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A Spatially Selective Composite 90° Radiofrequency Pulse

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Recently, a number of pulse sequences have been proposed that utilize rf inhomogeneity to limit spatially the size of the observed part of the sample (*1–3*). All these sequences rely on 180° pulses that are sensitive to rf field strength; i.e., to rf field inhomogeneity. Both Shaka and Freeman (*1*) and Tycko and Pines (*2*) have developed composite 180° spin-inversion pulses that are very sensitive to rf field strength. By phase cycling of such a 180° pulse in a 90°–180°(composite)–Acquire sequence, one can then observe exclusively signals that have undergone a 180° spin flip, i.e., signals from a part of the sample that experiences a certain rf field strength (*3*).

Here, a different approach to limiting the effective sample volume studied is presented. We propose the use of a composite 90° pulse that is very sensitive to the rf field strength. For reasons of simplicity, the effects of rf offset will be neglected in the following discussion. The simplest sequence for such a rf sensitive 90° pulse is α_x–α_y–α_{-x}–α_{-y} (**I**). For small flip angle α ($\ll 90°$), the NMR system behaves linearly and the net result of pulse **I** is zero. For $\alpha = 90°$, pulse **I** rotates magnetization from the z to the x axis. For arbitrary α one can easily derive that a magnetization component M_z, of unit intensity, is rotated to a position

$$M_x = -sc^2 + sc^3 + s^3 \qquad [1a]$$

$$M_y = sc - sc^2 \qquad [1b]$$

$$M_z = c^4 + 2s^2c \qquad [1c]$$

with $s = \sin\alpha$ and $c = \cos\alpha$.

Figure 1a gives a graphic presentation of these components as a function of flip angle. Even better localization can be obtained with the composite pulse: α_x–α_y–α_{-x}–α_{-y}–α_{-x}–α_{-y}–α_x–α_y (**II**). The effect of this pulse on z magnetization is shown in Fig. 1b. A pulse α_x–α_y–α_{-x} (**III**) has the opposite effect and selects against parts of the sample for which $\alpha = 90°$ (Fig. 1c). This pulse has been discussed previously by Shaka and Freeman as one of the simplest rf selective inversion pulses, and for $\alpha = 90°$, this pulse corresponds to a 90° rotation about the z axis. Note that all three pulses **I**, **II**, and **III** are very sensitive to small phase imperfections and rf amplitude imbalance.

We demonstrate the use of pulses **I**, **II**, and **III** for limiting the effective sample volume in a high-resolution probe. On our NT-500 spectrometer, the resonator coil is of outdated design and a significant amount of signal is picked up by the leads of

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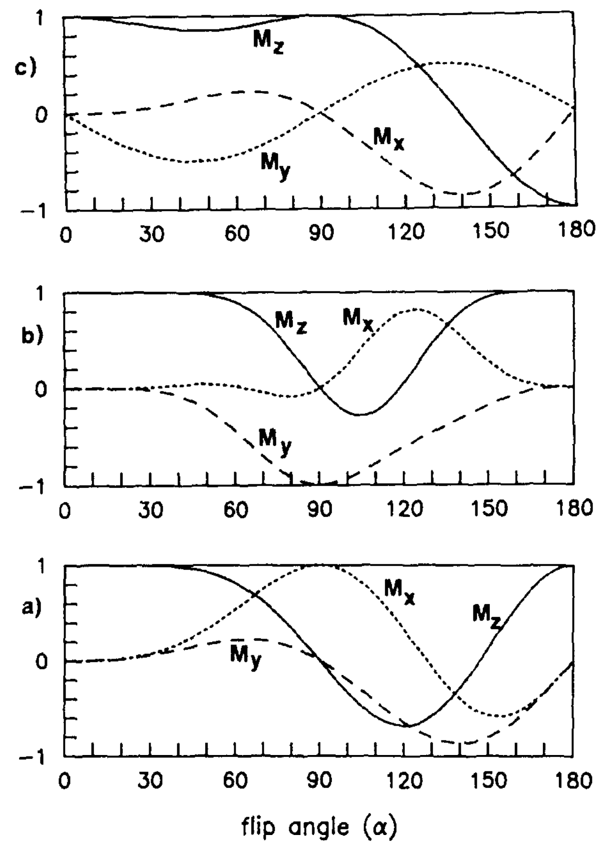

FIG. 1. The effect of the composite pulses (a) **I**, (b) **II**, and (c) **III** on a magnetization vector of unit intensity that is initially aligned along the z axis. The flip angle, α, represents the flip angle of each individual pulse within the composite pulse unit.

this coil. This spurious signal comes from an inhomogeneous H_0 region of low rf field strength and gives rise to a broad hump under the resonance. This hump is a particular nuisance when one works with samples dissolved in H_2O because saturation of the H_2O resonance with a monochromatic rf field will not saturate this hump. Consequently, after H_2O presaturation followed by a single 90° pulse, the H_2O hump will remain. An example of this is shown in Fig. 2a, for a 50 mM solution of angiotensin-II in 80% H_2O/20% D_2O. A 15 Hz rf field was used for 2 s prior to the 90° pulse to saturate the H_2O resonance. Figure 2a shows that the H(C_α) resonances of His, Tyr, and Phe residues are largely obscured by the residual base of the H_2O resonance. Figure 2b shows the result obtained when pulse **I** is used for excitation of the spectrum. As mentioned before, the hump originates from a region of the sample that experiences low rf field strength and is therefore not excited by the use of the composite pulse **I**. Figure 2c shows the result obtained when pulse **II** is used for excitation. In this case, little improvement is obtained over pulse **I**, which suggests that the residual H_2O signal is caused by pulse imperfections (phase and amplitude imbalance) or originates from

