TABLE OF CONTENTS

I. INTRODUCTION TO FOURIER TRANSFORM NMR

A. Introduction

In the familiar frequency swept nmr experiment the sample is irradiated with a slowly changing radio frequency and the absorption of energy observed. The resulting continuous wave (cw) nmr spectrum is simply a plot of this absorption vs. frequency. This is known as a spectrum in the frequency domain.

The cw nmr method is quite adequate for the study of samples of moderate concentration when the nucleus of interest has a high natural abundance and sensitivity. On the other hand, if a relatively weak signal can be expected because of low concentration or abundance, a single sweep through the spectrum will not produce enough information for detailed analysis. In this case, the signal can be enhanced by signal averaging techniques.

Signal averaging involves the sampling of the spectrum at regular intervals and the conversion of each sample into a binary number which is then stored in the memory of a digital computer. During each successive sweep, data points are summed with those observed during previous sweeps.

Assuming that each sweep starts at the same frequency and covers the same spectral region, the signal will add coherently with each sweep. Meanwhile, any random noise associated with the weak signal will add at a rate roughly proportional to the square root of the number of sweeps. If N is the number of sweeps, then the signal to noise ratio obtained by signal averaging is given by

$$\frac{\text{signal enhancement}}{\text{noise enhancement}} = \frac{N}{\sqrt{N}} = \sqrt{N}$$

The total signal to noise is therefore a function of the square root of the number of sweeps.

Signal averaging of cw nmr spectra has been well described in the literature.[1] However, it suffers from the significant drawback that the time required to perform the experiment is extremely long. For instance, if each cw sweep requires 100 seconds, then to obtain a tenfold improvement in signal to noise, it is necessary to take 100 sweeps. This experiment occupies 10,000 seconds or 6.6 hours.

It would be more efficient if instead of irradiating at one frequency at a time, we could irradiate at all frequencies in the range of interest at once. We could imagine this experiment as taking place using a multichannel spectrometer.[2] This hypothetical spectrometer contains one rf oscillator for each data point to be recorded in the computer. Thus, if we had been recording 4000 data points in our cw signal averaging experiment, we would require 4000 rf oscillators, each irradiating at frequencies separated by 1/4000th of the frequency range of interest. Clearly the "sweep" could be completed in much less time, approaching 1/4000 the length of a cw sweep.

The above experiment is clearly a thought experiment, limited by instrumental costs and engineering impracticality. However, this signal averaging efficiency can be approached by the pulsed Fourier transform experiment described below.

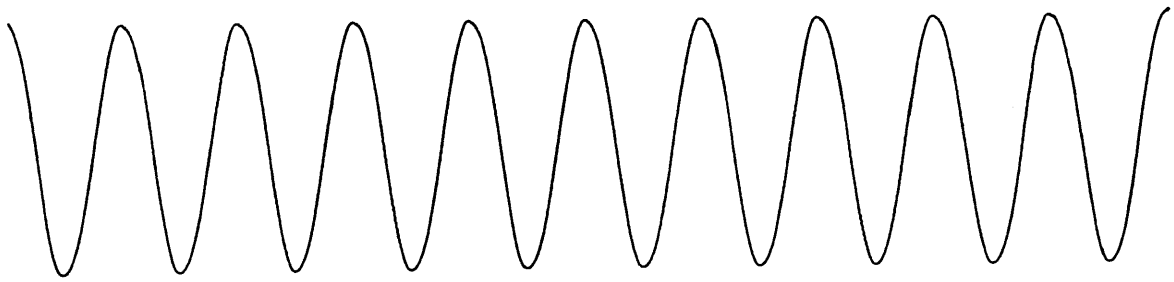
B. Pulsed Fourier Nmr

The theory of the pulsed Fourier experiment has been described by Ernst and Anderson.[3] In this experiment, a single short intense burst of rf energy is used to tip the magnetization of all the nuclei from the z-axis parallel to the magnetic field into the xy plane. There they precess and this magnetic precession induces a current in a receiver coil positioned in the xy plane.

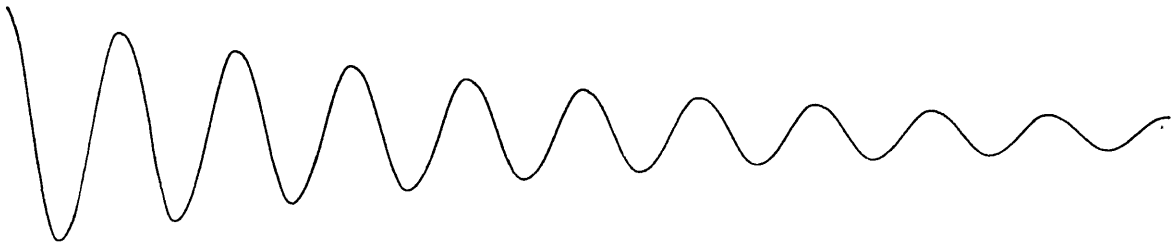
Since all the nuclei are precessing at their respective Larmour frequencies, they are inducing oscillations in the receiver coil proportional to their resonance frequencies. This differs from the cw nmr experiment in that the resonance frequencies of all these nuclei are observed at once. Clearly this is a close relative of the hypothetical multi-channel nmr spectrometer described above.

C. Time Domain Spectra

Let us now consider the nature of the signal observed in the above experiment. If a single nuclear species were observed in this way we would expect to induce a single sine wave in the receiver coil:

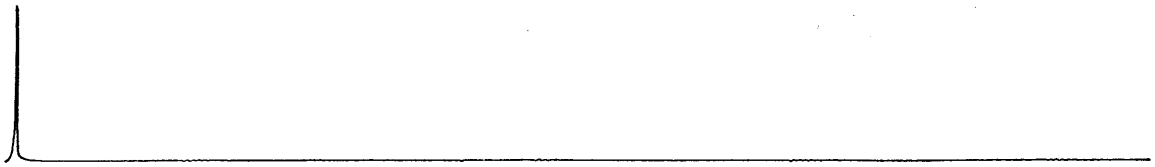


Since the magnetization decays from the xy plane back to the z-axis after the pulse is turned off, the form of this signal would be more like

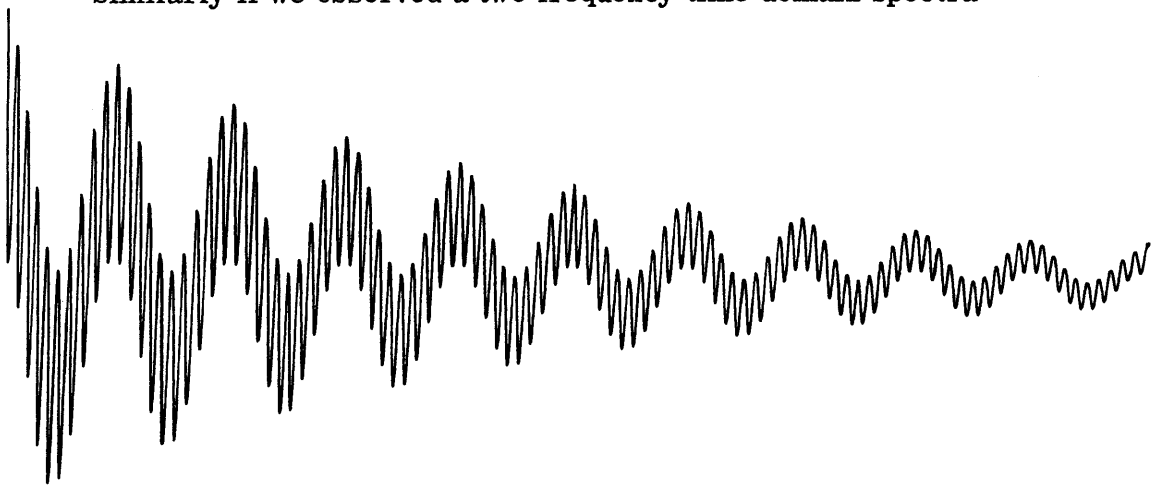


This damped sine wave is a plot of signal intensity vs. time and is thus called a time domain spectra. Since there is only one frequency observed here, we can easily measure it by simply measuring the distance between cycles of the sine wave.

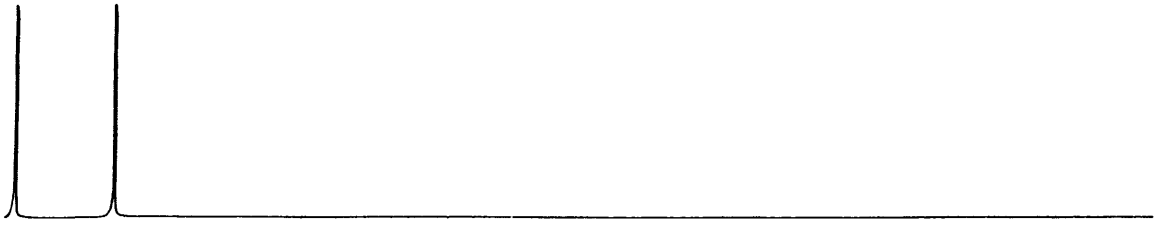
If we decided to make a plot of absorption versus frequency from this spectra we could do it by precessing the period of the sine wave, and plotting the one point frequency spectra.



Similarly if we observed a two frequency time domain spectra

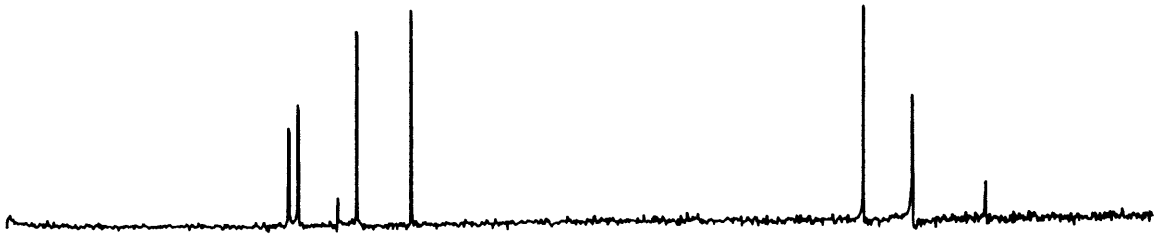


we could convert it to a frequency domain spectra in the same way:



This conversion which we have been doing by inspection is readily performed mathematically by a process known as Fourier transformation. Thus a complex array of frequencies observed in the time domain

is readily converted to the frequency domain by this calculation:

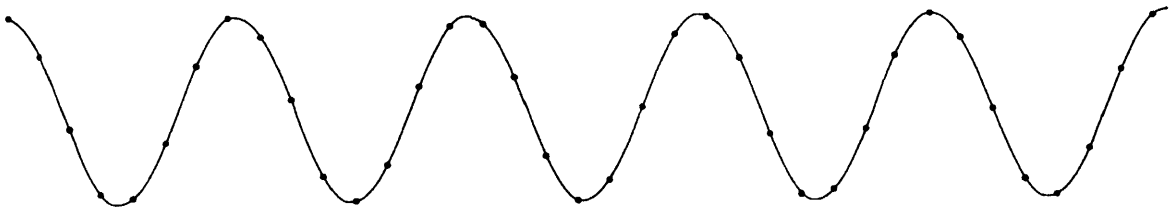


Obviously, this frequency domain spectrum is identical with that obtained by conventional cw techniques.

D. Sampling

Since data is acquired in the time domain during the FT nmr experiment, the rate of data acquisition, or sampling frequency, is directly related to frequency range which can be observed by the computer. Data are stored in memory as discrete points which are separated in time by a fixed sampling interval. This sampling interval or dwell time determines the frequency range which can be stored in the computer.

