THE AUTOMATED MEASUREMENT OF SPIN-LATTICE RELAXATION TIMES

Description and Instructions for T1 PROGRAM/II

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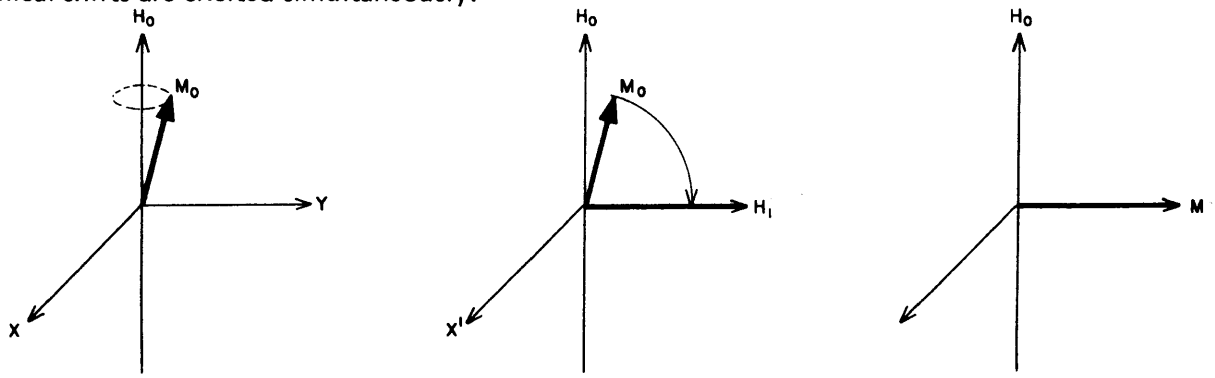
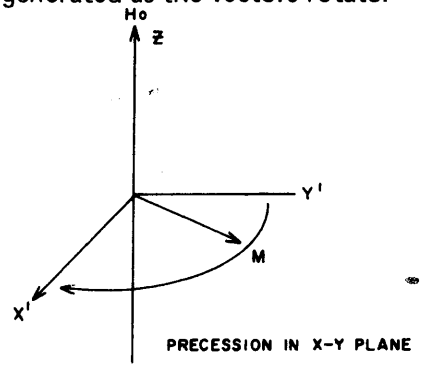
I. DESCRIPTION OF THE METHOD

In conventional FT-Nmr, the single 90° pulse is used to tip the magnetization of all the nuclei for which $\gamma H_1/2\pi \gg$ their chemical shifts. If we picture the nuclei in question as at equilibrium in the magnetic field, they precess around the field H_0 forming a vector M_0 precessing at their resonance frequency or Larmor frequency (a). In our figures, since it is difficult to represent this precession, we shall draw these vectors in a coordinate system which is also rotating at the Larmor frequency. This frame of reference is generally called the rotating frame. If a high energy rf pulse H_1 is applied in the xy plane, we can consider it as a rotating vector in the xy plane. The result will be to tip the magnetization M_0 into the xy plane if both H_1 and M are precessing at the same frequency (b, c). In fact, if the rf frequency is ω_0, it will cause the tipping of all vectors having Larmor frequencies such that $\gamma H_1/2\pi \gg \omega - \omega_0$. Thus, a large range of chemical shifts are excited simultaneously.



(a) (b) (c)

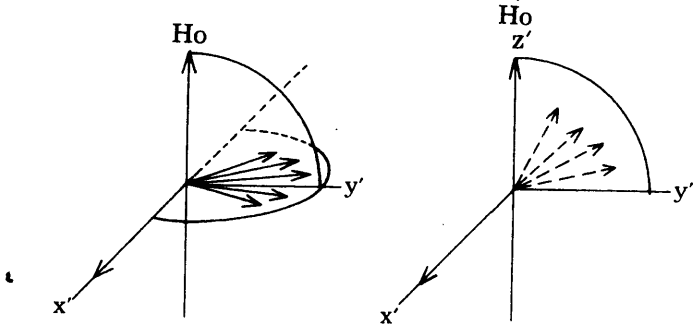
While these vectors are in the xy plane, they are still precessing at their respective Larmor frequencies and as rotating magnetic vectors, induce currents on the receiver coil also positioned on the xy plane. These currents will have a sinusoidal character, generated as the vectors rotate.



PRECESSION IN X-Y PLANE

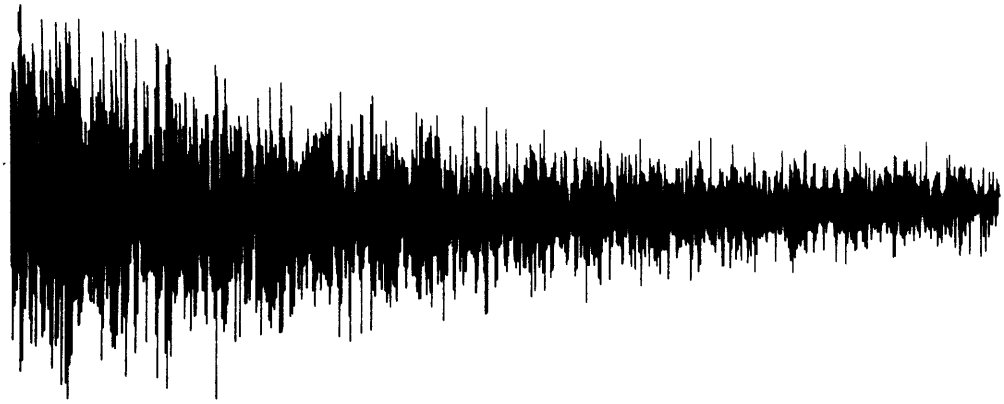
Following this pulse, the system has a tendency to return to equilibrium by two relaxation processes called longitudinal and transverse relaxation, or spin-lattice (T_1) relaxation and spin-spin relaxation (T_2). This latter process is often combined with field inhomogeneity contributions to produce the parameter T_2^*.

In our rotating frame, we can see that T_1 is the tendency for M to return to the z-axis from the x-y plane and T_2 the tendency for the vectors of the individual nuclei to dephase with one another in the x-y plane.



effect of T_2^* effect of T_1

For these reasons, the observed sinusoidal signal does not persist but tends to decay after the perturbing pulse has been removed. Thus, the recorded nuclear response is a decaying sinewave, called a free-induction decay.



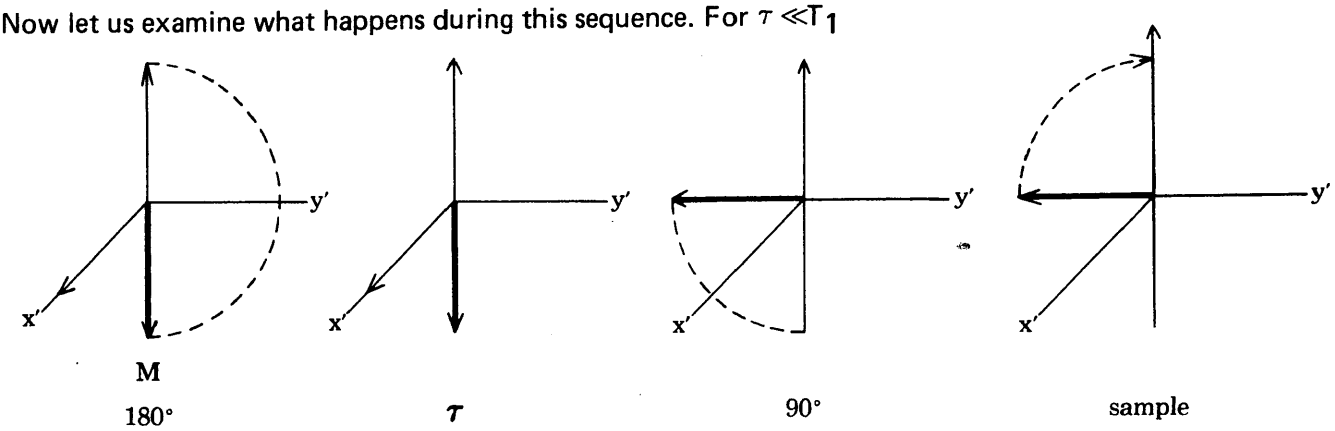
Let us now consider the method of measuring T_1 developed by Vold, et. al.[1] which has been referred to as the inversion recovery or partially relaxed Fourier transform spectroscopy.[2] In this method, the system, assumed to be at equilibrium, is excited with two rf pulses, a 180° pulse and a 90° pulse, separated by a delay time τ. For each spectrum in the set, this pulse spacing is varied. Following the 90° pulse, the free induction decay is sampled as usual and followed by a fixed delay T which must be at least 5 times the longest T_1 in the system, to allow for complete recovery of the magnetization.

The pulse sequence, then, is abbreviated

$$[180 - \tau - 90 - (\text{sample}) - T]_n$$

where n is the number of spectra to be summed.

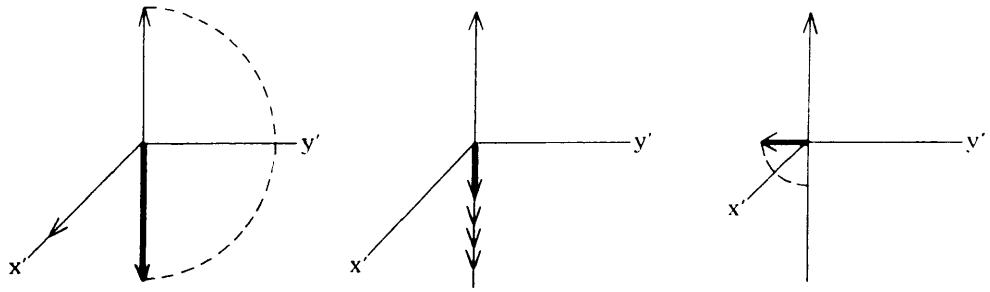
Now let us examine what happens during this sequence. For $\tau \ll T_1$



$$\tau \ll T_1$$

the 180° pulse rotates the magnetization M into the -z axis. If the delay time τ is quite short, very little relaxation will occur and the 90° pulse will cause rotation of the vector M into the x-axis from which it slowly decays back to +z while sampling occurs. Since this is roughly equivalent to a 270° pulse, it is not surprising that it produces a signal 180° out of phase with that produced by a 90° pulse, or, in other words, an inverted peak.

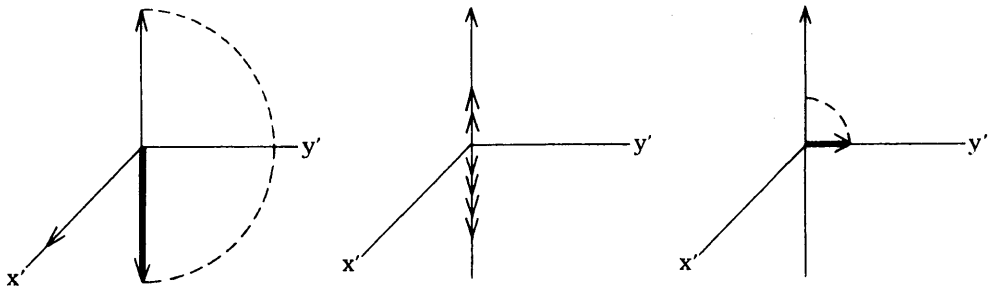
In the case where $\tau < T_1$ some spin-lattice relaxation will occur during the time τ. During τ, the vector M is "shrinking" up the -z axis during τ so that when the 90° pulse occurs a smaller negative signal occurs.



180° τ 90°

$\tau < T_1$

When $\tau \cong T_1 \ln 2$ the magnetization will be passing through the origin of our coordinate system and a null or zero signal will be observed for this line. As τ becomes longer, the signal will become a small positive peak as the magnetization relaxes into the positive z-axis as shown below.



180° τ 90°

$\tau > T_1 \ln 2$

Finally, after a time $\tau \gg T_1$, recovery from the 180° pulse will be complete and the 90° pulse will produce a full positive intensity signal.

To take full advantage of this technique, one simply selects a range of values for the pulse interval τ and allows the data system to accumulate a number of scans at each value. These data can then be stored on disk after each scan and processed all at once at the end of the experiment. This disk storage approach saves processing time during data acquisition and allows non-destructive experimental determination of the most effective exponential and/or trapezoidal window and phase correction constants. It also allows the production of stacked offset (isometric) plots without introducing the worry of pen skipping during data readout, since any spectrum can be replotted from disk if necessary.

II. LOADING THE PROGRAM

Introduction

The T1 PROGRAM/II tape (NIC-27-40327 or later) can be used with 1080's, NMR-80's (or NIC-80's) and BNC-12's. It is compatible with Bruker, TTI-Varian, JEOL and CAMECA spectrometers. A slightly revised version can be used with the CAMECA spectrometer to always make D3 = D2 - 11 usec.

T1 PROGRAM/II is used with the Nicolet 293 Controller and the Nicolet 294 disk system to control spectrometer pulses, and acquire sequential spectral data; each spectrum is stored on disk in files having similar names but sequential numbers. The data can then be viewed, processed as a group to the same parameters and plotted stereoscopically. If the data are from inversion-recovery T_1 experiments the T_1's can be calculated and printed out along with the standard deviation and calculated intercept.

The program allows the entry of pulse widths and spacings. Up to 30 different τ-values can be entered in any order. A number of τ_∞-values can be entered and all will be used in the calculation of the T_1's.

Program Loading

The T1 PROGRAM/II tape is provided as a single large tape containing a number of modules and routines. It requires that DEMON/II be loaded and will not work with the earlier DEMON/I. To minimize its size, two commonly used sections of sizeable length have been omitted. These are the FT sine look-up table and the floating point package. They can be incorporated, however, by loading the FT-Nmr program from disk. Any Nicolet, TTI or Bruker version of the FT program can be used as they all contain the sine look-up table at addresses 2000-3000 and FPP72 at 6000-7577. The sine look-up table will be used from memory. However, the floating point package must be stored as a file on disk named FPP72 before loading commences. (FPP72 is not complete in FT-Nmr-1974 and the actual FPP-1972 tape must be loaded and stored on disk as "FPP72" if this is the only program in use.) The file may be either protected to unprotected as desired. The following sequence is recommended for successful loading.

1. Start DEMON/II at 7600.
2. LOAD FTNMR — Load the FT program
3. STORE FPP72 6000-7577 — Store a copy of Floating Point 1972
4. Place the T1 PROGRAM/II tape in the reader
5. BIN — Start the Binary Loader.

Either a low speed or a high speed reader may be used to load this program. However since the tape stops several times and writes segments on disk, the non-incremental NIC-297 or NIC-297C reader cannot be used to load this tape.

After the tape has loaded, it will have written the following modules on disk:

- T1CNFG – The configurator module
- T1PRGM – The bootstrap module
- T1EXEC – The master control module
- T1PROC – The data processing module
- T1CLEC – The data collection module
- T1PLOT – The plotting module
- T1CALC – The calculation module
- T1CONS – A table of constants common to all modules.

During loading from paper tape, addresses 100000 – 100241 in data memory are used. This does not happen when the program is run later from disk.

Use of T1CNFG

To start the program after loading the tape the first time only, type

RUN T1CNFG

This starts the configurator program which asks a number of questions regarding your system. Answer them as indicated. This program sets a number of flags in the T1EXEC module regarding system type which are then used during data acquisition, plotting and knob display. If there is no FPP72 file on disk, the program will type NO FPP72 and exit to DEMON/II.

The T1CNFG module types out the following:

T1 PROGRAM/II CONFIGURATOR
TYPE RETURN IF COMPUTER IS A 1080
TYPE "N" IF NMR-80 or BNC-12:

This question sets a flag which assumes that the parameter knobs are on the NIC-293 if the system is a 1080 and are on the NMR-80 mainframe if the system is an NMR-80 or BNC-12. (These latter two systems are identical except for the name.)

TYPE "T" IF RF SYSTEM IS TT-1010, RETURN IF OTHER:

This question differentiates the XL-100 10,000 step digital plotter from xy plotters. It also assumes a radically different 293 patch panel use of the digital I/O lines for controlling the TTI interface to the spectrometer. If this question is answered with a T, the remaining questions are skipped.

If the above question is answered with a Return the program asks

TYPE RETURN IF X-Y PLOTTER, "D" IF DIGITAL:

A digital plotter is one which is driven step by step along the x-axis. These steps are produced at the PULSE1 output at the rear of the NMR-80 or banana plug J6 on 1080's. A reverse pulse comes from PULSE2 on NMR-80's and jack J5 on 1080's. These pulses are 400 nsec long and can be stretched using an interface available from Nicolet, if needed. If the plotter is an x-y plotter, it is then connected to the standard outputs at the rear of the data system.

If the above question is answered with a D, the program prints

ENTER NUMBER OF PLOTTER STEPS FULL SCALE:

Any positive integer can be entered here, followed by a Return.

For any non-TTI system, the program next prints

TYPE "Y" IF COMPUTER CONTROLS RECORDER PEN LIFT:

Answering Y to this question deletes Carriage Returns at the start and end of each plot.

Regardless of which options are selected above, the program will type

ILLEGAL MEMORY LAMP WILL NOW FLASH IF < 32K

This tests for the existence of more than 16K of data memory. If 20K of data memory is found, the front panel is assumed to be one reading 2, 4, 8 and 16K starting and 2, 4, 8, 16 and 32K size. Otherwise it is assumed to read 1, 2, 4 and 8 starting and 1, 2, 4, 8 and 16K size. This information is used in display and block size calculations. The wired measure processor already knows the status of the buttons independently of this test.

Lastly, the program types

T1 PROGRAM/II NOW LOADING

There is then a pause while the computer finds, loads and runs the T1PRGM bootstrap module. When the program has finished loading, it starts and prints an ampersand (&).

Use of the T1PRGM Module

Every time the T1 PROGRAM/II is to be used after the first, it is sufficient to type

RUN T1PRGM

as the flags regarding system type were set and stored on disk during a single running of T1CNFG. The T1CNFG program need only be re-run if the characteristics of your system change, as for example, if the pen lift is automated or if the computer is being used on two spectrometers.

If any modules are missing on disk, the program will print, for example,

NO FPP72

and exit to DEMON/II.

This module acts as a look-up program for the various modules stored on disk during the loading of the tape. This means that they can be changed and re-stored individually as each time T1PRGM is run, a new internal table of their disk positions will be created. This information is stored in T1EXEC, which is then started, printing the &.

Command Conventions

Whenever the T1 PROGRAM/II prints an ampersand (&), it indicates that it is ready for a new command. It displays the block selected by the pushbuttons while it is waiting. Each command consists of two characters. The second character actually executes the command. No Return need be typed. A Rubout character aborts any command when typed as a second character and serves as an error exit from many routines asking for parameters, when you do not desire to continue execution of that command.

Commands which involve entry of a constant always print out the old value and allow entry of a new one. If only a Return is typed the old value is retained.

File Name Conventions

DEMON/II recognizes 6-character file names for loading and storing programs and spectra. The T_1 program uses four characters to define a file name group. The last two characters may vary from 01 through 99, indicating the sequential position of that file within the group.

Any command which operates on a file will print out the file name which the program currently remembers followed by a space. The file name will always end in 01 and is to be taken to mean the entire group of names from FILE01 through FILE99, however many may be present on the disk.

After the space you may type a Return if this is the file which you wish to operate on and a new file name if you wish to operate on a different one. The new file name may be up to four characters. The program automatically types 01 after four characters have been entered. To continue execution, type a Return. If less than four characters are desired, you may type a Return after 1, 2 or 3 characters and the program will fill all remaining spaces with zeroes.

Thus, using the PR command as an example, where the text typed by the user is underlined

PR = ETPR01 SPC201

or, for less than four characters, a Return is typed following the A.

PR = SPC201 A00001

Users having more than one disk drive can take advantage of the ability of DEMON/II and T1 PROGRAM/II to utilize up to four disks. The T_1 program must be on disk 1, but can collect and process files on any disk drive. The entire filename group must be on the same disk, however. The unit number is specified by following the filename with a dash, a D and a number between 1 and 4. Thus, to collect data on disk 2, one simply types

GO = FILEØ1–D2

and to process files on one disk and put the results on a second disk, one types

PR = FILE01-D2
REPLACE? N
NEW FILE NAME = SPEXØ1–D1

III. COMMANDS USED IN T_1 PROGRAM/II

The following commands are available in T1 PROGRAM/II. They are listed by module and are marked with an asterisk (*) when they differ from similar commands of other Nicolet programs.

Executive Module

MO – Calls DEMON and writes out current T1EXEC and T1CONS
LI – Link together up to 13 commands
AU – Execute the linked list
PR – Process the specified files. Write a data file containing processing data.
NB – Jump to 114700, where high Nicobug must already be stored.
CB – Change blocks so that displayed region is now the total real part.

