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NMR APPLICATIONS NOTE NUMBER 5

Pulsed Homonuclear Decoupling Techniques

Introduction

It is often suggested that problems involving homonuclear decoupling and other double irradiation techniques cannot be solved adequately using pulsed-Fourier methods. This, of course, is not entirely true, since pulsed decoupling techniques have been suggested by Anderson,[1] Hewitt,[2] and others[3-5] and are, in fact, part of several commercial spectrometer systems.

In one commercial method, the time between data points is utilized to turn on and off a low power decoupling frequency which is adjusted to irradiate some multiplet which is to be decoupled from another. This method has been shown to be of great utility when the Nicolet 1080 data system is used, since a signal related to the sampling frequency is readily available for gating the decoupling frequency.

However, this method does restrict one to a particular decoupling frequency for each spectral width to be observed. In nearly all cases, the harmonics of this gating frequency lie far outside the spectral window and cause no problems, but for maximum versatility we decided to design a method of decoupling which would not be dependent on the sampling frequency.

Experimental Method

In this method, the NIC-293 General Purpose Controller is used to generate the rf pulses, the decoupling pulses and the receiver gating. This is accomplished by using one pair of timers as the 90° pulse and recovery time, a second pair as the decoupling pulse and delay, and two more to gate the receiver so that these pulses do not reach the data system. This is accomplished as shown in Figure 1.

As can be seen from the diagram, the timer pair P1 and D1 represent the rf pulse and its associated delay. In this case, the pulse is 2 usec and the repetition rate 5 sec. The second timer pair P2 and D2 represent the decoupling pulse and its associated delay. These are set to 80 usec and 100 usec respectively. The instrument used was a Bruker HX-90E with all pulses controlled by the NIC-293 Controller. The actual program was FT-Nmr 1972 with an NUS overlay tape allowing control of the pulses. Each pair of timers is so configured that it can be started by raising and lowering LEV5 and stopped by holding LEV5 high.

Once the timers are running, the end of D1 retriggers P1 and the end of D2 retriggers P2. At the same time these timers trigger the pulses, they also trigger timers P3 or D3 respectively, either of which will produce a 100 usec pulse. These pulses are used to gate the receiver at the IF frequency of the Bruker spectrometer. Thus, whenever the rf pulse or the decoupling pulse is turned on, the receiver is gated for 100 usec. These gatings may or may not occur at times associated with the sampling of data points on the FID, but the times can easily be adjusted to minimize this interaction. In general, occasional gating does not harm the information in the FID, since it only truncates parts of some data points.

Results and Discussion

Figure 2 shows the undecoupled nmr spectrum of ethylbenzene (50% v/v $CDCl_3$) obtained from four scans of 8K time domain points. This expanded plot represents the frequency range from 51.27 to 289.55 Hz, where TMS has been set to zero Hz. The sample was off-the-shelf and contained an impurity as marked.

Figure 3 shows the same spectral region with irradiation of the triplet as marked in Figure 2. The collapse of the quartet is nearly perfect and represents only minimal experimentation to find the exact irradiation frequency.

It has been suggested that the determination of the exact decoupling frequency would be much harder in FT-Nmr because there is so little to observe in the free induction decay. We have not found this to be the case, and in fact feel that pulsed homonuclear decoupling offers at least one distinct advantage. This is that the decoupling frequency can be determined with high precision digitally by printing out the peaks in the undecoupled spectrum. In fact, if the left most frequency point in the spectrum is assigned the value of the carrier frequency position using the cursor, then the printout will give the absolute setting of the decoupling channel. Alternatively, the cursor can then be set to the middle of the triplet, and the frequency read off directly. In actual fact, the negative of the carrier frequency is used because of the sign conventions of the printout. The frequency of the center line of the triplet was used as an estimate of the proper decoupling frequency and in a few small increments total collapse of the quartet was achieved.