Let us consider first a low frequency sine wave:

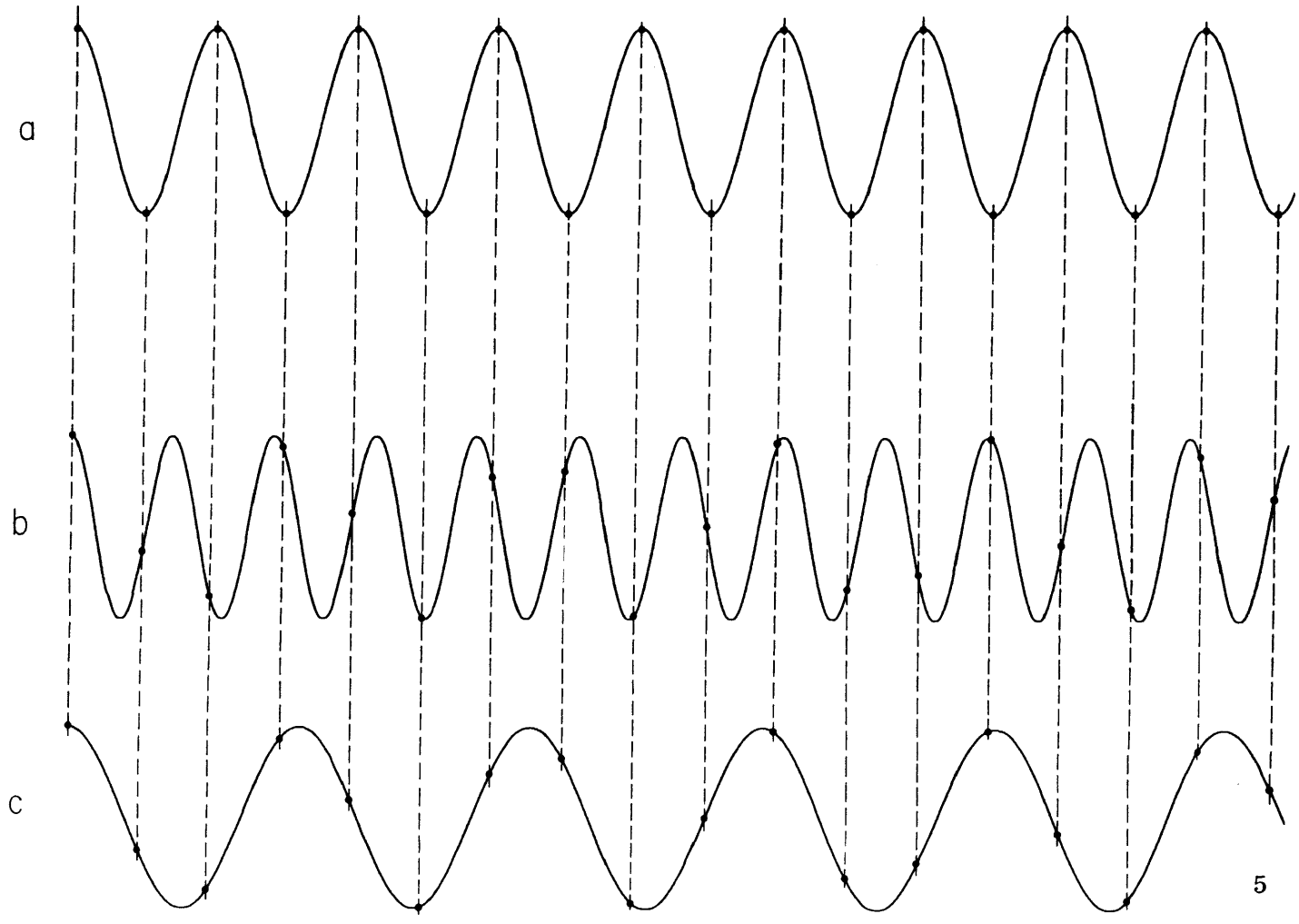


If it is sampled at the rate shown by the dots, there is clearly more than enough information to define this sine wave to any computer program.

At higher frequencies, the number of data points per cycle decreases until at a frequency equal to exactly half the sampling frequency there are just enough points to define each cycle of the sine wave. This is shown in Figure 1a. Clearly, it takes 2 points to define a sine wave. Thus if the sampling frequency is S, the highest frequency that can be accurately represented is S/2. This frequency is called the Nyquist[4] frequency.

In the event that the sampling rate is insufficient to define a sine wave, the data points taken will seem to the computer to define a lower frequency. Figure 1b shows a frequency of $S/2 + \triangle F$, where S/2 is one half the sampling frequency and $\triangle F$ is an arbitrary increment.

Figure 1c shows a frequency of $S/2 - \triangle F$, again sampled at the Nyquist frequency S/2. The position of the dots on the frequency $S/2 + \triangle F$ and those on $S/2 - \triangle F$ are identical when both are sampled at the rate S. Thus, a frequency which is greater than the Nyquist frequency by $\triangle F$ hz will appear exactly the same as a frequency which is $\triangle F$ less than S/2. In other words, frequencies higher than the Nyquist frequency will appear in the signal averaged spectrum but "folded back" as if they are lower frequencies. This fold-back phenomenon is also referred to as aliasing.



For pulsed Fourier data acquisition, the experimenter sets the pulse irradiation frequency to be near one end of the spectral region of interest. It does not matter which end, except for polarity, since the frequency range is S/2 on either side of the pulsing frequency. For this reason, one cannot generally pulse at a frequency in the middle of a group of nmr lines since they will fold back on each other to produce a virtually uninterpretable spectrum.

The spectroscopist generally sets the sampling rate to cover the center range where nmr lines are expected to occur, to avoid foldback. He then sets the input filter to have a cut-off frequency similar to the Nyquist frequency. It is not possible to acquire data over a smaller range than the entire densely populated frequency range, and use the input filter to filter out other strong nearby frequencies, since no existing filter network has that sharp a cut-off point.

The 1080 utilizes four-pole Butterworth filters, having an extremely linear frequency response. The characteristics of these filters is such that the level of signal passed is decreased to 0.707 (or 3 db) at the specified cut-off frequency. (The 3 db point is by definition the cut-off frequency of a filter.) For each doubling of frequency beyond the cut-off frequency, the level of signal which is passed decreases to .076 of that at half that frequency.

For example, if the filter is set to a 5000 Hz bandpass, and the signal level is one volt, the filter will pass 1 volt at low frequencies, and at 5000 Hz, it will pass 0.707 volts. At 10,000 Hz, however, the filter will pass 0.076 x 0.707 or .053 volts. At each successive doubling of frequency, the level of signal passed will be 0.076 of what it was at half that frequency.

II. THE NICOLET FOURIER TRANSFORM NMR PROGRAM

The Nicolet Fourier Transform Nmr Program is a sophisticated collection of easily executed routines for pulsed-Fourier nmr data handling on the 1080 Data System. It contains the fast Fourier transform, phase correction, several window functions, peak printout and display and plotting routines. Once loaded it should reside permanently in program memory unless another program is specifically loaded.

A. Loading

The Nicolet FT-Nmr program consists of a large number of subroutines and a sine look-up table used in the FT calculations. Rather than providing the sine look-up table on the paper tape, a short routine has been provided which calculates the sine look-up table during tape loading. This calculation requires about 8 seconds, while reading in the look-up table would require over 150 seconds by a low speed reader. Thus, the loading time has been considerably shortened by this procedure.

Since the FT-Nmr tape actually interrupts loading to perform the sine look-up table calculation, it is absolutely essential that the Binary Loader which is used be that contained in Nico-Loadeon (NIC-80/S-7115-B). Use of earlier Binary Loaders will result in destruction of the Loader and will prevent the tape from loading further. All new Nicolet 1080's contain this loader, and all 1080 owners have been provided with copies of this loader. If you have any doubts regarding which loader is present, load the Nico-Loadeon program as described in the Loading Programs or the Programming section of the 1080 manual.

To load the FT-Nmr program, proceed exactly as with the loading of other binary tapes:

(1) Be certain that both the wired and stored processors are stopped by pressing Stored Program Stop and Wired Program Stop.
(2) Set the switch register to 7777_8. In this position, the right hand 12 switches are up and the left hand 8 down.
(3) Set the low speed reader switch to Free.
(4) Place the tape, printed side up, in the Teletype reader.
(5) Depress Load PC and press Execute.
(6) Depress Continue and press Execute.
(7) Turn the low speed reader switch to Start.

The tape should read in. If the loader halts without reading any tape, the loader program has been destroyed and must be reloaded. When the tape has read in about 1/4 of the way, the tape will stop and the computer will calculate the sine look-up table. DO NOT remove the tape or turn off the reader or computer at this point. Read-in will automatically continue after about 8 seconds. When loading is complete, the computer will halt. To start the program, press the Stored Program Start button. The Teletype will respond with a carriage return-line feed and print a dot. The FT-nmr program is then ready for commands.

B. Command Format

All commands are two characters in length. Commands should be entered only following the dot. Typing the first character causes the screen to go dark and the program to wait for a second character. Typing the second command character causes that command to be executed at once. Always wait for the Teletype to print the first character of the command before typing the second. To abort the command without execution, type an illegal second character such as a RUBOUT. The program will respond to any illegal command or a Rubout by typing a question mark, followed by a carriage return, line feed and a new dot. By convention, all commands operate only on the displayed portion of the spectrum. When the displayed section is not that upon which the last Fourier transform was performed, an error message is given.

Following is a complete list of the FT-Nmr program commands. They are described in detail in the succeeding chapters.

COMMANDS FOR NICOLET FOURIER TRANSFORM NMR PROGRAM

Measure

SW - Set Spectral Width
DW - Set Dwell Time
ZE - Zero displayed memory section
GO - Jump to Measure mode and take N sweeps

Window Functions

TC - Enter Time Constant for exponential multiplication
EM - Exponential Multiplication
T1 - Enter first Trapezoidal address
T2 - Enter second Trapezoidal address
TR - Multiply FID by fraction between ∅ and 1 for addresses between ∅ and T1 and a fraction between 1.∅ and ∅ for addresses between T2 and the last data point

Transform

BC - Baseline Correction
FT - Fourier Transform displayed data

Phase Correction

CC - Calculate Constants to be used by AP
AP - Calculate Constants and perform semi-automatic phase correction
PA - Enter zero order phase correction constant
PB - Enter first order phase correction constant
PC - Perform manual phase correction using PA and PB
TP - Print out Total Phase correction performed since last FT

Peak Printout

SF - Enter Spectrometer Freq. in MHz
OF - Enter sweep Offset
MI - Enter Minimum Integral to be printed out
PP - Print out all peaks in displayed region

Region Selection

F1 - Enter one frequency limit
F2 - Enter second frequency limit
IR - Intensify specified region
  X - expand to full display
  C - recontract display
  P - Plot out intensified region
  L - List peaks in that region
  Return - return to normal display

Cursor Display

CU - Display cursor at entered address, enter number and follow with Return
  L - left one point
  R - right one point
  ML - move left
  MR - move right
  S - stop moving
  F1 - enter F1 for IR
  F2 - enter F2 for IR
  A - assign a frequency to that address
  Return - exit to normal display

Data Manipulation

AC - Add constant. Spectrum position controlled by DC level pot. Set input to GND. Exit with Return.
ID - Integrate Display. Baseline level controlled with DC level pot.
  P - Plot Integral
  Return - return to normal display
MC - Magnitude Calculation
DC - Enter Data Transfer multiplier constant
DT - Multiply data region selected by Measure by DC and add to region selected by Readout
MV - Move data selected by Measure into region selected by Readout

Output

PL - Plot data. Press Plotter Autoslew or Realtime, and type Return
  F - to plot faster
  S - to plot slower
  Return - return to display when done
PU - Punch out data in displayed region

Automation

LI - Link together up to 15 commands, use two Returns to return to display
AU - Execute linked list

III. SETTING UP THE DATA SYSTEM FOR DATA ACQUISITION

A. Introduction

The 1080 data system consists of two processors operating on the same memory: a wired processor for data acquisition and a stored program processor for calculation and data manipulation. The stored processor can be used to control the wired processor as a sort of hardwired subroutine, or the wired processor can be used entirely independently of the programmable capabilities of the 1080. In the following discussion, it is assumed that the processor has been installed with an operating pulsed-Fourier nmr spectrometer. For installation instructions, consult the Main Frame section of the manual.