Data Collection Module

NS – Number of spectra to be taken
GO – Begin data acquisition. Prints out total time, based on SC and checks for available space before beginning.
CO – Continue data acquisition after interrupt
DL* – Delete file group (formerly DE)
DE* – Enter delay time for BNC-12 or NMR-80
P1 – Enter width of 180° pulse
P2 – Enter width of 90° pulse
P3 – Extra, unused pulse
P4* – Extra, unused pulse
D1 – Enter up to 30 delay times
D2 – Enter repetition rate
D3 – Extra, unused delay
D4* – Extra, unused delay
ON – Turn on pulses. Also called by GO and SE
OF – Turn off pulses. Also called by program startup, and exit from GO or SE
SW – Enter spectral width. Calculates and prints dwell.
DW* – Enter dwell time. Calculates and prints spectral width
SE – Enter setup mode
VI* – View input
CD* – Continuous display
AD* – Add data
SD* – Subtract data
PT* – Positive trigger
NT* – Negative trigger
AR* – Auto-recur
SC* – Number of scans per spectrum. Works with 1080's if Autostop is set to 1.
IN – Increment for setup mode
ZE – Zero measure selected area
OV* – Override duty cycle protection
NV* – Non-override of duty cycle protection
LS – List acquisition parameters
HS* – Enable homospoil pulse (TTI systems only)
HR* – Homorestore. Disable homospoil pulse (TTI systems only)
WP – Number of pulses to wait between tau value changes
TI – Enter title
CP – Change stored parameters of a given file
TT – Print out total time that an experiment will take
LD – List out delay times and pulse widths
AV – Begin signal averaging in memory – without zeroing memory

Processing Module

EP* – Expansion and phase correction (requires phase knobs)
EC* – Expansion and phase correction using point last selected by CU
EM – Exponential multiplication
TC* – Time constant entry. Prints out Hz broadening if SW is entered correctly
FT – Fourier transform displayed area
PK* – Phase correction from last setting of phase knobs
BC – Baseline correction
SR* – Spectrum reverse of last FT'd block
PA – Enter zero order phase correction
PB – Enter frequency dependent phase correction
PC – Manual phase correction of last FT'd block
TP – Print out total manual phase correction since last FT
T1 – First trapezoidal apodization point
T2 – Second trapezoidal apodization point
TR – Perform trapezoidal apodization
NC – Print out last FT's normalization constant
DC – Enter multiply constant for AT
DF – Designate area from which data is to come
DT – Designate area to which data is to go
AT – DC*DF+DT→DT
MV – Move DF into DT

Plot Module

PL – Plot display block
OP – Offset parameter entry
LP – Length of plot in % of full scale
CU – Cursor mode
ID – Integrate display
IX* – Integrate expanded region
PX* – Plot expanded region
SP – Stacked plot of entire displayed area
IS – Integral scale factor
AC – Add Constant
SX* – Stacked plot of expanded region
IR – Intensify region
VW* – View successive files in series (formerly VI command)
VX – View successive files in series displaying only expanded regions
F1 – Examine and enter one boundary of intensified region
F2 – Examine and enter other boundary of intensified region

Output and Calculation Module

SO – Spectrum offset
SF – Spectrometer frequency (MHz)
MI – Minimum intensity
PP – Peak printout
XP – Peak printout of expanded region
GL – Grand list
UI – Use intensities in T1 calculation
UA – Use area in T1 calculation
CT – Calculate T1's of displayed area
CX – Calculate T1's of expanded region

* Indicates commands new to this program. VI, CD, AD, SD, PT, NT and AR operate only on NMR-80's and BNC-12's. SC operates on 1080's only if the Autostop is set to 1. HS and HR operate only with TTI systems. The EP, ID, IX and AC commands require phase knobs.

IV. ACQUISITION MODULE COMMANDS

SW -- Spectral Width

The value of SW, the spectral width, is entered in Hz. It can vary from 50000 (50 kHz) to .4768 Hz. The sampling time per point (or dwell time) thus varies from 10 usec/point to 1.048 sec/point. Note that since it takes two points per cycle to define a sine wave, the computer can sample at 100 kHz but can define a spectral width of only 50 kHz.

When the entry of SW is terminated with a Return the program prints out the exact sweep width, the dwell time in microseconds and the acquisition time for that setting of the pushbuttons. (In 1080's the Measure buttons are read, in NMR-80's the single row of Readout-Measure buttons is read.) Thus, for entry of a spectral width of 5000, the following occurs:

```
&SW=      5000.000  11000
SW =     11111.111
AQT =        0.184  SEC
DW =        45.000
```

11000 is entered
Exact spectral width is 11111.111 Hz

DW – Dwell Time

This command is redundant with SW, allowing entry of the sampling rate as the time per point or dwell time. When this command is terminated with a Return the corresponding SW and AQT are printed out and stored.

AD, SD -- Add Data, Subtract Data (NMR-80, BNC-12 only)

The value which is digitized at the A-to-D converter is either added to or subtracted from memory depending on whether AD or SD was last typed. In order that the external switching between add and subtract may be used on the NMR-80, the program must be in the AD state. This is the normal, or default option.

PT, NT, AR – Positive Trigger, Negative Trigger, Autorecur (NMR-80, BNC-12 only)

These commands allow triggering of the data system on the rising or falling edge of a trigger pulse depending on whether PT or NT is set. If Auto Recur is entered, triggering occurs automatically at the end of the previous sweep.

VI -- View Input (NMR-80 and BNC-12 only)

This allows display of the signal as it is digitized regardless of the contents of memory. This is useful in adjusting the spectrometer gain so that the signal just fills the ADC. The signal should fill one scope division on either side of zero at the following vertical display scale setting and digitizer resolution settings. All settings are not available on any machine. The possible 1080 and NMR-80 resolutions are combined in the table below.

Digitizer Resolution	Vertical Display Scale Setting (for filling two divisions)
12	2048
10	512
9	256
8	128
7	64
6	32
5	16

CD – Continuous Display (NMR-80 and BNC-12 only)

During Continuous Display, the entire spectrum is displayed regardless of delay time or sampling rate. This is the display mode of preference for general averaging and is set as the default mode within T1 PROGRAM/II.

ZE – Zero the Area Selected by the Measure Buttons

The ZE command zeroes the area which is selected by the Measure buttons in 1080's and by the single row of buttons in NMR-80's. It is of little utility except in conjunction with the AV command, since both the SE and GO commands also zero memory before starting.

OV, NV – Override, Non-override of Duty Cycle Protection

The program normally requires that all pulses be less than 201 usec and that delay D2 be greater than 1 msec. If the user wishes to override this provision for use in a Homospoil T_1 sequence, for example, typing OV disables this protection. Typing NV re-enables it.

SC – Number of Scans per Spectrum

The SC command allows entry of the total number of scans which are to be taken per spectrum. This number is necessary for NMR-80's and BNC-12's, but is an option for 1080's. It will only work properly in the 1080's if the Autostop counter is set to 1. Since in 1080's the computer stays in Measure until all scans on the Autostop have been taken, the Autostop value is therefore multiplied by SC. In general, it is desirable to set the Autostop to 1 and let the software take care of the sweep count, as this does allow the correct total time to be printed out. In this mode in 1080's, the Sweeps Completed display will always read zero.

The SC command should be distinguished from NS. SC is the number of scans per spectrum and NS is the number of spectra in the set.

SE – Setup Mode

The setup mode is provided for optimizing the pulse width for a 90^o, 180^o or 360^o pulse. In this mode, only a single pulse can be given the sample and the amplitude of the resultant FID can be observed on the display. P2 becomes the pulse whose width is varied by a preselected increment. To prevent the P1 pulse from reaching the rf equipment, disconnect the cable from BC1 to AA1. In TTI systems this is unnecessary; setting P1 = 0.1 disables it completely. Then, set the value of D2 to a time greater than 5 times the largest T_1 in the sample. Finally, set D1 and P1 to very small values, such as 1 usec each. These each become part of the total pulse interval. Then, enter the desired pulse increment using the IN command. It is generally most useful to set the Autostop Counter and SC to 1 sweep.

Typing SE zeroes the Measure area of memory, turns on the pulse sequence and records the next fid. The program returns to software control, displaying the accumulated spectrum and waiting a new command. The following commands allow the manipulation of the pulse widths:

I	increment the pulse width by IN
D	decrement the pulse width by IN
R	zero memory and take a new scan
CR	exit from the SE routine

If the pulse width is incremented beyond 200 microseconds the program will type a question mark and exit from the SE mode. During the SE mode, the pulse train remains on. It is not restarted by the R command, and there may be some delay between the R and the actual triggering of a sweep.

IN – Enter the increment for the SE mode

The value of IN is entered in microseconds. If it is greater than 26.214 milliseconds a question mark is typed.

NS – Print the number of spectra to be taken or enter the number to be taken

If a T_1 experiment is to be performed, NS will type out the number of τ values which have been entered in D1 to be used during data acquisition. If there is only one value entered in D1, the program becomes a kinetics program and will allow acquisition of up to 99 successive spectral files named FILE01 through FILE99. In this case, the command NS will allow entry of the number of successive spectra to be obtained. When there is more than one D1, NS will print out the number of entries but will not allow entry of any number.

P1, P2, P3, P4 – Enter the widths of the 180° and 90° pulses

Typing P1 or P2 causes the pulse length to be printed out and allows entry of a new pulse length. The program assumes that the value is in microseconds. P3 and P4 are not used on the basic program but are loaded when P3 and P4 are typed and may be used as homogeneity spoiler pulses, or as receiver gating levels if desired. The maximum pulse width is limited by software to 200 usec. Longer pulses will cause a ? to be typed. This is designed to restrict the duty cycle of the spectrometer pulse gates. It can be changed if desired using the OV command.

D2, D3, D4 – Enter the recovery time T and other delays

Typing D2 allows examination and entry of the second delay time D2 which is commonly used as the pulse repetition rate. This parameter is assumed to be in seconds. D3 and D4 are not used by the basic T_1 program but can be used for receiver gating or homogeneity spoiling if wired into the pulse sequence. The minimum allowable value of D2 is .001 sec. This is a software limitation to restrict the duty cycle, but it can be changed if desired, using the OV command. Some signal to noise enhancement can occasionally be gained by adding 1/4 of an AC cycle to D2; for example D2 = 1.0125 sec for AC current of 60 Hz or 1.010 for 50 Hz.

D1 – Enter the list of variable delay times

Typing D1 allows examination and entry of the list of delay times stored in the list. As many as 30 different τ values can be entered. The times are assumed to be in seconds as in D2. After each entry is terminated with a Return, the program automatically goes on to list the next one in the table and allow its modification. To get out of the list at any time, enter a zero value for the last parameter. To get out of the list at some point short of the end, type an ALT MODE. This key is labeled ESC on some Teletypes. Note that data acquisition will continue until a zero value of D1 is encountered in the list.

ON, OF – Turn the pulses on and off

Assuming that the patch panel configuration given in Chapter IX is used, these commands will allow the pulses to be turned on and off on command. The pulses are also automatically turned on by a GO, CO or SE command and are disabled when this process is complete. If D2 $<$ .001 sec, a ? will be typed and the pulses will not be turned on. This error protection is removed by the OV command.

GO – Go, begin data acquisition

When GO is typed the program will type = followed by the previously referred to filename. At this point you can enter a new four-character filename or type a Return, which will leave the old filename intact.

The four-character filename can be composed of any four printing characters and should be terminated with a Return. If less than four characters are entered followed by a Return, the remaining characters will be zeroes. The last two characters are always 01 and are automatically printed by the program if a Return is typed with less than four characters or upon the typing of the fourth. If the entered characters are ABCD, this creates the beginning of a series of files which will be named ABCD01, ABCD02, ABCD03, etc., and are used during data acquisition of successive spectra. If the filename that has been entered already exists in the disk the error message ABCDØ1 USED will be printed.

The program then checks the disk for sufficient space to store all of the files that will be collected. If there is not, the message INSUFFICIENT DISK SPACE is printed. You must then delete enough files that sufficient space is available. The DEMON/II directory listing routine combines adjacent empty file spaces and it is sometimes sufficient to list the directory and try again.

The program next prints out

TITLE =

and allows entry of up to a 51 character title which is stored on disk with the spectra. Typing a Rubout while entering the title aborts the entire GO routine and the title must be re-entered after again giving the GO command.

Following the title entry the program calculates the total time required for the experiment and prints it out in minutes or hours. For this calculation to be correct in 1080 systems (as opposed to the NMR-80 series) the Autostop counter must be set to 1 and the total number of scans entered using the SC command.

Collection of spectra then begins. The program prints out the tau value of the current spectrum and then begins acquiring it. Averaging can be stopped at the end of any sweep by typing CTRL/Q and at the end of any group of sweeps by typing Q. Each file is written onto disk following the acquisition of the total specified number of scans and the program then waits for the next 90^{o} pulse before changing the tau value and going back into measure. Each new tau value is printed on the Teletype. If WP, the number of waiting pulses, is > 1 they will be counted off here before returning to measure.

The sweep counter display in NMR-80 and BNC-12 systems shows both the spectrum number and the scan number. The spectrum number is multiplied by 100000 and the scan number is shown as the lowest significant digits of the counter. For example, scan 12 of spectrum 3 would be shown as 300012.

When the averaging is complete the program stops and returns to the executive module and types an &. The files written on disk will be named ABCD01, ABCD02, etc. (or whatever four-character name was selected). An additional file named ØØABCD will be created containing the pulse widths, delays, dwell time and title, where the symbol Ø is used to represent a space. Memory overflow will be prevented in BNC-12 and NMR-80 systems only.

CO – Continue averaging after interruption

The CO command allows continuation of averaging after an interruption caused by typing Q. Accumulation of spectra on disk continues until all non-zero values of D1 are obtained, or until NS has been satisfied if there is only one entry in the D1 table. No attempt should be made to continue after aborting with CTRL/Q.

DL – Delete all files having the first four characters specified

The DL command will echo the current filename and allow entry of a new filename of up to four characters or of a Return. This indicates that all files from FILE01 through FILE99 are to be deleted as found in the directory. Since this is a major deletion of information, the program prints CONFIRM: and waits for the character Y before actually proceeding with deletion. If files named ØØFILE or ØFILE0 have been created, these are also deleted. If there are no files having these names, the message NO SUCH FILES is printed. To abort this command without deleting anything, type a Rubout instead of a filename or instead of the Y.

TT – Print out the total time the experiment will require

This command simply calculates the total experiment time, converts to minutes or hours depending on the size of the result and prints it out. The TT command uses the currently entered values for SC and the delays. For 1080's it assumes that the Autostop is set to 1 and that the total number of scans is entered in SC. The GO command automatically calls TT and prints out the total required time.

WP – Number of pulses to wait after changing D1

The program automatically waits at least one additional pulse cycle before changing D1 so that it is changed immediately after a 90° pulse. If the program is to wait additional cycles before acquiring more data, this number of cycles should be entered in WP. This is useful in progressive saturation experiments, to re-establish pulse equilibrium.

LD – List out Delay Times and Pulse Widths

This command lists the values of P1 – P4, all D1's and D2-D4's currently stored in memory. This listing can be aborted by typing Q.

HS, HR – Homospoil and Homo Restore

These commands are used only in TTI systems to enable or disable a gate which allows a homospoil pulse to be triggered at a user selectable time. The pulse is normally triggered after the 180° by the patch connection from BC3 to AC5. Any rising edge will trigger the Homospoil pulse and can therefore be patched into AC5, depending on the desired experiment.

AV – Average Data into memory

This command allows averaging of data into memory. The pulse train is turned on and SC scans are taken. Memory is not zeroed unless the ZE command is specifically given.

TI – Enter Title and CP – Change Parameters

The TI command allows entry of a title up to 51 characters long. This command is automatically called during the GO command thus automatically writing a file onto disk with the correct title. The TI command is useful only if a new title is to be written into an existing file or if a file group created with another program or manually is to have a title added.

The GO command always writes an additional file with two leading blanks onto disk, called for example ØØABCD if the file name is ABCD01. This file contains the pulse widths, the delay times, sampling rate and number of scans, as well as the title. During processing of the files, a second data file containing processing parameters such as TC, PA, PB, phase knob settings, expanded region, spectrometer frequency, and T1 and T2 is written, and named ØABCD0. The CP command rewrites both of these files using the information currently in memory. These files having leading spaces in their names cannot be deleted by the DEMON/II DELETE command, but are deleted using the TIPROGRAM's DL command.

To be sure that this updating of information is non-destructive, you should first be sure that the correct current data files have been loaded into memory by typing LS. After reading the data listed by LS, make any necessary corrections and type CP. The program will allow entry of a file name and then, following a Return, will type

CONFIRM:

You must answer this with a Y for the change to be made on disk.

The Change Parameter command is useful if you wish to change the offset before a GL command, as the offset is stored on disk and will be read in before the GL is started. Further, files created with the 1973 version of T1PRGM (running with DEMON/I) will have the pulse widths correct but will not have the correct title, and processing parameters.

LS – List acquisition parameters of a particular file group

The LS command prints out the parameters used in acquisition and processing of a file group. If you wish to

print out those currently in memory rather than those associated with an existing set of files, enter a non-existent filename.

All of the parameters which are printed out are self-explanatory, with the possible exception of TA and TB. These are the total manual phase correction values which have been applied using PA and PB. The values used by the knob routine EP are not converted to degrees and are therefore not included. They are saved on disk, however, and are loaded whenever that file group is loaded. The T1 and T2 printed out are not nuclear parameters, but rather are the addresses used in any trapezoidal apodization. The NC is the FT normalization constant used during processing of the entire file group. This listing can be aborted at any time by typing Q.

```
&LS= DODE01

DODECYL ALCOHOL IN C6D6
P(180)=      100.000 USEC
P(90)=        50.000 USEC

TAU VALUES
=          0.100 SEC
=          0.200 SEC
=          0.299 SEC
=          0.400 SEC
=          0.499 SEC
=          0.600 SEC
=          0.699 SEC
=          0.800 SEC
=          0.899 SEC
=          1.000 SEC
=          1.499 SEC
=          2.000 SEC
=          2.499 SEC
=          3.000 SEC
=          3.499 SEC
=          3.999 SEC
=          5.999 SEC
=          7.999 SEC
=          9.999 SEC
RECOVERY TIME=        14.999 SEC
P3=          0.100 USEC
D3=          0.001 SEC
P4=          0.100 USEC
D4=          0.001 SEC
TOTAL SCANS=       32

NO. OF FREQ DOMAIN POINTS =    2048
SW=      1501.501
DW=       333.000
DE=         0.000
SO=         0.000
TC=         0.500
SF=        25.144
TA=         0.000
TB=         0.000
T1=         0
T2=         0
NC=         2

&
```

Since the LS command reads in data from disk, previous value of all the parameters are lost.

V. PROCESSING MODULE COMMANDS

Many of the commands summarized below are exact copies of those used in Nicolet's FT-Nmr programs. However, they are described for completeness.

FT – Fourier Transform Displayed Region

The FT command performs a fast Fourier transform on the displayed region of memory. It is the user's responsibility to be sure that that region contains the entire free-induction decay. At the time of the transform, the T1 program remembers the size and position of this block. This data is used in phase correction routines and frequency calculations.

TC – Enter Time Constant for EM

This allows entry of a time constant, as a pure number. This is the power of e which is to be used in producing the decaying exponential used in EM. If the spectral width (SW) is correctly entered, the program will also print out the number of Hz broadening produced by use of this window.

EM – Multiply Displayed Region by Exponential Window

The exponential window is useful in producing enhanced signal-to-noise or narrower lines, as discussed in the FT-Nmr manual. The free induction decay will be multiplied by exp (TC x i/N) where N is the number of data points and i is the index of each point. It is the user's responsibility to see that the entire fid is displayed before giving the EM command. If a negative TC is chosen, signal-to-noise will be enhanced at the expense of some line broadening. If a positive TC is chosen, lines will be narrowed and some fine structure may appear, but signal-to-noise will be worsened in the process. The utility of this approach has been demonstrated recently by Schaeffer.[3]

T1, T2 – Enter Trapezoidal Apodization Points

These points are entered as decimal addresses, so that the first point is numbered 1 and the last 4096, 8192 . . . depending on the block size used. T1 is entered as the number of addresses from the left edge of the display to be apodized and T2 as the number of addresses from the right side to be apodized.

TR – Perform Trapezoidal Apodization on the Displayed Area

TR multiplies all points between address 1 and address T1 by a rising diagonal and all points between the last T2 and the last by a falling diagonal window. In other words the multiplication

$$P_i' = Pi \times T1/i \Big|_{i=1}^{T1} \quad \text{and} \quad P_j' = P_j \times (\text{last}-j)/T2 \Big|_{j=\text{last}-T2}^{\text{last}}$$

are performed.

Trapezoidal apodization is most useful in removing small pulse feed-through effects at the beginning of free induction decays and reducing the very end of the free induction decay to zero before an FT with zero filling.

BC – Baseline Correct the Displayed Region

This command is automatically called by FT, TR and EM. It simply sums the entire displayed area and makes this integral equal to zero by subtracting or adding some number to each point. In general, this command need not be given separately unless unusual fid asymmetry requires it.

NC – Print Out the Normalization Constant Used in the Last FT

Since the Fourier transform involves a large number of multiplications, the program must continually scale the data so that it does not become larger than that which can be handled by a 20-bit word. This is

recorded in memory as the normalization constant NC. It is the number of shifts necessary to keep the data scaled. This is, in other words, the number of powers of two which the data have been divided by. During processing of a file group, the program keeps track of the normalization constant and keeps it constant for the entire group.

PA, PB – Zero Order and First Order Phase Correction Constants

PA is the number of degrees that the phase of the entire spectrum will be rotated during PC. PB is the frequency dependent phase correction term, giving zero correction to the first point and the specified number of degrees to Nyquist frequency point. These are entered in degrees. Note that PA = +270 and PA =–90 are equivalent. Further PA = 90 and 450 are equivalent. However, PB = +90 and PB = +450 are distinctly different as the 450° entry rotates the entire spectrum phase around 1¼ times, putting a phase "twist" run in the middle of the spectrum.

PC – Perform the Manual Phase Correction Entered in PA and PB

PC performs the phase correction specified in PA and PB on the last transformed block. If a frequency domain spectrum has been loaded from disk of a different size or location that this last block, the block location must be changed using the CB command.

