The Configuration and Demonstration of a
Rapid Scan Correlation Fourier Transform
Nuclear Magnetic Resonance Spectrometer

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ABSTRACT

THE CONFIGURATION AND DEMONSTRATION OF A RAPID SCAN CORRELATION FOURIER TRANSFORM NUCLEAR MAGNETIC RESONANCE SPECTROMETER

Geoffrey John Nesbitt

A nuclear magnetic resonance correlation spectrometer has been constructed, and shown to be a useful complement to the magnetic resonance facilities already present in this Department. This thesis first describes the theory behind the principles of the spectrometer operation, which then support the decisions necessary to configure the complete instrumental hardware and software systems. The spectrometer capabilities are demonstrated, under a variety of conditions, culminating in its application to a problem whose solution would be very difficult, if not unobtainable, by any other method. Finally, future applications are suggested, and conclusions drawn upon the text.
I know who John Galt is.
ACKNOWLEDGEMENTS

The multifaceted nature of this thesis dictates a rather lengthy compendium, in order to place credit and thanks where they belong. My standard reply to all the people who have contributed efforts, throughout the course of this project has been: "... get in line! ". Brevity shall be exercised, hopefully without offence. First, I would like to offer my most humble thanks to Dr. L. D. Colebrook, who has honored me with his attention as my very learned research supervisor.

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Chapter 1

INTRODUCTION

The field of Nuclear Magnetic Resonance (NMR) has seen phenomenally fast growth from conception to the state at which technology now stands.

When Bloch$^1$ and Purcell$^2$ first demonstrated NMR in bulk samples, the experiment was simply the observation of a nuclear resonance and the determination of its magnetic moment. The observation of the chemical shift$^3$ ushered the technique into the role of an analytical tool, finding employment in structure elucidation. At this time, the standard method to obtain high-resolution spectra was the continuous wave (CW) experiment. This procedure requires the continuous excitation to be slowly swept through the resonance condition in order to approximate the steady state solutions to the Bloch equations.$^4$ Under these circumstances the sweep rate is of the order

$$\frac{1}{2 \times T_2} \text{ Hz/sec (often < 1 Hz/sec)}$$

where $T_2$ = spin-spin relaxation time

Very little power is introduced to the sample, hence the system is perturbed only slightly and a weak signal procured as a result.

In 1966, Ernst and Anderson$^5$ capitalized on ground work laid previously by Torrey$^6$, Hahn$^7$, and Fourier$^8$, to establish that the Fourier transformation (FT) of the free induction
decay observed upon irradiation, with a short intense radio frequency (RF) pulse, could yield high resolution NMR spectra also. Further, the entire spectrum can be obtained with a single pulse, on a time order of $3^*T_2$ (after which the FID is reduced to 45%), and the magnetization vector is tipped from the equilibrium value (for a 90° pulse) yielding an increase in sensitivity (relative to the CW experiment).

To a large degree the quickly developing computer industry and the elucidation of the "fast Fourier transform" by Cooley and Tukey have been responsible for the Pulse FT method becoming the most popular and convenient mode to obtain high resolution NMR spectra.

One significant difference between the CW and pulse FT methods lies in the execution of the experiment. The pulse technique requires the entire spectrum to be excited during each scan, while the CW mode allows selection of any specific part of the spectrum. This becomes important when there is a particularly large solvent peak in the sample, which would cause dynamic range problems in the pulse experiment but could be skirted in the CW mode by not scanning that portion of the spectrum.

An alternative approach to the above techniques is found in the rapid passage (RP) experiment. Similar to the CW method the spectrometer is simply swept through the resonance under fast passage conditions. This results in magnetization being left in the x-y plane (see later), which produces a
ringing wiggle beat pattern that persists a time $3^*T_2$
after resonance.

This is useful only if the ringing artifact can be
removed in order to obtain the high resolution spectrum wished.
It has been shown that the cross-correlation of this
distorted fast passage response with a function representing
either a reference line recorded under fast passage conditions$^{11}$ or a theoretical calculated lineshape$^{12}$ will result in
an artifact-free spectrum. The method necessitates the use of
Fourier transformations and has thus been coined Rapid Scan
FT Spectroscopy. This offers a mode of operation comparable
to pulse techniques in many ways:
-approximately equivalent signal to noise (S/N) ratio.
-comparable resolution depending on the $T_2$ of sample.
-approximately the same time required for a single scan.
-control of the sweep rate allows regulation of the power input and hence the tip angle of the bulk magnetization vector, which in turn affects the sensitivity.
-dynamic range problems can be skirted by simply not exciting that portion of the spectrum containing the unwanted (problem) line.

This technique has seen further enhancement with the
addition of solvent suppression methods$^{13}$, wing processing$^{14}$, and has been demonstrated measuring spin-lattice relaxation times,$^{15,16}$ and applications in biological systems$^{16,17}$. 
The purpose of this thesis is to demonstrate the resurrection of an aging CW instrument in the form of a Rapid Passage Correlation NMR spectrometer, and the successful application of its unique capabilities to a chemical problem. This will be accomplished within the text by first presenting a discourse on the theoretical background of the experiment and the computational methods critical to the project. The hardware arrangement will then be discussed and explained as a consequence of the theoretical requirements of the experiment. The software configuration follows in detail with an operational flowchart demonstrating the step by step processing of the data. The experimental chapter will substantiate the previous performance claims and illustrate the functional application of the spectrometer over a range of operating conditions. Finally, conclusions will be drawn from the text and possible future development/evolution of the instrument suggested.
Chapter 2
Section 1

THEORY OF NUCLEI IN A MAGNETIC FIELD

Nuclear magnetic resonance is possible because some nuclei act as though they possess the properties of spin and angular momentum. The property of spin confers upon the nuclei a magnetic moment which is proportional to the magnitude of the spin and may be described as shown in equation 2.1.

\[ \mathbf{J}_n = g_n \mathbf{B}_n \mathbf{I}_n \]

where

- \( g_n \) = nuclear g-factor
- \( B_n \) = Nuclear magneton \( \frac{e\hbar}{2MC} \)
- \( I_n \) = Nuclear spin quantum number

The properties of the nuclear magneton do not change, e and \( M \) are the charge and mass of the proton respectively, \( C \), the speed of light and \( \hbar \) Planck's constant over \( 2\pi \). \( g_n \) is a dimensionless constant whose contribution depends upon the nuclei under observation. Hence, only \( g_n \) and \( I_n \) change to modify the equation to fit the characteristics of any nuclei. Quantum mechanics predicts the value of \( I \), being a characteristic of the isotope in question and a consequence of its atomic mass and number.

