METHODS FOR THE NMR IMAGING OF SOLIDS USING MULTIPLE PULSE SEQUENCE

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Abstract

Two new multipulse sequences for the NMR imaging of solids and other short T_2 materials have been developed. The two techniques share the common feature of using time dependent magnetic field gradients. They have been used to obtain two-dimensional images of a variety of solid samples. Their relative merits are compared and discussed.

Introduction

The principle difficulties with the NMR imaging of solids arise because of the characteristically short transverse spin relaxation times T_2 found in solids. Large field gradients must be imposed to produce spatial localization of the nuclear spins in the sample. This increases the signal decay rate further and means that much of the signal is lost in the apparatus dead-time following the excitation pulse. Moreover r.f. pulses applied in the presence of large field gradients must be of sufficient amplitude to cover the increased spectral width of the NMR signal. A third difficulty is that in solids the spin-lattice relaxation time, T_1, is usually much longer than T_2 so that the actual data acquisition time ($\approx T_2$) is very much shorter than the repetition period ($\approx 5T_1$) for projection accumulation and noise averaging.

Two different multipulse techniques described in this paper have been devised to overcome some of these problems. They share the common features of applying a long sequence of r.f. pulses with pulse intervals less than T_2 and of using rapidly driven sinusoidal gradients at a frequency corresponding to an integer multiple of the pulse repetition frequency so that the pulses are always applied when the gradient passes through zero.

In the first method a single 90x pulse, in the presence of an oscillating field gradient produces a train of Hahn-type echoes. These echoes can be held up by a sequence of 90y pulses which produce a train of solid-echoes (1-4). In the second method a multiple pulse line-narrowing sequence designed specifically for imaging is used. Some of the fundamental ideas of multipulse imaging were first demonstrated in the early work of Mansfield and co-workers (5). More recently Miller and Garroway (6) have refined the technique to include oscillating gradients but they use a low frequency so that pulses are applied in the presence of the gradients.

Theory

Method 1

In its simplest form this method does not provide any line-narrowing, but simply uses a sinusoidal field gradient of sufficient strength to resolve the broad lines. The basic experiment consists of a 90x pulse synchronized to the time of zero field gradient, thus removing the requirement for large r.f. power. After one period of the field gradient oscillation the spins refocus to produce an echo. Echoes will continue to form after every field gradient cycle with an amplitude envelope decaying with characteristic time T_2. An image may be formed from the first and/or subsequent echo envelopes provided a method of non-linear sampling (7) is used to correct for the variation of the field gradient strength during data collection. The optimum choice for the oscillating field gradient period, 2τ, depends on the dead-time (τ_d), the natural T_2 of the sample and the signal decay-time with the field gradient present (T_2^*). We require that

(1) the entire echo forms away from the dead-time:

$$\text{i.e. } 2\tau \geq 2\tau_d$$

(2) the echoes are clearly separated:

$$\text{i.e. } 2\tau \geq 2T_2^*$$

(3) there is sufficient signal available:

$$\text{i.e. } 2\tau \leq T_2.$$

In our experiments we could satisfy these three criteria conveniently by choosing $2\tau \approx T_2/2$.

A multipulse development of this scheme is to produce a train of solid echoes (1-4) thus preserving the transverse magnetization well beyond T_2. In order to apply the pulses with the correct r.f. phase for all nuclei they must be timed to occur when the magnetization is refocussed by the oscillating field gradient. The 90y pulses are therefore applied at the peaks of alternate Hahn echoes using the sequence

$$90_x\, 2\tau\, (90_y\, 4\tau)_n.$$

The unaffected echoes (i.e. those appearing at $((4n+2)\tau)$ are used in the data capture. Note that the whole of each echo profile is captured, not just the peak height. Summation of these echoes will improve the signal-to-noise ratio if spatial variation of T_2 can be ignored.