B. Start-Up

To begin operations with the 1080, assuming that the FT program is loaded, turn on the power by turning the key to the right. If the scope has been turned off, turn it on as well. Turn the Teletype switch to LINE and press Stored Program Start on the 1080 console. The Teletype should respond with a carriage return-line feed and print a dot. The scope should be displaying whatever section of memory is currently selected on the Readout Allocation pushbuttons. The readout allocation buttons allow viewing of any section of memory which actually exists. If a section is selected which does not exist, the Illegal Memory lamp will flash and a straight line indicating all zeroes will be displayed.

The Readout wired program can also be used to view memory by stopping the stored processor and pressing the Readout button. The exact same display will be available as during stored operation. The main advantage of the wired Readout program is that it is somewhat faster than the stored program and will display larger areas of memory without perceptible flicker. In the most common mode of operation, the CRT Readout button along the top of the 1080 should be depressed during wired program display. This causes each point of the display to be displayed for about 20 usec. Depressing the CRT Realtime button will cause each point to be displayed for a time selected by the Dwell time switches of the sweep plug-in. The rate can be increased to about 11 usec per point without any smearing. This is desirable only when examining 16K or 32K displays.

The Program Protect button protects the program memory stack from being destroyed by the wired Measure program and from being viewed by the Readout program. The program area is considered by the wired processor to be the next 4K after the last existing memory stack. It can be accessed for viewing or signal averaging when the Program Protect button is not depressed. This is generally not a good idea, however, since it could destroy the stored FT-Nmr program.

The Vertical display scale switch controls the vertical magnitude of the displayed data. It is simply a switch for multiplying or dividing the display by 2, and operates under either hardware or software (stored program) display. The Horizontal display scale switch controls the size of the display (in thousands of data points) which is displayed full scale across the scope. In general, this size should be the same as the number of data points selected by the Readout Memory Size buttons.

If the Horizontal Display Scale Size is larger than the selected Readout Size, the display will fill only a fraction of the scope; if the Horizontal Size is smaller than the selected Readout Size, the display will overlap itself on the scope. This feature can be useful for comparing spectra in adjacent sections of memory by overlapping them, but it may be confusing to the novice if it is not expected.

C. Clearing Memory - ZE

To begin signal averaging, it is necessary to set the memory segment to zero where averaging is to take place. This is not done automatically, since it could destroy valuable data if averaging is commenced by accident. There are two ways of zeroing data memory:

(1) During Readout mode, while the spectrum is displayed, depressing both the Erase and Enable buttons will zero the displayed memory segment.

(2) During stored program operation, typing the command ZE will zero the displayed memory segment.

D. Entry of Constants

Throughout the Nicolet 1080 FT-Nmr program, the convention of constant entry is as follows:

(a) The command is given to enter a constant.
(b) The program types out an equals sign followed by the current value of the constant.
(c) The value is left unchanged if the user types a carriage return.
(d) The value is changed if and only if a new value is typed followed by a carriage return.
(e) A typing error can be corrected by striking a Rubout. The program will echo with a backslash (\) and allow re-entry of the entire constant.

Constants which are generally considered integers are printed out as integers. Those which may have a fractional value are printed out as floating point numbers in scientific notation. In this notation scheme, the number is reduced to a value between 1.0 and 9.999 and the exponent adjusted accordingly. Since the Teletype has no superscript capabilities, it is conventional to represent the exponent as an integer following the character E. For instance, the value 5000 is represented as

$$5.000E3, \text{ meaning } 5.000 \times 10^3.$$

Constants may be entered in any desired format. Thus, the program will accept

5000	5.000E3	
+5000	+50.00E2	
+5000.	0.5000E4	
5000.0	50000E-1	as equivalent numbers.

The only restrictions on input are that it contain less than eleven significant figures. If more than eleven figures are typed the program will type a backslash and await fresh input. It is also required that there be no spaces embedded in the number, between the sign and the number, between the number and the E or between the E and the exponent.

E. Selection of Data Acquisition Rate - SW and DW

In the pulsed-Fourier nmr experiment, the rate of data acquisition determines the frequency range or spectral width acquired by the data system. To acquire data in a 5000 Hz range of chemical shifts, the chemist adjusts the pulse frequency to sit at one end of the range of interest and the sampling frequency to allow acquisition of 5000 Hz of data beyond that irradiation frequency. This sampling frequency would be 10,000 Hz.

Since it is more convenient for chemist to think in terms of sweep width than in terms of dwell time or sampling frequency, the FT-Nmr program contains a command for performing this conversion. To enter the spectral width, type SW. The program will type out the last entered value for the sweep width and allow its modification. Before typing Return, select the size of the memory segment into which the transient is to be averaged using the Measure Memory Size button. When Return is typed, the program will type back the correct setting for the dwell time thumbwheel switches such that this sweep width is observed. The program also calculates the number of Hertz per data point that will appear in the transformed spectrum, using the Measure Size button. Since roundoff errors may occur because of too few significant figures at high sampling frequencies, the program will also indicate the exact sweep width that dwell time will produce. For example, to enter a sweep width of 5000 Hz, the following operation is performed, assuming that the Stored Program is already running. The user enters the underlined characters.

```
.SW=0.000E-1 5000 (Measure Size is selected, and Return typed)
SET DW = 100 ×     1 USEC
EXACT SW=5.000E3
```

The user then sets the dwell time digi-switches to 0100 and the multiplier to 1. At this time it is also advisable to set the Input Filter of the digitizer to the same cutoff frequency as the sweep width.

The Dwell Time is also automatically calculated and stored for examination by the user. However, the actual setting of the clock time must be done by the user, since the program cannot tell whether the SW-80 sweep control is in place or whether some other plug-in has been inserted instead.

The user can enter the dwell time directly in a similar manner to that which the sweep width was entered. This has no value to the data acquisition process, but is used so that the program can calculate the sweep width of the displayed region for later use by the peak printout routine. The command DW allows examination of the current remembered dwell time in microseconds and its modification if desired. The program does not respond with a sweep width but does calculate the sweep width corresponding to that dwell time and store it internally. It may be examined by typing SW.

Because of the versatility of the 1080 as a signal averager as well as a stored program computer, the user must specifically tell the program the sweep width or dwell time he is going to use in an experiment. This is true because the stored processor has no way of knowing what operation the wired processor has performed independently. At the time of the entry of this constant, the Measure Memory Size button must be set to the size of the region where data is to be stored. If it is changed after the SW or DW are entered, the number of Hz per data point will be incorrectly calculated and this error will be reflected when the peaks are printed out by the computer. It will have no effect on data acquisition.

F. Beginning Data Acquisition - GO

The actual beginning of signal averaging may be initiated by one of two methods. The first is to depress Stored Program Stop, set the Autostop counter to the desired number of sweeps and depress Measure. Signal averaging will begin upon receipt of the first trigger and continue until the number of sweeps set on the Autostop counter is completed, or until Wired Program Stop is depressed. If Wired Program Stop is depressed, data acquisition will terminate at the end of the current sweep.

The second method of initiating signal averaging is using the GO command from the FT program. This command automatically halts the stored processor and initiates the Measure program. The sweep counter is zeroed and the number of sweeps on the Autostop counter are performed. Control is then returned to the Stored Program. If Wired Program Stop is depressed during this mode, the data acquisition will halt at the end of the current sweep and the stored program will restart.

On early 1080's having digitizer plug-in serial numbers below 52, the GO command will only halt the stored processor. Data acquisition will not begin until the Measure button is depressed. It is possible to make a minor hardware modification to allow the Automatic Measure command to work. This is desirable for complete experiment automation. Consult the factory for details.

It should be noted that both the ZE command and the Enable-Erase combination erase the section of memory selected by the Readout Memory switches, and that these switches contol only what section of memory is displayed. Data is added by the Measure program into that section of memory selected by the Measure Allocation switches. It is generally good practice to see that the Readout and Measure buttons select the same area of memory before beginning data acquisition.

G. Hardwired Display

During data acquisition, the contents of memory may be examined in any of three modes: View Input, View Memory and Continuous Display. These are controlled by the corresponding buttons on the 1080. The View Input mode displays only the input signal as it enters the digitizer, and at the rate it enters the digitizer. This is valuable during setup to assure the user that a signal is indeed entering the digitizer.

Once the user is satisfied with the signal, he may switch to Continuous Display, which shows the entire memory block selected by the Readout Allocation switches irrespective of the sampling rate. This unique feature is possible because the wired program operates in an "interrupt" mode, allowing flicker-free display at any sampling speed. Since the Readout and Measure switches are entirely independent, it is quite possible to view one section of memory while signal averaging into another.

The View Memory mode allows the user to examine memory at the rate data is being stored. The user will see a dot moving across the scope which represents the sum of the current sweep with the contents of memory. In all three modes, the Vertical and Horizontal Display Scale switches are operative.

H. Signal Conditioning

Before beginning a long signal averaging run, it is desirable to condition the input signal as much as possible. Set the Display mode to View Input and examine the input signal while sweeping. The signal should be centered on the scope, indicating no DC bias to the signal. If it is not, the DC level control on the digitizer should be adjusted before continuing. Otherwise, the DC bias will fill the memory word up quite rapidly, allowing only short-term averaging.

The delay time is most easily set while viewing the input signal as well. The principal reason for a delay is to prevent any pulse feed-through into the free induction decay signal. The delay is generally on the order of 0.5 to 2.0 times the dwell time, depending on the spectrometer. Pulse feed-through can easily be detected by viewing the input signal and looking for clipping at the beginning of the decay. Adjust the delay time by rotating the thumbwheel switches to increase the delay until this clipping disappears.

If the clipping appears to persist through any significant portion of the free induction decay, adjust either the signal preamplifiers in the spectrometer or the Volts Full Scale switch to cut the signal down to size. When the digitizer is set in the 9 bit position and the Vertical Display scale is set to 256, the signal should just fill one scope division on either side of zero for the signal to utilize the digitizer's full resolution. If the signal is significantly smaller than this, the digitizer is not being used most efficiently, and the Volts Full Scale switch or the spectrometer amplifier settings should be modified. When all parameters have been optimized, halt data acquisition, erase memory, and begin signal averaging again.

I. Digitizer Resolution

The 1080 digitizer provides hardware controlled switch selectable resolution for maximum signal averaging versatility. This feature is most useful when a very weak signal is being averaged. There is no reason to signal average with more precision than the signal to noise ratio, since this will simply fill up the memory word with noise more rapidly than necessary. Thus, when a very low signal to noise ratio is present, it is desirable to use a smaller digitizer resolution, so that averaging can proceed longer without overfilling the memory words.

J. Systematic Noise Reduction

All digitizers produce some systematic noise as part of the conversion process. This noise is coherent from sweep to sweep and will add together to fill up memory just as a DC level would. This systematic noise becomes apparent only in very long experiments of perhaps 100,000 sweeps or more, but in such experiments, it is desirable to reduce it as much as possible.

The 1080 Systematic Noise Reduction feature allows the reduction of this coherent noise by inverting the signal input to the digitizer on alternate sweeps and then alternately adding or subtracting the result from memory. Thus, on one sweep the signal is converted as is and added to memory, and on the following sweep, it is inverted (negated) before conversion and then subtracted from memory. These operations produce the same amount of signal averaging as if the inversion and subtraction process were not performed, but with the important difference that any noise produced within the digitizer is subtracted out on alternate sweeps.

In order to use this systematic noise reduction feature, it is necessary that the pulse repetition rate be adjusted so that there are at least two milliseconds of delay between the end of one sweep and the beginning of data acquisition for the next sweep. This is necessary to allow for the switching time of relays within the digitizer.

K. Long Term Averaging

Before leaving the system for long term averaging, turn down the scope intensity to avoid burning a dot in the scope, and turn off the Teletype to decrease mechanical wear. THE 1080 POWER KEY-SWITCH SHOULD NEVER BE TURNED OFF UNLESS BOTH THE WIRED AND STORED PROCESSORS ARE STOPPED. Failure to observe this warning may cause the destruction of some memory locations.