If the nuclei are placed in a magnetic field, the interaction between the magnetic moment and the field produces a torque which may be described classically as the vector product of the two, and pictured in Figure 2.1.
By substituting equations 2.1 into 2.2 we generate a Hamiltonian equation which models the coupling of the moment with the field, which will provide an explicit solution enabling the measurement of the nuclei energy.

(2.3) \[ H = -g_n B_n H_0 I_z \]

Quantum mechanics predicts multiple spin states through the variable \( I_z \) in equation 2.3, each with peculiar energy levels. Classically, Newton's law dictates that this coupling is also equal to the rate of change of the angular momentum \( \mathbf{U}_n \). \( \mathbf{U}_n \) has only one degree of freedom within the constraints imposed by equation 2.3, the rate of precession about \( H_0 \). The result is that the magnetic moment vector precesses about the field direction with a characteristic frequency, known as the Larmor frequency, \( \omega_0 \) where
(2.4) \[ |\omega_0| = 2 \pi V_o \]

where \( V_o \) (Hz) is the frequency of precession of the magnetic moment about \( H_o \).

Bringing equation 2.3 under closer scrutiny it should be obvious that for any nuclei with \( \omega_0 \), the application of the static field through \( H_o \) will effect a separation of the spin states observable in the Hamiltonian. In order to detect the presence of these energy levels, a tool is needed to perturb the system to enable transitions between the levels, which may then be measured. This materializes in the form of a circularly polarized radio frequency energy, usually applied along the x axis of the classical picture, illustrated in Figure 2.2a. The two possible states for \( U_n \) defined by \( I_z \) are shown in line with \( H_1 \), the perturbing field. If \( H_1 \) is varied through \( \omega_0 \) the resonance is observed. The equivalent quantum mechanical picture is portrayed in Figure 2.2b.

Examining equation 2.5, it is apparent that in a given magnetic field, the resonance condition requires a unique precession frequency for each distinct nucleus. If the magnetic moment is thought of as a top, then in a spin \( I = \frac{1}{2} \) system the top may have two orientations when placed in the field, anti or parallel to the field direction.

This is realized quantum mechanically in the form of the two energy levels shown in Figure 2.2b. A transition can occur at the resonance condition if the top receives
\[ h\nu = g_N\beta_N H = \Delta E \quad (2.5) \]

Figure 2.2
the unique amount of energy $hv$ dictated by Planck's law. The transition will happen only when this condition is met exactly; this provides the exclusive nature of the magnetic resonance experiment. By varying either $V$ or $H_1$ in equation 2.5, a transition can be caused peculiar to a particular nucleus, as an exact solution to equation 2.5.
Section 2

BOLTZMANN AND THE RESONANCE PHENOMENON

Until this point the discussion has considered only the behavior of a single isolated nucleus, while in practice the N.M.R experiment measures the mean behavior of a bulk sample in a very complicated magnetic environment. Boltzmann theory predicts that, left to its own devices, the populations of each energy level will approach an equilibrium derived from all the forces which affect the magnetic environment of the sample, shown in Figure 2.3. Given a two spin system, the Boltzmann equation (2.6) can be used to describe the population distribution at equilibrium.

\[
\frac{n_+}{n_-} \text{ equilibrium} = \exp \frac{\Delta E}{kT} = \exp \frac{-U_n H_0}{kT}
\]

(2.6)

The transitional probability from each state is equal in both directions. Upon irradiation with \( H_1 \), the applied field, a forced equilibrium can be reached which results in saturation of the population levels. No detection of transitions would occur at this point if it were not for the presence of natural relaxation mechanisms which allow the system to dissipate the energy.

These processes can be characterized in the form of two measurable relaxation rates which represent the two most important pathways, shown in Figure 2.4.
Two spin system

1. = Zeeman interaction
2. = Direct spin-spin interaction
3. = Nuclear spin-electron interaction
4. = Direct spin-lattice coupling
5. = Indirect spin-lattice via electrons
6. = Shielding and polarization via electrons
7. = Coupling of nuclear spins to sound fields
The isochromats above illustrate a classical picture of the effect of the two dominant relaxation pathways $T_1$ and $T_2$, on the vectors of the magnetic moments.

A. $T_1$ causes the distribution of the nuclear moments along the $z$ axis.

B. $T_2$ causes a dephasing of the spins in the $x$-$y$ plane.
When describing the bulk sample it is necessary to introduce a bulk magnetization vector $M$ which represents the mean of the individual nuclear vectors. In Figure 2.4 equations 2.7 and 2.8 model the two dominant relaxation pathways. $T_1$ is derived in terms of probability since the rate of return to equilibrium via the spin lattice is directly related to the original population condition under the experiment and the transitional probability of these populations changing. $T_2$ can be thought of most easily as a dephasing of the nuclear vectors via spin-spin interactions and field inhomogeneities. The NMR experiment works because, when the R.F. energy that is used to perturb the system forces the population levels from their natural equilibrium, these pathways act as a lever to restore the Boltzmann distribution. At room temperature the distribution is weighted such that a greater number of vectors (actually nuclei) reside in the lower energy level.

**THE BLOCH EQUATIONS**

The relaxation times, $T_1$ and $T_2$ are predicted by a set of equations postulated by Bloch which describe the behavior of the bulk magnetization vector, $M$, in the presence of an applied R.F. field. The approach used was to first model the effect of the applied field upon the bulk magnetic moment.
Figure 2.5

The Figure above illustrates the states possible for the spin vectors representing the nuclei in the bulk sample. The terms used in equations 2.10, 2.11, 2.12, can be visualized clearly, showing example contributions.
(2.9) \[ \frac{dM}{dt} = \gamma M \mathbf{H} \]

This may be expanded to account for each separate component of \( M, M_z, M_x, M_y \), where the field components \( H_z, H_x, H_y \), would by convention be the fixed ( \( H_z = H_0 \) ) and rotating fields respectively. In order to account for relaxation mechanisms the following assumptions were made:

1. \( M_z \) would decay to \( M_0 \) (equilibrium) by entirely first order processes with a time constant \( T_1 \).
2. \( M_x, M_y \) would decay to zero by the first order time constant \( T_2 \).

