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Historical Perspective

Recollections of REDOR

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ABSTRACT

Rotational-echo, double-resonance NMR (REDOR) is an experiment designed to measure heteronuclear dipolar couplings in solids and is most often used to obtain structural details in solids. A brief history of its inception and development is presented.

Interview with the author(s).

A video interview with the author(s) associated with this Historical Perspective and the original article can be found in the online version, at doi:10.1016/j.jmr.2011.08.011.

I studied for the Ph.D. degree under the direction of Mark Conradi. At that time Mark had a strong interest in characterizing atomic and molecular motions in solids, including very slow motions. Consequently, we used a variety of NMR experiments to characterize these motions, including relaxation time measurements, hole burning and selective inversion. The hole burning experiments [1] were based on the stimulated echo pulse sequence and impressed upon me the importance of manipulating the nuclear spins to obtain information.

When I joined the Schaefer group as a postdoctoral student, double-cross polarization (DCP) was being used to detect ^{13}C—^{15}N interactions [2]. This triple-resonance magic-angle spinning experiment had required Schaefer, Stejskal and McKay to build a 200 MHz triple-resonance spectrometer for solid state NMR. The main difficulty with DCP was getting quantitative internuclear distances. My inspiration for REDOR [3,4] was the description of the SEDOR experiment on a copper–cobalt alloy presented in Slichter's book [5] and a desire to contribute to measuring ^{13}C—^{15}N dipolar couplings under high-resolution magic-angle spinning conditions. I was familiar with Slichter's book because it was the text used in a graduate course taught by Conradi, but I do not recall if we had gone over the SEDOR section. After reading over the SEDOR experiment, it was clear that SEDOR would not work with magic-angle spinning because of the spatial averaging which occurs every rotor cycle; an experiment with a train of pulses applied synchronously with the sample rotation would be required. Indeed, my very first attempt at REDOR placed two π pulses per rotor cycle on the ^{15}N channel and a single refocusing π pulse on the ^{13}C observe channel.

A nice feature of Jake's 200 MHz spectrometer was that it had an oscilloscope that displayed the pulse sequence and each free induction decay (FID) in real time. The ^{13}C and ^{15}N rf pulses were diode detected via a capacitive rf pickup located in the triple-resonance probe and displayed on one channel of the oscilloscope. The other channel of the oscilloscope sampled the voltage of the FID just prior to being digitized. During each scan the rf pulses were displayed along with the corresponding free induction decay. Since our test compounds were ^{13}C—^{15}N labeled amino acids, the individual ^{13}C FIDs were easily observed in real time on the scope.

The first REDOR experiment was performed in Spring of 1987 at Monsanto's Creve Coeur research facility on a ^{13}C, ^{15}N labeled asparagine sample. It was programmed on the Nicolet-based spectrometer to alternate scans between no dipolar dephasing and dipolar dephasing. I still remember the excitement of the very first time the experiment was run. Alternating scans on one channel of the oscilloscope showed ^{15}N pulses blinking between off and on, and the other channel showed corresponding FID traces blinking between a big ^{13}C signal and virtually no ^{13}C signal. It worked and was fantastic to behold!

Fig. 1 shows two partial pages from May 14, 1987 out of my stenographer's notebook of the REDOR experiment on labeled asparagine. The $\Delta S/S_0$ values were being compared to DCP. Jake la-