IV. FOURIER TRANSFORMATION AND WINDOW FUNCTIONS

A. Baseline Correction - BC

The signal averaged free induction decay may contain a small residual DC bias that prevents the average value of the data points from being zero. If this is the case, a huge spike is produced near zero frequency which has no physical meaning. Hence, it is almost always advisable to perform baseline correction before transformation. The command BC takes the sum of all displayed data points, divided by the number of points and subtracts this average value from all points, so that the average value is zero. This command is called automatically if either the TR or EM commands are used. BC is required in these cases because the window function must operate on the data only and not on any constant DC offset.

B. Fourier Transformation - FT

The command FT initiates a Fast Fourier Transform of the data currently displayed and replaces it with the frequency domain spectrum consisting of N/2 real points and N/2 imaginary points corresponding to the cosine and sine transforms of the data. The classical calculation method consists of multiplying each data point by all possible sine waves up to the Nyquist frequency. This method clearly requires N^2 multiplications, where N is the number of data points. The method used in the Nicolet FT-Nmr program was discovered by Cooley and Tukey[5], and accomplishes the same thing, but requires only N log (N) multiplications. It makes use of the fact that sine waves which are harmonically related have certain redundancies. The transform times for the FT program are as follows:

Number of Time Domain Points	Time in Seconds
1K	2
2K	4.2
4K	8.9
8K	23
16K	47
32K	103

C. Exponential Multiplication - EM and TC

It is not always desirable to transform the free induction decay without the application of certain smoothing functions. It is possible to improve the signal to noise of a frequency domain spectrum by manipulations in the time domain. Smoothing can be accomplished in the frequency domain, but generally introduces more distortions.

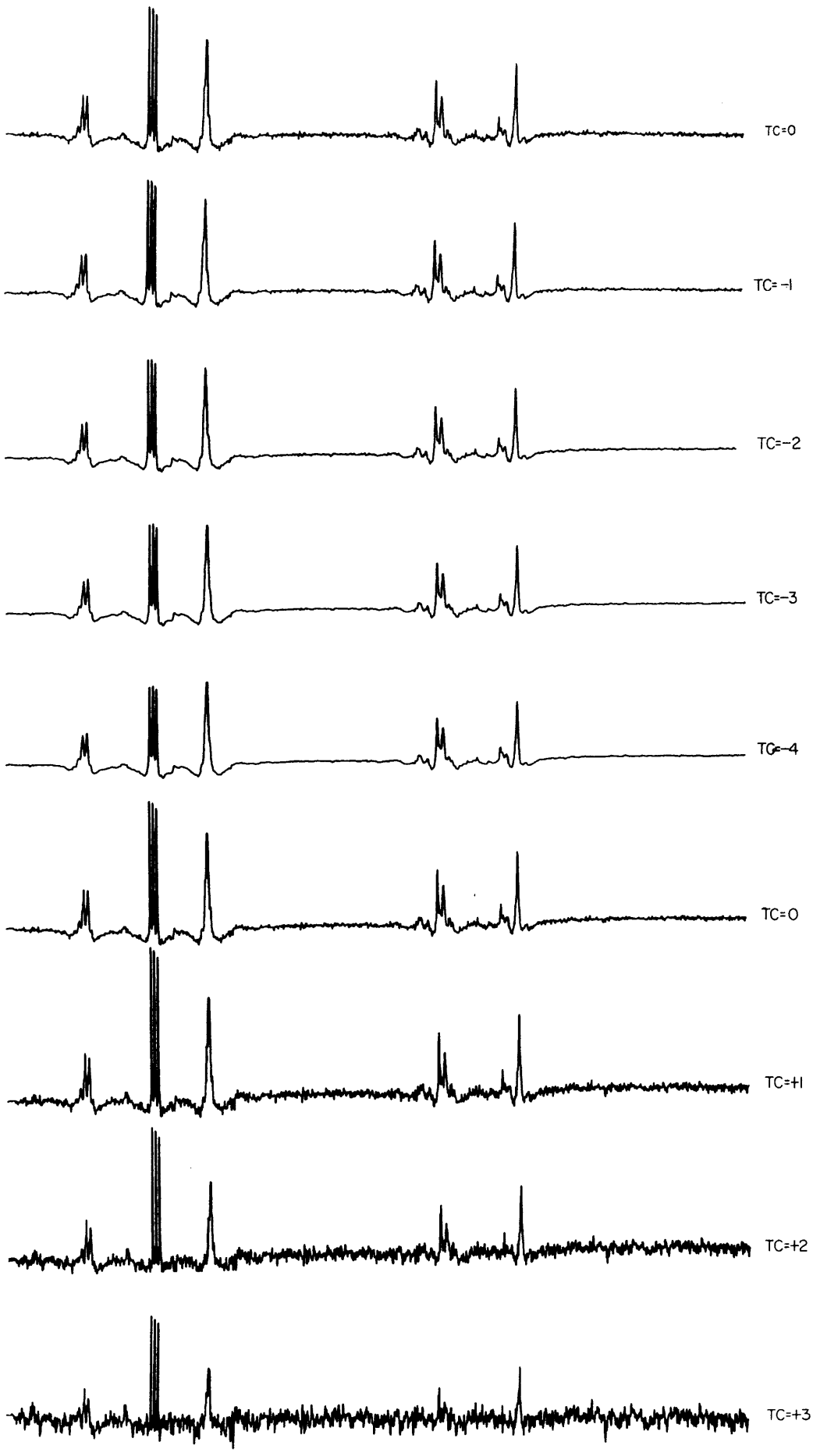
Multiplication of the free induction decay by an exponentially decaying function can increase apparent signal to noise markedly. The cost for the spectroscopist is some additional line broadening. The command EM multiplies the data by an

exponential having a time constant entered by the command TC. During this multiplication, each data point is multiplied by exp (iTC/N) where N is the number of data points and i is the index of the current point, i varying from 0 to N-1. Thus, the first point is multiplied by e^0 or 1.0 and the last data point by e^{TC}. Baseline correction is automatically called by the EM command.

It seems intuitively reasonable that multiplying by a decaying exponential would improve the S/N, since most of this noise contribution appears in the "tail" of the free induction decay where the signal has more or less died out. If this tail is forced toward zero the amount of noise in the transformed spectrum will be less, but the lines will have broadened somewhat.

The mathematical justification for this particular window function is simply that the Fourier transform of an exponential decay is a line having a Lorentzian shape. This is not surprising, since the free induction decay is governed by T_2^* which is indeed exponential in nature, and which is the cause of the observed Lorentzian line shape in conventional cw nmr spectra.

The constant TC is entered by typing TC and entering it in the usual manner. It should be noted that TC is usually entered as a negative number. Entering a positive TC will allow multiplication by a positive exponential. This has the effect of increasing the apparent noise level, but producing narrower lines, or enhancing resolution. This is illustrated on the following page.


TC=0
TC=-1
TC=-2
TC=-3
TC=-4
TC=0
TC=+1
TC=+2
TC=+3

D. Trapezoidal Window - T1, T2 and TR

It is often found that a small amount of pulse feed-through may exist even after introducing what is apparently a sufficient delay. This feed-through may manifest itself by a rippling baseline having a frequency of 2 or 3 Hz in the transformed spectrum. One of the easiest ways to cure this problem is by using the trapezoidal window function TR.

The limits of the trapezoid are specified by entering addresses T1 and T2 relative to the beginning and end of the spectrum. T1 and T2 are entered as integers between 1 and the size of the spectrum. The command TR multiplies the spectrum by a diagonal line starting at 0.0 and moving up to 1.0 for data points between the first data point and the data point at address T1, and by a fraction between 1.0 and 0.0 for data points starting at address T2 and proceeding to the end of the spectrum. If T1 is zero no multiplication is performed at the beginning of the FID and if T2 is zero, no multiplication is performed at the end of the FID. The first data point address is therefore 1, to be consistent with the usage of the hardware cursor.

The principal use of the downward diagonal window produced when T2 is enabled is that of forcing noise in a long free induction decay tail to zero. This will increase the signal to noise of the transformed spectrum, but at the expense of some line shape distortion. It is generally preferable to force the tail of a FID to zero by judicious choice of a TC for the EM command rather than by using the T2 window.

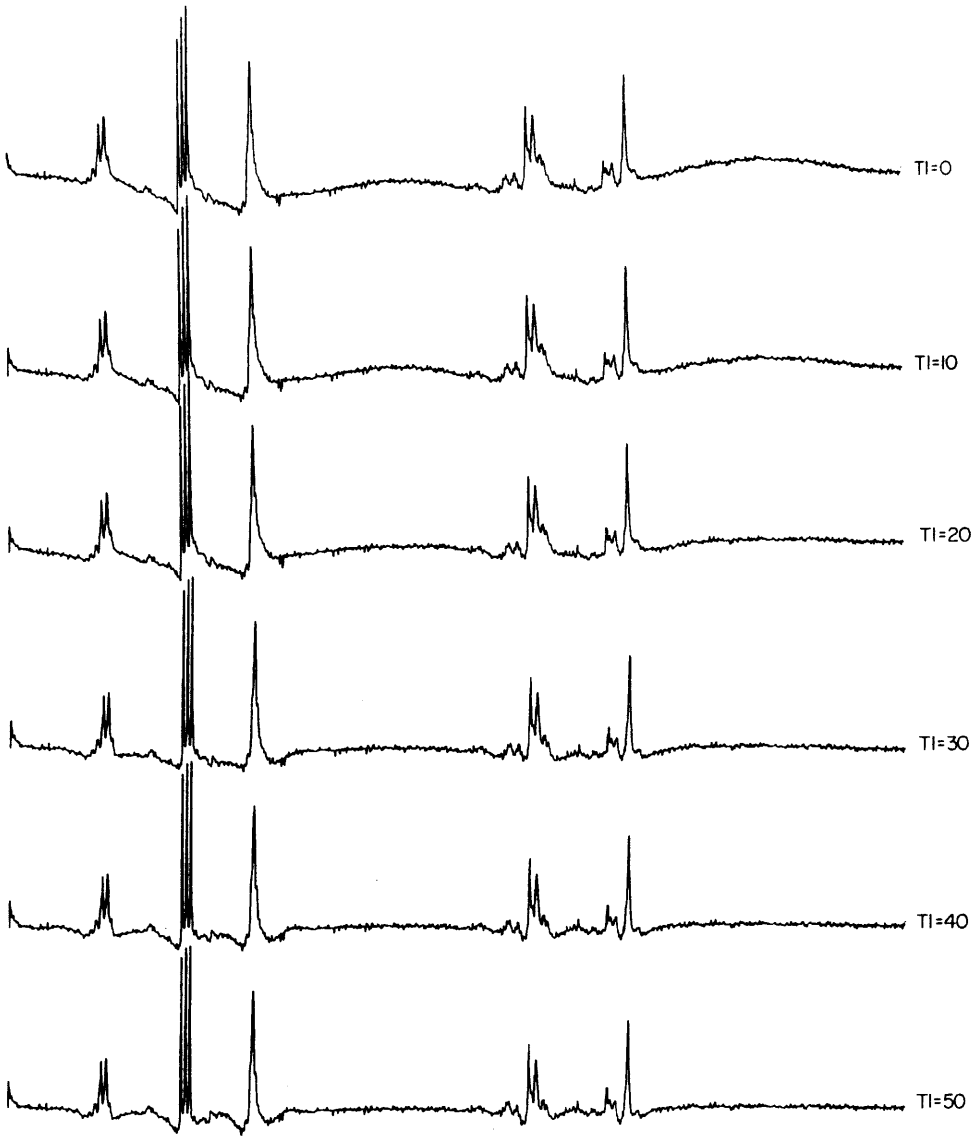
In summary, to suppress pulse feed-through, the following commands may be given:

```
.T1=     0 50
.TR
```