Method 2

The second approach we have adopted is to design a multiple-pulse line-narrowing sequence specifically for solid state NMR imaging. Unlike traditional sequences such as MREV-8, (8-10) a major design criterion is that all the pulse windows are of the same length τ so that sinusoidal gradients of period 2τ can be used. The sequence is further designed so that it removes inhomogeneous broadening effects due, for example, to chemical shift and inhomogeneous magnetic fields as well as dipolar broadening. Furthermore, the sequence retains maximum sensitivity, through the so called scaling factor, to resonance offsets toggled in alternate windows.

The sequence adopted, which fulfils the above requirements, is

$$90_{-y}\,\tau\,(90_{-x}\,\tau\,90_{-y}\,\tau\,90_{-x}\,\tau\,90_{-x}\,\tau\,90_{-y}\,\tau\,90_{-x}\,\tau)_n.$$

For spins experiencing an oscillating gradient of local amplitude, B_g, the spins precess about an effective field along the z direction at a scaled frequency of $(\gamma B_g/3)$. The magnetization is observed in every sixth window and recorded once per cycle throughout the sequence to build up a free induction decay which can be Fourier transformed to obtain a profile in the direction of the gradient. The gradient is rotated between sequences to build up a 2D image. A full discussion of the properties of the sequence is presented elsewhere (11).

Results

Method 1

A two-dimensional proton density image of a sample consisting of two pieces of rubber ($T_2 \approx 700\mu s$) of thickness 1mm and separated by 2mm, is shown in Figure 1. The image was reconstructed from 18 profiles each one formed using a single echo. The gradient amplitude was 40 Gcm^{-1} and the period, 2τ, was $200\mu s$.

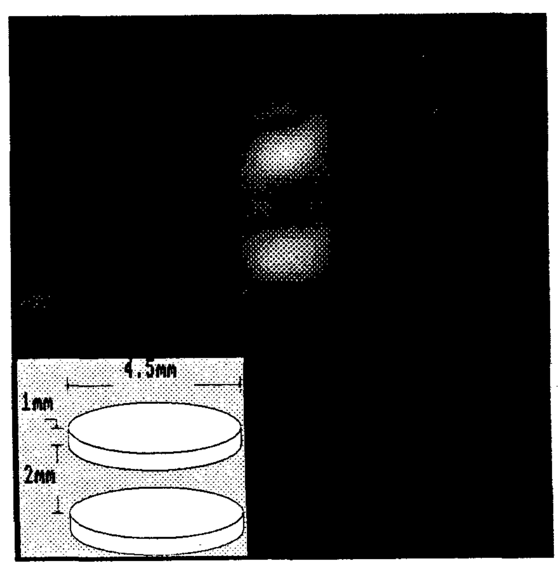

Figure 1 Two-dimensional proton density map of two red rubber discs as shown in the inset obtained by method 1 as described in the text.

Figure 2 demonstrates the S/N improvement possible using multiple 90y pulses to hold up the magnetization. One of the one-dimensional projection profiles used to create Figure 1 is shown in Figure 2(a). Figure 2(b) shows the result of using the multiple pulse scheme with summation of the first 10 echoes following the initial 90x excitation pulse. The S/N ratio has been improved by a factor of about two as expected.