TP – Print Out the Total Manual Correction Since the Last FT

The TP command prints out the total PA and PB since the last FT was performed. This does not include any knob corrections.

SR – Spectrum Reverse

SR reverses the real and imaginary parts of the last transformed block. This can be useful when the carrier is placed on the high frequency side of a spectrum, giving a spectrum whose frequencies are reversed in presentation. The only purpose of this command is to reverse the spectrum from right to left for peak printout or plotting. Phase correction can still be performed but the sense of the frequency dependent term is reversed as well.

EP – Expand and Phase Correct Using Phase Knobs

The EP command is unique to the Nicolet package and to T1 PROGRAM/II. It allows a knob-controlled zoom expansion of any region of the real part of the spectrum, followed by real-time phase correction. The NMR-80 digitizer resolution must be set at 12 bits.

1. Expansion

When EP is first typed, the program immediately displays the entire real part of the last transformed block. The left hand knob controls position and the right hand one the expansion size. The knobs are read according to relative position, so that whatever position they are found in at the beginning of the routine is regarded as the "zero" position. Rotating knob A to the left should move the spectrum to the left and rotating it to the right should move the spectrum to the right. Rotating Knob B to the left expands the spectrum around the middle and rotating it to the right contracts it. Should you run out of knob range while using the expansion routines, position knob A at about mid-range and knob B at its right end and type R. This resets the relative position of the knobs to full scale and allows re-expansion using the full range of the knobs.

Exit from the EP command to the T1 command decoder is by typing Return. At the time Return is typed, the program remembers the knob current expansion in frequency units which are then used whenever a command involving the expanded region is given, such as PX, SX, VX, XP, CX, and F1 and F2.

2. Phase Correction Display

While in the expanded display of EP, typing P will allow entry to the phase correction mode. It is important that the spectrum be expanded before entering the phase mode, as the display will be too slow to be readable if too many points are being displayed.

As the phase correction mode begins, knob A controls the spectrum position as before but knob B now controls spectrum phase rather than expansion. Upon entry to this routine knob A controls the zero order or non-frequency dependent phase term and it should be used to phase the line having the bright spot on it correctly. This line is the one which has been found to be the largest in a magnitude spectrum and the bright spot should be on the top of it. Once the line having the bright spot is in phase, the frequency dependent phase correction can be performed in a uniquely convenient way.

Typing B while in the phase correction mode, changes the meaning of knob B from zero order phase mode to first order phase mode. During this B mode the phase of the peak having the bright spot on it will be held constant and the frequency dependent phase of all other lines will be rotated around it. This should allow phase correction to take place without iteration. To check lines at the other end of the spectrum for their B phase, simply move knob A to display this portion of the spectrum and adjust the phase accordingly. If, at any time the phase knob runs off scale at either end, move the knob to the other extreme and type K. This resets the knob value to zero.

3. Phase Correction in Memory

The phase correction during display is on the display only. Memory is unchanged by all these display manipulations. To perform the displayed correction on the contents of memory, simply type P or C. C will phase correct and return to the expanded display mode with the expansion unchanged. P will phase correct and return to display the full spectrum.

To exit from the phase correction mode without doing anything, simply type R to reset the knobs and return to the expansion mode or Return to return to expanded display.

The complete set of commands in the expanded display mode is summarized below:

EP – enter expand and phase correction routine
- R – reset knobs so that current position is "zero"
- P – enter phase correction mode. Knob B is initially zero order phase
  - B – make knob B first order phase (B-mode phase) and hold cursor point phase constant
  - A – make knob B zero order phase (A-mode phase)
  - K – reset the value of knob B
  - R – reset knobs and return to full display
  - C – perform phase correction in memory, and return to expanded display
  - P – perform phase correction in memory, reset expansion to full scale and return to expanded display routine
- A – enter phase correction mode and add result to previous correction. Commands are the same as under P.
- Return – Exit to EP without resetting knobs

Return – Exit from EP

4. Remembering the Constants and Region of Expansion

All of the phase corrections that are performed during a phase correction display are remembered by the program. If you exit to EP and then re-enter the phase mode using A the corrections are summed. These numbers are not remembered as degrees and therefore are not printed out by the TP command. However, it is a simple matter to correct the spectrum in a single iteration as the cursor brightened line is held constant in phase while the frequency dependent term is varied.

The region last expanded is also remembered when the program exits from EP, and these two limits can be found by examining frequencies F1 and F2. If your system does not contain phase knobs, expanded regions can be specified by F1 and F2 directly or within the cursor mode.

PK – Phase Correct According to Last Setting of Knobs in EP Routine

The PK routine phase corrects the last Fourier transformed block to the parameters which were used when the last phase correction (or group of corrections) was done on memory by the EP command.

EC – Perform EP but Use a Point Selected by CU

The EC command expands the display in the exact same way as does EP. However, when the phase correction mode is entered by typing P, the intensified point is that last selected by the cursor routine. This is useful in cases where the strongest peak is not the most convenient one to phase correct, as in the case of a solvent peak or an address zero spike caused by residual DC level in the fid.

DF, DT – Enter Data From and Data to Regions

After typing DF or DT, the program awaits a Return. The position of the Readout pushbuttons is remembered and the DT and DF starting addresses are used in the AT and/or MV commands.

AT – Additive Transfer

The size specified by the readout pushbuttons at the time of AT is used to define a block size. The block of this size starting at the address specified by DF is multiplied by the entered constant DC and added to the block specified by DT. The sum is stored in the DT block and the DF block is unchanged. This can be used for spectrum addition or subtraction.

DC – Data Transfer Constant

The constant to be used in AT can be entered in the usual fashion.

MV – Move Data

The block starting address is defined by DF, the size by the buttons at the time of MV and the destination by DT. The DF block is moved to DT. The previous contents of DT are lost, DF is unchanged.

VI. EXECUTIVE MODULE COMMANDS

MO – Call the DEMON/II Monitor

This commands writes the current parameters of the T1 PROGRAM on to disk by copying T1EXEC and T1CONS back onto disk and then jumps to 7600, calling the DEMON/II monitor. The program can be restarted by simply giving the DEMON command GO.

CB – Change Blocks

The current block size of a processed file is remembered by the program for use in phase correction and peak frequency calculations. Should a new frequency domain spectrum be loaded, which has a different size, this must be indicated by typing the CB command while the entire real part is displayed. If a time domain spectrum is loaded or acquired, the block size is automatically changed when an FT command is given.

LI – Link Commands

The LI command allows the linking of up to 13 commands to be executed as a group. The commands must be typed immediately after the LI without spaces. For instance, to link together EM, FT and PK, you type LIEMFTPK followed by two carriage returns. The list can be aborted at any time by typing Rubout during entry. If an illegal command is entered, this is detected, the entire list is cancelled and a ? is printed.

AU – Automate; Execute Linked List

The AU command executes the commands in the linked list. This operation is performed only on the displayed area of memory and commands which require keyboard interaction, such as constant entries, still require this interaction in the AU mode.

NB – Jump to 114700

This command is intended for debugging of routines added by users. It causes a jump to 114700, where Nicobug/II is assumed to be resident. If no program is there, disaster may result.

PR – Process a Group of Files According to AU

This command causes a group of files having the same first four characters to have the commands in the LI list executed upon them. The result is placed either in a file of the same name or in a new file name group. Assuming the commands have already been entered in LI, we can use this command by typing:

PR = ABCD01 SPXP01 Old file name echoed. New one entered. 01 appended.

REPLACE?

If the REPLACE question is answered Y, the processed data replace the original data on disk. In general, this is not a good idea, as various manipulations can always be performed on the time domain data to produce differing frequency domain spectra, but little change can be effected on frequency domain data once the free induction decays have been deleted. Thus, whenever there is room on the disk, it is advisable to answer REPLACE? with an N.

If REPLACE is answered with any character but Y, the program prints

NEW FILE NAME = Ø1

The use can then enter a new file name for the processed data. If this file name already exists on disk, the program will print ABCD01 USED, where ABCD01 is the existing file name. A good practice to conserve

disk space is to keep only tree-induction decays permanently on disk, and have one file name which is always used for processed data, such as TEMP01.

Processing will then commence with each file being ready into memory, operated upon by the commands in the LI List and stored on disk in the new file which was specified. If there is not enough disk space available for the processed files, the message INSUFFICIENT DISK SPACE is given. The program will return to the command decoder and type an & when it is done.

> NOTE: The first file of the group should contain peaks of average intensity as the scaling constant for the entire set is computed from the FT normalization constant used in processing the first file. If the first spectrum contains mostly nulled peaks, some of those spectra having larger intensity peaks may be off scale.

If you inadvertently end up in a situation where the first spectrum has mostly nulled lines, simply interchange the first spectrum with another having greater intensity. This can be done using DEMON/II as follows: where we interchange SPECØ1 and SPECØ6.

```
LOAD SPECØ1
STORE TEMP : B                    Set buttons to display entire fid
LOAD SPEC Ø6
STORE SPECØ1 : P
DELETE : Y
LOAD TEMP
STORE SPEC Ø6 : P
DELETE : Y
DELETE TEMP
DELETE : Y
```

The underlined portions are printed by DEMON/II. The order of the D1's must also be changed in the list for accurate T_1's to be calculated, using the CP command.

VII. PLOT MODULE COMMANDS

The plot module contains the cursor display, integration display, view file group routines and the single and stacked plot routines. There are described below.

CU – Display Cursor

The CU command works exactly as in the FT-Nmr program. When CU is typed, a number is printed out representing the current cursor position. This number will be zero the first time the program is used. The cursor position is a decimal number starting with the left-most address of the last transformed block as address 1. The highest address will be 2048, 4096 or whatever the displayed block size is. Following the entry of a new number, typing Return displays the selected region with a bright spot on the specified address. This cursor can then be shifted right or left by typing R or L to step it one point at a time in either direction or can be started moving in either direction by typing MR or ML for move right and move left. The commands are not echoed on the Teletype. Once the cursor has started moving, it can be stopped by typing S.

The address of the cursor can then be examined and assigned to a display expansion limit by typing F1 or F2. These commands assign the current position of the cursor to one end or the other of a region to be expanded. When F1 or F2 is typed, the program prints out the current cursor address, the corresponding frequency and the absolute value of the contents of that address. This is shown below:

```
&CU=          0  1500                          1500 is entered
F1=      1319      1356.445        364   ML is typed (not printed), then S, then F1
F2=      1384      1324.707       9041   MR is typed, then S, then F2

&
```

This thus defines a new F1 and F2 for an expanded region to be used in expanded region commands such as IR, IX, PX, XP, SX, VX and CX. The last region specified by either the cursor mode, F1 and F2 directly or EP is the one remembered and used in these commands.

In the cursor mode, it is also possible to assign a particular point to a given frequency. This is done by placing the cursor on the peak of interest, for instance, TMS, and then typing A. The program will print an equals sign and any number can be entered. This will allow the assignment of a frequency to that point. This will affect the offset of the spectrum recorded in memory.

Exit from the cursor routine is accomplished by typing a Return. The complete set of commands available in the cursor mode are:

- R – step right
- L – step left
- MR – move right
- ML – move left
- S – stop moving
- A – assign a frequency to this point
- F1 – assign this point to F1
- F2 – assign this point to F2
- Return – exit from the CU mode.

ID – Integrate Display

This program allows the user to integrate the displayed region of a spectrum. It displays the integral and allows the knobs to be used to vary the slope and curvature of the integral, corresponding to the DC and baseline tilt of the original spectrum. Knob A controls the curvature and Knob B the slope.

When the integral is properly adjusted, it can be plotted by typing P. If, during the plot, the integral would go off scale, it can be reset by typing R. This raises the pen and moves it back to zero. The pen can then be lowered when desired by typing P again. As in the plot routine discussed below, F and S control faster and slower plotting speeds and Q will interrupt the plot immediately.

The integral commands are:

ID – Integrate display
P – plot displayed integral
R – raise pen and reset to zero
P – lower the pen again
F – plot faster
S – plot slower
Q – interrupt plotting
Return – exit from ID

IS – Integral Scale

The IS command controls the overall normalizing factor used in calculating the integral and may vary from -15 to +15. It is set at 5 on the supplied tape as a median value. This value should allow most integrals to be plotted to any desired height by simply varying the vertical display scale switch. Should you find that you wish to plot the integral of a very small region of low intensity, the value of IS may be decreased somewhat. Each step increases the value of the final integral by a factor of 2.

This IS feature also allows absolute integrals to be obtained from different spectra and accurately compared. Integrals plotted at the same vertical display scale setting and with the same IS and NC can be compared directly. Any combination of the Vertical Display Scale and IS can be varied to give the same values if NC differs. For example, if NC = 1 in one spectrum and IS = 6 and the plot is obtained with VDS at 2K, a directly comparable integral of a spectrum whose NC = 2 can be obtained by plotting at VDS = 4K or by plotting at VDS at 2K with IS = 6.

In general, vary VDS or IS by the difference between the two NC's. The easiest way to make sure that the FT normalization constants of two or more spectra are the same is to process them as a group using the PR command. This can be accomplished either by acquiring them using the GO command, or if this is not convenient, acquiring them one at a time, exiting to DEMON and storing them so that they have the same first four characters in their file names and the last two characters Ø1, Ø2, Ø3, etc.

AC – Add constant

After typing AC, the two parameter knobs control the spectrum vertical position and tilt. This DC and tilt are applied only to the display and are added to memory only if Return is typed. If any other character is typed, the program exits to the Executive module without changing memory.

VW – View the Spectra Specified by Filename

Typing VW allows entry of a four-character filename and upon typing Return loads FILEØ1 into memory. The file is loaded into that portion of memory which it originally occupied, and any sub-portion of that memory may be viewed by selecting it using the Readout buttons. The associated data files are also loaded when VW is called so that the correct constants are in memory.

To view the next file in the series, type N. The filename will be incremented by one and that file loaded into memory directly. If you have reached the end of the list or if you pass through a file which has been deleted for some reason, the displayed portion of memory will be zeroed. If no such file exists, the display will also be zero.

To back up through the list, type R once for each step. After you have stepped through the files back to FILEØ1, the R command will have no further effect.

To discover which file you are currently viewing, if you have lost count, type the number symbol, #. The number of that file will be printed out. To discover the τ value (D1) which produced it, type T. It will be printed out in units of seconds.

To exit from the VW command mode, type a Return.

In summary, the VW commands are:

VW – View
- N – next
- R – reverse
- # – print file number
- T – print tau value of this spectrum

Return – exit from VW

VX – View the Expanded Region of the Spectrum

This allows viewing of the last expanded region defined either by EP, CU or F1 and F2. All commands are the same as VW.

F1, F2 – Examine and Enter Limits or Region

The F1 and F2 commands allow the user to examine or enter the frequency limits of the region to be used in expanded mode commands. They may be entered in either order. The command prints out the current remembered value and allows entry of a new one.

IR – Intensify Region

The IR Command allows intensification of the last defined expanded region. Typing X will then expand the intensified portion of the display to fill full scale. Typing C recontracts the display and typing Return exits from IR.

Plotting Commands

This program provides facilities for the production of stacked plots using the commands:

- LP – Enter length of plot in terms of percent of full scale (used only in single plots).
- OP – Enter offset parameters X and Y in terms of percent of full scale
- PL – Plot the currently displayed spectrum region, using the offset parameters. Check OP and LP before calling PL.
- SP – Stacked Plot. The SP command types out the current filename and allows entry of a new one. Upon typing a Return, the program asks

  # TO PLOT =

  and allows entry of a number. This allows less than the entire range of spectra to be plotted. After a Return is typed, the program asks the question

  ST. WITH TAU =

  and allows the entry of the first tau value which is to be plotted.

The spectrum having a tau value equal to that specified is then loaded into memory. The Recorder should then be turned on with the pen in the Up position. When a Return is typed, the recorder will be returned to the left side. The pen should then be placed in the Down position and a second Return typed. The spectrum will then be plotted out. During plotting, the available commands are:

F – to plot faster
S – to plot more slowly
Q – to abort the plot. Typing a Return will cause the display to return.

At the end of this plot, the pen should be lifted and a new carriage Return typed. This will return the pen carriage and load the spectrum having the next greatest tau value. Note that the spectra are sorted into order of increasing tau value regardless of their order of acquisition. Each spectrum is plotted after the cumulative X and Y offset is added to it. This process continues until all spectra are plotted or until there are no spectra having greater τ-values. If this occurs, this will be the last spectrum plotted. Newer 1080's and NMR-80's contain an automatic pen enable and pen lift command which can be used for total automation of the stacked plotting process. In this case, the wait for carriage returns is removed when the question regarding pen lift is answered Y during T1CNFG. Consult the factory for details on installing this modification in older machines.

The rate of pen lifting at the beginning of each plot can be changed by changing the contents of location 3776 of the T1PLOT module. This is discussed in chapter XII. Digital plotters can be advanced using PULSE1 and returned using PULSE2.

Plotting a Single Spectrum

The PL command plots out that region of the spectrum which is currently displayed on the scope including the entered offset parameters OP and the length of plot LP. This command can be used to simply plot out any given spectrum, or it can be used to determine the proper offset and gain values for the extremes before beginning a stacked plot.

To plot out a single spectrum, be sure that the Offset Parameters are both zero and that the plot length (LP) is set to 100%. Then type PL, followed by a Return. The carriage will return to the left side and wait for the pen to be lowered. Typing another Return will cause the spectrum to be plotted out. At the end of the plot, the computer waits for another Return so that the plotter can be turned off before the display returns.

Setting Up for a Stacked Plot

The inclusion of the offset parameters will allow the user to plot out the first and last spectra and then the first and second spectra to assure that the alignment and overlap is as desired. In this case, it is up to the user to set the plot length (LP) to the proper value. The general formula for calculating the desired plot length is 100 - (n-1)x, where n is the total number of spectra to be plotted and x is the x-offset per spectrum. The n-1 term arises because the first spectrum is not offset, although all the others are. For instance, if 15 spectra were to be plotted, each with a 2% offset, the plot length would be 100 - (15-1)2 or 72%. This calculation is performed automatically by the SP program using the # TO PLOT = question, but this number will not have been set if a stacked plot has not been initiated with this number of spectra and this offset. Examples of stacked plots are shown on the following pages.[4]

Expanded Region Plotting PX, SC

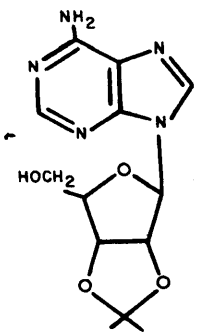
The last defined expanded region can be plotted using the PX command. Similarly a stacked plot of expanded regions can be obtained by typing SX. The commands under SX and PX are identical to those used under SP and PL.

Inverted Stacked Plots

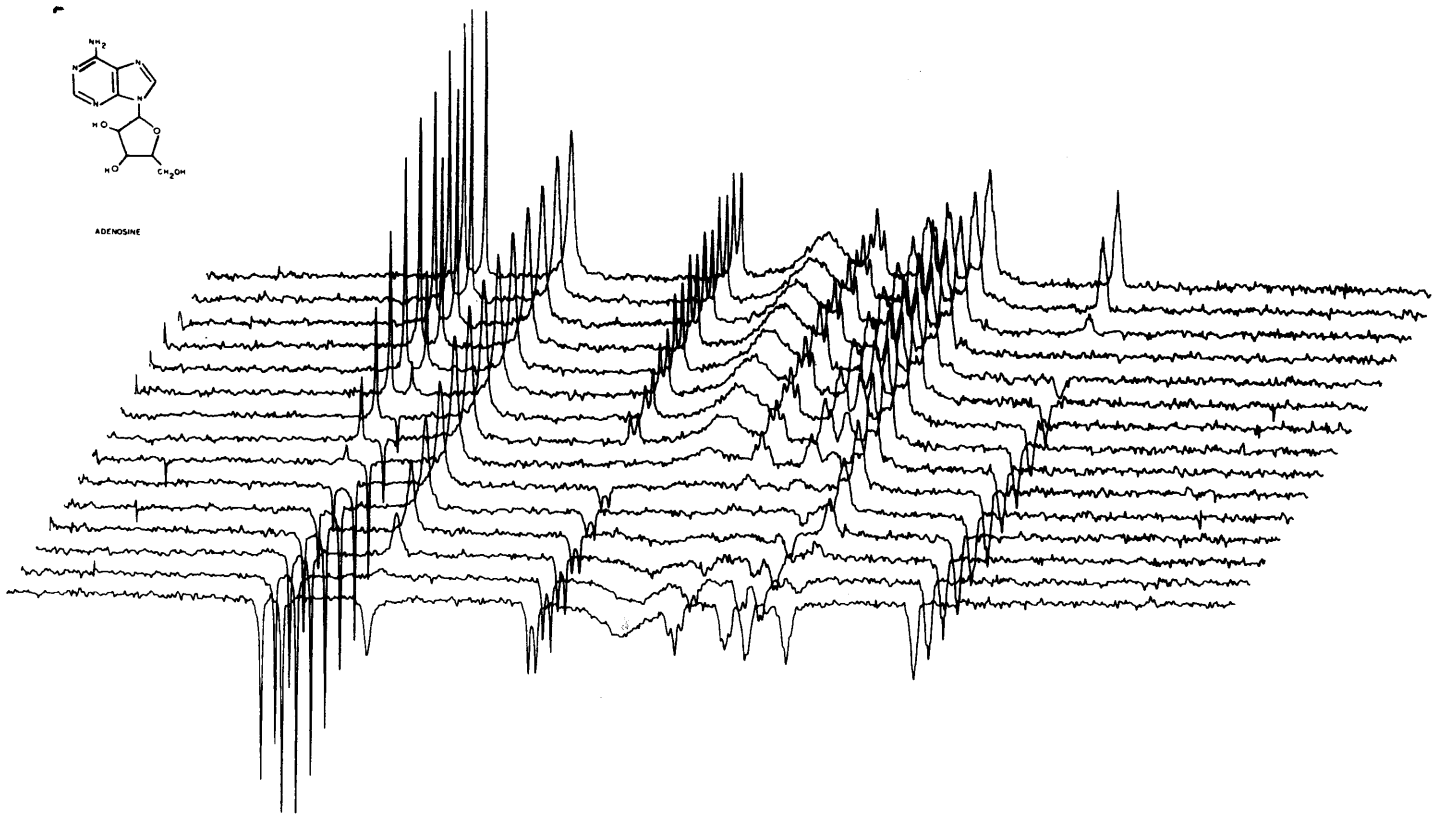
Plots which have all of the peaks pointing inward have the advantage of using less paper vertically and allowing greater vertical amplitude per spectrum. This can most easily be accomplished by phase correcting all spectra so that they are 180° out of phase. This can be confusing, however, if not carefully interpreted.