The result is the equations presented below:

(2.10) \[ \frac{dM_x}{dt} = \gamma ( M_y H_0 + M_z H_1 \sin wt ) - \frac{M_x}{T_2} \]

(2.11) \[ \frac{dM_y}{dt} = \gamma ( M_z H_1 \cos wt - M_x H_0 ) - \frac{M_y}{T_2} \]

(2.12) \[ \frac{dM_z}{dt} = - \gamma ( M_x H_1 \sin wt + M_y H_1 \cos wt ) - \frac{(M_z - M_0)}{T_1} \]
Chapter 2
Section 3

EXCITATION AND MEASURING TECHNIQUE

In the classic CW experiment, the field or frequency is swept slowly through the spectrum such that the stationary solution of the Bloch equations yields analytical solutions, under certain limiting conditions. The criteria are that the applied field $H_1$ is small, and the sweep rate is slow enough to establish a steady state where the time derivatives of the equations are zero. Accordingly, we get equation 2.13 as a result.

\[
\begin{align*}
\frac{dM_x}{dt} &= \frac{dM_y}{dt} = \frac{dM_z}{dt} = 0 \\
\end{align*}
\]

Since the spectrometer measures the frequency component of the magnetization, the magnetic flux through the receiver coil induces an alternating potential which it can be shown yields two signals in the $x,y$ plane.\textsuperscript{18}

1. Absorption signal, 90° out of phase with $H_1$, proportional to the $V$ component of $Mxy$.
2. Dispersion signal, in phase with $H_1$, proportional to the $U$ component of $Mxy$.

The signal components, $U$ and $V$ represent the electromagnetic radiation as two rotating vectors out of phase with each other, this will be covered in more detail in Chapter 3.

Both the phase and magnitude are important, and each signal can be obtained separately by means of an radio-
frequency phase-sensitive detector as the spectrometer is swept through the resonance condition. This affords us a measuring technique and is illustrated vectorally by the isochromats in Figure 2.6.\textsuperscript{19}

If the experimental arrangement is such that a receiver coil is placed along the x axis then the detected signal will be

\begin{equation}
S = A \frac{\partial M}{\partial t} \text{ } x
\end{equation}

and the absorbance maximum will be

\begin{equation}
S \propto \frac{H_1}{1 + \gamma^2 H_1^2 T_1 T_2}
\end{equation}

Some important conclusions can be drawn from this:

1. Under adiabatic slow passage conditions (eqn. 2.16), as the perturbing excitation reaches resonance the system at that point must absorb all the energy introduced by the excitation.
2. In order to avoid saturation the power level of the excitation must be carefully balanced.
3. The bulk magnetization vector is pushed only slightly from equilibrium and a weak signal results.

From the adiabatic theorem we know that equation 2.16 must be satisfied in order for the spectrometer passage to be considered adiabatic.\textsuperscript{20}
Figure 2.6

A. formation $M_z$ and alignment with $H_0$.

B. tipping of $M$ by $H_1$ causes $M_{xy}$ formation.

C, D, and E. relaxation to equilibrium.
\[ (2.16) \quad \frac{dH_0}{dt} \ll X \cdot H_1^2 \]

In liquids, the ratio of the spectrum width to the line width is very large, meaning the relative time spent searching a line is short with respect to the total scan time. The result is that in an unpopulated sample the entire spectrum must be scanned, and at a power level which will not saturate the populated parts of the spectrum.

When this requisite is ignored the Bloch equations no longer accurately describe the system. In practice, this results in a non-Lorentzian line shape with spurious ringing caused by excess magnetization left in the x-y plane after resonance. Figure 2.7 illustrates the artifact, but the explanation is best delivered using Figure 2.6.

As the resonance condition in 2.6b is reached, \( H_1 \) is rotating in the x-y plane at the Larmor frequency \( \omega_0 \). Immediately after resonance the Larmor frequency has changed as a result of the sweeping excitation and \( H_1 \) now finds itself beating against \( M_{xy} \), as shown in Figure 2.6c. This is the cause of the wiggle observed after the peak.

From the Bloch equations we know that \( M_{xy} \) decays with the characteristic time \( T_2 \). In principal the envelope should contain information with respect to this decay. Unfortunately, field inhomogeneities cause nuclei in the bulk sample to experience slightly different values of \( H_0 \) and their vectors quickly dephase causing relaxation. In fact, this envelope is a better estimate of field homogeneity than
Figure 2.7

A. Fast passage scan of a formyl proton showing residual ringing. $\sim 50 \text{ Hz/sec}$

B. Slow passage run of same. $\sim 2 \text{ Hz/sec}$
anything else, and it is common procedure to shim up the field against a single line wiggle beat pattern.

In order to drive the system into the fast passage region, equation 2.17 must be satisfied experimentally.

\[
(2.17) \quad b' \gg \frac{1}{2 \pi T_2^2} \quad \text{where } b' = \text{sweep rate (Hz sec)} \quad T_2 = \text{natural decay time}
\]

Concurrently, to minimize the system saturation, which should then yield the greatest peak height for the given sweep rate, equation 2.18 must be optimized.\(^{10}\)

\[
(2.18) \quad S_{op} = (\delta H_1)^2 T_1 T_2 = 1 + 3.01 b' T_1 T_2
\]

At its upper limit \( S_{op} = 3.01 b' T_1 T_2 \) for an infinite power input.

The sweep rate, \( b' \), must be optimized in accordance with the last two equations. This is difficult unless the operator has a priori intuition concerning the relaxation values for the system under investigation, but certainly these values can be guessed at. If the expectations are that a natural line width of 1 Hz is desirable, then the minimum value for \( b \) would be only 20 Hz by equation 2.17 while equation 2.18 would only be limited by the available transmitter power.
In general, it can be stated that the pulse method usually yields a better S/N ratio, with the difference closing as the sweep rate in the rapid scan experiment increases, but the sensitivities are comparable. If equation 2.19 describes the time between scans, then

\[
T = \frac{V_t + 3T_2}{V'} \quad \text{where} \quad V' = \text{sweep rate} \quad V_t = \text{sweep width}
\]

therefore the time given by \(\frac{V_t}{V}\), is necessary to sweep the entire spectrum while \(3T_2\) accounts for the time required for the last line scanned to decay. From this it is possible to conclude that at low \(T_1\) values the \(3T_2\) term lowers the sensitivity, while at high \(T_1\)'s the contribution would be negligible and the rapid scan has approximately equal sensitivity to pulse methods.
Chapter 2
Section 4

THE FOURIER TRANSFORM

The Fourier transform (FT) finds wide application among problems involving vibrations or oscillations. In order to describe a harmonic process it is necessary to employ a mathematical series which can precisely represent all the components present in the system. The Fourier series is particularly well suited to this case since, simply stated, it is a series whose terms are composed of periodic functions. By definition, at the limit of the sum the Fourier series may be replaced by an integral of the same name.