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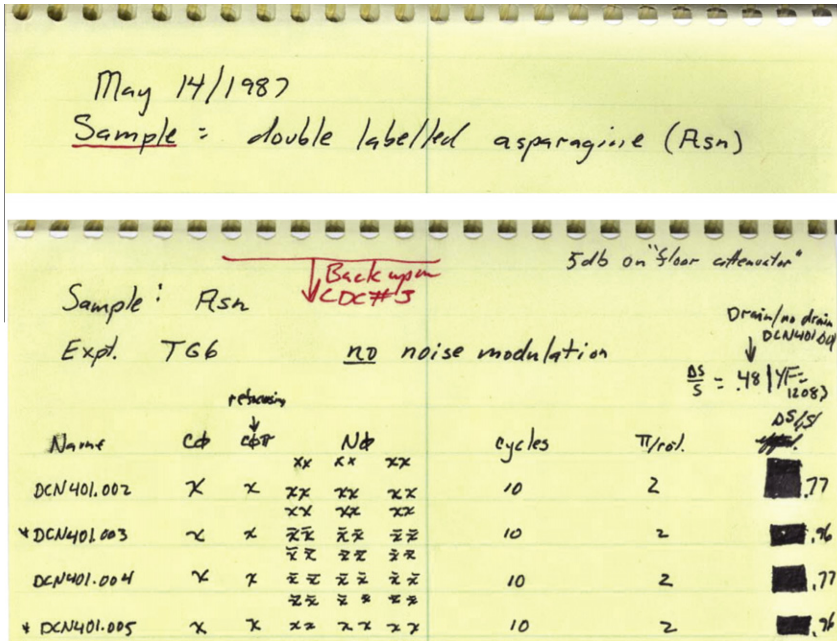

Fig. 1. Shown are parts of two consecutive pages out of my 6″ by 8 1/2″ notebook used in the first REDOR experiments. Page 1 of the notebook (top) shows the May 14, 1987 date that the experiments started. The following page (bottom) shows some of the first files and experiments that were done on that day. The Cϕ column is the ^{13}C cross-polarization phase, and the Cϕπ column is the phase of the single ^{13}C refocusing π pulse. The number of rotor cycles was 10, and each rotor cycle had two ^{15}N π pulses per rotor cycle. The Nϕ column shows the phasing pattern of the ^{15}N π pulses. For each file, the upper row of ^{15}N phases represents the phases of the ^{15}N π pulses before the ^{13}C π pulse and the lower row represents the phases of the ^{15}N π pulses after the ^{13}C π pulse. Effects of pulse phasing on REDOR were already evident. For example, files DCN401.002 and DCN401.004 were experiments with all ^{15}N π pulses being the same phase throughout the experiment (either all *x* or all −*x*). Files DCN401.003 and DCN401.005 were experiments with all ^{15}N π pulses having different phases before and after the ^{13}C π pulse. The $\Delta S/S_0$ values depended on the phasing of the ^{15}N π pulses.