Changing two locations in the T1PLOT module will allow spectra to be plotted in order of decreasing delay time. There are:

	from	to
4446	405164	5104
4467	5104	405164



ISOPROPYLIDINE
ADENOSINE



ADENOSINE

```
&LS= IP2D01 TEMP01


ADENOSINE IN CDCL3
P(180)=          8.900
&LS= TEMP01

ADENOSINE IN CDCL3
P(180)=          8.900 USEC
P(90)=           4.400 USEC

TAU VALUES
=           0.001 SEC
=           0.010 SEC
=           0.030 SEC
=           0.069 SEC
=           0.100 SEC
=           0.130 SEC
=           0.170 SEC
=           0.200 SEC
=           0.299 SEC
=           0.400 SEC
=           0.499 SEC
=           0.699 SEC
=           1.000 SEC
=           1.499 SEC
=           2.000 SEC
=           4.999 SEC
=           9.999 SEC

RECOVERY TIME=         29.999 SEC
P3=           0.100 USEC
D3=           0.001 SEC
P4=           0.100 USEC
D4=           0.001 SEC
TOTAL SCANS=          1

NO. OF FREQ DOMAIN POINTS =    2048
SW=       1000.000
DW=        500.000
DE=          0.000
SO=          0.000
TC=          2.000
SF=        100.000
TA=          0.000
TR=          0.000
T1=          0
T2=          0
NC=          0

&
```

VIII. DATA OUTPUT AND THE CALCULATION OF T_1's

The following commands can be used to list out the data acquired from the T_1 program.

SO – Spectrum Offset

This command allows entry of the frequency offset from the right end of the spectrum. This is the same as the FT-Nmr OF command.

SF – Spectrometer Frequency

Enter the spectrometer frequency in MHz for the peak printout parts per million calculation.

MI – Minimum Intensity

Enter the minimum intensity peak to be picked in the PP and GL.

PP – Peak Printout

The peak printout command prints out the title currently in memory and the peaks in the entire displayed area. It assures that the right end if zero Hz plus any offset entered using the SO command or the A(Assign) subcommand of the CU (Cursor) command. The columns printed out are line number, cursor address, frequency, parts per million intensity and integral. The intensities and integrals are signed and unnormalized, allowing direct comparison of the intensities between various spectra within a given run. A typical example is shown below.

```
&PP
DODECYL ALCOHOL IN C6D6
     NO.   CURSOR      FREQ.        PPM      INTENS.      AREA
      1      193    1358.642     54.034      32700       70752
      2     1193     626.220     24.905      21464       62180
      3     1217     608.642     24.206      20964       58568
      4     1292     553.710     22.021      67868      287752
      5     1297     550.048     21.875      32336       81104
      6     1304     544.921     21.672      31620       78832
      7     1312     539.062     21.439       3216        5236
      8     1424     457.031     18.176      24044       54228
      9     1537     374.267     14.884      32276       54704
     10     1840     152.343      6.058      18100       40128

&
```

XP – Peak Printout of Expanded Region

This command is identical to PP, but only those peaks in the expanded region are printed out.

GL – Grand List

The GL command allows entry of a file name and lists out the peaks in all of the spectra in that file name group. The title is printed out and the name of each file is also printed as shown below. This listing can be aborted at any time by typing Q.

CT – Calculate T_1's

This command is unique to the Nicolet T_1 software package. It allows automatic calculation of T_1's from the processed data stored on the disk. The program compiles a list of intensities or of integrals for each peak in the spectrum and performs a least squares analysis to fit a straight line to the equation.

$$\ln (1 - A/A_\infty) = \tau / T_1 + \ln 2$$

Thus, a plot of ln $(1-A/A_\infty)$ vs τ gives a line with slope $-1/T_1$ and theoretical intercept of .693. The program scans through the list of τ-values for the longest one and finds all spectra accumulated at that τ-value. It then picks each peak in all of these τ_∞ spectra and averages their intensity or area. This average value of A_∞ is then used in calculating each A/A_∞ term. The spectra may be acquired in any order and as many τ_∞ values as desired may be used. The associated data files containing the pulse width delays and spectral widths are automatically loaded.

The actual equation which is implemented is[5]

$$T_1 = \frac{(N)\ \Sigma\ \tau_i^2 - (\Sigma\tau_i)^2}{(N)\ (\Sigma L_i\tau_i) - \Sigma\ L_i\ \Sigma\ \tau_i}$$

where $L_i = \ln\ (1 - A_i/A_\infty)$ and N is the number of spectra other than those at $\tau\infty$.

The intercept and standard deviation are also calculated. The intercept is given by

$$B = \frac{\Sigma L_i\ \Sigma\tau_i^2 - \Sigma L_i\ \tau o\ \Sigma\tau_i}{(N)\ \Sigma\tau_i^2 - (\Sigma\ \tau_i)^2}$$

The deviation of each point is given by $d_i = L_i + \quad /T_1 - B$

and the standard deviation by

$$\left[\frac{N\Sigma d_i}{(N-2)\ [\Sigma\tau_i^2 - (\Sigma\tau_i)^2]}\right] 1/2 \cdot T_1^2$$

To use the CT command, type CT and enter the name of the desired file name group. The associated data files containing pulse widths, delays and spectral widths will be loaded automatically. The title and a header are printed out and calculation begins. Since this is a reasonably lengthy process, it can be aborted at any time by typing Q.

Both the standard deviation and the intercept give useful information regarding the quality of the data used in the calculation. The standard deviation should be as small as possible, of course, and the intercept should be 0.693 (ln2).. Standard deviations can sometimes be reduced by deleting some of the spectra between 0.8 (5 x T_1) and 5 x T_1, as these are all essentially τ_∞ values for many spectra.

```
&CT= TEMP01

DODECYL ALCOHOL IN C6D6

 NO.   CURSOR      FREQ.        T1(SEC)        STD. DEVN.    INTERCEPT
  1      193     1360.002    0.875 +-          0.032         0.499
  2     1193      626.347    0.686 +-          0.066         0.636
  3     1217      609.251    1.599 +-          0.022         0.646
  4     1292      554.265    0.629 +-          0.043         0.831
  5     1297      550.599    1.041 +-          0.101         0.291
  6     1304      545.467    1.323 +-          0.016         0.579
  7     1424      457.488    0.863 +-          0.070         0.437
  8     1537      374.642    2.343 +-          0.047         0.655
  9     1840      152.496    3.495 +-          0.189         0.718

CALCULATED USING INTENSITIES
&
```

UA – Use Areas in the Calculation of T_1

Typing this command sets a program flag such that areas of picked peaks are used in the calculation of T_1's. The message CALCULATED USING AREAS is printed at the end of the list.

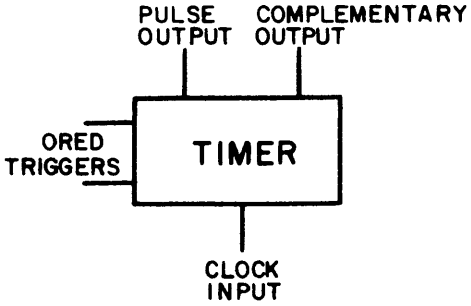
UI – Use Intensities in the Calculation of T_1's

Typing this command causes intensities to be used in the calculation of T_1's. The message CALCULATED USING INTENSITIES is printed at the end of the list.

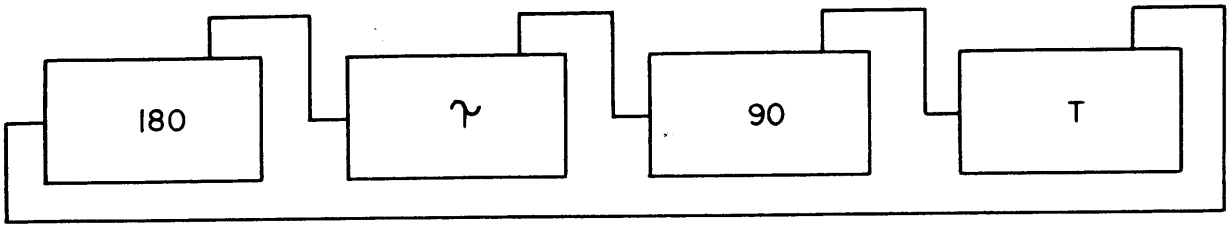
IX USE OF THE NIC-293 IN MULTIPLE PULSE EXPERIMENTS

The NIC-293 is a versatile interface controller for an infinite variety of laboratory experiments. It has facilities for controlling up to eight timers, eight levels, eight sense lines, four contact closures, two digital-to-analog converters and an eight-channel multiplexed analog-to-digital converter.

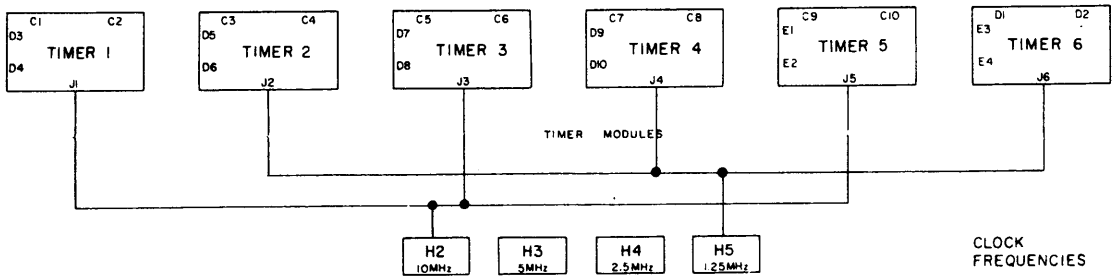
In the inversion-recovery pulse sequence, four timing modules are used, two for the pulse widths and two for the inter-pulse intervals. These are connected in a circular series so that the end of the 180 triggers the beginning of τ, the end of τ the beginning of the 90, the end of the 90 the beginning of the recovery time and the end of the recovery time the beginning of the 180. We will represent each timer as a rectangle having two ORed trigger inputs on the left end, the clock input on the bottom and the output and complementary output on the top as shown below.



The level marked pulse output is high when the timer is counting and the level marked complementary output is high when the timer is not counting. Thus the complementary output goes from low to high at the end of the timing interval and this transition from low to high can be used to trigger the next timer. The entire chain of four timers is represented thus:



The rate at which each of these timers counts is determined by the clock frequency which is connected to it. This frequency is available from the patch panel at four terminals which contain 10 MHz, 5 MHz, 2.5 MHz and 1.25 MHz. The times selected for the T1 measurement program are 10 MHz for the two pulse widths, allowing a resolution of 0.10 usec in the selection of pulses and the 1.25 MHz rate for the two inter-pulse delays. The T1 program assumes that the timers 1, 3, 5 and 7 are connected to 10 MHz and timers 2, 4, 6 and 8 to 1.25 MHz as shown below.



Clock Frequency Connections in the NIC-293 to Timers 1-6

There are two further points which must be considered in the design of the complete pulse experiment. It should be possible to turn the sequence on and off conveniently and prevent a lock-up mode where all the timers become zero and cannot trigger each other, such as might happen during a power failure. In addition, it should be possible to obtain the levels corresponding to the two pulse widths on a single line to be connected to the rf gating circuitry.

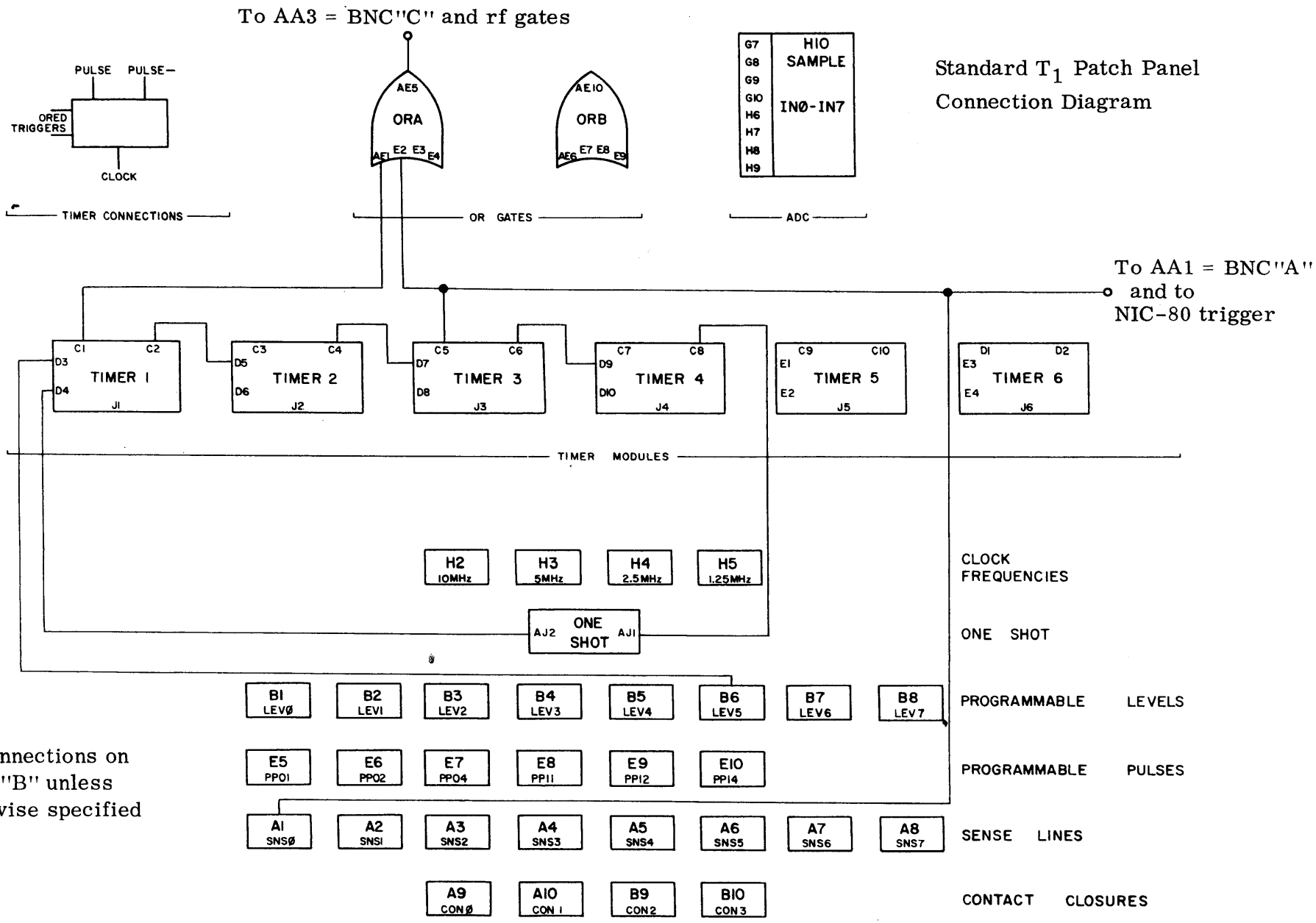
The latter requirement is easily satisfied by simply taking the positive outputs of the two pulse width timers and ORing them together using one of the 293's OR gates. The requirement for turning the sequence on and off is satisfied by inserting a short (100 nsec) "one shot" in the pulse line and including a second input to a timer in the form of one of the programmable levels. Since the two trigger inputs to each timer are ORed together, a high level at one of the two inputs would effectively prevent a trigger at the other. If the input from a programmable level is high, a rising level from another timer will not cause a trigger. This stops the chain. If the programmable level is lowered, raised and lowered again it provides the rising level to start the sequence and goes low again to prevent inhibiting the next cycle. Thus the one-shot is triggered by the end of the recovery time and it in turn triggers the beginning of the 180.

The timing sequence is turned off by raising a programmable level under software control, thus preventing a trigger to that timer from occurring. The complete timing sequence, then, is shown on the next page.

> CAUTION: The 293 Controller should be treated with some care. It contains timers which will provide pulses of highly reliable width and spacing as long as power is applied. If the power to the 293 is disconnected, the state of these timers becomes indeterminate and the resulting pulse duty cycle may not be that desired when power is applied. It is therefore recommended that power be applied continuously to the 293. The widths of the various pulses are loaded into the timers when the values are typed and when GO or SE is typed. A hardware duty cycle limiter is available from Nicolet to protect rf pulse equipment. Consult the factory for details.

Phase knobs on the 293 require that Knob A be connected to pin AI1 and Knob B to AI2. The program requires the following patches:

AI1 – BG8
AI2 – BG7
BE5 – BH10


To AA3 = BNC"C" and rf gates
PULSE
PULSE—
ORED TRIGGERS
CLOCK
TIMER CONNECTIONS
AE5
ORA
AE1 E2 E3 E4
AE10
ORB
AE6 E7 E8 E9
OR GATES
G7
G8
G9
G10
H6
H7
H8
H9
HIO SAMPLE
INØ-IN7
ADC
Standard T_1 Patch Panel Connection Diagram
To AA1 = BNC"A" and to NIC-80 trigger
C1 C2 D3 D4 TIMER 1 J1
C3 C4 D5 D6 TIMER 2 J2
C5 C6 D7 D8 TIMER 3 J3
C7 C8 D9 D10 TIMER 4 J4
C9 C10 E1 E2 TIMER 5 J5
D1 D2 E3 E4 TIMER 6 J6
TIMER MODULES
H2 10MHz
H3 5MHz
H4 2.5MHz
H5 1.25MHz
CLOCK FREQUENCIES
AJ2 ONE SHOT AJ1
ONE SHOT
B1 LEVØ
B2 LEV1
B3 LEV2
B4 LEV3
B5 LEV4
B6 LEV5
B7 LEV6
B8 LEV7
PROGRAMMABLE LEVELS
E5 PP01
E6 PP02
E7 PP04
E8 PP11
E9 PP12
E10 PP14
PROGRAMMABLE PULSES
A1 SNSØ
A2 SNS1
A3 SNS2
A4 SNS3
A5 SNS4
A6 SNS5
A7 SNS6
A8 SNS7
SENSE LINES
A9 CONØ
A10 CON1
B9 CON2
B10 CON3
CONTACT CLOSURES
All connections on panel "B" unless otherwise specified

X. EXAMPLES OF THE USE OF T_1 PROGRAM/II

Setting Up

Before proceeding to data acquisition, the sampling rate (dwell time) must be adjusted so that sampling is proceeding at twice the highest frequency in the spectrum, as described in the FT-Nmr manual. To do this, simply type SW and enter the desired spectral width. The program will print out the proper setting for the 1080 dwell time thumbwheel switches. For instance, for a spectral width of 5000, type SW = 5000 and the program will instruct you that DW = 100.

At the time the command SW is typed, the Measure Size button must be set to the size of the free induction decay to be acquired. If you decide to change the number of data points, set the new Measure Size button and re-enter SW. It is at this time that the program calculates the number of Hz per point for later peak printout.

At first, it will be necessary to determine the exact pulse width necessary to produce a 180° or 90° pulse. This can be done easily using the SE (Setup) routine. First, the 293 is converted for use in a single pulse experiment by removing the patch panel connector from timer 1 to the OR gate. This wire runs from BC1 to AE1. Disconnecting at AA1 is sufficient. (This is unnecessary in TTI systems.) Then, the only pulse reaching the rf equipment is pulse 2 from Timer 3. Then select a sample with a strong signal and a reasonably short relaxation time. Benzene saturated with Cr $(AcAc)_3$ is often used in C-13 experiments.

Then set the value of P1 to 0.1 usec and D1 to .001 sec. This makes these times negligible with respect to the total repetition rate selected by D2. Set D2 to a value equal to 5 or more times the longest T_1 of the sample in the probe. Set P2 to an estimated value of a 180° pulse and IN to some small incremental value such as 0.5 usec. Set the Autostop counter and SC to 1 sweep and enter the Setup mode by typing SE. Observe the amplitude of the free induction decay produced during the single measure scan. If it does not appear to be too well nulled, increment or decrement the pulse width by typing I or D and type R to initiate a new Measure scan. Continue adjusting the pulse width by typing more I's or D's and taking new scans, until the resulting signal is as well nulled as possible. When the pulse width has been properly adjusted, type Return to exit from the setup mode and examine P2 to determine the value of the 180° pulse. Set P2 to one half this value to obtain a 90° pulse and set P1 to the width determined for the 180° pulse.