In summary, the techniques of homonuclear pulsed decoupling have been found to be extremely easy to achieve using the Nicolet 1080 and 293 with the Bruker HX-90E spectrometer. The direct digital control of pulse widths and delays coupled with the versatility of the pulse sequence, allows easy achievement of most pulse experiments. In fact, the same techniques can also be used for related techniques such as solvent suppression and spin tickling.

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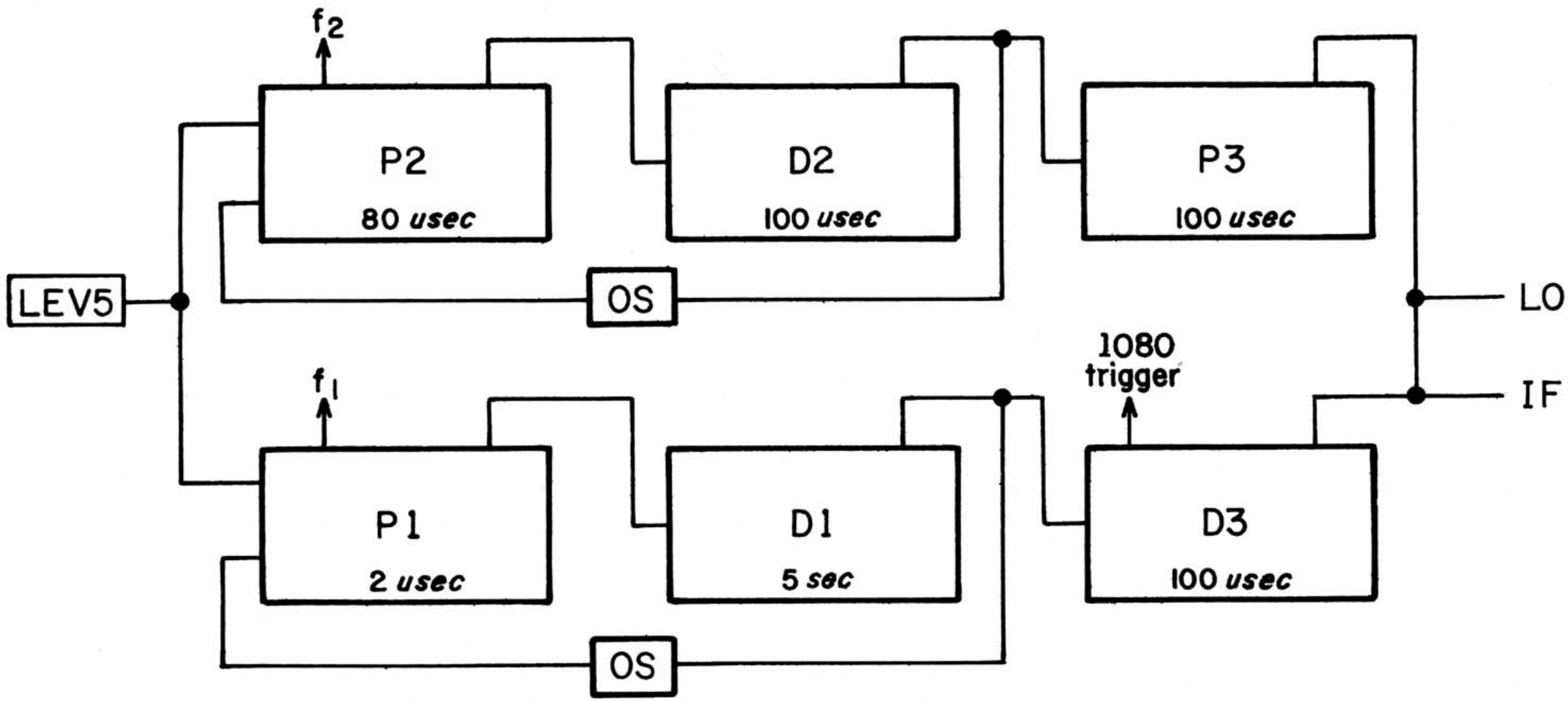
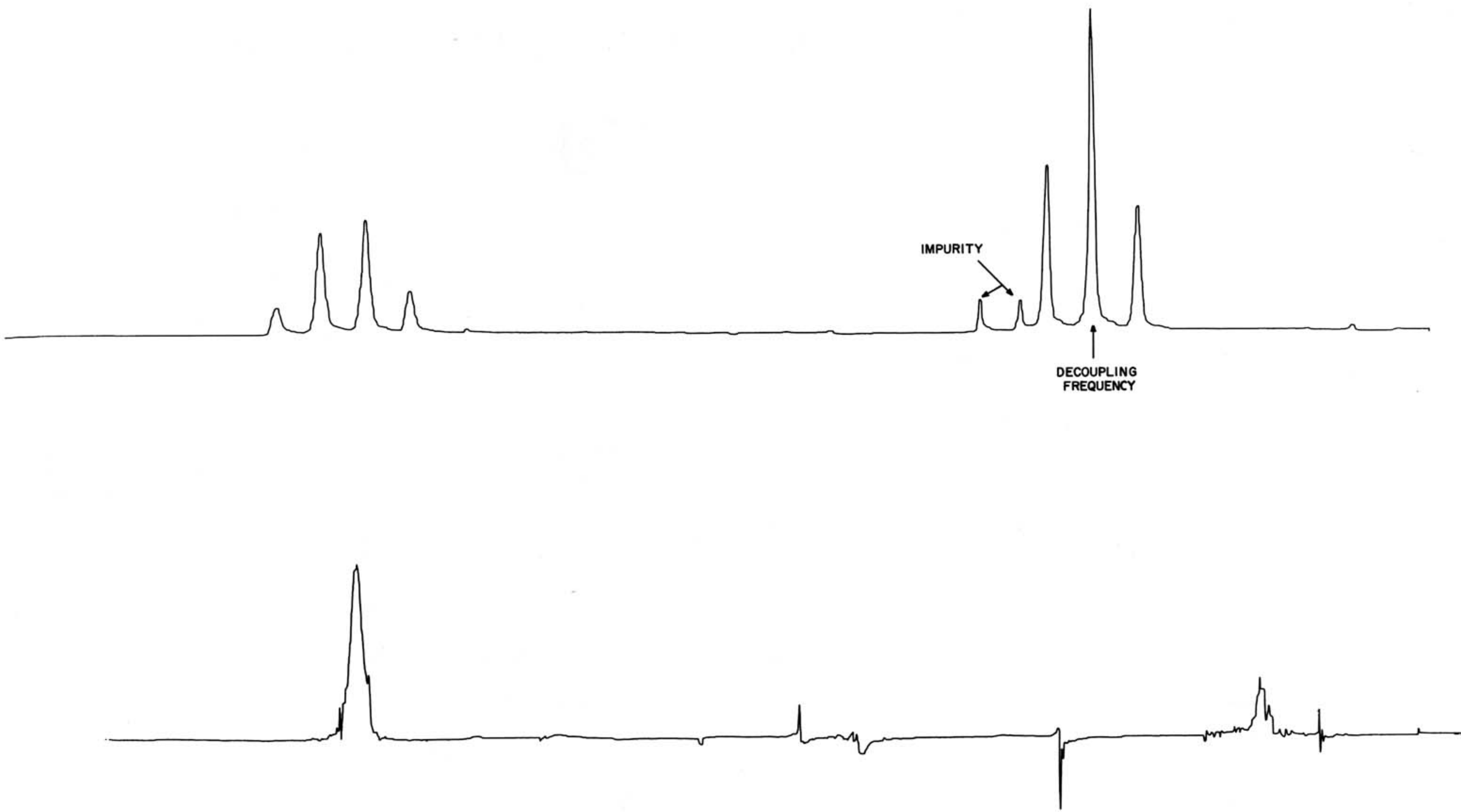


NIC-293 PATCH PANEL DIAGRAM FOR HNFT EXPERIMENT


IMPURITY
DECOUPLING FREQUENCY

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