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Improved Convection Compensating Pulsed Field Gradient Spin-Echo and Stimulated-Echo Methods

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The need for convection compensating methods in NMR has been manifested through an increasing number of publications related to the subject over the past few years (*J. Magn. Reson.* 125, 372 (1997); 132, 13 (1998); 131, 126 (1998); 118, 50 (1996); 133, 379 (1998)). When performing measurements at elevated temperature, small convection currents may give rise to erroneous values of the diffusion coefficient. In work with high resolution NMR spectroscopy, the application of magnetic field gradients also introduces an eddy-current magnetic field which may result in errors in phase and baseline in the FFT-spectra. The eddy current field has been greatly suppressed by the application of bipolar magnetic field gradients. However, when introducing bipolar magnetic field gradients, the pulse sequence is lengthened significantly. This has recently been pointed out as a major drawback because of the loss of coherence and of NMR-signal due to transverse relaxation processes. Here we present modified convection compensating pulsed field gradient double spin echo and double stimulated echo sequences which suppress the eddy-current magnetic field without increasing the duration of the pulse sequences. © 2000 Academic Press

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When performing diffusion experiments in solutions or low viscous systems, it is important to have a homogenous heating of the sample and an accurate temperature control of the system. If this is not achievable, one should make use of double spin or stimulated echo sequences in order to suppress effects caused by convection within the sample studied.

Already in 1954 Carr and Purcell (*8*) noted that even echoes in a CPMG train were convection compensated. When assuming that an ensemble of molecules are experiencing a constant velocity throughout a pulse sequence, the double pulsed field gradient spin echo sequence (*9*) will suppress convection artifacts in a diffusion experiment. The drawback when using a monopolar double pulsed field gradient spin echo sequence is the occurrence of the eddy-current magnetic field at the time of acquisition. This transient magnetic field is induced due to the switching of the gradient pulses and may lead to errors in baseline, phase, and signal intensity in the FFT spectra. In order to simultaneously compensate for convection and reduce the induced eddy-current magnetic field at the time of acquisition, one has applied bipolar magnetic field gradients during motional encoding and decoding (*1, 6*). However, a recent publication (*7*) points out that a major drawback to applying bipolar pulsed magnetic field gradient sequence is the duration of the sequence. The lengthened duration may make it unsuitable for example in diffusion studies of large molecules where transverse relaxation times are short. It is therefore evident that a shortening of the bipolar pulsed field gradient sequences will improve the experimental setup and the quality of the experimental data set.

By applying preparatory magnetic field gradients prior to the ordinary double PFGSE-sequence but with opposite polarity as shown in Fig. 1, the eddy current field will be greatly suppressed while the double spin echo sequence will be the shortest possible. The echo attenuation for the sequence is written (*8*)

$$\ln \frac{I}{I_0} = -2\gamma^2 D g^2 \delta^2 \left(\tau - \frac{\delta}{3} \right). \qquad [1]$$

When it is crucial to include a storage period of the NMR signal between motional encoding and decoding, in order to have a proper attenuation of the NMR echo-signal, a double pulsed field gradient stimulated echo sequence should be employed. Stimulated echo sequences of this type have been suggested by Pelta *et al.* (*10*), where two preparatory gradients were placed in the Z-storage interval of an ordinary PFGSTE sequence. In the double stimulated echo sequence we suggest (Fig. 2), one preparatory gradient pulse is placed in the first Δ-interval while the last three are placed in the second Δ-interval. The echo attenuation is then written

$$\ln \frac{I}{I_0} = -2\gamma^2 D g^2 \delta^2 \left((\Delta + \tau) - \frac{\delta}{3} \right). \qquad [2]$$

We have deliberately placed three preparatory gradients in the last Δ-interval while only one gradient in the first. Then the degree of dephasing by the *z*-spoiler gradients in the two

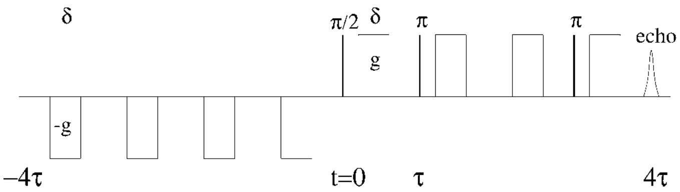

FIG. 1. A double pulsed field gradient spin echo with a preparatory gradient sequence of opposite polarity.

intervals is not equal, and unwanted coherence transfer pathways as $p \to 0 \to 1 \to 1 \to [0, 1 \; or \; -1] \to 1 \to 1$ are crushed. This simplifies the phase cycles needed in the experiment. In order to have a most effective cancellation of the eddy-current field, it is important to have the pulse pairs of opposite polarity as close together as possible (Fig. 2).