In summary, the Teletype commands below allow you to determine the proper pulse widths for your experiment.

```
*RUN T1PRGM

&P1=        46.000   .1
&D1=        19.999   .001
&P2=        23.000   15
&D2=        19.999   15
&IN=         0.000   .5
&SEIIRDDDDR
&P2=        14.000   7
&P1=         0.100   14
&
```

Make P1 and D1 negligible compared to repetition rate.

Pulse widths are loaded into the timer when entered.

Approximately 180° pulse width of 15 microseconds

Repetition rate of 15 seconds

Pulse increment of 0.5 microseconds

Set Autostop to 1 scan

Enter Setup mode to be 1 sweep. Increment twice, take another sweep. Decrement 4 times, take another scan and exit.

180° pulse is 14 usec. Set P2 to 90° pulse width or 7 usec

Set P1 to 180° pulse or 14 usec

It is not generally necessary to determine pulse angles each time a new experiment is run. Unless there is a marked alteration in sample characteristics or spectrometer configuration the flip angles will remain relatively constant for each nucleus studied. Some workers prefer to determine the pulse width necessary for a 360°

pulse rather than a 180° pulse. They feel that the null observed in the free induction decay is much cleaner and more easily observed. In this case, of course, the 90° pulse has one fourth the width of the 360° pulse. Further, the waiting time of 5 x T_1 is no longer needed.

Determining the Delay Time (Tau Value) Range

Once the pulse widths have been determined it is necessary to select a range of tau values such that all peaks will begin inverted, and all will recover their total positive values during the longest delay. This is usually best determined by running the shortest and longest delays individually and transforming them before beginning the process of data acquisition. To do this, set D1 to some long value such as 30-60 seconds and set the second D1 value to zero. Then acquire the data in the SE Mode. Here we are using the SE mode with both pulses connected. Set the Autostop counter or SC to a sufficient number of scans to obtain fair signal to noise. After data acquisition, transform and phase correct the spectrum and ascertain that all expected peaks are visible and fully recovered. The PRFT 180 - τ - 90 sequence does require an accurate A_∞ value, so this last value should be determined with some care. Several τ_∞'s may be entered to allow averaging to take place during T_1 calculations.

Then proceed to the shortest τ-value, which might be, for instance, around .05 seconds. Acquire data at this value and transform and phase correct it using the same phase correction constants. If all peaks are not fully inverted, try the experiment again using a shorter delay time.

When both the shortest and longest delays have been accurately determined, enter the entire list of delays, in any order, interspersed with the τ_∞ values just determined. Having several τ_∞ values and entering the τ's in random order allows some compensation for system instability. The value following the last τ in the D1 table must be zero. This zero is a signal to the automated processor to stop acquiring data. The D1 values should be entered spaced so that there will be a sufficient number of data points on the curve for each line's relaxation to calculate its T_1. If there is one line with a much longer T_1 than the rest, the values of D1 should probably spread out as D1 increases.

To perform the operations described in this section, the following commands would be used.

```
&SC=        50  1                Set scan counter (and Autostop) to 1
&D2=        14.999

&SW=      1501.501  5000         Set spectral width
SW =      5000.000
AQT =        0.819  SEC
DW =       100.000
&P1=        14.000               Check pulse widths

&P2=         7.000

&D1=         0.001   15          Set τ∞ delay
=         0.000

&SE                               Take one scan

&FT                               Transform
&EP                               and Phase Correct
&D1=        14.999   .05         Set very short
=         0.000

&SE                               Take one new scan

&FT                               Transform
&PK                               And correct as done in last EP
&D1=         0.050   15          Enter list of taus
```

```
=          0.000   .1
=          0.000   .3
=          0.000   .5
=          0.000   15
=          0.000   7
=          0.000   3
=          0.000   .7
=          0.000   2
=          0.000   5
=          0.000   15
=          0.000   0

&SC=          1  32                Reset scan counter
&TT                                And check total time
TOTAL TIME =          2.095   HOURS

&
```

Acquiring Data

When all of the above parameters have been optimized, you are ready to acquire data. Generally, you should select a four-character filename which describes the compound under investigation. Then, after assuring yourself that the spectrometer homogeneity, lock and decoupling power are optimally adjusted, simply type GO, enter your filename and title, and allow the data system to acquire the data. The total time required will be printed out. If this is a particularly long run, it is also a good idea to turn off the Teletype. However, if the Teletype is left running, the τ -value for each spectrum in the series will be printed out before acquisition of that file begins. To find out where you are in the series, simply compare the Teletype listing with that of the original D1 entry list. If the SC option is used with 1080's with the Autostop set to 1, the sweep counter will always show zero. However, the τ-value printout and the total time calculation should give a sufficient gauge of the experiment's progress.

The sweep counter display in NMR-80 and BNC-12 systems shows both the spectrum number and the scan number. The spectrum number is multiplied by 100000 and the scan number is shown as the lowest significant digits of the counter. For example, scan 12 of spectrum 3 would be shown as 300012.

Should it be necessary to abort the experiment, the 1080 can be stopped by pressing both stop buttons. As an unconditional stop, you can cause a halt even during a long delay by changing the Measure Size buttons while holding both Stop buttons in. NMR-80 systems can be stopped unconditionally by pressing the Stop button in the upper right hand corner. More gentle stopping conditions include typing Q which halts at the end of the next spectrum or CTRL/Q which halts at the end of the next scan. Data acquisition is aborted in NMR-80's if memory is about to overflow.

The printout during a GO command is shown below:

```
&SC=          1  32
&GO= ABCD01  BULI01

TITLE = BUTYLLITHIUM PYRIDINE ADDUCT IN TMED
TOTAL TIME =          2.095   HOURS
      14.999
       0.100
       0.299
       0.499
      14.999
       6.999
       3.000
       0.699
       2.000
       4.999
      14.999
```

Processing the Files

To determine the proper parameters for data processing, leave the final spectrum in memory following the completion of automated data acquisition if it is a τ_∞ value. Should you need another spectrum, it can be reloaded from disk simply by exiting to the monitor (MO) and LOADing a τ_∞ spectrum. For example, if the chosen filename for data acquisition was SPEX, and the eleventh was a τ_∞ value, LOAD SPEX11 would reload this last one for data processing. The VW command can also be used to load this spectrum.

All data processing operations are performed in memory. The disk files are only altered if the program is told to do so by answering Y to REPLACE? It is important to obtain the best possible line shape and signal to noise as well as phase correction before beginning processing of all the files on disk. To do this transform the τ_∞-value spectrum and correct its phase. It may well be advisable to perform some exponential weighting before transformation, and if the signal to noise is not too good, try repeating the transformation with a TC of -2 or -3.

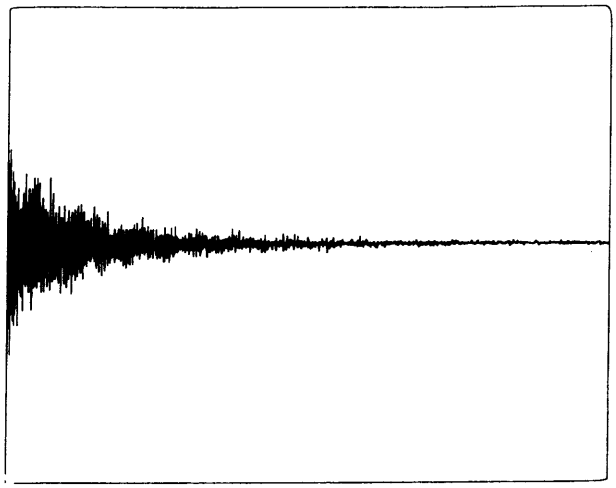
In the case of carbon-13 lines, it is sometimes desirable to use a positive TC of +.5 or +1 to narrow the lines, even at the expense of signal-to-noise, since the intensities will then be more useful in the calculation of T_1's. The peak areas will be unchanged.

Examples of EP Phase Correction

These next pages illustrate the process of Fourier transformation and phase correction.

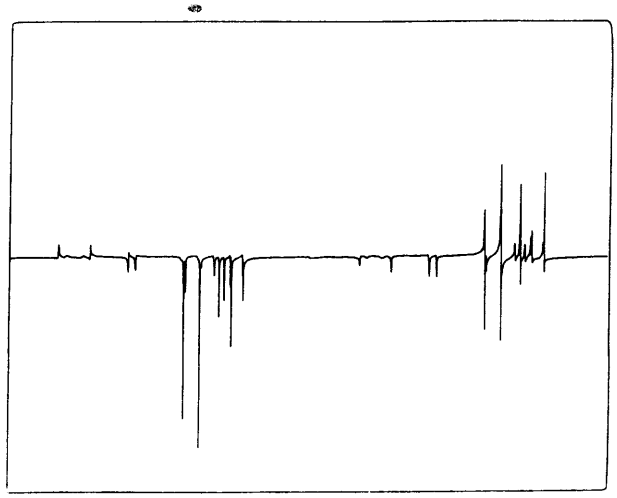
After loading into memory a spectrum obtained at a τ_∞ value, we set the Readout buttons to display the entire free induction decay and type

FT

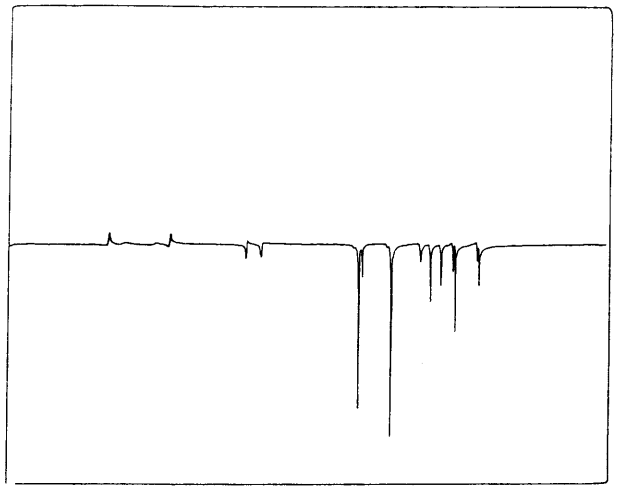


Some seconds later, the resulting spectrum will be displayed, showing both the real and imaginary Fourier components, but both out of phase. We will use the EP command to correct the phase of the real part. To do this we type

EP



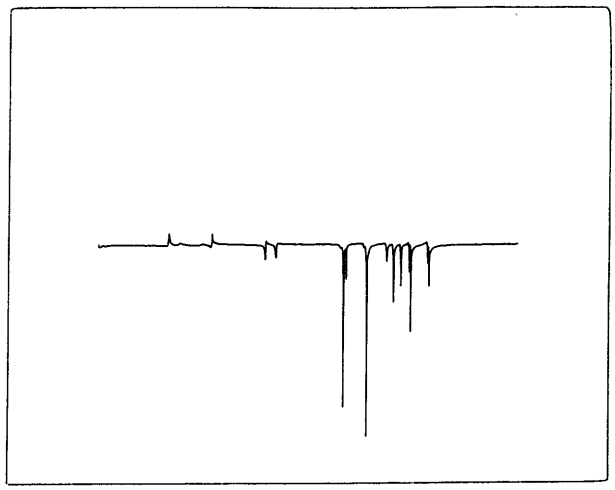
The display will ignore the current setting of the pushbuttons and will show the real part of the last transformed block, in this case the left half of the above spectrum. At this time the knobs are active and control the starting address and size of the displayed spectrum. The left knob controls the starting address and the right one the expansion. If we anticipate expanding the spectrum fairly far, we



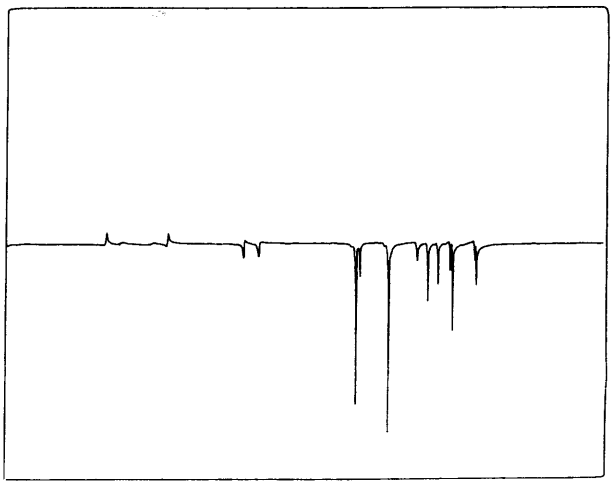
rotate the size knob all the way to the right, giving a spectrum which is actually contracted from its normal presentation.

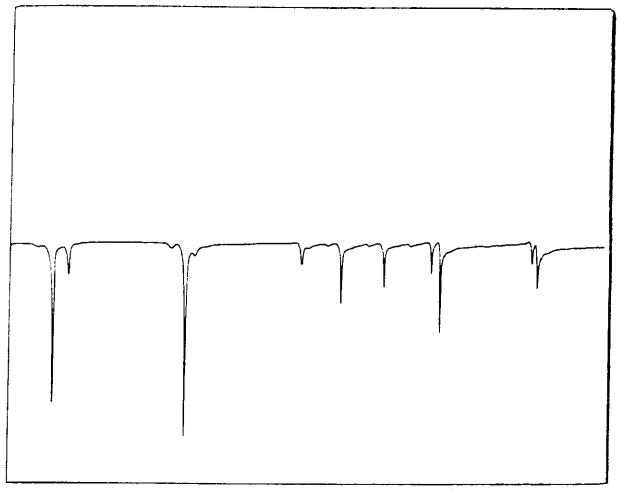
The knobs, however, have only a relative position and they can be reset so that their current position is considered "zero" by typing

R. (These single letter sub-commands are not printed on the Teletype)



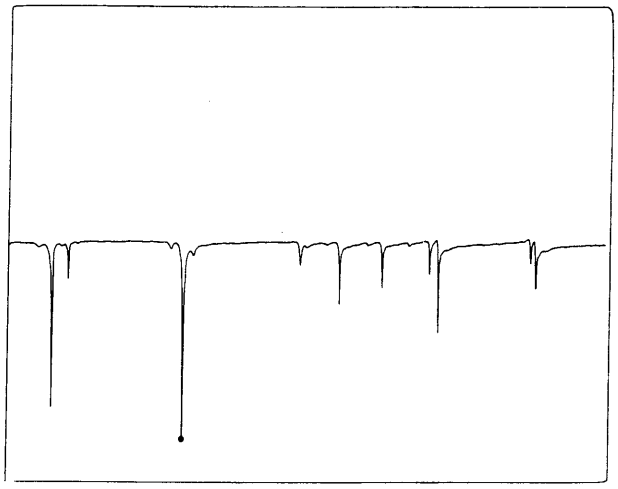
After typing R, the spectrum will be displayed full scale and can be expanded by turning knob B counterclockwise and shifted left or right using knob A. Expand the spectrum so that only some of the larger peaks are displayed



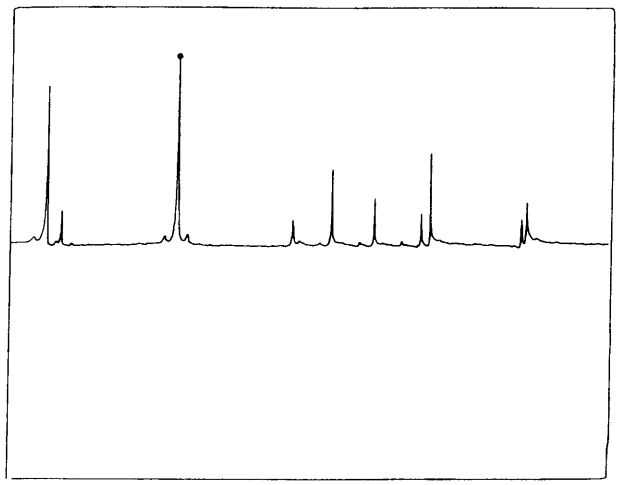


as shown here. Then, type P to go into phase correction mode.

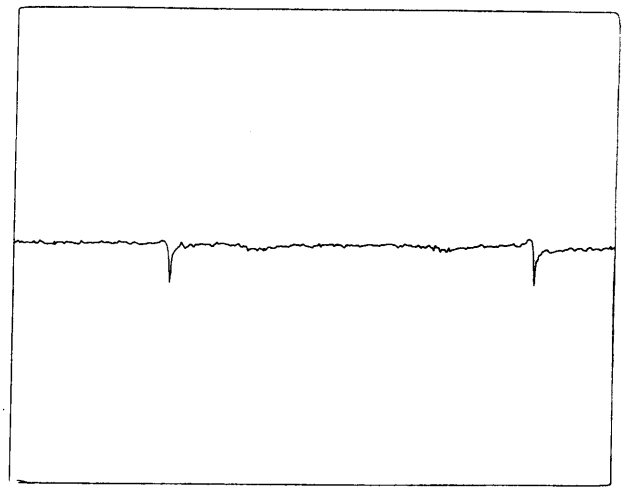
The largest peak in the entire spectrum will now appear with an intensified dot on it. This peak may or may not be in the current display but can easily be found by shifting the spectrum to the left or right using knob A (the left hand Knob).



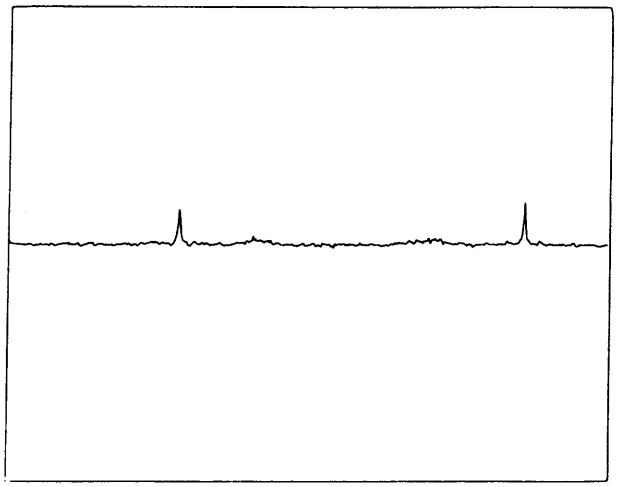
Now, to phase the spectrum, adjust knob B so that the phase of the line having the intensified point on it is as perfect as you can make it. The vertical expansion of the spectrum can be controlled using the Vertical Display Scale switch as usual. When the line having the cursor is properly phased, type B and



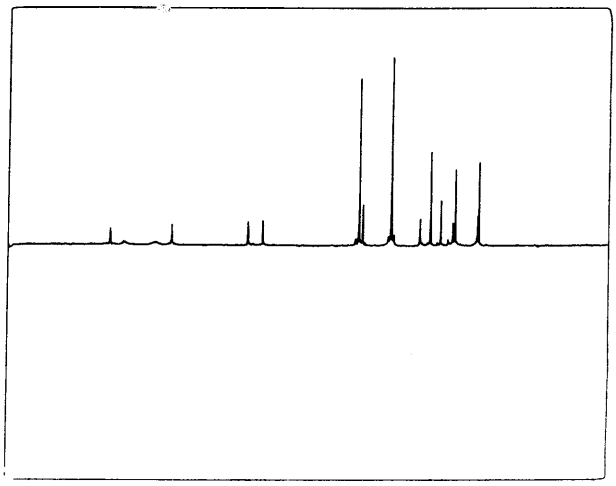
shift the display to show peaks at the other end of the spectrum. The right hand knob will now correct the frequency dependent phase term while leaving the phase of the line having the cursor on it constant. Phase peaks at this end of the spectrum



so that they look like this. Then, examine the entire spectrum by moving the left hand knob back and forth. If all peaks seem to be in phase, the spectrum can be phase corrected by typing either P or C. If C is typed, the spectrum remains expanded after correction, and if P



if typed, the spectrum is displayed recontracted as shown here. If, at this time some small additional correction seems advisable, the spectrum can be re-expanded and rephased as using the A (add) sub-command..



However, once you exit from EP by typing Return, additional corrections will only be added if performed by re-entering EP and using the A sub-command.

At this time, any spectrum offset (SO) which is to be used in future GL or CT commands should be entered, as the PR command immortalizes this value on disk.

When the phase correction and signal-to-noise have been optimized on this spectrum, enter all processing commands in the LI command and enter the values contained in TP (total phase correction), in PA and PB. If the EP phase correction mode is used, the command PK should be used in the LI string to perform this same correction on all spectra in the file group. Then process the spectra using the PR command. If the question REPLACE? is answered Y the free induction decay spectra on the disk are replaced with the processed data. It is generally not a good idea to replace these files on the disk unless there is very little space remaining on the disk. Replacing the files would then preclude reprocessing them with new TC or TR parameters if this is necessary. Instead, it is good practice to store only your FID's on the disk and keep one file called, say, TEMP for the processed results.

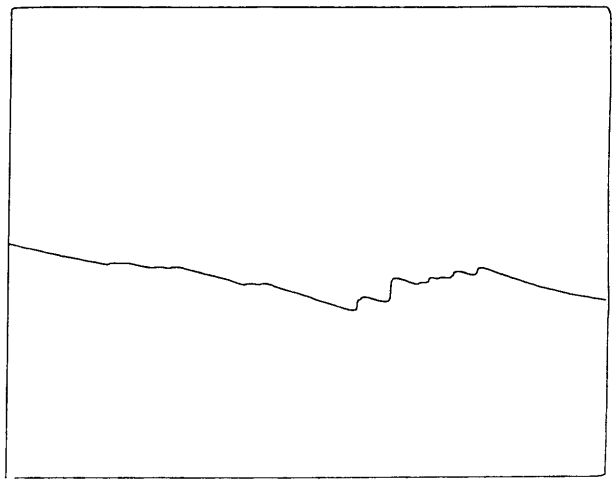
The data processing of these spectra can be aborted by typing Q. This will halt the processing after the next spectrum is complete. It is generally not advisable to halt by pressing STOP, as this may interrupt during a disk transfer and cause a loss of information or even a disk "crash."

