SEPARATION OF THE DIFFERENT ORDERS OF NMR MULTIPLE-QUANTUM TRANSITIONS BY THE USE OF PULSED FIELD GRADIENTS

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Any order of transition can be detected separately in a two-dimensional multiple-quantum spin-echo experiment by applying a matching pair of pulsed field gradients. The method is based on the fact that the rate of defocusing and refocusing in an inhomogeneous magnetic field is proportional to the order of coherence. Natural line widths can be obtained for each order of transition.

1. Introduction

Multiple-quantum transitions (MQT) in NMR spectroscopy were mentioned as early as 1956 [1]. Recently new methods have been published describing the excitation and detection of multiple-quantum transitions in quite different and more practical ways [2–5]. One of these methods [2] generates MQT coherence in a homonuclear coupled spin system by means of two non-selective 90° pulses separated by a time interval τ. The coherence which is created then evolves during a time t_1, after which another 90° pulse partly transfers this MQT coherence back to observable single-quantum coherence, which is detected during the time t_2 (fig. 1). Fourier transformation of the 2D time signal, with respect to t_1 and t_2, gives a 2D frequency spectrum, with information about the coherence which existed during the evolution period presented along the ω_1 axis. In general, along the ω_1 axis we find resonance lines which correspond to all orders of transitions in the coupled spin system, while along the ω_2 axis only the single-quantum transitions observed during t_2 are visible.

A more simple 2D spectrum, which contains only MQT resonance lines corresponding to a selectable order of transitions can be obtained by combining the results of various measurements with phase-shifted 90° pulses [5–8]. The phase-shifter needed to obtain this separation of orders can be quite complicated. As will be shown, similar results can be obtained if pulsed magnetic field gradients are applied. This new extension relies on the fact that the sensitivity to magnetic field homogeneity is proportional to the order of coherence considered. This is also the reason that coherence transfer echoes arise during the detection period at different times t_2 for different orders [9]. Wokaun and Ernst [10] suggested that these coherence transfer echoes could be used for the transverse relaxation study of MQT coherence. However the overlap of the different echoes with the non-echoing part of the signal causes trouble in this case.

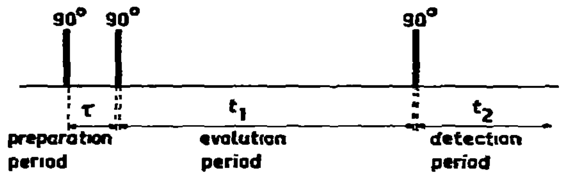

Fig. 1. Pulse sequence used to create and detect multiple-quantum coherence of all orders by way of a two-dimensional Fourier transform experiment.

With the new method it is possible to suppress all signals except a set of echoes which correspond to a selectable order of quantum transitions, by applying pulsed field gradients with different lengths of time during the evolution and detection periods. This makes it possible to obtain the MQT relaxation rates in a very simple way.

2. Effect of magnetic field gradients on MQT coherence

A detailed description of the effect of magnetic field gradients on MQT coherence has been given by Maudsley et al. [9]. They calculate that in the experiment of fig. 1 the contribution to the magnetization $M_{y(kl),(mn)}(t_1, t_2)$ of coherence between the levels m and n during the evolution period and the levels k and l during the detection period in a completely homogeneous magnetic field is given by

$$M_{y(kl),(mn)}(t_1, t_2) = 2\exp(-t_2/T_{2kl})\exp(-t_1/T_{2mn}) \times [\mathrm{Re}(Z_{kl,mn})\cos(\Delta_{(kl),(mn)}) - \mathrm{Im}(Z_{kl,mn})\sin(\Delta_{(kl),(mn)}) + \mathrm{Re}(Z_{kl\,mn})\cos(\Sigma_{(kl),(mn)}) + \mathrm{Im}(Z_{lk,mn})\sin(\Sigma_{(kl),(mn)})], \quad (1)$$

where $Z_{kl,mn}$ is a complex amplitude, determined by the kind of preparation ($t < 0$) and the mixing pulse at $t = t_1$ [2,5].

$\Delta_{(kl),(mn)}$ and $\Sigma_{(kl),(mn)}$ are given by

$$\Delta_{(kl),(mn)} = \omega_{0kl}\,t_2 - \omega_{0mn}\,t_1, \quad (2a)$$

$$\Sigma_{(kl),(mn)} = \omega_{0kl}\,t_2 + \omega_{0mn}\,t_1. \quad (2b)$$

In fact eq. (1) shows the contribution of the density matrix elements $\sigma_{mn}(t_1)$ and $\sigma_{nm}(t_1)$ oscillating with angular frequency ω_{0mn}, to the magnetization $M_{y(kl),(mn)}$ which rotates during the detection period with angular frequency ω_{0kl} and originates from $\sigma_{kl}(t_2)$ and $\sigma_{lk}(t_2)$.