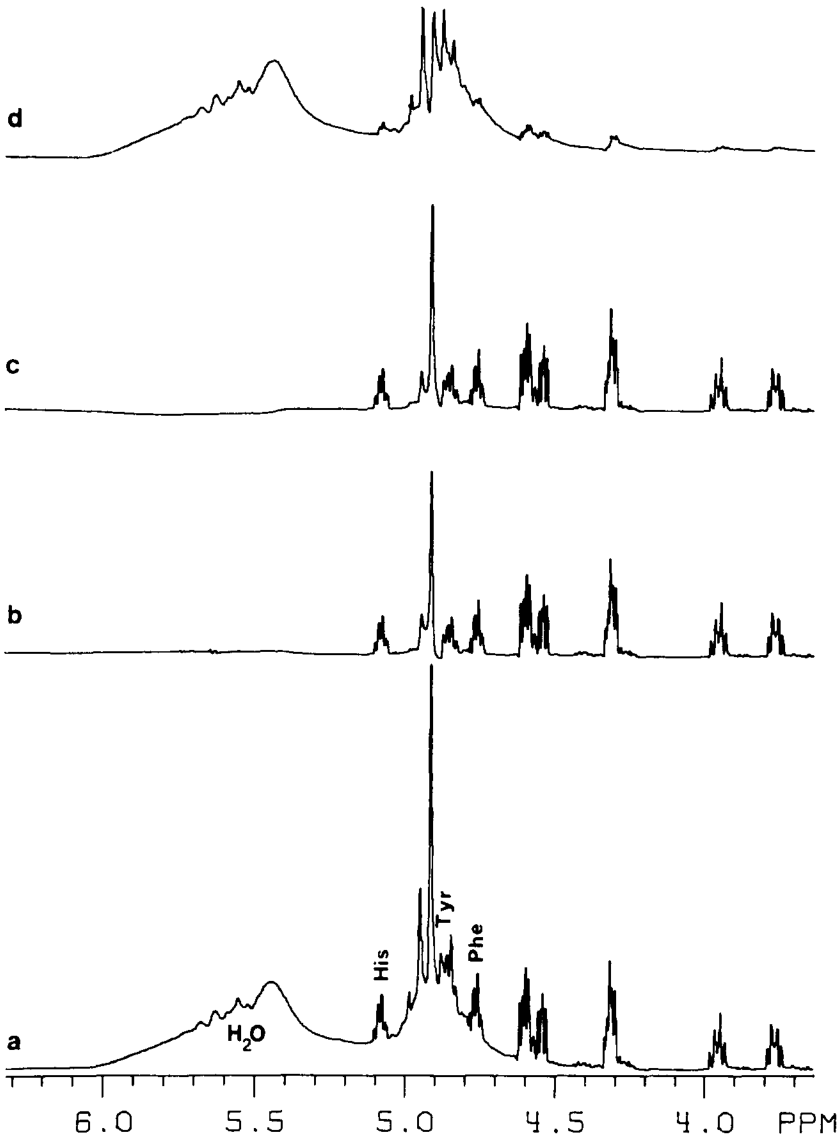

FIG. 2. ^1H 500 MHz NMR spectra of a 50 mM solution of angiotensin-II in 80% H_2O/20% D_2O, at pH 3. Each spectrum results from 32 scans and water presaturation with a 15 Hz rf field has been employed for a period of 2 s prior to excitation. The spectra have all been processed and recorded under identical conditions apart from the excitation pulse used. For spectrum a, a regular 90° pulse was used. For spectra b–d pulses **I**, **II**, and **III**, respectively, were, used. The spectra are all drawn to the same absolute scale. Therefore, spectral intensities are directly comparable.

a part of the sample that is in a strong rf field region. Figure 2d shows that the experiment can also be reversed; i.e., the signal in the strong rf field region can be suppressed if pulse **III** is used for excitation, again with α set to about 90° for the strong rf field region.

Of course, the pulses presented here can be used in combination with phase cycling of composite rf selective 180° pulses (*1–3*) to further limit the effective size of the sample. The main advantage of the rf selective 90° pulses is that no phase cycling is needed to obtain localization of the sample and therefore, dynamic range problems can be significantly alleviated.

It should be noted that resonance offset affects both the rf selectivity of the composite pulses and the amount of excitation obtained for $\alpha = 90°$. In this respect, it is interesting to note that the resonance offset effect is not symmetric (upfield vs downfield from the carrier position), due to the asymmetric structure of the composite pulses. The development of composite rf selective 90° pulses that are less sensitive to offset effects will be desirable for applications like *in vivo* spectroscopy, where the rf field strengths are often limited.

The application shown here, limiting the observed part of the sample to the strong rf field region, is beneficial in high-resolution NMR studies not only for water suppression but also for all types of 1D and 2D experiments that are sensitive to rf field inhomogeneity. Replacing the initial 90° pulse by a composite 90° pulse (**I** or **II**) is easily done and does not require additional phase-cycling steps in the experiment. This type of pulse may also be applicable to *in vivo* experiments when surface coils are used, especially since the rf field produced by such coils varies strongly with position in the sample.

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