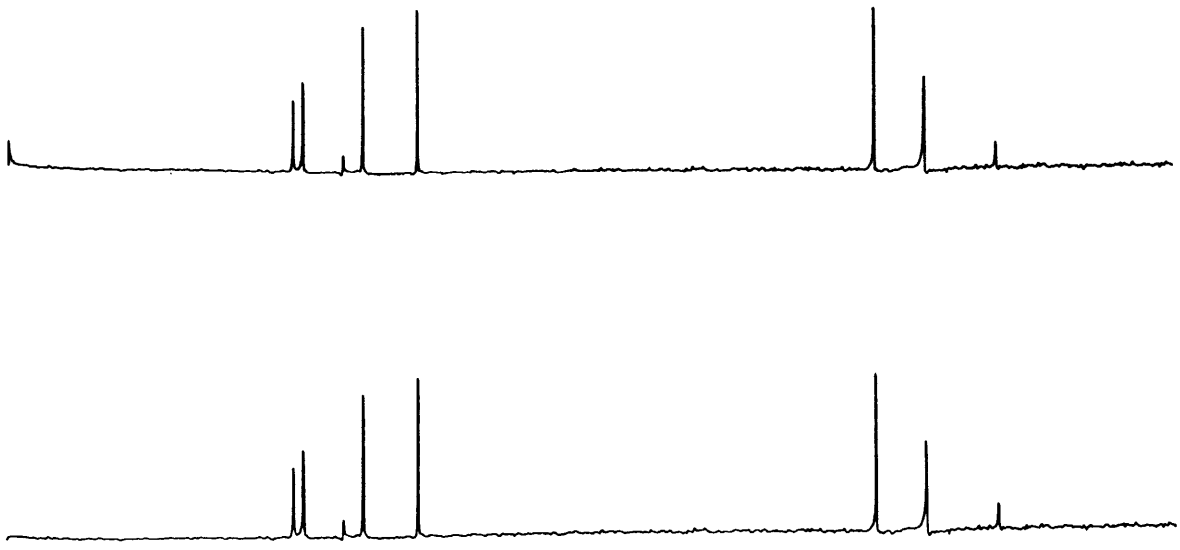
The command TR then multiplies the first fifty points by i/50, where i is the index of the point.

Baseline correction is automatically called internally to the TR routine.

The examples below indicate the effect of varying T1's on a 4K free induction decay having some pulse feed-through. Note that as the number of points which are multiplied increases, the pulses appear to sit in little "valleys."



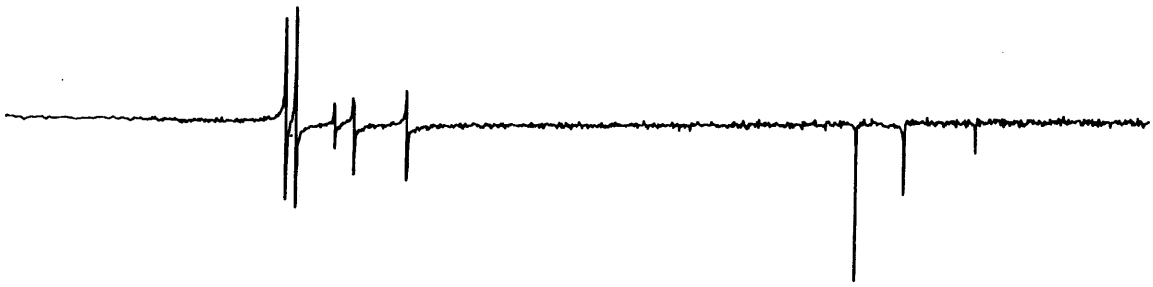
The transformed data may sometimes have a small spike at the left end of the spectrum, at zero Hz, caused by a small residual DC bias not removed by BC. This spike may be removed using the TR command with only T1 set.



V. PHASE CORRECTION

A. Introduction

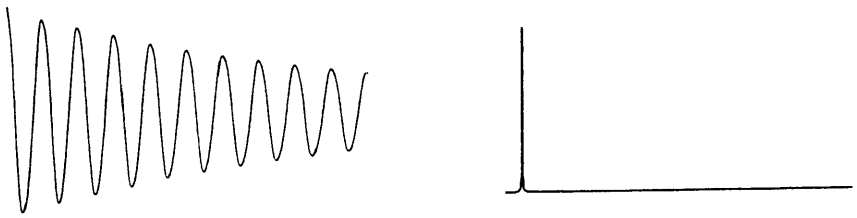
The Fourier transform of a free induction decay produces two spectra, each containing half as many points as the original FID. Those are called the real and imaginary parts, or the cosine and sine transforms. Under ideal conditions, these two spectra should correspond to the absorption and dispersion mode spectra respectively. However, a number of physical phenomena often cause the absorption and dispersion mode phase information to be "mixed" between the two spectra.



There are three major causes of mixed phase information:

(1) Spectrometer phase detector setting,
(2) Delay between pulse and start of data acquisition,
(3) Filter settings.

The spectrometer phase detector is usually optimized at the beginning of a series of spectra, using a strong sample containing sharp peaks. Just as in cw spectroscopy, the smallest changes will affect this parameter: variation in sample tubes, solvents, or even spinning rate may affect the phase of the information entering the detector. This effect is a zero order one, which causes the same shift in phase for each data point, regardless of frequency. Examples of out of phase and in phase cosine waves are shown below, along with their transforms.



The remaining two factors, delay time and filters, have first order effects on the spectrum. That is, at frequency zero, the phase shift is zero and at the highest frequency in the spectrum, the phase shift is large. It is customary to refer to this first order phase shift in terms of the phase angle shift of the highest frequency. A 170° first order phase shift is one in which the first frequency domain point has zero phase shift ane the last one 170° of phase shift.

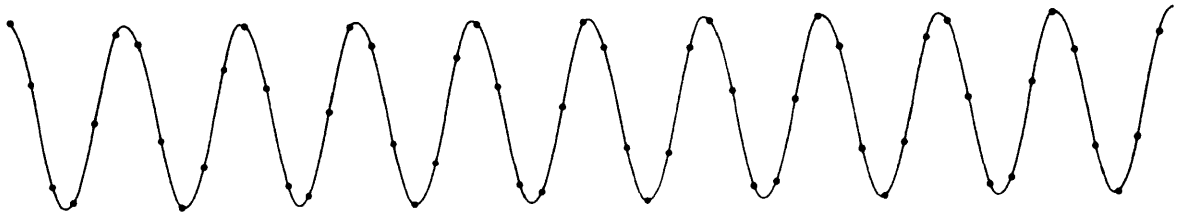
The delay time causes a frequency dependent phase shift related to the dwell time. The highest frequency point will be shifted by an amount equal to 180° × Delay/ Dwell. In other words, for each dwell time unit of delay there will be a first order phase shift of 180°. Note that in the case of first order shifts, a 0° shift and a 360° shift are not equivalent. In the case of the 360° shift, the highest frequency point is "wrapped" around 360° in phase from the first point, causing the phases of the data points to spiral in the phase plane around one complete circle, much as shown in the phase-frequency model below.

Logically, one can also see that first order phase shifts can be greater than 360°, and can in fact attain almost any number of degrees. For instance, if the dwell time in a particular experiment is 30 usec and the delay time 300 usec, then the first order phase shift will be

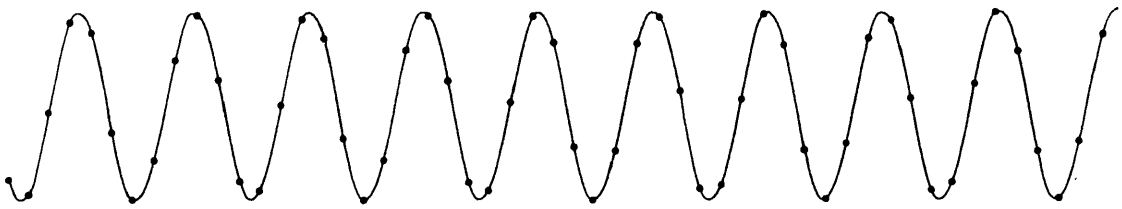
$$\frac{\text{300 usec dwell}}{\text{30 usec delay}} \times 180° = 1800°$$

This is equivalent to a spiralling of the phase information in five complete circles.

Let us now consider a physical explanation for this phase shift. While the zero order shift is quite easy to explain in terms of phase detector settings, the first order shift is a little harder to grasp. We will first return to our discussion of sampling. Recall that the sine waves comprising the FID are sampled at a constant interval called the dwell time:

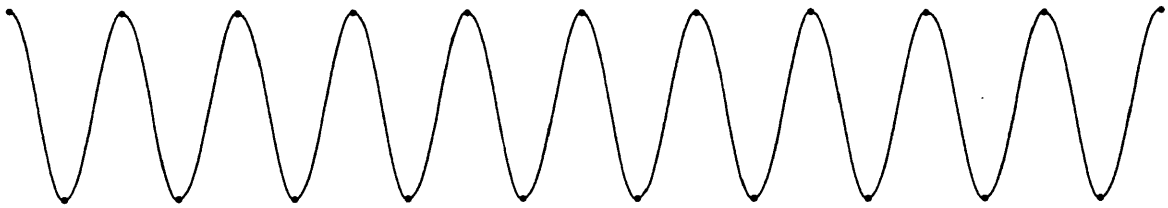


We have assumed that these waves are sampled starting exactly at 0° as the first point of the sine or cosine wave. Let us now assume that a delay of 2 dwell times is introduced for instrumental reasons, such as to minimize pulse feedthrough.

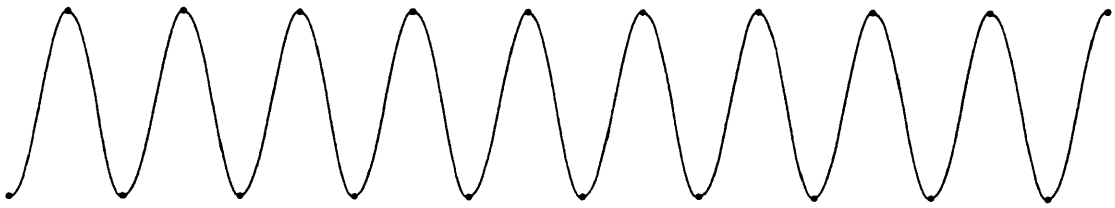


As you can see, the omission of the first two data points causes the phase of this line to begin at about 75° instead of at 0°. This means that this line when transformed to the frequency domain will be 75° out of phase.

Let us now consider a line of much higher frequency, one at the Nyquist frequency, or at one half the sampling frequency. At this frequency, there are only two data points per cycle of the sine wave:



If, at the high frequency, we introduce a one dwell time delay, we will have wiped out 180° of phase information, so that the wave will start at 180° instead of at 0°.



Thus, at this frequency, the highest one represented in the FID, the delay of one single dwell time (or of one address) will cause a 180° phase shift. It follows from this that a 2 address delay would cause a 360° phase shift, and so forth.

A line which is "folded back" or aliased from a frequency higher than twice the sampling rate will have the first order phase dependence that it would have if it were actually observed at its correct frequency. Thus, a folded back line will seem to have an anomalous phase relative to lines around it. If a line appears to be folded back, then alter the irradiation frequency and obtain a new spectrum. If all lines move in the same direction except the suspicious one, it is folded back.

A line may also appear to have anomalous phase if its spin-lattice relaxation time, T_1, is widely different from that of other lines in the spectrum and if the pulse repetition rate is greater than 5 times this longest T_1. In this case, the nuclear magnetization will not have relaxed back to the +z axis before the new pulse begins.

The third cause of phase shifts are the characteristics of the filter used to limit the spectrum bandwidth. In the Nicolet 1080, 4-pole Butterworth filters have been chosen because of their extremely linear phase characteristics. The 4-pole filter causes first order shift of -180° if used in the system. This does not vary appreciably with the cutoff frequency selected. Thus, the total formula for determining the first order phase shift is given by

$$\frac{\text{delay time}}{\text{dwell time}} \times 180° - 180°$$

Phase correction is performed by convolving all points in the real and imaginary spectra with a cosine and sine wave. Zero order phase correction is performed by

$$x_j' = x_j^{real} \cos [A] - x_j^{imag} \sin [A]$$

where j is the index of the point, and A is the zero order phase correction angle.

