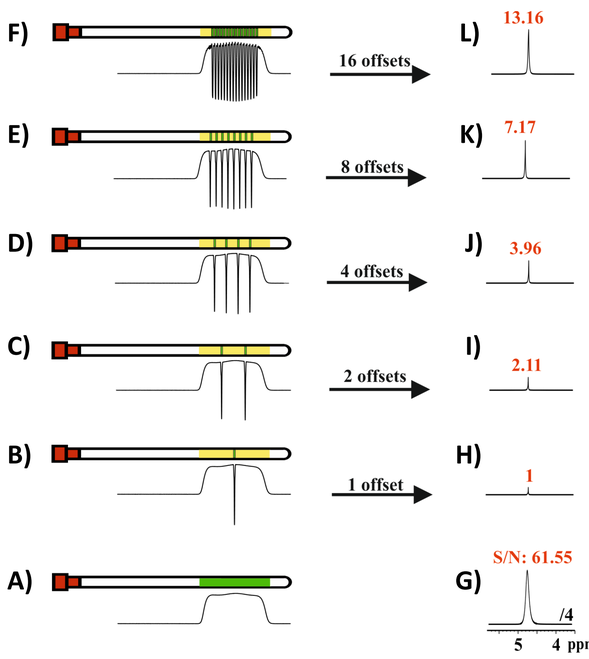


Figure 2: A-F) Schematic z-profile of a 99.96% D_2O sample (pulse sequence used shown in Fig. 1A) using a multiple-frequency pulse with 0 (G_s=off), 1, 2, 4, 8 and 16 different offsets, respectively; G-L) se-SPFGE spectra (pulse sequence used shown in Fig. 1B) using a multiple-frequency pulse with 1, 2, 4, 8 and 16 different offsets and with the experimental signal-to-noise ratio related to the conventional ^{1}H NMR spectra (I). In all experiments, a 20ms Gaussian-shaped 180º ^{1}H pulse was simultaneous applied with an encoding gradient of 0,865 G/cm.

Application of multiple-frequency pulses

As a proof of the method, we have applied it on a sample of ibuprofen, that contains a relative simple ^{1}H spectrum (Fig. 3A), and on a sample of cyclosporine, which presents a more complex ^{1}H spectrum (Fig. 4A).

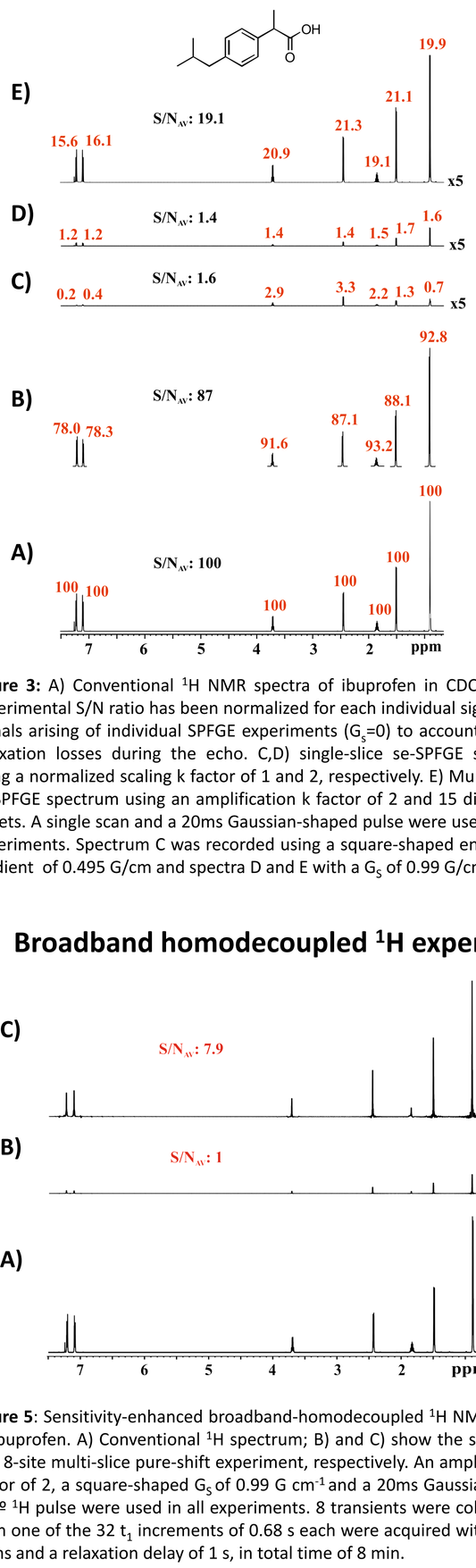


Figure 3: A) Conventional ^{1}H NMR spectra of ibuprofen in $CDCl_3$. The experimental S/N ratio has been normalized for each individual signal. B) Signals arising of individual SPFGE experiments (G_s=0) to account for T_2 relaxation losses during the echo. C,D) single-slice se-SPFGE spectra using a normalized scaling k factor of 1 and 2, respectively. E) Multi-slice se-SPFGE spectrum using an amplification k factor of 2 and 15 different offsets. A single scan and a 20ms Gaussian-shaped pulse were used in all experiments. Spectrum C was recorded using a square-shaped encoding gradient of 0.495 G/cm and spectra D and E with a G_S of 0.99 G/cm.