This integral may undergo transformation between two domains where the function is preserved coherently and exactly in both domains, but defined in different units, related directly through the transform. The transform may take different forms depending upon the nature of the system, but will be composed of a number (perhaps infinite) of (co-)sinusoidal components at various frequencies, each with a given amplitude and initial phase, as illustrated in Figure 2.8. The purpose of Figure 2.8 is to show an example component and the relationship possible between the two domains. By inspection, in Figure 2.8C, the real and imaginary vectors are 90° out of phase with each other, leading to the observation that a combination of sin and cos terms can describe the whole function.
A. Example sinusoidal component $A \cos (2\pi ft + \phi)$
both period and phase shift along x axis.

B. Function in A. decomposed as sum of two contra-
rotating vectors. Only real component of vectors
add, by inspection imaginary parts always cancel.

C. Three dimensional spectrum of part of function.

The time for one rotation of a vector equals one
period, all at the same frequency. Equivalence of
representation is obvious: $A \cos \phi = \frac{A}{2}(e^{i\phi} + e^{-i\phi})$
Both Fourier sine and cosine transforms are symmetrical about \( t=0 \), the cosine being an even function, the sine odd. These transforms alone allow the description of systems with either purely even or odd symmetry, a serious limiting condition.

The linear combination of the two transforms generates a new transform which will model all functions of arbitrary symmetry. This equation may be expressed by a Taylor expansion in exponential notation, as shown in Figure 2.9.

**FIGURE 2.9**

\[
\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} + \ldots
\]

\[
\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \ldots
\]

\[
\exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots
\]

by Euler \( \exp(i\phi) = \cos(\phi) + i\sin(\phi) \).

The special properties of \( i \) accommodate the symmetry and preserve the orthogonality of the sine and cosine functions. Finally a notation can be ventured which represents the Fourier transform.\(^{22}\)

\[
(2.20) \int h(t) \exp(-2\pi ft) \, dt = \int h(t) \left( \cos 2\pi ft - i \sin 2\pi ft \right) \, dt
\]
The transform pair may now be presented, depicting the relationship between the two domains.

\[
H(f) = \int_{-\infty}^{\infty} h(t) \exp(-j2\pi ft) \, dt
\]

\[
h(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} H(f) \exp(j2\pi ft) \, dt
\]

The practical advantages of the Fourier transform are realized in the algorithm of the fast Fourier transform (FFT). This is an especially time efficient method of processing the discrete Fourier transform (DFT).

The particular strategy employed in the program used in this thesis is a decimation in time algorithm, for the special case where \( N \), the number of points in the array to be processed, is a power of two. The effectiveness of this algorithm is achieved by the reduction of the number of complex operations (multiplication or addition) necessary to perform the transform. The form of the discrete digital expression for the FT is shown in equation 2.22.

\[
H(f) = \sum_{k=0}^{N-1} h(t) W_n^{kf} \quad \text{for } f = 0,1, \ldots, N-1
\]

where \( W_n = \exp\left(-j\frac{2\pi}{n}\right) \)

Intrinsically, it must take \( N \) operations to find the value of one \( H_f \), hence \( N^2 \) operations to find all \( N \) \( H_f \) values.

Using the Cooley-Tukey procedure, the array is split into two sums, one for \( n \) even, another for \( n \) odd points.
\[
(2.23) \quad H(f) = \sum_{t=0}^{N/4-1} h_{2t} W_t^{2tf} + \sum_{t=0}^{N/4-1} h_{2t+1} W_n^{(2t+1)f}
\]

The total \(N\)-point DFT may be found by combining the two \(N/2\) point DFT's according to the relationship,

\[
(2.24) \quad H(f) = \sum_{t=0}^{N/4-1} h_{2t} W_{n/2}^{tf} + W_n^f \sum_{t=0}^{N/4-1} h_{2t+1} W_n^{t+1f}
\]

since \(W_{n/2} = W_n^2\)

\[
(2.25) \quad H(f) = A_f + W_n^f B_f
\]

To process the two \(N/2\) point arrays requires only \(2 \times (N/2)^2\) operations. If the two \(N/2\) point arrays are further divided into \(N/4\) point arrays, and so on until each sub-array contains only one point, the transform of which is itself, the complex arithmetic required is only that necessary to recombine the sub-divisions of the array. This is how the \(N \log_2 N\) relationship is derived which dictates the number of calculations required to perform a FFT using the Cooley-Tukey algorithm.
Chapter 2
Section 5

CORRELATION

The dFT adheres to the same principal relationships between Fourier transform pairs as does the continuous FT. In particular, one of these properties is very useful with respect to our intent, for it states that the convolution of the FT's of two functions is proportional to the FT of the product of the two functions. Thus if $H(f) \rightarrow h(t)$ and $G(f) \rightarrow g(t)$ are both FT pairs then

$$H(f) \ast G(f) \propto \frac{1}{2\pi} \left( h(t) \ast g(t) \right)$$

where $\ast$ defines the operation of convolution.

This theorem allows the arduous task of a conventional discrete convolution product to be replaced by the direct multiplication of the two functions in the Fourier domain. Of further significance is the generalization of the properties of the convolution theorem to generate an equivalent supposition for the correlation operation.

The consequence of this becomes important in light of the fact that the time domain measurement of an NMR signal (the free induction decay) and the frequency domain equivalent (absorption mode) are Fourier transform pairs. The result is an elegant data manipulation which allows access to a huge array of digital processing techniques.
If the data gathered from the experiment, \( F(w) \), is in the frequency domain, then upon FT the array is now described as a function of time, \( f(t) \). In the time domain our function models a naturally decaying exponential, and may be treated digitally as such.

At this stage the signal can undergo exponential multiplication, convolution,\(^{31,32,38}\) cross correlation,\(^{33}\) trigonometric multiplication,\(^{34}\) digital smoothing,\(^{35}\) and filtering\(^{36}\) or any other operation acting coherently on an exponential function.