First order phase correction is performed by

$$x_j' = x_j^{real} \sin [_j B/N] + x_j^{imag} \cos [_j B/N]$$

where N is the total number of frequency domain points and B is the first order phase correction constant.

In actual practice, these two equations are combined and executed simultaneously. The sign of the phase correction constants have been specified as the sign that must be entered to perform the required correction. Thus, if the spectrum appears to have a 190° first order phase shift, the value +190° is entered to perform this correction.

B. Determining the Necessary Phase Correction Constants - PA, PB and PC

In the Nicolet 1080 FT nmr data system, the phase correction constants are referred to as PA and PB, where PA is the zero order constant and PB the first order constant. A general procedure for phase correcting such a spectrum is to first remove any gross first order phase shifts by entering a value for PB as shown above. Then enter a zero value for PA and type PC to perform the actual phase correction.

For example, if the delay were 220 usec and the dwell time 100 usec, the phase correction process would be as follows:

$$PB = \frac{220}{100} \times 180 - 180 = (2.2-1) \times 180° = 216°$$

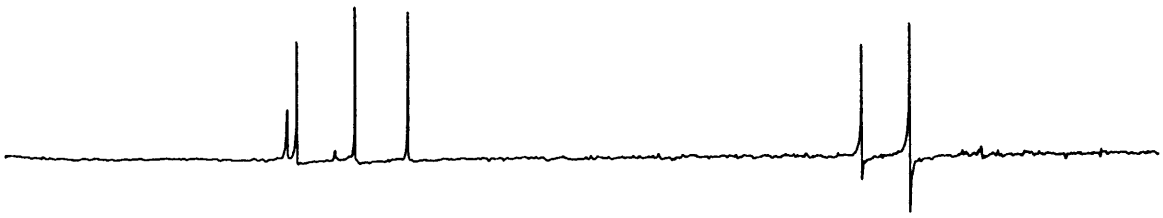
. PB = 216
. PA = ø
. PC Phase correction performed

Once this gross shift has been removed, any new shifts can be removed by first correcting some low frequency peak to be in phase using PA with PB set to zero. For instance in the following spectrum, the low frequency peak

appears to be 45° out of phase. Note that for PA, 45° and -315° are equivalent. This is not true of PB. The following operation will bring the first peak into phase:

. PB = ø
. PA = 45
. PC

The result is

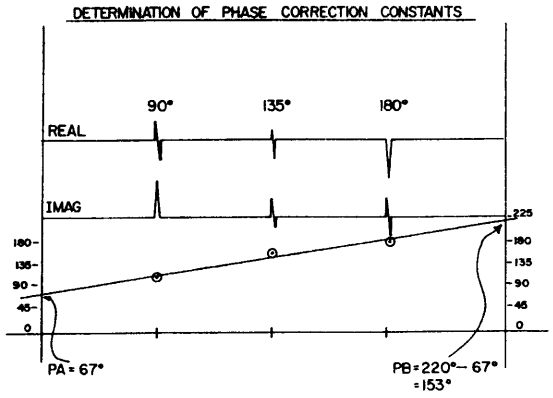


From this resulting spectrum, we can easily determine a value for PB that will bring the upper peak into phase:

.PA = ø
.PB = -60
.PC

C. A Combination Method for Determining Phase Correction Constants

Since the phase correction routine is very fast, requiring only one or two seconds, it is not unreasonable to separate PA and PB when correcting a spectrum. However, it is possible to perform both corrections simultaneously. This is accomplished by examining the scope display and estimating the phase of several lines. This is done most effectively by looking at both the real and imaginary parts, and comparing them with the chart on the preceeding pages. The phase of several points is then plotted versus frequency. This is shown in the example below.



The intercept at zero frequency is the value of the zero order phase correction constant PA. The intercept at the Nyquist frequency is PB + PA. PB is determined by simply subtracting PA from this intercept.

D. Semi-Automatic Phase Correction - AP, CC

The calculation of PA and PB from the intercepts of a line extending from 0 to the maximum frequency is performed by the command AP. It works by picking the two largest peaks in the power spectrum (sum of the squares of real and imaginary). The peaks are picked so that the second line found is at least 12.5% of the total spectrum width from the first peak. Furthermore, the last 12.5% of the spectrum is excluded because the filter may introduce somewhat nonlinear phase shifts at higher frequencies.

The phase of these two lines is determined by taking the ratio of the intensity of the real and imaginary peaks. A line is "drawn" through these two peaks and PA and PB calculated from the intercepts. The command AP initiates this calculation. The PA and PB are calculated and printed out, and the correction then takes place.

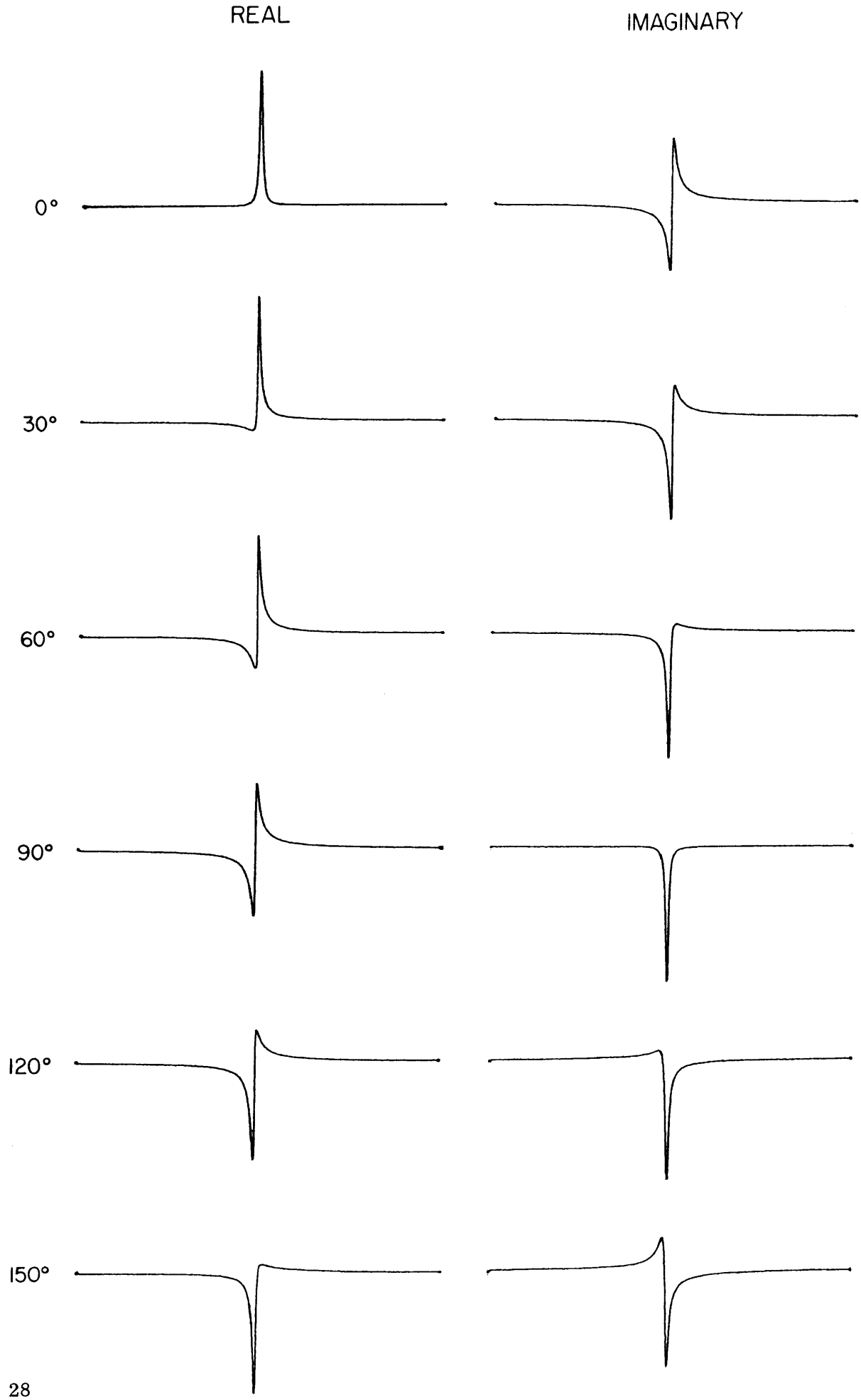
This semi-automatic method is obviously useful in many cases. However, it is limited and the limitations should be clearly recognized by the user. AP will work best if

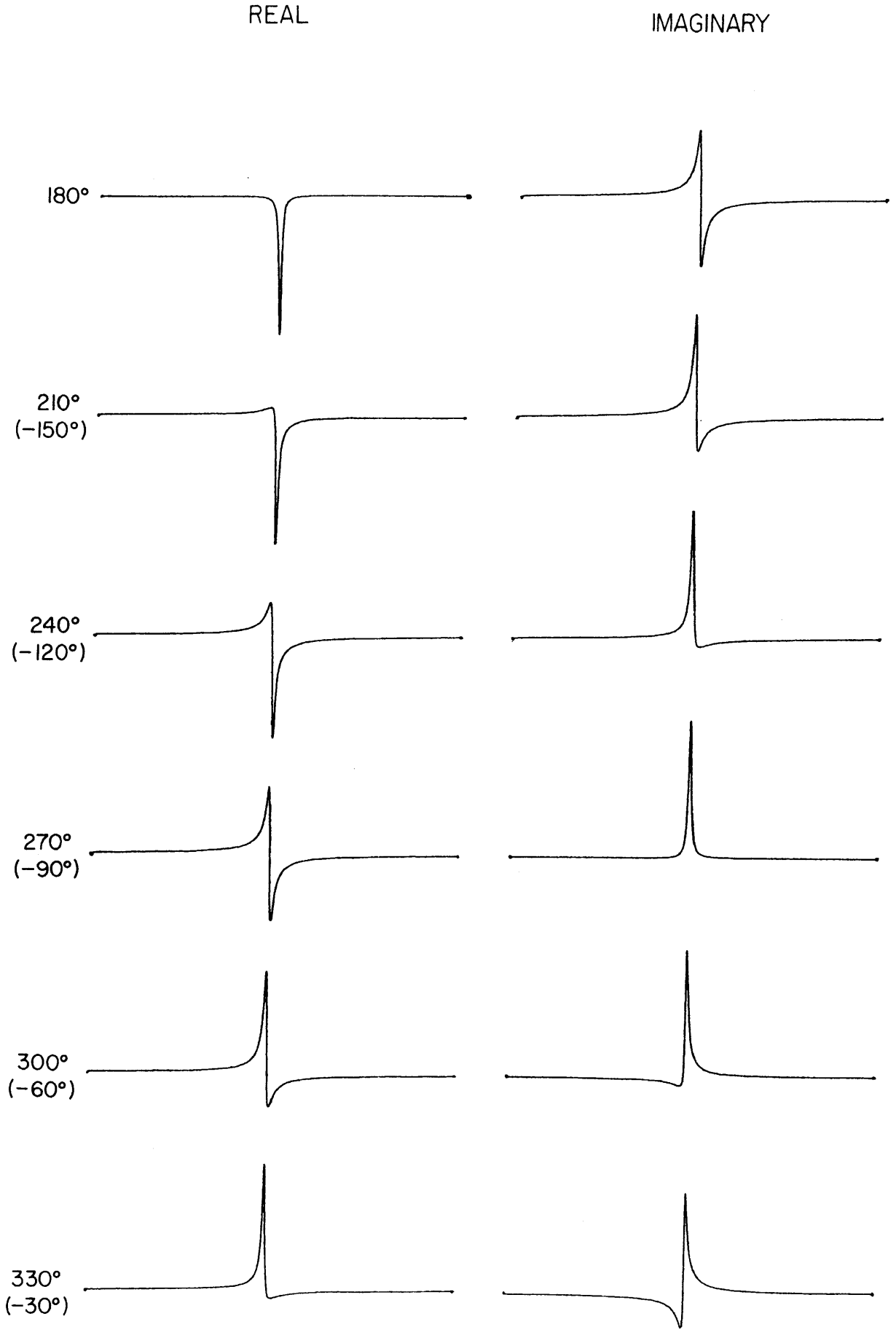
(1) the peaks have a high signal to noise,
(2) the lines are not too broad,
(3) the lines are well spread out through the spectrum,
(4) there are no out of phase peaks on the spectrum resulting from very long T_1's or folded back lines,
(5) the first order phase correction is no more than about $\pm$ 180°.