When employing the double stimulated echo sequence instead of the double spin echo sequence, one must be aware of the fact that a successful suppression of convection depends on a constant velocity term experienced by each individual spin throughout the pulse sequence. As the storage period is increased, the validity of the constant velocity approximation may become poorer.

The diffusion experiments were performed with Bruker Avance DMX200 and DRX600 spectrometers. On the DMX200 we had access to approximately 900 G/cm while on the DRX600 a maximum gradient of 63 G/cm was achievable. Distilled water was used for the calibration measurements. The water was slightly doped with $CuSO_4$ to reduce the relaxation times and thereby reduce the recycle delay.

Before applying the double PFGSE and PFGSTE sequences in the presence of convection, it is necessary to check the linearity of the attenuation on a homogeneous sample with no convection present. If the attenuation is nonlinear as a function of the applied gradient strength, this implies that an unwanted signal contributes to the echo attenuation. Figure 3 shows the two pulse sequences performed on distilled water at room temperature, and it is evident that the $\ln(I/I_0)$-attenuation is linear to below -6. This indicates that we indeed are recording the wanted coherence transfer pathway, and other pathways are suppressed satisfactorily without using *xy*-spoiler gradients (*11*).

When investigating the effect the preparatory gradient pulses

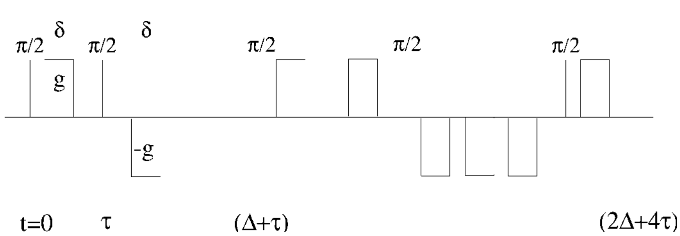

FIG. 2. A double pulsed field gradient stimulated echo with gradient pulses of opposite polarity in the store intervals.

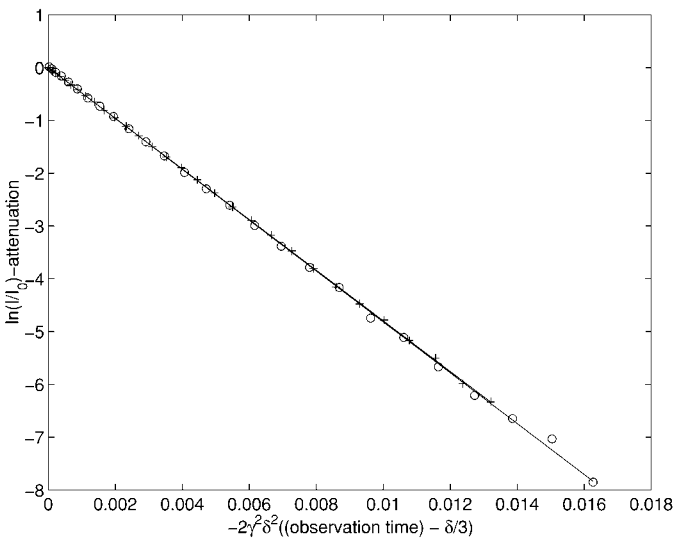

FIG. 3. The $\ln(I/I_0)$-attenuation of distilled water using the double stimulated echo (○) and double spin echo (+) sequences. The solid line indicates linear fits which coincide for the two experiments.

have on the eddy-current transient field, we have studied the deuterium lock signal with and without the use of preparatory gradient pulses in the double echo sequences. As the lock signal is very sensitive to changes in the magnetic field, one should expect to see effects as shown in (*6*). Figure 4 shows how the application of preparatory gradient pulses significantly reduces the eddy-current field.

The impact of this reduction in the eddy-current field, is that both phase and baseline errors in the FFT spectra should be reduced. Figure 5 shows an improvement of the FFT-spectra of a CH_3 group in valine.