The correlation multiplication yields the important components, \( h(t) \), without preserving the wiggle beat ringing, and upon retransformation back to the frequency domain we have the signal of interest, \( H(w) \). This is illustrated graphically in Figure 2.10.

**FIGURE 2.10**

\[
\begin{align*}
F(w) \otimes G(w) & \quad \longrightarrow \quad H(w) \quad \text{frequency domain} \\
\downarrow \text{FT} & \quad \uparrow \text{iFT} \\
f(t) \ast g(t) & \quad \longrightarrow \quad h(t) \quad \text{time domain}
\end{align*}
\]

The processing algorithm employed has come under close scrutiny\(^{37}\) and several options are theoretically available. For reasons that will be made evident in latter discussion the physical restraints of the hardware at hand impose criteria for making the decision determining which method to employ.
The derivation will be presented here at a level where these restrictions play no role.

The linear response of a spin system can be written as a Fourier transform pair.

\[ F(w) = \int f(t) e^{-iwt} dt \quad \Rightarrow \quad f(t) = \frac{1}{2\pi} \int F(w) e^{iwt} dw \]

In NMR convention, \( F(w) \) would be the result obtained from a slow passage experiment while \( f(t) \) could represent a typical response from a pulse spectrometer.

The correlation operation may be justified treating the system classically or quantum mechanically, the linear response method will be presented here. In order to show the analytical proof of the correlation operation within the context of the NMR experiment it will first be necessary to describe the spin system, \( F(w) \).

The response of the sample to an arbitrary excitation, \( E(t) \), can be modeled by

\[ R(t) = \int \phi(\tau) E(t-\tau) d\tau \]

where \( \phi(\tau) = 0 \) for \( \tau < 0 \) (causality condition).
The excitation can be further described as

\[(2.27) \quad E(t) = e^{i \int w_t dt} = e^{ibt^2} \frac{1}{2} \]

where \(w_t = b^2 t\) for a linear rf field swept at \(b\) rad \(\text{sec}^{-2}\).

Substituting into equation 2.26 we get,

\[(2.28) \quad R(t) = \int_{0}^{t} \mathcal{G}(\tau) e^{ib(t-\tau)^2} d\tau \frac{1}{2} \]

The detected component of the response, \(R(t)\), must be in phase and at the same frequency as the applied rf field \((H_1)\). This is obtained by multiplying \(R(t)\) by \(e^{-ibt^2} \frac{1}{2}\) and is analogous to phase sensitive detection. \(40\)

This gives us

\[(2.29) \quad F(w) = R(t) * e^{-ibt^2} \frac{1}{2} \]

which upon substitution by equation 2.28 and factoring, yields,

\[(2.30) \quad F(w) = \int_{0}^{t} \mathcal{G}(\tau) e^{ib(t^2-2t\tau)} d\tau \frac{1}{2} \]

Now taking the forward transform of \(F(w)\) we have an expression of the system in the time domain.

\[(2.31) \quad f(t) = \int_{-\infty}^{\infty} F(w) e^{iw_t} dw_t \]
Substituting equation 2.30 into 2.31 and knowing \( w_t = b^t \), we get equation 2.32.

\[
(2.32) \quad f(t) = \frac{1}{2\pi} \int \frac{1}{\omega(t)} \left( e^{i(\omega^2 - 2\omega t)} \right) e^{i\omega t} \, dt \, d\omega
\]

After factoring and rearranging this can be written as equation 2.33.

\[
(2.33) \quad f(t) = \frac{1}{2\pi} \left[ e^{i\omega(t-t)} \right] \int \frac{1}{\omega(t)} \left( e^{i\omega t} \right) \, d\omega \, dt
\]

In equation 2.33 the definition for the inverse FT for the Dirac impulse function is underlined. Once recognized, it provides us with a tool to simplify the equation since by definition the transform of the product of a function multiplied with an impulse function, is the function itself. Substituting the Dirac function into equation 2.33 we have

\[
(2.34) \quad f(t) = \int \delta(t) \left( e^{i\omega t} \right) \, d\omega = \delta(t-t) \, dt
\]

and finally, after multiplication, equation 2.35,

\[
(2.35) \quad f(t) = \delta(t) e^{ibt^2} \frac{1}{\sqrt{2}}
\]

By inspection, it is obvious that multiplying equation 2.35 by the term \( e^{-ibt^2} \), in this case the function we have designated \( g(t) \), the original time response is retrieved to
yield the free induction decay signal $\varphi(t)$. This is the justification of the multiplication of our muddled time response by the complex conjugate of the theoretical line shape.

\[ h(t) = f(t) * g(t) = \varphi(t) \frac{e^{ibt^2} + e^{-ibt^2}}{2} \]

(2.36) \quad h(t) = \varphi(t) !

To obtain the final slow passage spectrum it is only necessary to find the inverse FT of $\varphi(t)$ in equation 2.36.

(2.37) \quad H(w) = \int_{-\infty}^{\infty} h(t) e^{-iwt} dt

which yields the approximation to the slow passage spectrum.

Glancing back at Figure 2.10 it is now possible to write down the first rudiments of a flow chart dictating the steps required to perform the actual correlation operation:

1. Start with the frequency data $F(w)$
2. Perform forward FT to get $f(t)$
3. Multiply by $g(t) \left( \exp \frac{-ibt^2}{2} \right)$ to get $h(t)$
4. Perform inverse FT to get $H(w)$

This will be expanded in chapter 4.
Chapter 3

INTRODUCTION

The most basic instrumentation required to perform a modern CW NMR experiment using a crossed coil probe is shown schematically in Figure 3.1. The theoretical background has already been treated in Chapter 2, the purpose of this chapter is to substantiate the implementation of the experiment with the actual electronic components necessary to meet the criteria established in Chapter 2. A summary is given followed by an explicit description of the system employed in this thesis.