Obviously, if these criteria are not satisfied the program will have some trouble calculating a meaningful straight line from which to obtain the intercepts. While in some cases it may be obvious whether or not the command AP will produce the desired results, in other cases it may be more difficult. For these borderline cases, the command CC (calculate constants) will print out the values of PA and PB which would be used by AP without actually performing the corrections. One can then examine these constants and decide whether or not to perform the correction.

In general it is desirable to remove any large first order phase shifts before attempting AP since the phase angles calculated by AP are only meaningful within $\pm$180°.

A complete table of phase angles is given on the following pages. The sign of the angles given is that required to bring the lines back into phase.


REAL
IMAGINARY
0°
30°
60°
90°
120°
150°


REAL
IMAGINARY
180°
210°
(−150°)
240°
(−120°)
270°
(−90°)
300°
(−60°)
330°
(−30°)

E. Total Phase Correction Performed - TP

At any time the command TP will cause the total phase correction performed since the last FT command to be printed out.

F. Block Selection Errors During Phase Correction

The 1080 FT-Nmr program assumes that the entire real and imaginary spectrum are displayed during phase correction commands CC, PC and AP. If the area displayed differs from the area upon which the last FT was performed, the message WRONG BLOCK? is typed. To force phase correction of the displayed area type F. To return to the display without performing the erroneous calculation, type Return.

The only reasons that one might have for typing F are if a paper tape spectrum has been loaded since the last FT or if there are two or more sets of data in memory simultaneously. One might also wish to force the program to phase correct a new area if one is generating a sine wave for test or demonstration purposes by phase correcting a straight line.

VI. DATA OUTPUT ROUTINES

A. Plotting - PL

Following phase correction the spectroscopist will generally desire to plot out the spectrum as it resides in memory. The FT-Nmr program contains a unique constant speed plot routine which enables the user to make extremely neat plot outputs of his data.

Early signal averaging devices plotted out data by simply slowing down the point display. If the excursion between points was small the plotter pen easily negotiated the jump, but if a large jump occurred the pen usually would skip. This generally necessitated very slow plotting speeds or very unevenly plotted spectra.

The constant speed plot routine which is provided by the FT-Nmr program overcomes this limitation by drawing a straight line which contains all y-axis points between actual data points. Thus the pen is always moving at the same speed, whether horizontally or vertically and pen skipping is eliminated.

To initiate the plot routine, type PL. The program will display the first point of the spectrum and await further instructions.

The outputs to an x-y plotter are clearly marked on the back of the 1080. They are disconnected whenever any button except Plotter Realtime or Plotter Autoslew is depressed. This prevents the scope display from driving the plotter wild. To actually begin plotting, depress either Plotter Realtime or Plotter Autoslew and type Return. This will cause the plot to begin. Whatever section of memory is currently displayed will be plotted out.

The speed of the plot is controlled by typing the two commands

F - plot faster
S - plot slower

When the plot is finished, the last dot will be displayed until Return is typed. Turn off the plotter and/or depress CRT Readout before typing Return. The display will then return. This prevents the plotter pen from scribbling all over the plot while trying to follow the CRT display.

In summary, to plot out a spectrum

(1) Select the region of interest by depressing the proper Readout button
(2) Type PL
(3) Depress either Plotter Realtime or Plotter Autoslew
(4) Type Return
(5) F to go faster; S to go slower
(6) When plot is finished turn off plotter

(7) Depress CRT Readout
(8) Type Return.

The plotter drive from the x and y outputs is for an x-y plotter. To drive a y-d plotter, connect the y-axis output as usual, and connect the digital advance to pin J2, the Intensify pulse. This produces 16384 steps full scale on the recorder. For information on modifying the number of steps full scale, consult the factory.

B. Intensify Region - IR, F1, F2, OF

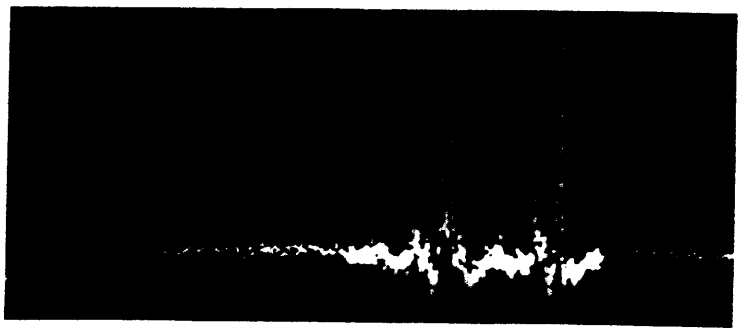
It is possible to expand any section of a spectrum to full scale using the IR command. This command causes the intensification of a region between frequencies F1 and F2.

F1 and F2 are entered as are all constants in the FT-Nmr program, by typing F1 or F2 and entering the desired frequencies. These frequencies are taken relative to any offset entered by the OF command. The program considers the right most data point to have frequency zero and the left most point to have the Nyquist frequency. This "left handed" frequency arrangement is used because it is common in both proton and C-13 nmr, since it is useful to report frequencies relative to TMS.

Let us suppose that we know that the right most frequency point has a frequency of 100 Hz and that the sweep width of the spectrum is 5000 Hz. To intensify and examine a region between 2000 and 3000 Hz, the following commands are needed. (We assume SW was entered before data acquisition.)

```
.OF = 0.000E-1     100
.F1 = 0.000E-1    2000
.F2 = 0.000E-1    3000
.IR
```

Following IR, the intensified region will look like that shown below:



To examine the intensified region in more detail, the command X will expand the display to full scale. The display will then appear as follows:

The sub commands available at this time are

X - Expand intensified region to full scale
C - Recontract to show entire spectrum and intensified region
P - Plot intensified region. Follow instructions under PL
L - List the peaks in the intensified region
Return - Return to the normal display

The plot of the expanded region proceeds exactly as described under PL except that the initiating command is P rather than PL. The carriage return at the end of the plot returns the normal display.

The L subcommand is identical to the PP command except that only peaks within the intensified region are listed.

It does not matter which frequency is assigned to F1 and which to F2; they are automatically arranged within so that the correct region is displayed rather than its complement. If frequencies are chosen so close together that they represent only one data point, the error message ?F1=F2 is printed when IR is typed.

Another method of specifying F1 and F2 is included as part of the CU command. F1 and F2 are stored as frequencies and the modification of the offset will leave them unchanged. The modification of the sweep width will automatically zero F1 and F2. If IR is attempted when SW has not been set, the error message ?ENTER SW OR DW will remind the user of this error.

C. Peak Printout Routine - PP, SF, OF, MI

All of the peaks in the displayed spectrum region can be listed on the Teletype by typing the PP command. The columns, as they are printed are cursor address, frequency, parts per million, and integral. The relevant commands are

. OF enter sweep Offset, to be added to zero (right) end

. MI enter Minimum Integral to be printed out. Peaks having an integral less than the value are suppressed

. SF enter the Spectrometer Frequency in megahertz. If the frequency was 60 MHz, the value 60 is entered. If SF = ø, the PPM column is omitted.

. PP Print out the peaks in the displayed region. The program assumes that all peaks are absorption mode and that the right end of the display represents ø Hz (plus the offset).

A typical peak printout will appear as shown below:

Cursor	Frequency	Parts Per Million	Integral
505	3.769E3	1.499E2 PPM	497
523	3.725E3	1.481E2 PPM	520
592	3.557E3	1.414E2 PPM	114
625	3.476E3	1.382E2 PPM	828
721	3.242E3	1.289E2 PPM	921
1524	1.281E3	5.097E1 PPM	1000
1611	1.069E3	4.252E1 PPM	746
1739	7.568E2	3.010E1 PPM	166

The printout routine detects virtually all fine structure; no threshold setting is required. The criteria for recognizing a peak are that

(a) it must rise above the mean noise,
(b) it must fall back below its maximum by an amount greater than the mean noise,
(c) it must either

i) fall back below the baseline noise, or
ii) begin to rise again by an amount greater than the mean noise.

Occasionally these criteria may pick out very small spikes on the baseline noise. These can be suppressed by adjusting the Minimum Integral criterion. The program automatically normalizes the integrals so that the largest peak has an integral of 1000. The program detects only absorption mode spectra and assumes that the entire spectrum is displayed, so that the right end is zero Hz plus the offset.

D. Cursor Display - CU

The Nicolet 1080 sweep plug-in contains a hardwired cursor which places an intensified dot on a selected decimal address in the displayed spectrum during Read-out Mode display. This cursor is useful in providing signals for signal averaging purposes.

The CU command allows the stored program processor to have access to equivalent information. Typing CU will produce an equals sign followed by the current value of the cursor. A new value of the address may be entered followed by a return. If CU = ø, the normal display returns. To examine address 1503, the following command is used:

```
.CU=        0    1503
```

The display is then shown with address 1503 intensified. Addresses are relative to the left end of the display. The first address is 1 rather than ø to be consistent with the hardware cursor.

While the intensified point is being displayed, the following subcommands are available:

```
     L - move the cursor left one point
     R - move the cursor right one point
    ML - start the cursor moving to the left
    MR - start the cursor moving to the right
     S - stop the cursor motion
    F1 - assign this address to limit F1 for the IR command
    F2 - assign this address to limit F2
     A - assign an entered frequency to this data point
Return - return to normal display
```

The F1-F2 assignment commands allow exact selection of the region to be intensified and expanded without guessing at frequency ranges. Furthermore, when F1 or F2 are typed the program automatically types out the frequency of that point, giving the user a method of determining the frequency of any line in the spectrum.

For example, to select a region for intensification and expansion type

.CU = 1053 1610 (Return)	The spectrum is displayed with point 1610 intensified.

To specify this point as the right end of the region to be expanded, type

F2 = 5.023E2	The program assigns this point to F2 and types out its frequency in Hz.

To move the cursor to the left, type

ML

and when the desired point has been reached, type

S — to stop the cursor motion. These commands are not echoed by the Teletype.

To assign the other frequency limit, type

F1 = 4.231E2 — This tells you the frequency of that point and assigns the left end of the region to be expanded.

To exit to the normal display, type Return.

Then, to intensify and expand the region, type

.IR followed by X.

The A command allows the assignment of any point to any desired frequency. This is useful for assigning a frequency to an internal standard such as TMS. However, the reference frequency can be any desired frequency; it need not be ∅. To use the A command, type A. The program will follow the A with an equals sign. Enter the desired frequency and follow with a Return. The value of the sweep offset is automatically adjusted after an assignment is made. To exit to the normal display, type Return again.

E. Punch Out Data - PU

Typing PU causes the program to punch out the contents of the displayed area of memory in binary format, which can be read in by the Binary Loader. Leader and trailer tapes are automatically punched, including a Rubout in the trailer.

This punch routine is not limited to the low speed Teletype. To modify this routine for use with a high speed punch, contact the factory for details.

VII. DATA MANIPULATION

A. Add Constant - AC

The command AC causes a constant to be added to the display whose value is selected by the DC-level potentiometer. To use the DC-level pot for a constant input, set the Volts Full Scale switch to GND, to prevent any input signal from affecting the AC command.