Because in practice the magnetic field will not be completely homogeneous there will be a constant space-dependent field $\Delta B_0(\bar{r})$. If also a time-dependent gradient $\Delta B(\bar{r}, t)$ is applied, the magnetic field can be described as

$$B(\bar{r}, t) = B_0 + \Delta B_0(\bar{r}) + \Delta B(\bar{r}, t). \quad (3)$$

In this case the resonance frequencies in a homonuclear coupled spin system with nuclei which have a gyromagnetic ratio γ are given by

$$\omega_{mn}(t_1) = \omega_{0mn} - \gamma\Delta M_{mn}\Delta B_0(\bar{r}) - \gamma\Delta M_{mn}\Delta B(\bar{r}, t), \quad (4a)$$

$$\omega_{kl}(t_1) = \omega_{0kl} - \gamma\Delta M_{kl}\Delta B_0(\bar{r}) - \gamma\Delta M_{kl}\Delta B(\bar{r}, t). \quad (4b)$$

ΔM_{mn} and ΔM_{kl} are the changes of total magnetic quantum numbers in the two transitions considered. If $\Delta B(\bar{r}, t)$ equals a constant gradient $\Delta B_1(\bar{r})$ during $0 < t < \tau_1$ and another gradient $\Delta B_2(\bar{r})$ during $t_1 < t < t_1 + \tau_2$ and zero for all other values of t, we obtain from eqs. (2) and (4) for $t_1 > \tau_1$

$$\Delta_{(kl),(mn)} = \omega_{0kl}t_2 - \omega_{0mn}t_1 - \gamma\Delta B_0(\bar{r})(\Delta M_{kl}t_2 - \Delta M_{mn}t_1) - \gamma[\Delta M_{kl}\tau_2\Delta B_2(\bar{r}) - \Delta M_{mn}\tau_1\Delta B_1(\bar{r})], \quad (5a)$$

$$\Sigma_{(kl),(mn)} = \omega_{0kl}t_2 + \omega_{0mn}t_1 - \gamma\Delta B_0(\bar{r})(\Delta M_{kl}t_2 + \Delta M_{mn}t_1) - \gamma[\Delta M_{kl}\tau_2\Delta B_2(\bar{r}) + \Delta M_{mn}\tau_1\Delta B_1(\bar{r})]. \quad (5b)$$

Following the arguments of Maudsley [9], eq. (5a) immediately shows that if the gradient $\Delta B(\bar{r}, t)$ is not applied (i.e. $\tau_1 = \tau_2 = 0$) for the value

$$t_2 = t_1\Delta M_{mn}/\Delta M_{kl}, \quad (6)$$

$\Delta_{(kl),(mn)}$ becomes independent of $\Delta B_0(\bar{r})$, this means independent of the static magnetic field gradients, i.e. an echo is formed whenever eq. (6) is fulfilled. As is clear from eqs. (1) and (5) only that part of the magnetization $M_{y(kl),(mn)}(t_1, t_2)$ which contains the $\Delta_{(kl),(mn)}$ terms refocuses, while the other part, containing the $\Sigma_{(kl),(mn)}$ terms defocuses further during the detection period. Because the observed transition has to be a single quantum transition ($\Delta M_{kl} = 1$) it is clear that an echo originating from a p-quantum transition during t_1, will appear at $t_2 = pt_1$. Generally, the echoes corresponding to different values of p will overlap each other, and will also interfere with the defocusing $\Sigma_{(kl),(mn)}$ magnetization components.

If we do apply magnetic field gradients $\Delta B_1(\bar{r})$ for a time τ_1 during the evolution period and $\Delta B_2(\bar{r})$ for a time τ_2 at the beginning of the detection period, in such a way that:

$$\Delta B_2(\bar{r})\tau_2 = \Delta B_1(\bar{r})\tau_1 p, \tag{7}$$

it is clear from eq. (5) that only $\Delta_{(kl),(mn)}$ terms for which $\Delta M_{mn}/\Delta M_{kl} = p$ are not influenced by these gradients applied. This means that if the gradient pulse is sufficiently strong, only the p-quantum coherence transfer echo will appear, while all other signals are eliminated because of the defocusing. If the gradients applied during t_1 and t_2 have opposite signs, in such a way that $\Delta B_1(\bar{r})\tau_1 = -p\Delta B_2(\bar{r})\tau_2$, substitution in eq. (5) shows that only the $\Sigma_{(kl),(mn)}$ terms, corresponding to p-quantum transitions during t_1, are not eliminated by the gradients applied. These signals can also be applied to obtain a MQT spectrum of a selected order p.