The spectrometer hardware is used to first perturb, then measure the electromagnetic transitions of a population of nuclei (bulk sample), between stationary energy states. The energy levels in the NMR experiment are a consequence of the permanent magnetic field furnished by the magnet pole faces. The stability of the magnet is largely a function of the magnetic power supply and associated monitoring circuitry (magnetic flux stabilizer and temperature controller). The excitation is stimulated by an RF oscillation supplied by the transmitter of Figure 3.1 through a transmitter coil aligned along the x axis. The detection and quantitative measurement of the induced signal is performed by a phase sensitive detector connected to a coil placed on the y axis. Both coils are housed in a probe which sits between the pole faces of the magnet and holds the
Figure 3.1  Basic NMR Spectrometer
sample under investigation. At the point of detection both the transmitter and the receiver are tuned to the Larmor frequency, completing the requirements for the resonance condition, and reaching a maximum according to the Bloch equations. The last component to be mentioned, shown in Figure 3.1, is the signal recorder. The recorder receives information derived from two sources, shown clearly in the Figure. Conventionally, the potential from the sweep coils is used to drive an analog motor which moves a bridge proportionally to the x axis. A separate motor drives a slide wire mounted on the bridge, with a pen attached to it. This is driven by the amplified signal from the receiver and draws the y axis absorption plot.

This concludes the general description of an NMR spectrometer, the specific configuration of the instrument used in this thesis will now be discussed. The modified arrangement of an HA-100 spectrometer is shown in Figure 3.2. Each component will be discussed to specify its role in the operation of the entire system.
Chapter 3
Section 1

The Magnet

A 100 MHz (2.348 Tesla) water cooled electromagnet is employed in this spectrometer along with the original power supply and V3520A temperature controller. The physical dimensions and mechanical criteria conform to the manufacturers specifications and have been covered in detail in other texts. The magnetic field must be both stable and homogeneous since, by the Larmor equation, a fluctuation of $H_0$ by an order of $10^{-9}$ yields a change in the resonant frequency of 1 Hz at 100 MHz, which is significant in a high resolution experiment. When the line broadening governed by the spin-spin and spin-lattice relaxation is less than that caused by the inconsistencies of the magnetic field then the spectrometer contribution is at the limit of resolution. The stability and homogeneity requirements are met by several actions detailed below:

Field Stabilization

The following list comprises the techniques employed in this spectrometer to achieve a stable magnetic field.

1. Insulation and temperature control are provided by a double wall casing and the V3520A temperature controller respectively. The V3520A is solenoid controlled to react to a thermistor resident in a reservoir tank where the water from the magnet cooling coils is continuously cycled.
A large amount of heat is generated from an electromagnet since a high intensity electrical current is routed through two main field coils which are wound around the circuit connected to the pole faces.

2. The output from the main transformer stages going into the magnet is rectified and filtered by current stabilization circuits present in the power supply itself.

3. Magnetic flux stabilization is supplied by the flux stabilizer which compensates for rapid changes in the magnetic field. This is accomplished by supplying a correction signal to the current stabilizer as a result of monitoring the magnetic flux through stabilizer pick up coils mounted on the pole faces and by supplying a current to the buck-out coils.

4. A field homonuclear lock is used by the V4354A controller with a separate channel provided for the lock modulation. For our purposes, the lock channel was operated at 2500 Hz, the V4354A having a dedicated potentiometer to control the power modulating the lock. The dispersion signal of the chosen reference side band (TMS, DSS, or H₂O) is monitored and current applied to the appropriate stabilizer coil to correct for the shift in magnetic field. See Figure 3.3 for explanation of channel frequency allocation.

Homogeneity

The homogeneity of the magnetic field varies as a result of sample state, sample tube quality, and of course, the
Figure 3.3

Lock is held at 0 Hz, sign change occurs upon drift. Feed back loop monitors sign and applies current to coils.

Figure 3.4
main field inhomogeneities. Attached to each pole face are shim coils arranged in pairs which apply supplementary fields of concisely regulated strength and geometry controlled by potentiometers housed in the V3531B unit.

Under normal operating procedures, the field homogeneity is shimmed empirically by observing the ringing of an intense singlet.(mentioned in Chapter 2, section 3) This is done before locking such that the signal is maximized to provide the largest possible lock and the most resolved signal possible. Spinning the sample in the probe also increases homogeneity since the magnetic field experienced by any nucleus in the x-y plane will be averaged.

The Sweep System

In order to detect the signal, some method is required to move the resonance condition past the detector. This may be done, as pointed out in Chapter 2, by either sweeping the frequency or the field. The pro's and con's of the two alternatives has recently been questioned in the literature, with the conclusion that both methods are equally sensitive being drawn.66 In our case, the lock frequency is held constant, modulated on a separate channel, while a weak ac is supplied to the sweep coils mounted in the probe, from the linear sweep module, originating from the V3530 sweep oscillator. This is represented diagrammatically in Figure 3.4. The V3530 houses the Wavetek oscillator which
responds to a voltage ramp output from the HP-1000 computer (0 to 10 volts) and is initialized by the operator calibrating trim potentiometers on the unit face while observing the V4315 frequency counter. This is the point where the frequency sweep is put under software control. The linear voltage ramp pushes the V3530 output between any two minimum and maximum settings dialed in by the operator viewing the frequency counter, in response to the polling computer program. This allows discrete digital control of the frequency linear sweep and replaces the usual CW analog drive.
Transmitter, Receiver, Probe.

The HA-100 is a crossed coil spectrometer, where the receiver and transmitter coils are perpendicular to each other, mounted on the x and y axis, respectively. They are housed in the probe body, a single piece of harmonically stable aluminium, this prevents interference from phonons, mentioned in Chapter 2, section 3. Also aligned in the probe are the sweep coils and the receiver preamplifier.

The close proximity of the two coils and local magnetic eddy currents make it necessary to balance the transmitter power with the emf produced in the receiver coil such that a zero potential is passing out of the probe from the receiver coil. This is accomplished with two sets of double paddles, coarse and fine, which tune the coils by changing the inductance of the probe.

Experimentally, the transmitter excitation is caused by applying plane polarized electromagnetic radiation in such a way that a component of the radiation rotates in the same direction as the spin precession, and induces a transition. The quartz oscillators in the V4311 unit supply the lock, analytical and transmitter channels with the appropriate amplified and attenuated RF energy.

The receiver detection signal is an induced emf potential in the coil which undergoes preamplification in the probe. Once out of the probe, the signal is further amplified and passed into a phase sensitive detector. The abs-
orption (v) or dispersion (u) signal, both present in the output, may then be obtained by the judicious adjustment of the phase angle by rotating a capacitive copper plate between the face of the detector, mounted on a calibrated dial, displayed on the V4311 unit front panel. The output of the phase detector depends upon the phase of the input signal relative to that of the reference signal and the slope of the line. It is well documented that the resistance of the tuned circuit is the absorption (real) mode, while the reactance yields the dispersion (imaginary) mode of data, and this is electrically how the signal is separated.
Chapter 3

Computer Interface

Any spectrometer using FT techniques requires a computer to process the data digitally. There are many options open to the NMR spectroscopist considering putting a spectrometer under computer control. 69, 70, 71 In the configuration presented here, there are three obvious functions the computer must perform:

1. Output control signals to run the experiment.
2. Input data from the experiment and output hardcopy.
3. Interface with the operator.