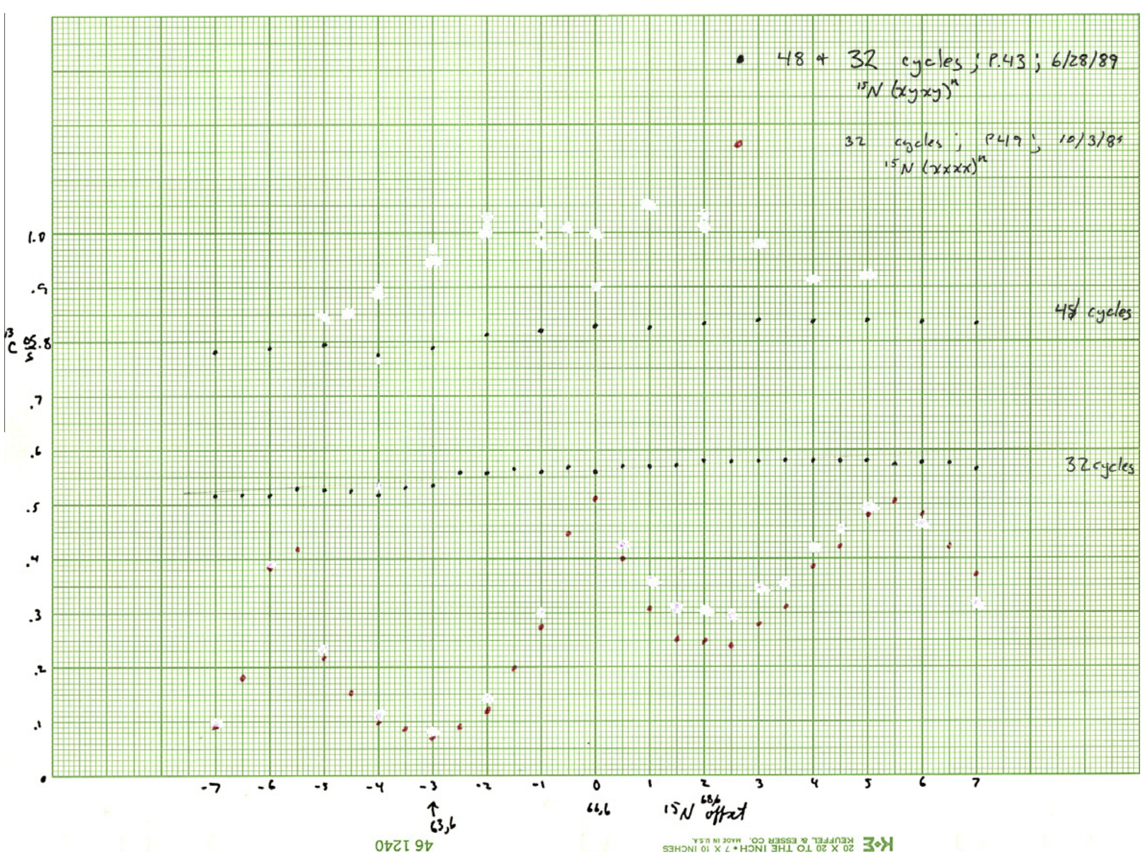

Fig. 2. The original plot showing the REDOR resonance offset dependence for all ^{15}N π pulses having the same phase (red) and for *xy*-4 phasing of the pulses. The *xy*-4 phasing restored the *z*-component of ^{15}N magnetization after each cycle and basically kept the ^{15}N magnetization from becoming scrambled. The 6/28/89 date should have read 9/28/89. The whiteouts show that the graph paper was previously used. This plot became Fig. 1 in Ref. [8].

ter commented that I would need a larger notebook. We quickly realized that resonance offset of the ^{15}N pulses was a substantial problem for REDOR, and early attempts to eliminate the problem were not successful. Later, I was having difficulty in refocusing transverse magnetization while developing the extended chemical shift modulation experiment (XCS) [6]. The XCS experiment used a train of π pulses on the observed channel to generate a spinning sideband pattern for the CSA that appeared to be taken at very slow spinning speeds even though fast spinning speeds were used. I soon discovered that if the π pulse train was phased in an *xyxyxy* fashion (named later as *xy*-4) then a remarkable improvement in transverse magnetization occurred and the XCS experiment was much improved. Starting with *xy*-4, Mark and I worked on this phasing scheme and developed *xy*-8 and *xy*-16 [7]. We did this by using vector models and came to the realization that all three components of magnetization were being refocused by these phase cycles. The restoration of the *z*-component of magnetization is particularly important because of the I_zS_z term in the dipolar Hamiltonian. The imperfections in restoring the *z*-component of the ^{15}N magnetization in the original REDOR experiment were causing the resonance offset problem. Simply phasing the REDOR π pulses according to *xy*-4 (originally, and subsequently with *xy*-8) eliminated the offset problem, and REDOR became very reliable and quantitative [8]. Fig. 2 shows the original plot on standard graph paper comparing REDOR with *xy*-4 phasing and all pulses being the same phase. The improvement using *xy*-4 was remarkable. The positions of the valleys in the $\Delta S/S$ values that occur for *xxxxxx* phasing were easily explained with our vector picture using the frequency offset and timing between adjacent ^{15}N pulses.

My time spent in the Schaefer lab was great! During the years that I was there, it was hard to leave the lab at night and I could not wait to get back in the lab in the morning because it was such an exciting time. Jake established a wonderful group of people. Most of his graduate students worked on REDOR related projects. The ones that I overlapped with were Susan Holl, Patricia Lani Lee, Allyson Christensen and Yong Pan. Mobae Afeworki was another graduate student in the group working on DNP projects. I was also fortunate to overlap with other postdoctoral students, including Drs. Vincent Bork, Mark Poliks and Asher Schmidt. I thoroughly enjoyed being with this group of people and discussing NMR. I learned a lot about NMR hardware during that time from the very talented Bob McKay. Best of all, I thoroughly enjoyed working with Jake. He had a lab where we could try new things and, more importantly, provided us with remarkable insight.

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