The digitizer resolution must be set to 9 bits to allow the pot to control the full range of the display. The Vertical Display Scale switch is active during this command, so that the ten-turn pot causes a full scale motion of the display at any Vertical Display Scale setting. When the addition is complete as desired, type Return to fix this addition in memory. To prevent addition from taking place, press STOP and restart the program by pressing Stored Program Start. This command can be used to shift the spectrum baseline to the bottom of the scope to obtain more vertical resolution.

B. Integrate Display - ID

The ID command causes the integral of the display to be taken and scaled to full scale display. Since a small DC level may remain in the signal, it may be removed by adjusting the DC-level pot to remove any slope from the integral display. Again, the Volts Full Scale switch should be set to GND and the resolution to 9 bits before using the DC-level pot as a line adjustment. The integral may be plotted by typing P. This begins the plot routine just as described under PL. Return must then be typed to initiate the plot.

C. Magnitude Calculation - MC

As a quick alternative to phase correction, the magnitude calculation routine provides a pseudo-absorption mode spectrum. The magnitude spectrum is defined as the square root of the sum of the squares of the real and imaginary spectra. It is equivalent to multiplying the complex spectrum by its complex conjugate. The MC command replaces the imaginary spectrum with the magnitude spectrum.

Once the MC has been performed the imaginary spectrum has been destroyed and it cannot be recalled. This prevents any possibility of further phase correction calculations. While the MC is useful as a quick guide, the "skirts" of the peaks tend to be a good deal broader because of the mixing of phase information inherent in this process.

By convention, the program assumes that the entire real and imaginary spectra are displayed when MC is typed, and that it is to replace the second half of the displayed area with the magnitude spectrum. If the displayed area differs in size or location from that upon which FT was last performed, the program types WRONG BLOCK?. To force the calculation of the MC of the displayed area, type F. To return to normal display without performing the calculation, type Return.

D. Move - MV

The command MV causes the contents of the memory section selected by the Measure Switches to be transferred to the area selected by the Readout Memory switches. If these are the same, this is a null operation. If the Size buttons do not agree, the message BLOCK SIZE? is printed. The previous contents of the Readout area are destroyed.

E. Data Transfer - DC, DT

The command DT causes the data specified by the Measure buttons to be multiplied by the constant DC and added to the area specified by the Readout buttons. If DC is still set to zero, the message ?DC=ø is printed. If the Size buttons do not agree, the message BLOCK SIZE? is printed.

This command can be used to add and subtract spectra, since DC can be either positive or negative, and either fractional or integer. It can be used to multiply the size of a spectrum, by selecting the same area for Measure and Readout. The constant DC is entered using the command DC in the usual way.

F. Automation of Experiments - LI, AU

The typical FT-Nmr experiment will probably consist of a large number of commands given in succession. For instance:

.ZE	zero the data array
.GO	begin signal averaging
.TR	trim off pulse feed through by trapezoidal multiplication
.EM	enhance signal to noise by exponential multiplication (TC entered earlier)
.FT	Fourier transform
.PC	phase correction (PA and PB entered earlier)
.PP	print out peaks in spectrum
.PL	plot out spectrum

It would be desirable to be able to call this entire string of commands repetitively for routine operation without the necessity of typing them individually each time. This facility is available with the LI (link) command.

The link command allows the linking of up to fifteen separate commands in a string. This string can then be called by giving the command AU, which will execute all of them before returning for more commands. To link together a string of commands, type LI followed by each two character command. The linked commands are not followed by carriage returns or spaces. To terminate the list of linked commands, type Return twice in succession. The list is then stored for use and the program responds with a new dot. If an illegal command is entered a question mark is typed,

the list is erased and a dot is typed to allow entry for a new command. If more than fifteen commands are typed in succession, a question mark is typed and the list is erased.

For example, to link together the commands shown above, the following characters would be typed:

. LIZEGOTREMFTPCPPPL

followed by two carriage returns. To execute this string automatically, the command AU is given. The list is not destroyed by use, and may be recalled by simply typing AU again.

It should be noted that commands which require operator intervention, such as the PL command, which requires that the plotter be turned on, the Plotter Realtime button be depressed, and that Return be typed, still require this same intervention when they are linked together. Thus, in the above example, all of the commands will be performed as listed up to the PL command, which will wait for Return to be typed before the actual plot begins.

TABLE II

LIST OF ERROR MESSAGES

.xx?	Illegal Command
.LI xxxxxxxx?	Illegal Command or more than 15 commands. Linked list erased.
WRONG BLOCK?	Phase correction or magnitude calculation attempted on a block other than the entire real and imaginary display produced by the last FT command. May be overridden by typing F to force compliance. To return to command made without executing PC or MC, type Return. This causes exit from the Linked list.
? ENTER SW OR DW	IR or PP is attempted when neither SW or DW has been entered. F1 and F2 must be entered after SW or DW.
? F1=F2	F1 and F2 are the same, so that intensification of a region is impossible.
? BLOCK SIZE	DT or MV attempted when Measure Size and Readout Size do not agree.
? DC=ø	DT attempted when DC = ø

APPENDIX I

USER MODIFICATIONS TO THE FT-NMR PROGRAM

The Nicolet FT-Nmr program has been designed so that users can easily write small additional subroutines for their own use and call them from the Command Decoder routine. Listings of the entire program are available upon request. However, the discussion below should be sufficient for a programmer to design and enter new subroutines in the body of the FT-Nmr program.

A. Commands

Each two character command is stored in a list in memory so that the first location contains the pair of ASCII characters, 9 bits per character, and the second location contains the address of the subroutine called by that command. The command list occupies locations 56-210, with locations 211-213 containing list terminator information. The routines and their addresses are listed on pages 43-44.

The commands are interpreted as follows: The two character command is entered from the Teletype and packed into one word so that the first character is shifted to bits 9 - 17, and the second character in bits 0 - 8. This packing allows one to read off the ASCII characters directly in octal. Thus, the command CU is stored as 303325, where 303 is the ASCII for C and 325 the ASCII for U. The next address in the table contains the subroutine address of the CU routine. The command interpreter performs a JMS indirect using this location as a pointer. For CU, the instruction JMS @ 57 is performed, or an effective JMS 1443. Illegal commands or zero commands are trapped by the interpreter to prevent the program running wild.

As is apparent, the following spaces are free to insert commands:

106-123, 142-143, and 172-175

B. Program Space

The FT-Nmr program contains free space on page 4000 which is reserved for user programs. Several of the programs in the Nicolet Users Society Library (NUS) utilize this space and this should be considered when loading more than one new routine into the FT-Nmr program. Locations 5213 through 5410 are available in the tape NIC-80/S-7202c-B. Later versions may contain less space and users should read the documentation accompanying these tapes before loading any new patches. The Nicolet Instrument Corporation applications staff is always ready to answer questions regarding such programs.

C. FPP-1972

The space on page 4000 was carefully preserved for users so that they could take advantage of the Floating Point Package pointer list which is available on this page. FPP-1972 operates in the exact same way as does FPP-1971, except that the pointers have been moved as shown on page 45. FPP-1972 also contains a new routine for integer output, called FIXOP. The format of this fixed point output is determined by the registers NUMD and PREDIG. NUMD is the total number of digits to be typed (leading zeroes are suppressed), and PREDIG is the number of digits before the decimal point to be typed. If NUMD = PREDIG, the output is in integer format. The routine is called by JMS @ FIXOP with the number in the FAC. A complete source tape of FPP-1972 is available from the NUS library.

```
/LOCATIONS 56 - 212 ARE THE COMMAND LIST
/FORMAT :  ASCII PAIR
/           SUBROUTINE ADDRESS OF COMMAND
     56  303325  COMAND, 303325 /CU
     57    1443    CU
     60  323327  323327  /SW
     61    4000  SW   /SWEEP WIDTH
     62  304327  304327  /DW
     63    4131  DW    /DWELL TIME
     64  320320  320320  /PP
     65    4154  PCKPRN   /PEAK PICKER
     66  315311  315311   /MI
     67    4446  MINI      /MINIMUM INTEGRAL
     70  306261  306261  /F1
     71    4513  F1SET
     72  306262  306262  /F2
     73    4522  F2SET
     74  315326  315326  /MV
     75    4562  MV
     76  304324  304324  /DT
     77    4536  DT
    100  304303  304303  /DC
    101    4641  DC
    102  317306  317306 /OF
    103    4645  OF
    104  323306  323306  /SF
    105    4651  SF



    124  324303  324303  /TC
    125    5021  TC    /ENTER TCONST
    126  305315  305315  /EM
    127    4714  EM    /EXPONENTIAL MULTIPLICATION
    130  324261    324261  /T1
    131    5076  T1
    132  324262  324262  /T2
    133    5102  T2
    134  324322  324322  /TR
    135    5025  TR
    136  315303  315303  /MC
    137    5127  MC
    140  332305   332305  /ZE
    141    5120  ZE

    144  320314  320314  /PL
    145    3001  PL    /PLOT
    146  320325  320325  /PU
    147    3141  PU    /PUNCH
    150  301303    301303
    151    3351    AC       /ADD CONSTANT
    152  311322    311322  /IR
    153    3424    IR       /INTENSIFY REGION
```

```
 154   320301   320301   /PA
 155     1401   GETA
 156   320302   320302   /PB
 157     1405   GETB
 160   320303   320303   /PC
 161     5660   MPKOR
 162   303303   303303   /CC
 163     5563   AUTOP
 164   301320   301320   /AP
 165     5672   APKOR
 166   324320   324320   /TP
 167     1412   TP
 170   306324   306324   /FT
 171      600   XFFT

*176
 176   311304    311304 /ID
 177      223    INTEG

 200   314311    314311  /LI
 201      463    LINK
 202   302303    302303 /BC
 203      545    BC  /BASELINE CORRECT
 204   301325    301325 /AU
 205      507    AU
 206   307317    307317 /GO
 207      541    GO
 210   215215   RTRT, 215215  /CRCR
 211       54    GSTART
 212 3777777  3777777  /TABLE TERMINATOR
```

```
/POINTERS TO FLOATING POINT PACKAGE 1972

5727    7524  FIXOP, 7524
5730    7553  NUMD, 7553
5731    7554  PREDIG, 7554

5732    6543  FLOP, 6543
5733    6544  MANDIG, 6544

5734    6712  FLIP, 6712
5735    6760  VFLAG, 6760

5736    6761  RCHAR, 6761
5737    6767  PCHAR, 6767
5740    6775  CARCNT, 6775

5741    7002  FACFAR, 7002
5742    7010  FACTEM, 7010
5743    7016  TEMFAC, 7016

5744    7024  GETAR, 7024
5745    7036  GETAC, 7036
5746    7050  PUTAC, 7050

5747    7214  FADD, 7214
5750    7255  FSUB, 7255
5751    7263  FNEG, 7263
5752    7350  FMULT, 7350
5753    7413  FDIV, 7413

5754    7466  FLOAT, 7466
5755    7473  FIX, 7473

5756    7556  ERRF, 7556

5757    7572  FACE, 7572
5760    7573  FACM, 7573
5761    7574  FACML, 7574

5762    7575  FARE, 7575
5763    7576  FARM, 7576
5764    7577  FARML, 7577

5765    6000  FSIN, 6000
5766    6114  FCOS, 6114
5767    6122  FARCTN, 6122
5770    6170  FRIP, 6170
5771    6176  FSQRT, 6176
5772    6311  FLOG, 6311
5773    6317  FLOGN, 6317
5774    6333  FSQAR, 6333
5775    6337  FEXP, 6337
5776    6345  FEXPN, 6345
```

BIBLIOGRAPHY

1. L. C. Allen and L. F. Johnson, J. Am. Chem. Soc., 85, 2668 (1963)

2. T. C. Farrar, Anal. Chem., 42 No. 4, 709A (1970)

3. R. R. Ernst and W. A. Anderson, Rev. Sci. Instr., 37, 93 (1965)

4. B. P. Lathi, "Communication Systems", 89, John Wiley & Sons, Inc., New York (1968)

5. J. W. Cooley and J. Tukey, Math. Comput., 19, 297 (1965)

INDEX