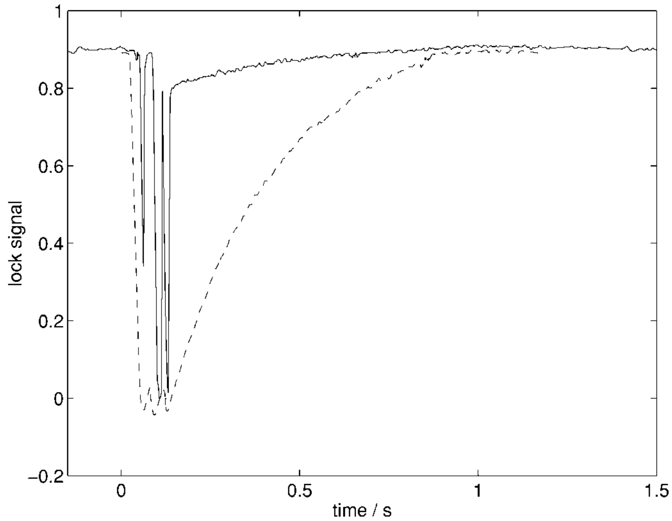

FIG. 4. Recordings of the lock signal during an ordinary double PFGSTE sequence (dashed line) and the proposed double PFGSTE sequence with preparatory gradient pulses (solid line).

Figure 6 shows the effect of introducing a double pulsed field gradient spin echo sequence as compared to a single pulsed field gradient spin echo sequence in the presence of convection. The system studied was a solution of acetonitrile at 15°C.

As expected, the double spin echo gives rise to a linear attenuation while the single spin echo is nonlinear due to a nonzero convection term. As the linearity of the double PFGSE attenuation is high, we find it reasonable to believe that the velocity pattern in the sample is stable at 15°C. The double PFGSE attenuation will then reveal the true self diffusion coefficient in the presence of convection.

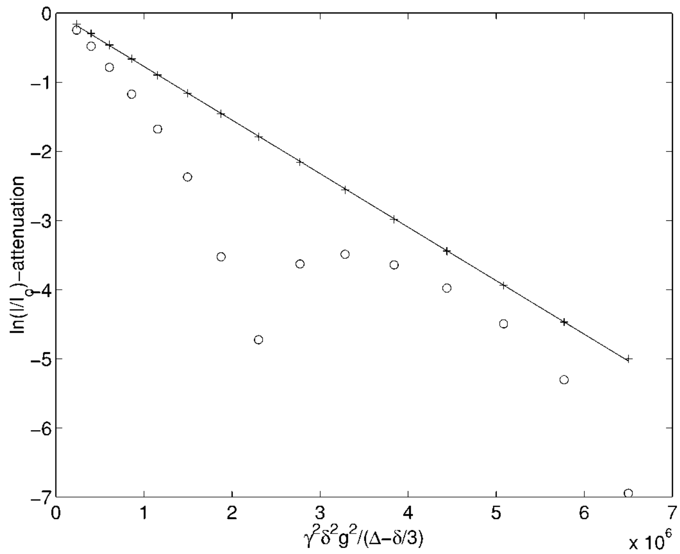

FIG. 6. A single pulsed field gradient experiment (○) and a double pulsed field gradient experiment (+) performed on acetontrile at 15°C.

CONCLUSION

We have shown that it is possible to make use of the ordinary double PFGSE and PFGSTE sequences for suppression of convection artifacts in the presence of a eddy-current field which is significantly reduced by preparatory gradient pulses. These gradient pulses do not lengthen the pulse sequences as the application of bipolar pairs of gradient pulses does. This makes the proposed sequences suitable when studying systems with short transverse relaxation times.

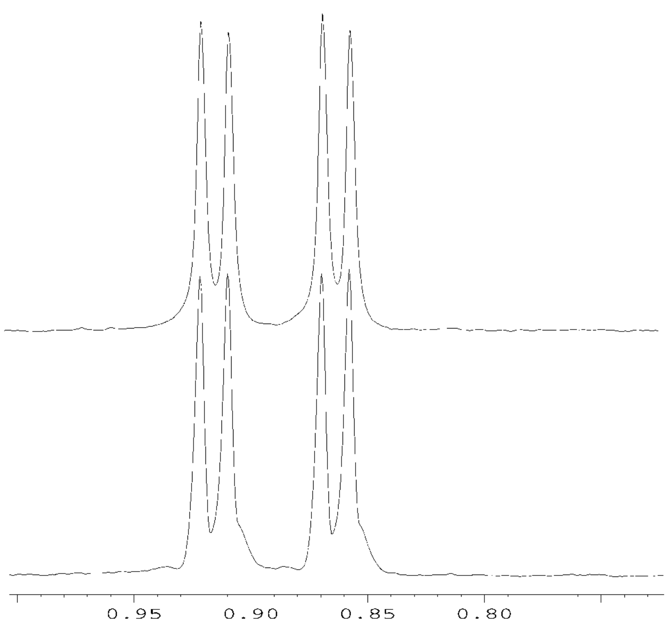

FIG. 5. Four peaks arising from two CH_3 groups in the amino acid valine. The lower FFT spectrum is recorded with the ordinary double PGFSTE sequence while the upper is recorded using the double PFGSTE with preparatory gradient pulses.

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