The operating parameters of the computer control network are a function of both the hardware and software involved. The intention here is to discuss the aspects of the computer components which affect the performance of the instrument. The programs are covered in detail in Chapter 4, and that is the most obvious point to discuss the attributes of the entire coordinated system.

HP-1000

The HP-1000 is a Hewlett-Packard minicomputer running under a HP-21MX-E processor with 32K of 16-bit word memory. An HP-7400A disc drive provides 4.9 M bytes of hard copy through one fixed, and one removable disc. Ancillary input-output (I/O) devices include a HP-2645A terminal, Digital
LA-120 terminal (employed as a printer), and a Nicolet Zeta 1553 digital plotter. The I/O between the HP-1000, and the Zeta plotter, or LA-120, is done through an RS-232C interface which is switchable, to allow remote operation from different lines hard wired to various rooms in the Department.

The HP-1000 runs on the HP RTE-2 operating system, and will run Fortran IV and Assembler languages.

AIM-65

The Aim-65 is a single board R-6502 based microprocessor with 4K 8-bit memory. The Aim-65 has an on board dot-matrix thermal printer, a 22 character light emitting diode (LED) display, and a full typewriter style keyboard.

The R6502 central processor unit runs a memory mapped I/O through an 8-bit parallel data bus. Because of the simplicity of the monitor program resident in the Aim, a separate assembly language program was written accessible through a function key on the keyboard. This program, shown in figure 3.5, sets the microprocessor in a polling loop. This loop monitors the keyboard and the designated data lines on the J-3 expansion port, searching for incoming data. In this configuration the Aim acts as a remote terminal, receiving data in both directions. The characters sent by the HP-1000 are input and displayed on the display, while the keyboard data is output on the chip-selected lines.
**Figure 3.5** AIM-65 Assembler Program and Flow Chart

```
START

INITIALIZE
STATUS
REGISTERS

GET I/O
STATUS REGISTER
CONTENTS

ANYTHING
THERE?

GET KEY
STATUS

KEY
DOWN??

GET KEY

OUTPUT TO
DISPLAY

IS
TRANSMIT
REGISTER
FREE??

OUTPUT TO
RS-232 MODEM

0300 78 SEI
0301 8D STA 8000
0304 A9 LDA #38
0306 8D STA 8003
0309 A9 LDA #8B
030B 8D STA 8002
030E AD LDA 8001
0311 29 AND #08
0313 DD BNE 0330
0315 20 JSR ECEF
0318 88 DEY
0319 30 BMI 030E
031B 20 JSR EC82
031E 20 JSR EF05
0321 48 PHA
0322 AD LDA 8001
0325 29 AND #10
0327 F0 BEQ 0322
0329 68 PLA
032A 8D STA 8000
032D 4C JMP 030E
0330 AD LDA 8000
0333 20 JSR E97A
0336 4C JMP 030E
```
INTERFACE

It is now possible to review the original three functions deemed necessary for computer control. The first two, experimental monitor duties, are accomplished by providing a ramp from 0 to 10 volts dc to the Wavetek in the V3530 unit. This allows discrete digital control of the frequency sweep through the experiment with an accuracy imposed by the timer internal to the HP-1000. To a certain degree, the limitations are controlled by the programming efficiency, but the NMR experimental time frame is many orders of magnitude slower than the speed approachable by an optimized assembly language program.

The input signal enters the HP-1000 through the Raytheon 14-bit analog to digital converter (ADC), via a 16-bit duplex register. The output signals exit through two dual 12-bit digital to analog converters (DAC). One DAC line provides the spectrometer sweep and scope x-axis, while the other has the scope y-axis.

The last function, operator interface, is performed through the Aim-65, using the program in Figure 3.5 and the circuitry shown in Figure 3.6. The R6551 is an asynchronous communication interface adapter (ACIA). It is completely programmable, with three internal registers which control the parity, interrupt status, baud rate, and other pertinent handshake parameters which ensure easy interface with a variety of host computers.
Figure 3.6  RS-232 Communication Interface

Pin #

(15) D\text{0}
(14) D\text{1}
(13) D\text{2}
(12) D\text{3}
(11) D\text{4}
(10) D\text{5}
(9) D\text{6}
(8) D\text{7}

(4) SYS \text{T}R\text{Q}
(U) SYS \text{\Phi}2
(V) SYS \text{R/W}

(18) CS\text{B}
(7) RES

(A) A\text{0}
(B) A\text{1}

+5V \text{GND}

2N5339

180Ω

4N25

2N2905

220Ω

RS-232C D-Connector
The three functions of the computer control system have been discussed with respect to the hardware components used to implement the network. The limiting step is the software, and that is discussed next.
CHAPTER 4

SOFTWARE

Control of the entire correlation process has been divided into three separate programs, each of which is compiled and run distinctly from the others. This is necessary because of the restrictive size of the host computer, but follows a natural separation present in the exclusive nature of each job.

Each program shall be explained presenting the operating algorithm and illustrations of the actual results. The duties of each are summarized here to enable an understanding of how the division of labor is accomplished between them.

1. NMRUN--Actually two programs, a Fortran routine for user interface and calculations, and an assembly language routine which actually runs the spectrometer during the experiment. This program in its entirety allows the user to run the experiment and write the data gathered as a disc file.

2. NMRAN--One large routine which performs all data manipulations necessary for coherent treatment of an NMR data file. This program reads a disc-file (presumably the result of NMRUN), allows processing, and writes the post operative file without affecting the original spectra file.
3. NMPLT—This program reads a disc file and plots the data on the digital Zeta plotter. The routine is in Fortran and utilizes Nicolet Zeta subroutines. The original file is preserved with no additional files created.

The usual sequence of operation is in the order that the routines have been presented. Because of the remote access to the spectrometer, only the programs NMRAN and NMPLT are run local to the HP-1900 and Zeta plotter. This is not inconvenient, since these two routines are run exclusively post manipulative to the experiment itself.