3. Experimental

As is clear from the previous section, the defocusing or refocusing magnetizations, which originate from MQT's of order p during the evolution period can be detected selectively by giving the right gradient pulses. In practice, during a short time τ_1, which is part of the evolution period, a strong linear gradient is created along the axis around which the sample is spinning, by sending a current through the appropriate shimming coils. Then at the beginning of the detection period a current of the same magnitude is applied in the same or opposite direction, during a time $\tau_2 = p\tau_1$.

If no gradient pulses are applied the three pulse program gives contributions of the defocusing and refocusing magnetization components, which originate from all orders (fig. 2a). If a pulsed gradient is applied only during the evolution period (fig. 2b), the detected magnetization originates only from zero quantum transitions (ZQT) and longitudinal relaxation during t_1. If the two pulsed gradients have the same length in time and magnitude, only the 1QT coherence transfer echo is visible (fig. 2c), if the second gradient lasts twice as long as the first, only the 2QT coherence transfer echo is visible (fig. 2d).

To minimize incomplete refocusing because of self-diffusion in the sample between the gradient pulses, the two gradient pulses should be as close as possible. This means that the "evolution gradient pulse" should be given at the end of the evolution period. For the same reason, the gradient pulses should not be made stronger than necessary. Which gradient pulse length is needed can most easily be checked experimentally. The gradient pulses applied during the evolution period in fig. 2 had a length of 5 ms. The signals shown in fig. 2 were recorded on a 7T HR-NMR spectrometer constructed at the Delft University of Technology [11].

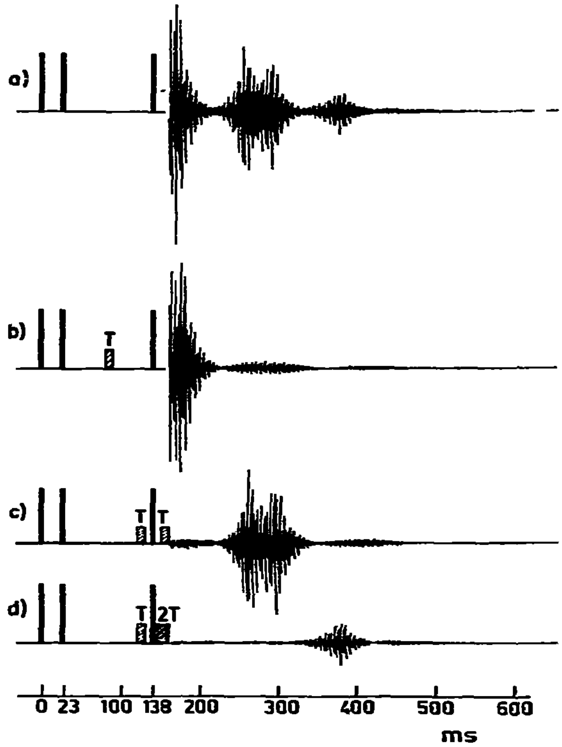

Fig. 2. Signals from an AX spin system after a three-pulse sequence, (a) without gradient pulses; (b) with a gradient pulse applied only during the evolution period; (c) with equal gradient pulses at the end of the evolution and the beginning of the detection period; (d) with the gradient pulse during the detection period doubled in length.

4. Discussion

When the method described above is compared with the other methods for separating the orders of multiple-quantum transitions by applying phase-shifted pulses [5–8] the following points are relevant.

In principle the field gradient method gives signal loss because all signals originating from orders other than the observed order are physically destroyed. So only one order of transitions per experiment can be studied. With the "phase-shift separation" method all orders can be measured in a single experiment, if sufficient data storage space is available.

Because the field gradient method destroys those components of magnetization which continue to defocus during the detection period, only coherence transfer echoes are acquired. This means that natural line-widths can be obtained by selecting suitable cross sections through the 2D frequency spectrum [12]. These natural line-widths can be used for the transverse relaxation study of MQT in a simple way [10].

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