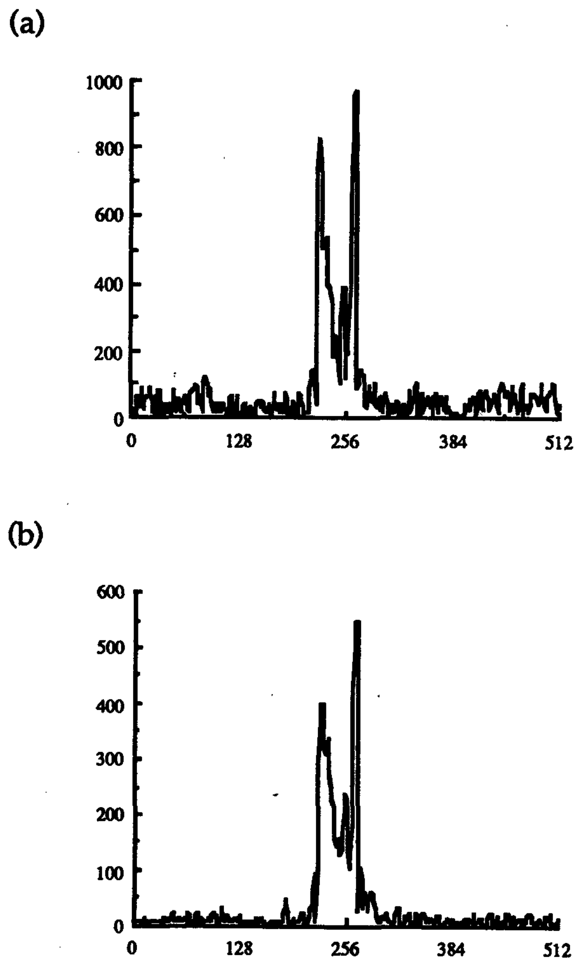

Figure 2 The S/N improvement possible using multiple 90_y pulses to hold up the magnetization.

Method 2

Figure 3 shows a fluorine density two-dimensional image without any attempt at slice selection across a teflon rod 7mm in diameter with a 65° wedge and central hole 2mm in diameter cut out along its length. This was obtained using the line-narrowing sequence. The image is made up of 36 profiles. The pulse gap used was 11μs with a 90° pulse length of 3μs. Each profile was averaged 5 times. The effective gradient strength was less than $2Gcm^{-1}$. Low frequency oscillations in the projection profile, due to defects in the multipulse sequence, give rise to a central artefact in the image. This artefact can be shifted away from the image information by adding a spatially constant field of less than 3.5G switched synchronously with the field gradient.

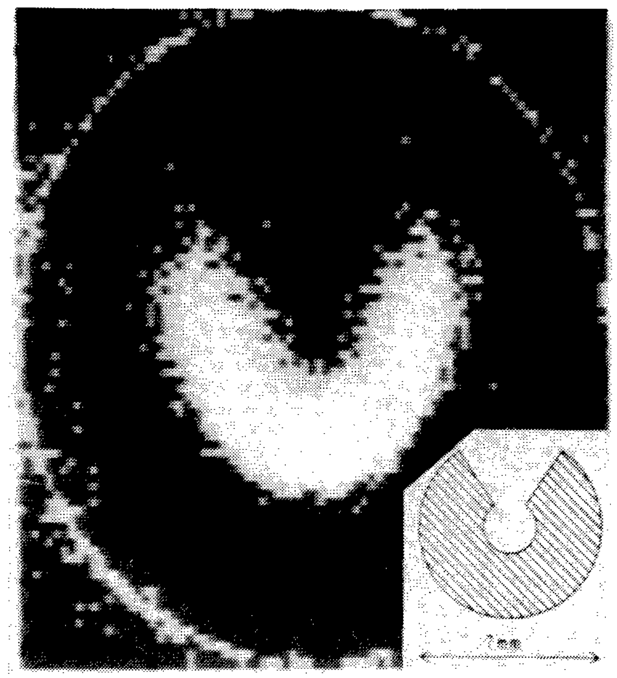

Figure 3 A fluorine density image across a teflon rod 7mm in diameter with a 65° wedge and a central circle 2mm in diameter cut out (see inset) obtained using method 2.

Discussion

Both methods use back projection of profiles. Whilst this overcomes the need to rapidly switch between gradients in different directions, the cost is represented by the relatively inefficient way k-space is covered.

The echo method is considerably easier to implement, specifically overcoming problems of dead-time and pulse intensity. However, it requires somewhat higher gradient strengths than the multiple pulse method. This is not too difficult to achieve since the gradient coils can be tuned to the gradient oscillation frequency. The multiple pulse method has the considerable advantage of working well in inhomogeneous magnets. Indeed we have noted that the line-narrowing achievable with long T_2 systems far exceeds the linewidth capability of our magnet.

The efficacy of the multiple pulse sequence described above is very sensitive to pulse defects. A much improved sequence is obtained by following the six pulse cycle by its Hermitian adjoint so creating a twelve pulse basic cycle. The magnetization is still observed in each sixth window.

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