Examples of the optimization and processing process are shown below.

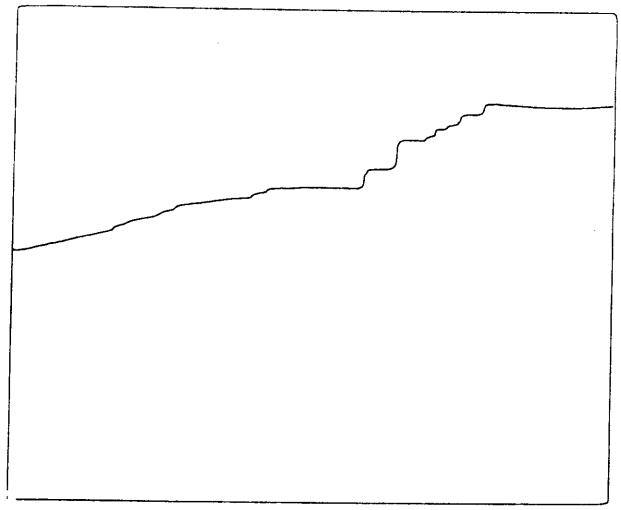
```
&MO
*LOAD BULIØ1

*GO

&TC=        Ø.ØØØ -2
      Ø.155  HZ BROADENING

&EM
&FT
&EP
&LIEMFTPK


&PR= BULIØ1
REPLACE? N
NEW FILE NAME=      Ø1 TEMPØ1
```

Integrate Display

Upon entry to the integrate routine by typing ID or IX, the scope will display an integral which may look like that pictured here. It has a downward slant because of a residual negative dc bias which should be removed prior to plotting. This can be done by slowly moving knob B until the presentation is more upright. The Vertical Display

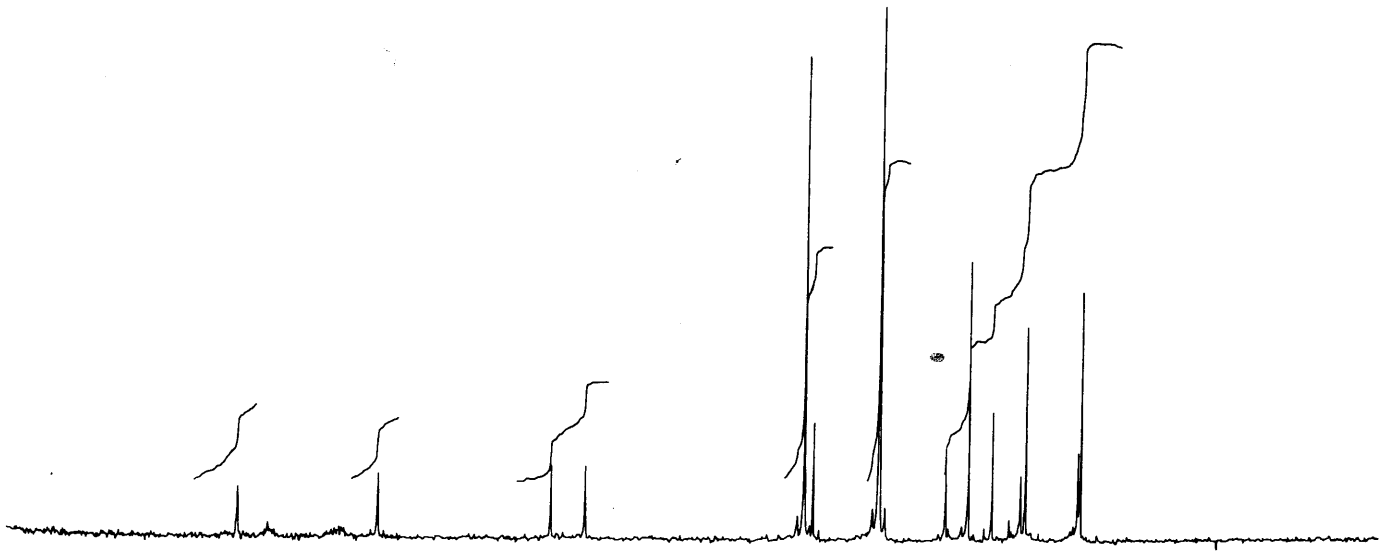


Scale switch can also be varied if desired. Knob A controls any baseline roll by adding a small address dependent constant. This will usually be used to square off rounded corners of integrals, so that the final result appears as shown on the right.



The plotting of the integral may be done as it is shown or with a more expanded plot, by increasing the vertical display scale. While this increase may place the entire integral off scale, the integral of any one peak may still be one scale or can be plotted using the R (reset) and P (plot) commands.

The R command resets the integral to zero at the time it is struck and raises the pen. The pen is lowered when P is struck to begin plotting the next peak integral as shown below:



Viewing the Result

After the data have been acquired and processed, they may be viewed successively using the VW command. After entering the filename, the program will pause to load the associated data files and then begin displaying the first file in the series. The N command displays the next sequential spectrum, the R command the previous one and the # command prints out the current file number. T is used to print out the corresponding value. Since the VW and VX commands load spectrum data files of D1's pulse widths and processing parameters, these commands will delete more recently entered information.

If you wish to view only some small region of the spectrum and study how it changes with time, the VX command allows viewing of the last defined expanded region. The subcommands remain the same.

Plotting the Spectra

In order to get a more thorough feeling for the data, it is useful to produce a "stacked" isometric plot of all the spectra for careful inspection. While a tightly stacked plot may not allow quantitative interpretation, it does allow qualitative analysis which may aid in later interpretation of other data. This stacked plot method was shown in the original paper on the 180-τ-90 sequence[1] and has since been popularized by a number of workers.[6]

Production of a publication-quality stacked plot, even in totally unattended operation, is a slow process, which may require one to two hours of work. However, since the spectra are stored on disk, this time need not be immediately after, or worse, during, acquisition.

In order to optimize the plot of 10 to 30 spectra, it is necessary to do several trial runs, to optimize (a) the plotting rate, (b) the x-axis offset, and (c) they y-axis offset. The x-offset should be chosen so that major line groups do not overlap in a confusing manner from one spectrum to another. Further, the y-offset is determined by the setting of the Vertical Display Scale switch.

When a stacked plot is performed, the program automatically calculates the proper plot length based on the number of spectra to be plotted and the x-offset per spectrum. For instance, if the x-offset were 2% and there were 12 spectra, 11 of them would be offset by 2% from each other and the total y-offset would be 22%. The maximum allowable plot length is therefore 100% - 22% or 78%. While this value is calculated for the SP command and stored in LP, it must be calculated by the user before trial plots of individual spectra may be made. Alternatively, a stacked plot may be started and immediately interrupted using Q, leaving LP with the correct value.

Generally, plotting the first two of these spectra will assure the user that peak overlap is as desired. The PL command includes the currently entered offset parameters but does not increment them. Thus, to plot the first spectrum of the series, OP X and Y should be set to zero. Then the spectrum should be loaded and plotted as usual. To plot the next spectrum, the offset parameters should be changed, and the second spectrum loaded using theVWcommand or from DEMON/II. To plot the last spectrum, to ascertain that the plot will stay on scale, the offset parameters should be changed to their maximum incremented values, and the last spectrum loaded. It is reasonable to assume that some unusually large peak may run off scale and clip at the top of the plot, but most of the peaks should remain on scale.

When you are satisfied that the entire set will plot properly, exit from the plot routine by typing Q followed by a Return and enter the stacked plot program. The command SP will ask for a four-character file name as follows:

```
SP   = TEMPØ1
# TO PLOT =
```

You can enter the total number of spectra or any number less than that, but those spectra plotted will be sequential in increasing τ value. The program will then request the tau value of the first file to be plotted:

```
ST. WITH TAU =
```

and allow entry of a τ-value. This feature allows the user to plot out a large number of spectra by breaking them into two or more groups on separate pages, so that they will be spaced for easier interpretation. The program awaits a Return and then moves the plotter carriage to the left side and awaits another Return allowing the pen to be lowered. The waits for Returns are omitted if the user indicated that the recorder pen lift is automated.

The total length of each plot, LP, is calculated for the x-offset and the number of spectra to be plotted. This frees the user from continually calculating LP under routine conditions.

Output of Acquisition Parameters

Before proceeding to other experiments it is probably a good idea to obtain a listing of the value of various parameters used in the experiment. These include the pulse widths, repetition rate, and the τ- values for the various delays. They also include the values for various constants which may be used to process the spectra such as the number of data points, the exponential multiplication time constant, phase correction parameters and apodization constants. The pulse widths and delays are stored on disk by the T_1 program and the GO command processing parameters during the PR command. The LS command generates this listing. It can be interrupted by typing Q.

The PP command generates a listing of all of the peaks in the currently displayed spectrum. The columns are line number, cursor address, line frequency, parts per million, intensity and integral. The frequencies are calculated using the total number of data points selected by the Measure Size button when the values for SW or DW were entered. Any offset is generated by SO or the A (assign) subcommand of the CU (cursor) routine. The PP listing can be interrupted at any time using the Q command.

The peak printout for all files having the same four-character name can be obtained by using the GL command. GL stands for Grand List. This is a rather lame mnemonic but most of the other possibilities have already been used. The GL command causes a peak printout of the displayed area of each spectrum. Such a listing might be useful if calculated T_1's seem out of line or for additional off-line calculations.

Calculation of T_1's

The CT command will allow entry of a four-character filename and then print out a title and header. The calculation of T_1's will begin by finding the first peak in each spectrum and compiling its intensity or area as noted by the UA or UI command. When all spectra of the group have been processed, the peak number, cursor position, frequency, calculated T_1 value standard deviation and intercept will be printed out. The calculation process can be halted at any time by typing Q.

The peak scanning routine starts at the beginning of the first τ_∞ spectra and remembers the position of each line so that it will find the same line in each spectrum. If no line is found in the vicinity of this line in a particular spectrum, a null is assumed and a zero intensity or area is entered for that line. To prevent calculations of T_1's of spurious lines, the program requires that four non-zero lines be found or the peak is rejected. Some small spurious peaks may also be suppressed by judicious use of the MI command. The MI used is that for the first τ_∞ spectrum in the set. If you have reason to believe that a particular spectrum in the set contains spurious information, it can be deleted by using the DEMON DELete command, which deletes only single files. Deletion of some of the spectra having longer τ's (close to τ_∞) may result in more accurate T_1's.

Calculation of T_1's will take a time proportional to the number of spectra in the set. Most of this time is spent accessing the disk and loading the various spectra. Once the spectra are read in, the actual least squares calculation proceeeds virtually instantaneously.

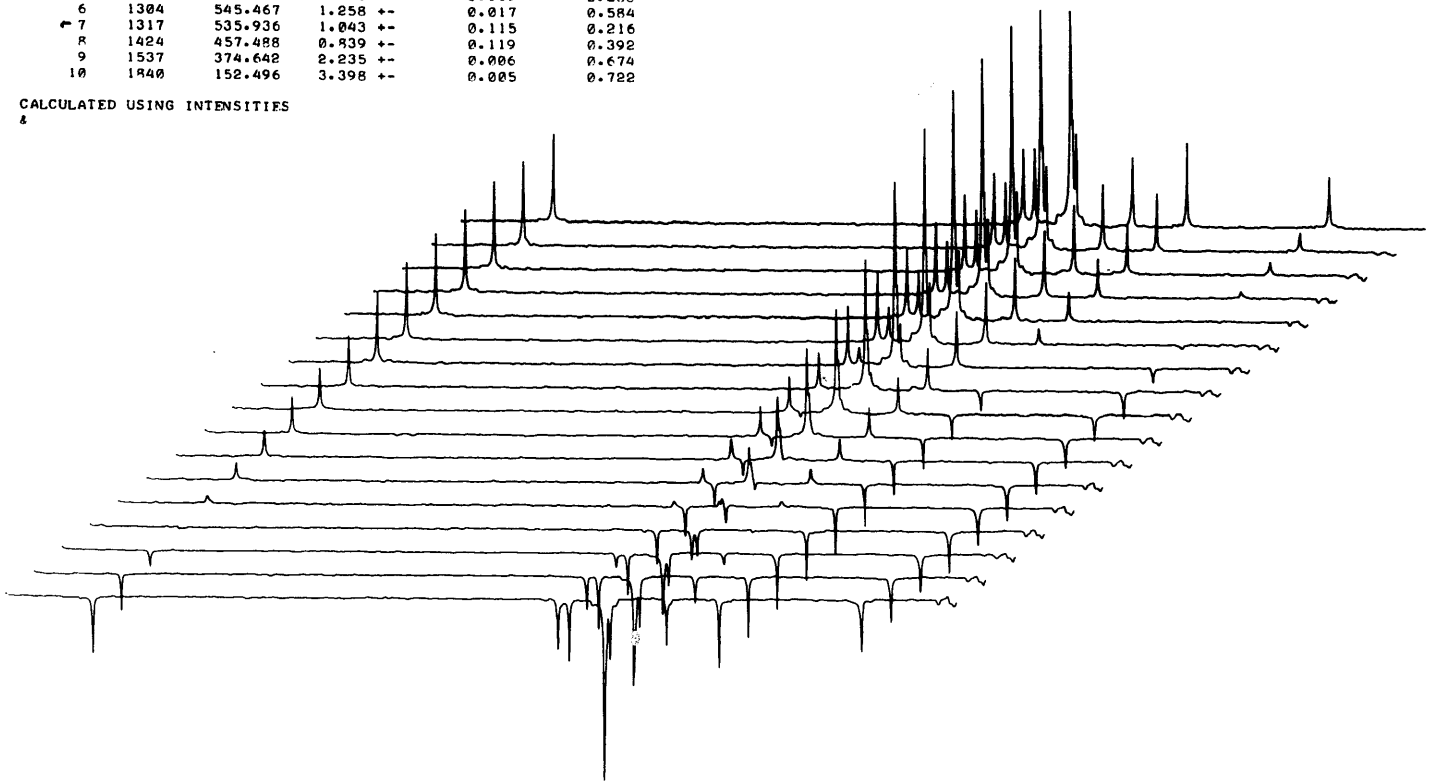
T_1's will be most meaningful in cases of well separated decoupled lines with good signal to noise. In the case of multiplets, the relaxation may be more complex and the resulting T_1 rather less meaningful. In these cases, it is generally advisable to calculate the T_1's using both areas and intensities and compare the results.

A complete spectrum,[7] shown with the CT and LS printouts is shown on the following page. The spectrum is that of dodecyl alcohol and was obtained on a Nicolet 1080 attached to an XL-100 with a TT-100 FT accessory.

DODECYL ALCOHOL IN C6D6

NO.	CURSOR	FREQ.	T1(SEC)	STD. DEVN.	INTERCEPT
1	193	1360.002	0.775 +-	0.179	0.497
2	1193	626.847	0.741 +-	0.042	0.570
3	1217	609.251	1.514 +-	0.005	0.673
4	1292	554.265	0.850 +-	0.076	0.518
5	1297	550.599	0.860 +-	0.119	0.288
6	1304	545.467	1.258 +-	0.017	0.584
7	1317	535.936	1.043 +-	0.115	0.216
8	1424	457.488	0.839 +-	0.119	0.392
9	1537	374.642	2.235 +-	0.006	0.674
10	1840	152.496	3.398 +-	0.005	0.722

CALCULATED USING INTENSITIES
&



LS= TEMP01

DODECYL ALCOHOL IN C6D6
P(180)= 100.000 USEC
P(90)= 50.000 USEC

TAU VALUES
= 0.100 SEC
= 0.200 SEC
= 0.299 SEC
= 0.400 SEC
= 0.499 SEC
= 0.600 SEC
= 0.699 SEC
= 0.800 SEC
= 0.899 SEC
= 1.000 SEC
= 1.499 SEC
= 2.000 SEC
= 2.499 SEC
= 3.000 SEC
= 3.499 SEC
= 3.999 SEC
= 5.999 SEC
= 7.999 SEC
= 9.999 SEC

RECOVERY TIME= 14.999 SEC
P3= 0.100 USEC
D3= 0.001 SEC
P4= 0.100 USEC
D4= 0.001 SEC
TOTAL SCANS= 32

NO. OF FREQ DOMAIN POINTS = 2048
SW= 1501.501
DW= 333.000
DE= 0.000
SO= 0.000
TC= - 3.000
SF= 25.144
TA= 0.000
TB= 0.000
T1= 0
T2= 0
NC= 1

XI. OTHER EXPERIMENTS

Single Pulse FT-Nmr

The T_1 program can be used for single pulse FT-Nmr be simply disconnecting the 180° pulse timer from the OR gate patch panel location AE1 and setting P1 and D1 equal to small values relative to the pulse repetition rate. Then, the user has the choice of straight, in-core signal averaging using the SE or AV commands or averaging and copying onto disk using the GO command.

Kinetic Studies

When there is only one delay entered in the D1 list, the GO command stores data in the files ABCDØ1, ABCDØ2, etc., without making any changes in the delay time between scans. The total number of spectra acquired per file is set by the SC command. The number of files which are acquired can be varied between 1 and 99 by entering the value using the NS command. During T_1 data acquisition the NS command prints out the number of D1's in the list but does not allow entry of a new number. However, when there is only one D1 in the list the NS command allows entry of the number of successive files to be stored on disk.

Nuclear Overhauser Effect Measurements

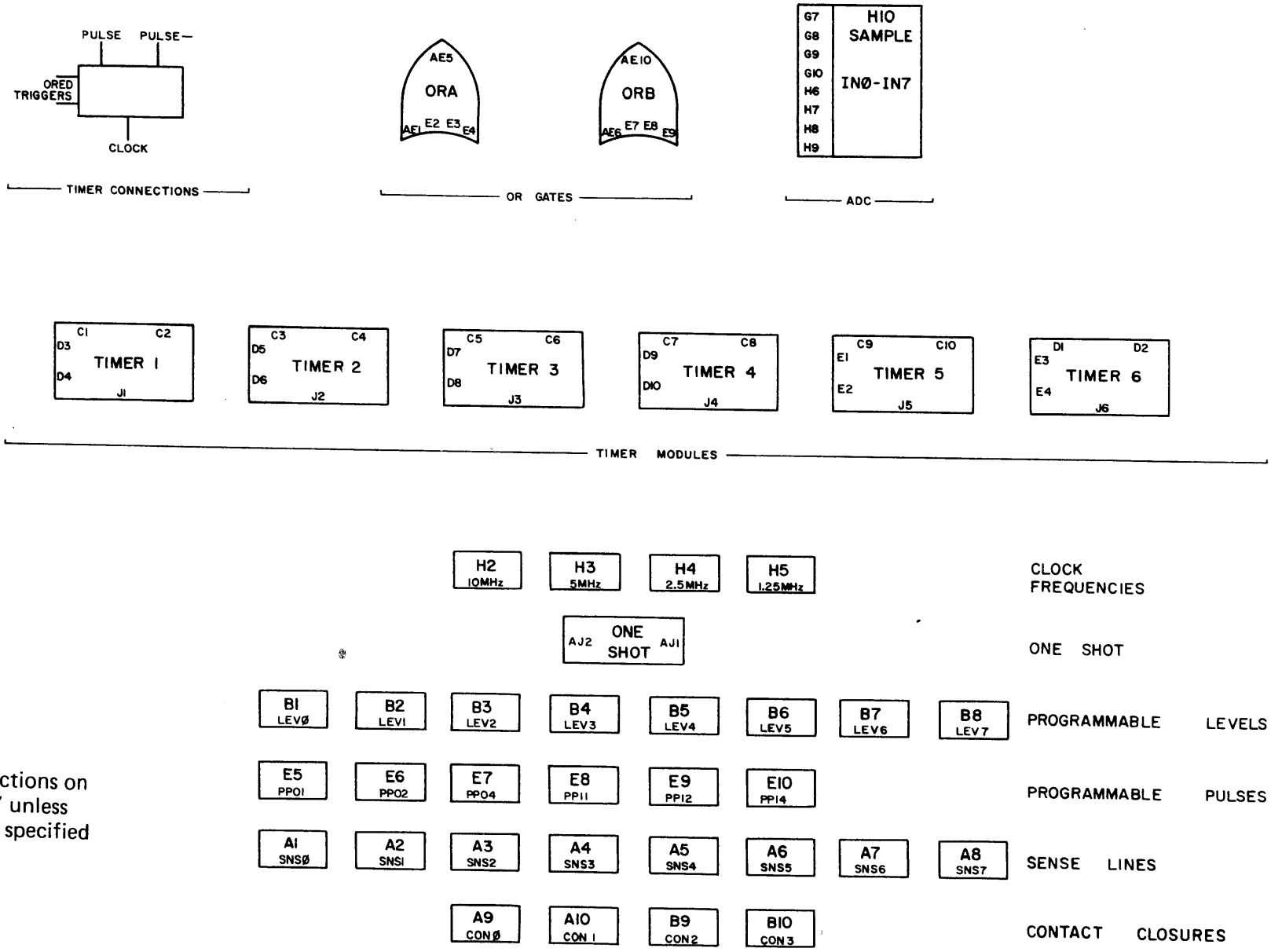
NOE Measurements are most often performed by measuring the integrals of spectra obtained under conventional single pulse FT mode with full decoupling and again with gated decoupling employed. In order for these data to be directly comparable, the various scaling factors must be kept constant. This can be accomplished by storing the fid's from the two experiments on disk and calling them, say, FIDØ01 and FIDØ02 (or any other 4-character file name followed by 01 and 02). Then, if they are processed together, the FT normalization constants will be equal and the intensities directly comparable.