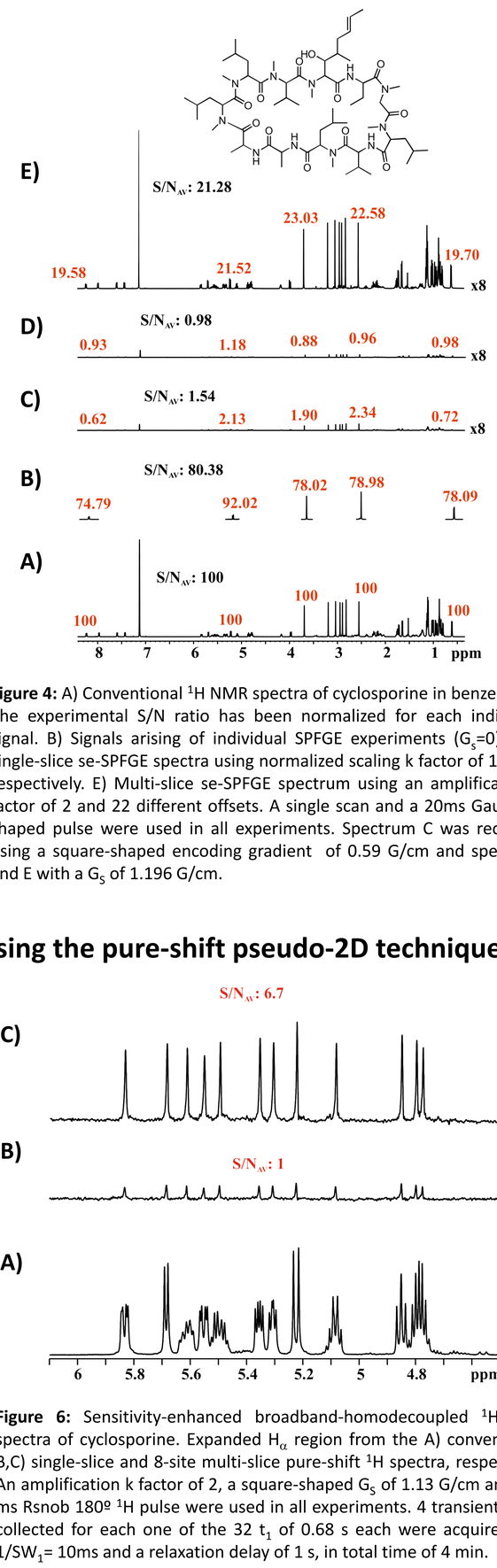


Figure 4: A) Conventional ^{1}H NMR spectra of cyclosporine in benzene-d6. The experimental S/N ratio has been normalized for each individual signal. B) Signals arising of individual SPFGE experiments (G_s=0). C,D) single-slice se-SPFGE spectra using normalized scaling k factor of 1 and 2 respectively. E) Multi-slice se-SPFGE spectrum using an amplification k factor of 2 and 22 different offsets. A single scan and a 20ms Gaussian-shaped pulse were used in all experiments. Spectrum C was recorded using a square-shaped encoding gradient of 0.59 G/cm and spectra D and E with a G_S of 1.196 G/cm.

Broadband homodecoupled ^{1}H experiments using the pure-shift pseudo-2D technique[2]

Figure 5: Sensitivity-enhanced broadband-homodecoupled ^{1}H NMR spectra of ibuprofen. A) Conventional ^{1}H spectrum; B) and C) show the single-slice and 8-site multi-slice pure-shift experiment, respectively. An amplification k factor of 2, a square-shaped G_S of 0.99 G cm^{-1} and a 20ms Gaussian-shaped 180º ^{1}H pulse were used in all experiments. 8 transients were collected for each one of the 32 t_1 increments of 0.68 s each were acquired with $1/SW_1$= 10ms and a relaxation delay of 1 s, in total time of 8 min.

Figure 6: Sensitivity-enhanced broadband-homodecoupled ^{1}H NMR spectra of cyclosporine. Expanded H_α region from the A) conventional; B,C) single-slice and 8-site multi-slice pure-shift ^{1}H spectra, respectively. An amplification k factor of 2, a square-shaped G_S of 1.13 G/cm and a 80 ms Rsnob 180º ^{1}H pulse were used in all experiments. 4 transients were collected for each one of the 32 t_1 of 0.68 s each were acquired with $1/SW_1$= 10ms and a relaxation delay of 1 s, in total time of 4 min.

Conclusions

- ✓ The simultaneous multi-slice excitation improves the sensitivity of slice-selective NMR experiments.
- ✓ The experimental effects on the NMR spectrum can be quickly monitored by recording se-SPFGE experiments.
- ✓ Easy implementation without need to modify existing pulse sequences, so can be immediately adapted to a wide range of applications.

References

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b)A. Aguilar, S. Faulkner, M. Nilsson, G. A. Morris, *Angew. Chem. Int. Ed.* **2010**, *49*, 3901-3903.

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