NMR Diffraction Revisited with a Modified CRAZED Double Quantum Imaging Sequence

C. Chin[1], X. Tang[2], L. Bouchard[2], W. S. Warren[2], F. W. Wehrli[1]

[1]Department of Radiology, University of Pennsylvania Medical Center, Philadelphia, PA 19104, United States, [2]Department of Chemistry, Princeton University, Princeton, NJ 08544, United States

Distant dipolar fields allow observation of intermolecular multiple quantum coherences. Recently, this phenomenon has been exploited to obtain structural information since these signals result from pairs of spins separated by the correlation distance (D_c). Here we show experimentally in a model system consisting of a 7×6 array of water-filled capillaries that capillary diameter and spacing can be retrieved by a CRAZED-type double quantum sequence. Using phase cycling, signal attributed to different coherence transfer pathways (M=0, 2, ±1) at various D_c could be isolated. For M=0, ±1, diffraction peaks occurring at $D_c=(2-M)\times\lambda/2$ could be observed, with λ being the inter-capillary spacing.

Introduction

The signal generated by distant dipolar interactions can be explained as resulting from the mean demagnetizing field (1) or, alternatively, from intermolecular multiple quantum coherence (*i*MQC) (2). The dipolar field giving rise to these effects is caused by distant spins separated by the correlation distance (2). Thus, *i*MQC NMR offers the potential to probe structure size at different scale by varying the correlation distance. If, in addition, the spin density varies periodically, an additional modulation occurs leading to diffraction-like phenomena (3). However, the predicted diffraction phenomena have so far not been observed experimentally. Here we applied a modified CRAZED DQ pulse sequence to probe size and spacing in an array of signal-producing capillaries and demonstrate the unique diffraction behavior for signal arising from different coherence transfer pathways (M=0, 2, ±1).

Materials and Methods

Experiments were carried out on a 4T GE Signa™ scanner using a modified CRAZED pulse sequence (Fig. 1). The imaging phantom was a 7×6 glass capillary array (o.d./i.d.=1.0/0.5 mm, and 10cm in length, Fig. 2). An array of parallel capillaries, spaced 2.5mm apart (containing saline) were placed perpendicular to $\mathbf{B}_o$, and imaged with TR/TE=5s/200ms, $\alpha=\pi/2$, $\beta=\pi/6$, τ=30ms, G_c=0.3G/cm, STH=15mm, NEX=4. The correlation distance, $D_c=\pi/(\gamma G_c T)$, was varied from 200 µm to 4.7mm by stepping T. In order to analyze the signal behavior of different coherence transfer pathways, data was acquired by varying the phase of the α-pulse (x, $-x$, y, $-y$) for each excitation and the resulting signals combined as indicated in Fig. 3. Measurements were performed when G_c applied parallel (x) and perpendicular (z, $=\mathbf{B}_o$) to the long axis of capillaries.

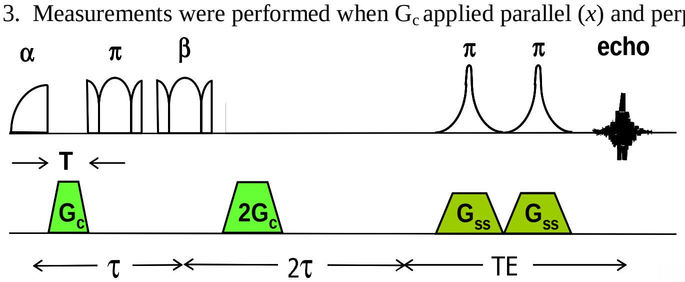
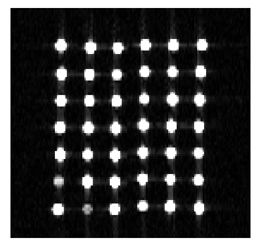


FIG 1 (left) Modified CRAZED pulse sequence. All RF pulses are adiabatic to ensure uniform excitation. The first π pulse refocuses the chemical shift and field inhomogeneity. The 1:2 correlation gradients (G_c) were used to select double quantum coherence, and the slice-selection gradient (G_{ss}) allows imaging a slab of sample. The α pulse was subjected to 4-step phase cycling (x, $-x$, y, $-y$). **FIG 2** (right) Spin-echo image of water-containing capillaries immersed in D_2O.



Results and Discussion

Figure 3 shows the signal intensity plotted vs D_c of each coherence transfer pathway after judicious combination of signals obtained by cycling the phase of α-pulse. It is noted that the double quantum filter gradients do not suppress the signal for coherence orders $M\neq 2$. It is straightforward to show that the periodicity in spin density causes diffraction peaks to appear when $D_c=(2-M)\times\lambda/2$, where λ=capillary spacing (2.5mm), along with k-th order diffraction peaks at D_c/k. The ZQC peaks are generated from dipolar interactions whose origin differs from that of ±SQC. As expected, no diffraction was observed when G_c was parallel to the long axis of the capillaries.

The 4-step phase cycling scheme applied here does not suffice to separate ±DQC. However, the signal can be weighted toward either + or –DQC by choosing $\beta=\pi/6$ or $5\pi/6$ (optimizing + or – DQC selection, resp.). A striking negative peak at D_c=1.25 mm in the DQC plot was attributed to a minimum in paired spins at this correlation distance (one half the capillary spacing). Finally, a change in slope is noted at D_c=0.5mm which occurs at D_c=i.d.

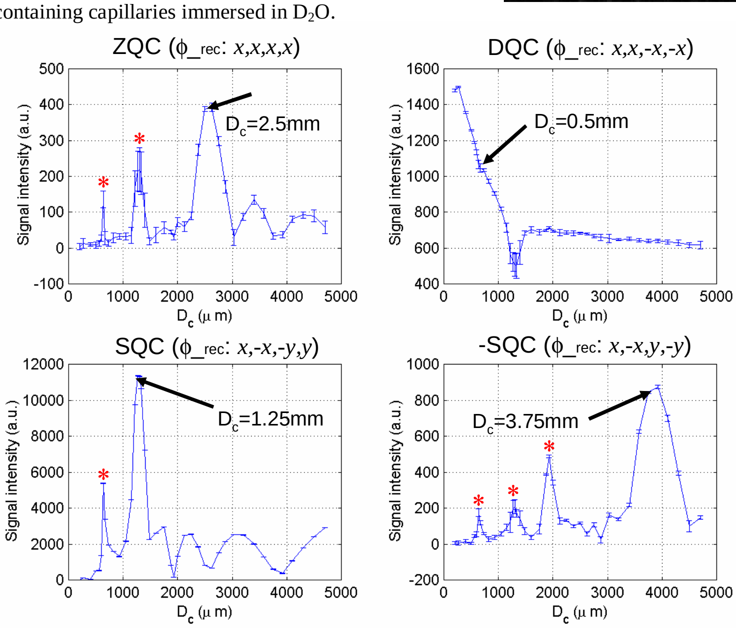


FIG 3 *i*MQC [M=0(ZQC), ±1(±SQC), 2(DQC)] signal intensity at different D_c values when G_c was applied along z (perpendicular to capillary direction). The signal combination mode is shown on top of each illustration, asterisks indicate location of higher-order harmonics.

Conclusions

These results are the first demonstration of diffraction phenomena resulting from long-range dipolar interaction involving structures with periodically varying spin density. The method may have potential for probing structural heterogeneity of biological materials.

References **1.** Bowtell R *et al*, J Magn Res **88**, 643 (1990). **2.** Warren WS *et al*, Science **262**, 2005 (1993). **3.** Robyr P *et al*, J Chem Phys **106**(2), 467 (1997).