The integral routines ID and IX also hold the scale factor constant, being determined by the command IS, and will allow direct comparison of plotted integrals. Further, peak printouts of the intensities and integrals will comparable whether the data were processed together or not, as they are multiplied by the FT normalization constants from the last performed FT.

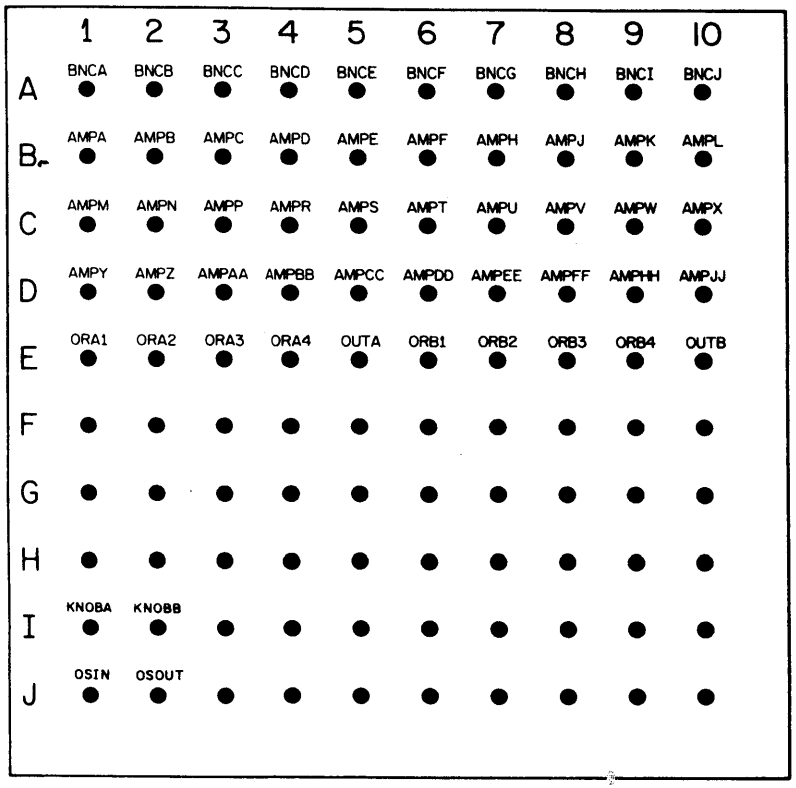
Homogeneity Spoiling Pulses

Contributions of the spin-spin relaxation time T_2 can be suppressed by the use of a pulse connected to the y-gradient which is activated following the 180° pulse. Those are usually observed as "phase errors" in spectra having the shorter τ values. The extra pulse P3 can be patched in to be triggered by the end of the 180° and this pulse patched to one of the BNC outputs at the rear of the 293. For figuring out complex patch panel configurations, a blank patch panel diagram is shown on the following page. Additional copies are in your 1080/NIC-80 manual. Homospoil pulses are a standard feature of the TTI-100 system and are described on page 14.

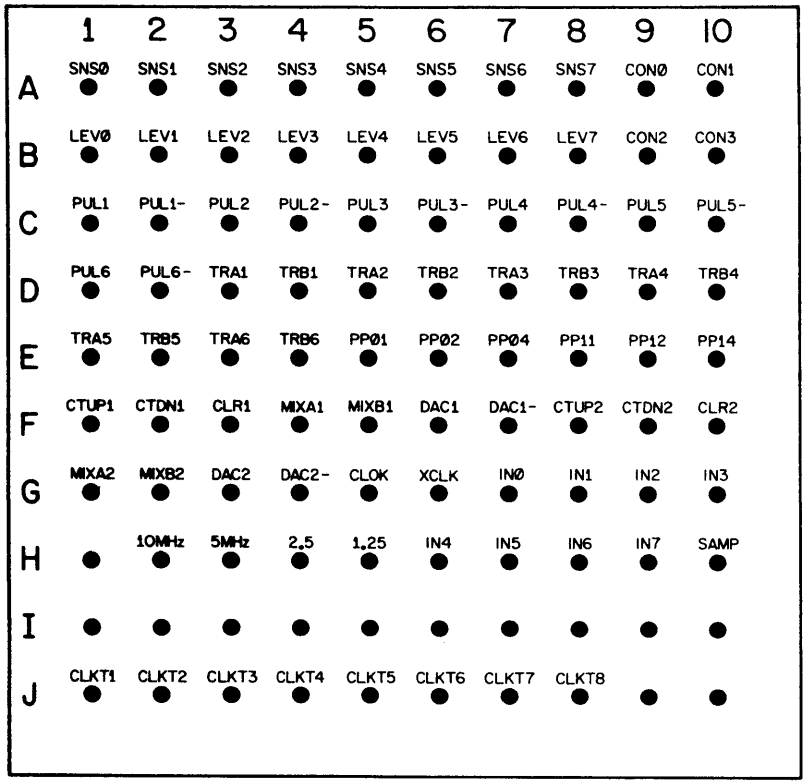
GENERAL PURPOSE CONTROLLER
PATCH PANEL DIAGRAM
NICOLET 293



All connections on panel "B" unless otherwise specified



A



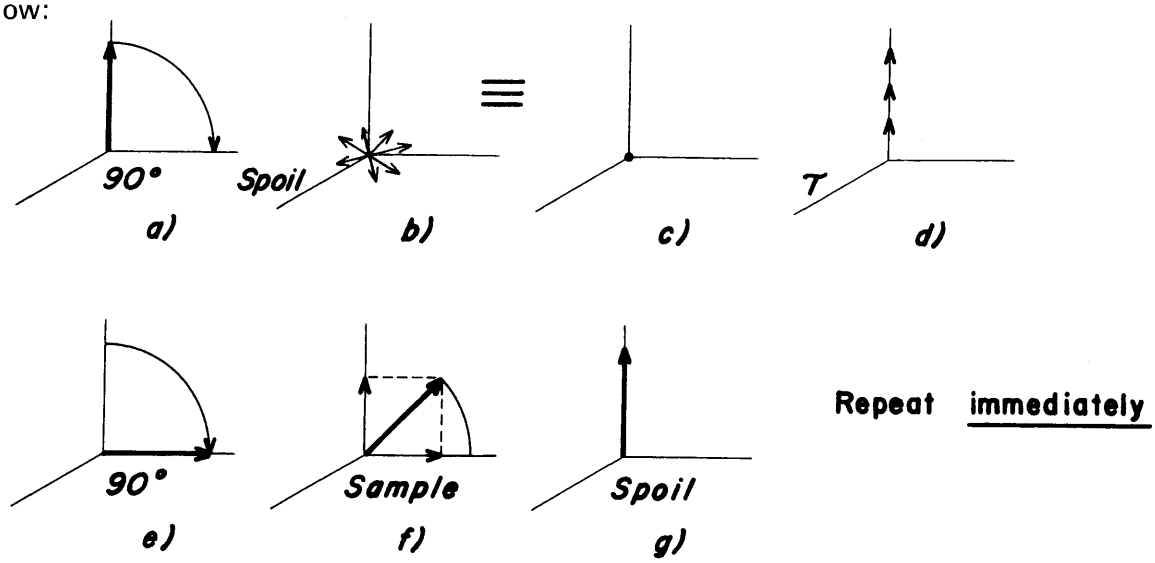
B

PATCH PANEL

A Homospoil Sequence for T_1 Measurement

Recently, methods for measuring long T_1's which do not require a lengthy 5 x T_1 waiting period between pulses have been suggested by Markley, Horsley and Klein,[8] Freeman and Hill[9] and McDonald and Leigh.[10]

The sequences involve the use of a pulse to "spoil" the homogeneity of the field for a brief time. Such pulses are easily connected to most spectrometers; details are available from the factory. The sequence is illustrated below:



Initially, a 90° pulse is applied to the system, forcing the magnetization into the x-y plane. This removes all z-magnetization. Here a homospoiling pulse is applied to the y-gradient, causing the vectors to dephase in the x-y plane as shown in b. The result is that the system has no net x-y magnetization as shown in c. The delay time τ is then used to allow z-magnetization to recover according to T_1, as shown in d. If τ is very short, there will be little or no recovery; if τ is long recovery will be essentially complete. After the time τ, a second 90° pulse is applied (e) followed immediately by sampling of the free-induction decay (f). After sampling, the magnetization will be partially recovered, having components in both the x-y planes and the z-axis. The x-y magnetization is removed by an additional homospoil pulse resulting in g. Figure g is exactly analogous to a and the sequence can be repeated immediately.

This sequence can be used on any Nicolet system having an NIC-293 with three timer boards or six timers. The sequence

$$-[90 - \text{spoil} - \tau - 90 - \text{sample} - \text{spoil}]_n$$

is patched so that P1 and P2 are the two 90° pulses, D1 remains τ, D2 the acquisition timing, P3 and D3 each one of the homospoiling pulses. These are patched as shown below.

In many systems, the conditions necessary for homogeneity to be "spoiled" are the grounding or pulsing of the shim coils for several milliseconds. The T1 PROGRAM/II software will not normally allow a pulse >200 usec, but this can be overridden by giving the OV (Override) command. The NV (non-override) command restores this protection.

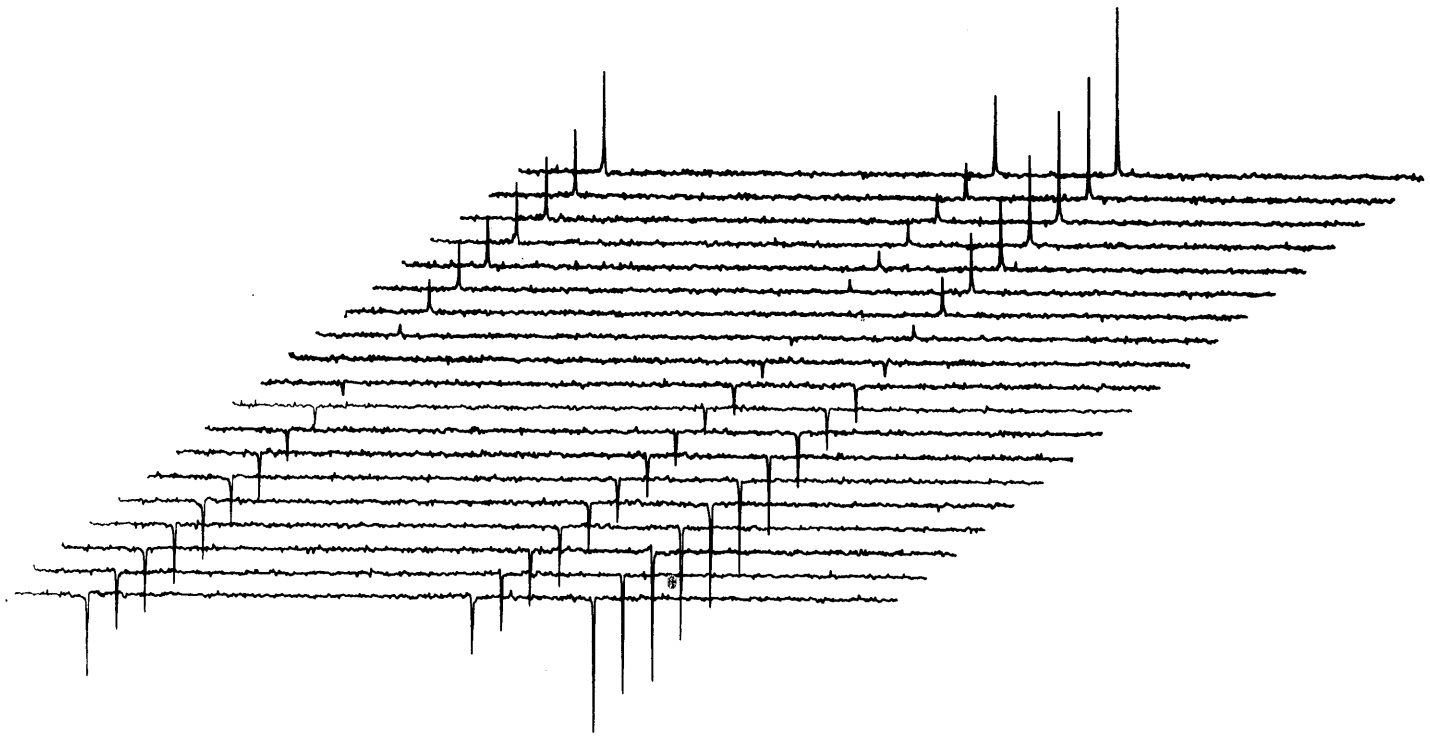
It has been our experience that these sequences are most applicable to systems having long T_1's. When very short T_1's are to be measured the shorter τ values may actually lead to sampling of the fid before the homogeneity has recovered.

Spectra produced by such sequences will start at null and move upward to fully recovered data. There are no inverted peaks since no 180° pulses are given. Care should be taken that the first spectrum in the set is not a set of nulled peaks, as the FT normalization constant is calculated from the first spectrum processed and this spectrum should have most of the peaks recovered so that the remaining spectra will be on scale. Inversion recovery and homospoil T1 sequence spectra of isobutanol are shown on the next page, along with a suggested patch panel diagram.

ISOBUTANOL PRFT

NO.	CURSOR	FREQ.	T1(SEC)	STD. DEVN.	INTERCEPT
1	192	1812.500	4.569 +-	0.013	0.726
2	1079	946.289	6.055 +-	0.016	0.812
3	1355	676.757	5.455 +-	0.013	0.651

CALCULATED USING AREAS



ISOBUTANOL PRFT
P(180)= 70.000 USEC
P(90)= 35.000 USEC

TAU VALUES
= 0.010 SEC
= 0.200 SEC
= 0.299 SEC
= 0.400 SEC
= 0.499 SEC
= 0.699 SEC
= 1.000 SEC
= 1.499 SEC
= 2.000 SEC
= 2.499 SEC
= 3.000 SEC
= 3.999 SEC
= 4.999 SEC
= 5.999 SEC
= 6.999 SEC
= 7.999 SEC
= 8.999 SEC
= 9.999 SEC
= 14.999 SEC

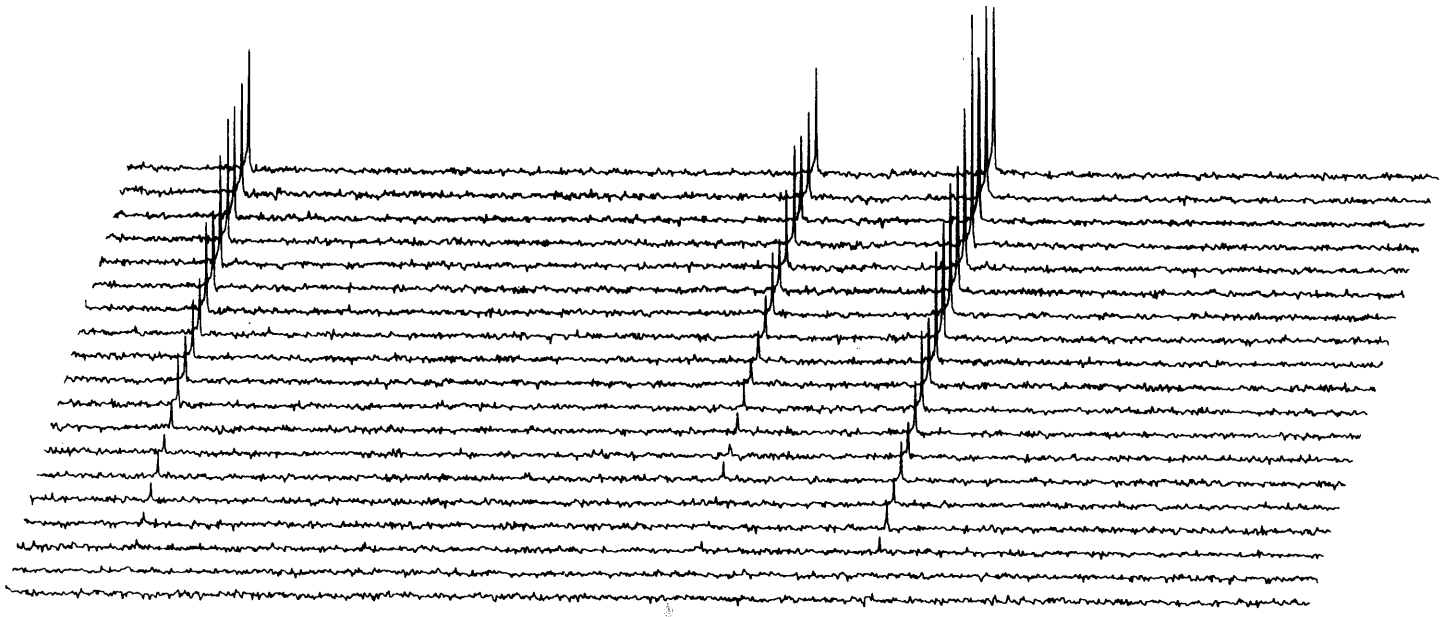
RECOVERY TIME= 14.999 SEC
P3= 100.000 USEC
D3= 0.001 SEC
P4= 0.100 USEC
D4= 0.001 SEC
TOTAL SCANS= 10

NO. OF FREQ DOMAIN POINTS = 2048
SW= 2000.000
DW= 250.000
DE= 0.000
SO= 0.000
TC= - 3.000
SF= 25.144
TA= 0.000
TB= 0.000
T1= 0
T2= 0
NC= 4

ISOBUTANOL MCDONALD LEIGH

NO.	CURSOR	FRFC.	T1(SEC)	STD. DEVN.	INTERCEPT
1	192	1812.500	5.307 +-	0.032	0.021
2	1079	946.289	7.082 +-	0.024	0.033
3	1355	676.757	5.813 +-	0.024	0.015

CALCULATED USING AREAS

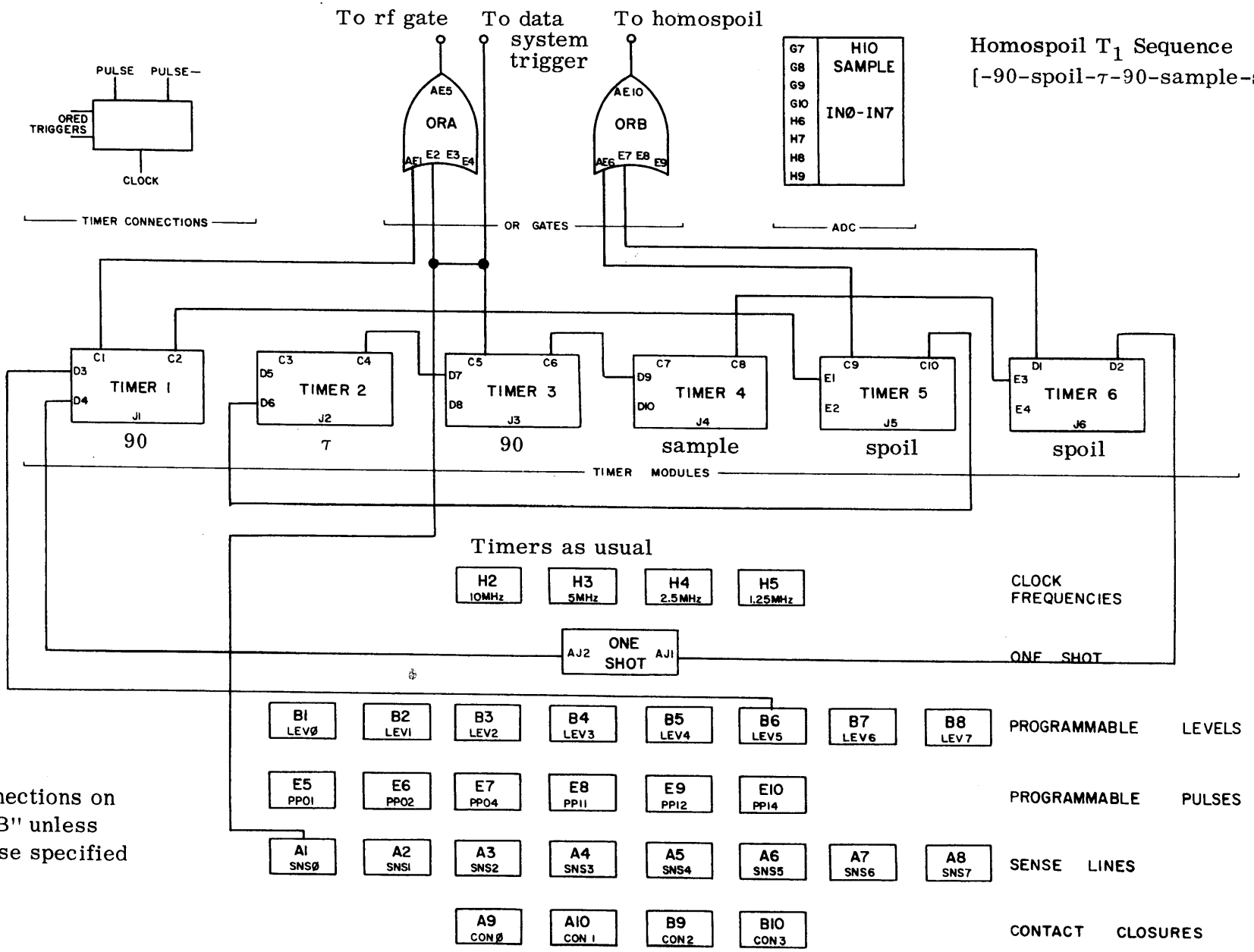


ISOBUTANOL MCDONALD LEIGH
P(180)= 35.000 USEC
P(90)= 8000.000 USEC

TAU VALUES
= 14.999 SEC
= 0.200 SEC
= 0.299 SEC
= 0.400 SFC
= 0.499 SEC
= 0.699 SEC
= 1.000 SEC
= 1.499 SEC
= 2.000 SEC
= 2.499 SEC
= 3.000 SEC
= 3.999 SEC
= 4.999 SEC
= 5.999 SEC
= 6.999 SEC
= 7.999 SEC
= 8.999 SEC
= 9.999 SEC
= 0.010 SEC

RECOVERY TIME= 1.099 SEC
P3= 35.000 USEC
D3= 0.008 SEC
P4= 0.100 USEC
D4= 0.001 SEC
TOTAL SCANS= 10

NO. OF FREQ DOMAIN POINTS = 2048
SW= 2000.000
DW= 250.000
DE= 0.000
SO= 0.000
TC= 0.000
SF= 25.144
TA= 0.000
TB= 0.000
T1= 0
T2= 0
NC= 0



Homospoil T_1 Sequence
[-90-spoil-τ-90-sample-spoil-]

All connections on panel "B" unless otherwise specified

Transferring T1 PROGRAM/II to Another Disk

It is not necessary to reload the tape to transfer the program to another disk cartridge. However, if a high speed reader is available, this is the most straightforward method.

If you have a 12K computer but no high speed reader the entire program can be loaded into core and transferred with only minimal manipulation. To understand what you are doing you should understand a little about how the program works. The table below shows the normal core locations of the various modules:

0-1777	2000-5637	5640-5777	6000-7577	7600-777
T1CNFG	T1PROC	T1CONS	FPP72	MONITOR Head
T1PRGM	T1CLEC		I/O SUPERVISOR	
T1EXEC	T1PLOT			
	T1CALC			

The T1CNFG and T1PRGM modules are present only at program start-up time. They perform some look-ups on disk and then load T1EXEC, T1CONS and FPP72. As needed, one of the four modules occupying 2000-5637 are loaded into core from disk and their commands executed. Thus, only one of them is resident at a time. The floating point package FPP72 is in core unless the DEMON/II I/O supervisor is in use. It always replaces FPP72 when done.

Now, to load all of these modules into core at one time, you simply make use of the DEMON/II program relocation feature. If a LOAD command is followed with an address the file is loaded starting at that address rather than at the one specified in the directory. This feature is demonstrated in the instructions below.

1. Start DEMON/II

2.
```
*LOAD T1EXEC

*LOAD T1PROC

*LOAD T1CONS

*LOAD FPP72

*LOAD T1CNFG 100000

*LOAD T1PRGM 102000

*LOAD T1CLEC 104000

*LOAD T1PLOT 110000

*LOAD T1CALC 114000

*BIN
```

3. Then, to swap out DEMON and load the entire program, type BIN (Return). This is very important, as otherwise locations 3000-7577 will still be on the disk swapping area instead of in core.

4. Switch the drive to LOAD, put in the new disk and when the drive is up to speed, start the computer at 7600.

5. Then store the modules which are in their proper locations as follows:

```
*STO T1EXEC 0-1777:P

*STO T1PROC 2000-5637:P

*STO T1CONS 5640-5777:P

*STO FPP72 6000-7577:P
```

6. Now we will successively store the moved files in a dummy file called DUM, then reload them into memory and store them correctly.

```
*STO DUM 100000-101777

*LOAD DUM 0

*STO T1CNFG 0-1777:0:P

*STO DUM 102000-103777
DELETE:Y
*LOAD DUM 0

*STO T1PRGM 0-1777:0:P

*STO DUM 104000-107777
DELETE:Y
*LOAD DUM 2000

*STO T1CLEC 2000-5637:P

*STO DUM 110000-113777
DELETE:Y
*LOAD DUM 2000

*STO T1PLOT 2000-5637

*STO DUM 114000-117777
DELETE:Y
*LOAD DUM 2000

*STO T1CALC 2000-5637

*DEL DUM
DELETE:Y
*RUN T1CNFG

T1 PROGRAM/II CONFIGURATOR
TYPE RETURN IF COMPUTER IS A 1080
TYPE "N" IF NMR-80 OR BNC-12:
```

XII. MODIFYING THE T1 PROGRAM

The T1 program operates through the T1EXEC module, which calls one of the four modules into memory which occupy 2000-5637. The table of constants which are referred to by all modules occupies 5640-5777. The command look-up scheme is therefore of two parts. First, the command is converted to two character packed ASCII so that the command AC, for example, becomes 301303.

The command list in T1EXEC is divided into groups by module and the first location in each sublist of commands contains the track on which that module can be found. This track address includes the unit number and has bit 19 set as a flag that this begins a new module. These track addresses are written into the T1EXEC program each time the T1PRGM startup program is run. Thus, the scanning for a legal command begins by running through the list within T1EXEC and keeping track of which tracks will contain the command if it is found.

If a match is found, that module is loaded from disk, whether or not it was already there, so that a fresh copy is always used. Then, a second command list is scanned within the module, occupying locations 5510-5637. In this list, the commands alternate with the subroutine addresses of the various routines, and if a match is found in this second list, the T1EXEC module performs a JMS to this address, starting that command routine.

Therefore, to modify the T1 program, you need to insert a command in both the T1EXEC module command list and in the module itself. The space available for adding commands are shown in the accompanying tables. They are designated by the BLOCK assembler command, which reserves the number of spaces given following the command.

Once you have written your patch tape, you must load it in a very specific way for it to be placed in memory properly. Let us assume that you additional command will be placed in the T1PLOT module. To add to this module, call DEMON and type:

```
LOAD T1EXEC
LOAD T1PLOT
BIN          and read in the patch tape. When tape has read in, restart DEMON at 7600 and type:
STORE T1EXEC 0-1777:P
DELETE:Y
STORE T1PLOT 2000-5637:P
DELETE:Y
```

Then, to reconfigure T1EXEC to contain the new version of T1PLOT, type:

```
RUN T1PRGM
```

This will look up the new locations of the various modules and load them into the table in T1EXEC.

Unused Space

The following space is available for patches in the various modules:

T1EXEC	1572	– 1573
T1CLEC	3702	– 3777
	4501	– 5507
T1PROC	3665	– 3777
	5467	– 5507
T1PLOT	3771	– 3775
	5062	– 5507
T1CALC	3746	– 3775
	4251	– 5507

The available space for commands and the location of various constants is shown in the following tables:

CONSTANTS FROM ALL MODULES --"T1CONS"

```
TITLE /CONSTANTS FROM ALL MODULES --"T1CONS"/
*5640
/CONSTANTS FROM ALL MODULES
   5640       1 P1, 1
   5641       1 P2, 1
   5642    2342 D1, 2342
DECIMAL
   5643       0 BLOCK 30
OCTAL
   5701    2342 D2, 2342
   5702       1 P3, 1
   5703    2342 D3, 2342
   5704       1 P4, 1 /COMMANDS USED BY EXPANDED NIC-293'S
   5705    2342 D4, 2342
   5706       1 SCANS, 1 /NUMBER OF SCANS
   5707       1 WAITPL, 1 /WAITING PULSES
   5710       0 D1FLAG, 0 /NUMBER OF ENTRIES IN D1 TABLE
   5711      46 CWORD, 46 /IA+PT+CD
   5712       0 NSPEC, 0 /NUMBER OF ENTRIED IN D1 TABLE
   5713       0 HOMFLG, 0 /HOMO SPOIL  ENABLED IF 1 IN TTI SYSTEMS
   5714       0 OKFLAG, 0 /OK TO DISREGARD DUTY CYCLE LIMITS
   5715     144 FDWELL, 144  /REGISTER LOAD VALUES
   5716       0 FDELAY, 0 /FIXED DELAY
   5717    4272 HZPPT; 2.44140 /HERTZ PER POINT FROM DW
   5720 1160777
   5721    4000 KSIZE, 4000 /2K REAL ASSUMED
   5722   32000 WIDTH; 5000  /SWEEP WIDTH
   5723 1161000

   5724   16000 DWELL; 100 /DWELL TIME
   5725 1440000
   5726  116000 DELAY;0
   5727       0
/TITLE TEXT GOES HERE
   5730  770000 NAME0, 770000
   5731       0 BLOCK 20
   5751       0 OFFSET, 0
   5752       0 0
   5753       0 TCONST, 0 /EM TIME CONSTANT
   5754       0 0
   5755       0 SFREQ, 0 /SPECTROMETER FREQUENCY
   5756       0 0
   5757       0 ATOTAL, 0 /TOTAL MANUAL PA
   5760       0  0
   5761       0 BTOTAL, 0 /TOTAL MANUAL B
   5762       0  0
   5763       0 TP1, 0 /T1
   5764       0 TP2, 0 /T2
   5765       0 GLOBAL, 0 /# OF SHIFTS TO KEEP FT ON SCALE

   5766  100000 KSTART, 100000 /ASSUMED START OF LAST FT BLOCK
   5767       0 FPAK, 0 /PA
   5770       0 0
```

```
5771        0 FPBK, 0 /PB
5772        0 0
5773        0 SVTHTA, 0 /SAVED KNOB PHASE CORN PARAMETERS
5774        0 SVADDI, 0
5775   116000 DCONST;0 /DATA TRANSFER CONSTANT
5776        0
5777   115203 115203 /FOR MICOBUG/11
```

T1EXEC COMMAND TABLE IN T1PRGM/II

```
TITLE "T1EXEC COMMAND TABLE IN T1PRGM/II"
*1574 /IMMUTABLE POSITION

/LEGAL COMMAND LIST - PAGE ZERO CMMANDS FIRST
   1574 2000000 COMLST, 2000000 /PAGE ZERO FLAG
   1575  316302 316302 /NB
   1576  114677 114677 /HIGH NICOBUG
   1577  315317 315317 /MU
   1600    1341 MONTOR
   1601  314311 314311 /LI
   1602    1072 LINK
   1603  301325 301325 /AU
   1604    1114 AUTO
   1605  320322 320322 /PR
   1606    1133 PROCES
   1607  303302 "C!T+"B /CB
   1610    1407 CB
   1611  215215 RTRT, 215215 /CR
   1612    1415 CRCOM

/COLLECTION MODULE
   1613 3777776 COLMOD, -2 /TRACK #
   1614  316323 316323 /NS
   1615  307317 307317 /GO
   1616  303317 303317 /CO
   1617  304305 304305 /DE
   1620  304314 "D!T+"L /DL
   1621  320261 320261 /P1
   1622  320262 320262 /P2
   1623  304261 304261 /D1
   1624  304262 304262 /D2
   1625  320263 320263 /P3
   1626  304263 304263 /D3
   1627  320264 "P!T+"4 /P4
   1630  304264 "D!T+"4 /D4
   1631  317316 317316 /ON
   1632  317306 317306 /OF
   1633  323327 323327 /SW
   1634  304327 304327 /DW
   1635  323305 323305 /SE
   1636  326311 "V!T+"I /VI
   1637  303304 "C!T+"D /CD
   1640  301304 "A!T+"D /AD
   1641  323304 "S!T+"D /SD
   1642  320324 "P!T+"T /PT
   1643  316324 "N!T+"T /NT
   1644  301322 "A!T+"R /AR
   1645  323303 "S!T+"C /SC
   1646  311316 "I!T+"N /IN
   1647  332305 "Z!T+"E /ZE
   1650  317326 "O!T+"V /OV
   1651  316326 "N!T+"V /NV
   1652  314323 "L!T+"S /LS
   1653  310323 "H!T+"S /HS
```

```
   1654  310322 "H!T+"R /HR
   1655  327320 "W!T+"P /WP
   1656  324311 "T!T+"I /TI
   1657  303320 "C!T+"P /CP
   1660  324324 "T!T+"T /TT
   1661  314304 "L!T+"D /LD
   1662  301326 "A!T+"V /AV
   1663       0 BLOCK 3
T=1000

/PROCESSING MODULE
   1666 3777776 PRMOD, -2 /TRACK #
   1667  305320 305320 /EP
   1670  305303 "E!T+"C /EC
   1671  305315 305315 /EM
   1672  324303 324303 /TC
   1673  306324 306324 /FT
   1674  320313 320313 /PK
   1675  302303 302303 /BC
   1676  323322 323322 /SR
   1677  320301 320301 /PA
   1700  320302 320302 /PB
   1701  320303 320303 / PC
   1702  324320 324320 /TP
   1703  324261 324261 /T1
   1704  324262 324262  /T2
   1705  324322 324322 /TR
   1706  316303 "N!T+"C /NC
   1707  304324 "D!T+"T /DT
   1710  304303 "D!T+"C /DC
   1711  304306 "D!T+"F /DF
   1712  301324 "A!T+"T /AT
   1713  315326 "M!T+"V /MV
   1714       0 BLOCK 3 /SPARES
/PLOT MODULE
   1717 3777776 PLMOD, -2 /TRACK #
   1720  317320 317320 /DP
   1721  320314 320314 /PL
   1722  323320 323320 /SP
   1723  314320 314320 /LP
   1724  303325 303325 /CU
   1725  326330 "V!T+"X /VX
   1726  311330 "I!T+"X /IX
   1727  320330 320330 /PX
   1730  323330 323330 /SX
   1731  311322 311322 /IR
   1732  311304 "I!T+"D /ID
   1733  326327 "V!T+"W /VW
   1734  306261 "F!T+"1 /F1
   1735  306262 "F!T+"2 /F2
   1736  311323 "I!T+"S /IS
   1737  301303 "A!T+"C /AC
   1740       0 BLOCK 3
```

T1EXEC COMMAND TABLE IN T1PRGM/I1

```
/OUTPUT AND CALCULATION MODULE
   1743 3777776 OPMOD, -2
   1744  323317 323317 /SO
   1745  323306 323306 /SF
   1746  315311 315311 /MI
   1747  320320 320320 /PP
   1750  330320 "X!T+"P /XP
   1751  307314 307314 /GL
   1752  325301 325301 /UA
   1753  325311 325311 /U1
   1754  303324 303324 /CT
   1755  303330 "C!T+"X /CX
   1756       0 BLOCK 5 /SPARES
   1763 3777777 -1 /END OF COMMAND LIST


/POINTERS TO FPP-1972
   1764    7524 FIXOP, 7524
   1765    7553 NUMD, 7553
   1766    7554 PREDIG, 7554
   1767    6712 FLIP, 6712
   1770    6760 VFLAG, 6760

   1771    7036 GETAC, 7036
   1772    7050 PUTAC, 7050

   1773    7466 FLOAT, 7466
   1774    7473 FIX, 7473


   1775    7573 FACM, 7573
   1776    7574 FACML, 7574
```

COMMANDS IN T1PROC MODULE

```
TITLE "COMMANDS IN T1PROC MODULE"
*5510
   5510  323322 COMNDS, 323322 /SR
   5511    3273 REVERS
   5512  305320 305320 /EP
   5513    4000 EP
   5514  305303 "E!T+"C
   5515    4004 EC
   5516  305315 305315 /EM
   5517    3001 EM
   5520  324303 324303 /TC
   5521    3066 TC
   5522  320313 320313 /PK
   5523    4504 PK
   5524  320301 320301 /PA
   5525    3531 GETA
   5526  320302 320302 /PB
   5527    3535 GETB
   5530  320303 320303 /PC
   5531    5367 CONVAB
   5532  302303 302303 /BC
   5533    3351 BC
   5534  324320 324320 /TP
   5535    3541 TP
   5536  306324 306324 /FT
   5537    4727 XFFT
   5540  324261 324261 /T1
   5541    3210 T1
   5542  324262 324262 /T2
   5543    3214 T2
   5544  324322 324322 /TR
   5545    3130 TR
   5546  216303 "N!T+"C /NC
   5547    3325 NC
   5550  315326 "M!T+"V /MV
   5551    3654 MV
   5552  304303 "D!T+"C /DC
   5553    3614 DC
   5554  304306 "D!T+"F /DF
   5555    2576 UF
   5556  304324 "D!T+"T /DT
   5557    3604 DT
   5560  301324 "A!T+"T /AT
   5561    3626 AT
   5562       0 BLOCK P1-#-2
   5636 3777777 377777?
```

COMMANDS IN T1CLEC MODULE

```
TITLE "COMMANDS IN T1CLEC MODULE"
/COLLECTION MODULE COMMANDS
*COMNDS
   5510  314323 "L!T+"S /LS
   5511    4000 LS
   5512  316323 316323 /NS
   5513    3433 NS
   5514  307317 307317 /GO
   5515    2000 GO
   5516  303317 303317 /CO
   5517    2111 CONTINUE
   5520  304305 304305 /DE
   5521    3003 DE
   5522  320261 320261 /P1
   5523    3372 P1SET
   5524  320262 320262 /P2
   5525    3376 P2SET
   5526  320263 320263 /P3
   5527    3410 P3SET
   5530  320264 "P!T+"4
   5531    3414 P4SET
   5532  304261 304261 /D1
   5533    3314 D1SET

   5534  304262 304262 /D2
   5535    3364 D2SET
   5536  304263 304263
   5537    3402 D3SET /D3
   5540  304264 "D!T+"4
   5541    3420 D4SET
   5542  317316 317316 /ON
   5543    2401 ON

   5544  317306 317306 /OF
   5545    2461 OF
   5546  323327 "S!T+"W /SW
   5547    3016 SW
   5550  304327 304327 /DW
   5551    3011 DW
   5552  323305 323305 /SE
   5553    3137 SE
   5554  326311 "V!1000+"I /VI
   5555    3203 VI
   5556  303304 "C!T+"D /CD
   5557    3230 CD
   5560  301304 "A!T+"D /AD
   5561    3210 AD
   5562  323304 "S!T+"D /SD
   5563    3215 SD
   5564  320324 "P!T+"T /PT
   5565    3240 PT
   5566  316324 "N!T+"T /NT
   5567    3426 NT
   5570  301322 "A!T+"R /AR
```

COMMANDS IN T1CLEC MODULE

```
5571     3234 AR
5572   323303 "S!T+"C /SC
5573     2777 NUMS
5574   311316 "I!T++"N /IN
5575     2537 IN
5576   332305 "Z!T+"E /ZE
5577     2530 ZERO
5600   317326 "O!T+"V /OV
5601     2522 OVRIDE
5602   316326 "N!T+"V /NV

5603     2525 NOVRID
5604   304314 "D!T+"L /DL
5605     2171 DL
5606   310323 "H!T+"S /HS
5607     4344 HS
5610   310322 "H!T+"R /HR
5611     4347 HR
5612   327320 "W!T+"P /WP
5613     4353 WP
5614   303320 "C!T+"P /CP
5615     4440 CP
5616   324311 "T!T+"I /TI
5617     4360 TITSET
5620   324324 "T!T+"T /TT
5621     3467 TIMCLC
5622   314304 "L!T+"D /LD
5623     4120 LPULSE
5624   301326 "A!T+"V /AV
5625     3641 AV
5626        0 BLOCK P1-#-2
5636  3777777 -1
```

COMMANDS IN T1PLOT MODULE

```
TITLE "COMMANDS IN T1PLOT MODULE"

*COMNDS
/COMMANDS
   5510  311304 "I!T+"D /ID
   5511    4133 ID
   5512  303325 "C!T+"U /CU
   5513    2224 CU
   5514  317320 "O!T+"P /OP
   5515    2571 ASPECT
   5516  320314 "P!T+"L /PL
   5517    2642 PL
   5520  314320 "L!T+"P /LP
   5521    2543 LP
   5522  320330 "P!T+"X /PX
   5523    2650 PX
   5524  323330 "S!T+"X /SX
   5525    2654 STACKX
   5526  311330 "I!T+"X /IX
   5527    4054 IX
   5530  323320 "S!T+"P /SP
   5531    2423 SP
   5532  311322 "I!T+"R /IR
   5533    3555 IR
   5534  326327 "V!T+"W /VW
   5535    2000 VW
   5536  326330 "V!T+"X /VX
   5537    2004 VX
   5540  306261 "F!T+"1 /F1
   5541    4763 F1
   5542  306262 "F!T+"2 /F2
   5543    4767 F2
   5544  301303 "A!T+"C /AC
   5545    4574 AC
   5546  311323 "I!T+"S /IS
   5547    4566 IS
   5550       0 BLOCK P1-#-2
   5636 3777777 -1
```

COMMANDS IN T1CALC MODULE

```
TITLE "COMMANDS IN T1CALC MODULE"
*COMNDS
/COMMAND LIST
/PLUG IN COMMANDS
   5510  320320 320320 /PP
   5511    3626 PP
   5512  330320 "X!T+"P /XP
   5513    3632 XPEAK
   5514  323306 323306 /SF
   5515    4201 SF
   5516  325301 325301 /UA
   5517    3672 UA
   5520  325311 325311 /UI
   5521    3675 UI
   5522  315311 315311  /MI
   5523    3430 MI
   5524  307314 307314  /GL
   5525    4000 GL
   5526  323317 "S!T+"O /SO
   5527    4175 SO
   5530  303324 "C!T+"T /CT
   5531    2000 CT
   5532  303330 "C!T+"X /CX
   5533    2004 CX
   5534       0 BLOCK P1-#-2
   5636 3777777 -1 /TERMINATOR
```

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