The programs themselves are presented in Appendix 1 for consultation.
Chapter 4
Section 1

NMRUN

This program runs the spectrometer, and creates a disc file to hold the data recovered from the experiment. There are really two major parts to this code, the controlling Fortran routine and the slave assembler code. Each will be treated separately, taking the lead from their mode of interaction.

It would be most helpful to consult Figure 4.1 for this discourse. The calculation of the running parameters is done to fit the requirements of the assembly language sweep program. The operator is polled for data, of which three responses must be accurate: the two readings off the frequency counter indicating the Wavetek settings, and the number of scans required. All other entries are taken to be estimates, with the real value resultant from the internal calculations returned at the end of the set-up loop. The operator then has the alternative of changing any variable. Because of the hardware configuration, only the acquisition time and the number of sweeps can be altered without repeating the entire set-up routine.

Once the sweep routine has been selected, the keyboard is locked out until the experiment is completed. The assembler routine returns to the calling routine where the acquisition parameters may be immediately changed if the operator was dissatisfied with the original result.
Figure 4.1

START

PRESENT MENU

WRITE??

RUN??

STOP??

Y

N

Y

A

N

FILE NAME??

WRITE FILE
LENGTH N

END.
DISPLAY TO DAC
INCREMENT ADDRESS
SCAN COMPLETE??
Y
N
PUT DAC TO 0
WAIT ON INTERR.
Y
N
WAIT.
OUTPUT SCAN# TO TERMINAL??
Y
N
OVERFLOW LIKELY NEXT SCAN??
Y
N
OUTPUT ASCII CODE TO TERM.
DIVIDE ARRAY
The assembly language code has three Fortran calls from NMRUN which access different subroutines. The three subroutines are responsible for calibration of the V-3530 Wavetek (RMIN,RMAX), and running the experiment on the HA-100 (SWEEP).

The experiment is run by providing a sweep ramp from 0 to 10 volts in 4096 steps, with data collection at each step. The ramp is calibrated by separate calls to RMIN(0V) and RMAX(10V) which are summoned by NMRUN to coincide with the Wavetek adjustment performed by the operator.

The SWEEP code call passes the pertinent values to the assembly routine to run the system clock and count the number of scans. All the calculations are performed in the NMRUN calling routine, the values are simply loaded into the variables with the call, no error checking is done after the call, inside the assembler routine.
Chapter 4
Section 2

NMRAN

The algorithm is discussed by section, since each processing function operates independently of the others and may be accessed in any sequence. The one assumption which the programmer is responsible for, is that the operator understands what order the different functions should be applied to yield a coherent result. An error checking monitor at this level would be quite complicated unless every step of the processing was put under program control. This would be relatively simple but would restrict the freedom of the operator to experiment with new procedures. There are also hardware memory limitations to be considered.

The actual use of NMRAN is demonstrated in Figure 4.3, which is an illustration of the steps taken typically through the processing of a raw spectrum file to yield the final correlated, phased, slow passage spectrum. No digital massaging was done, so that the final slow passage spectrum of orthodichlorobenzene would be comparable to the fast passage result. Only the sweep rate differs between spectra E and F in Figure 4.3. Obviously, the resolution in the correlated result is not equivalent to that of the slow passage spectrum, but this is simply a question of excessive sweep rate causing line broadening and this case is examined with an example in the experimental Chapter 5.
Sweep Rate = 147.0 Hz/sec
Digital Resolution = 7.56 pts/Hz
True Acquisition Time is 1.84 sec
Spectrum sweeps from 6.53 to 5.81 ppm

Sweep Rate = 2.26 Hz/sec
Digital Resolution = 7.56 pts/Hz
True Acquisition Time is 1.19.81 sec
Spectrum sweeps from 8.73 to 5.81 ppm
The purpose here is to illustrate the state of the array values at various steps through the processing procedure. The following histogram steps through the exercise typical in correlating a raw spectrum file, the appropriate diagram is indicated. For each step alphabetically.

1. read a disc file into the array.
2. scale the array---------------------------→ A
3. perform a forward real transform
4. scale the array---------------------------→ B
5. perform correlation multiplication------→ C
6. perform an inverse complex transform
7. scale the array---------------------------→ D
8. perform phase adjustment
9. pack-plot the result----------------------→ E
10. comparable slow passage plot-------------→ F

The flow chart is shown in Figure 4.4. The convention is to always present the operator with a menu of alternatives such that the options are plainly before him or her at all times. An unavailable or unintelligible response always returns the menu.
Figure 4.4

START

PRESENT MENU.

READ?? N WRITE?? N SHAPE?? N STOP?? N

Y Y Y Y

FILE NAME?? FILE NAME??

READ FILE LENGTH N WRITE FILE LENGTH N

A

END.
CORRELATION

The correlation calculation expects the array to be in first half real - second half imaginary order. The term which represents the theoretical line is not applied directly, but is reduced to a form simpler to implement in the calculation.

From Chapter 2, section 5, it is remembered that

\[ g(t) = \exp \left( -i b T^2 \right) \]

where \( b = \text{sweep rate} \frac{\text{rad}}{\text{sec}^2} \)

and \( T = \text{running time variable} \).

from Ozawa and Arata\(^{37}\) we know that

\[ (4.1) \quad \Delta t = \frac{1}{N \Delta f} = \frac{2 \pi}{N b \Delta t} \]

where \( \Delta t = \text{the change in time} \).

\( N = \text{number of points} \).

\( \Delta f = \text{change in frequency} \).

\( b = \text{sweep rate} \).

\( \Delta t = \text{time increment} \).

by definition in my program

\[ b = \frac{2 \pi \text{ SW}}{\text{AQ}} \]

where \( \text{SW} = \text{sweep width} \).

\( \text{AQ} = \text{acquisition time} \).

and \( \Delta t = \text{TCON} = \frac{\text{AQ}}{N} \)

substituting these into equation 4.1 we get

\[ (4.2) \quad \Delta t = \frac{2 \pi}{N \cdot 2 \pi \cdot \text{SW} \cdot \text{AQ}} \]

\[ \frac{\text{AQ}}{N} \]
From Ozawa and Arata\(^{37}\) we also know that \(\exp \left( \frac{b (k \omega t)^2}{2} \right)\)

is equivalent to \(\exp \frac{b \cdot T^2}{2}\)

We can now substitute for \(b\) and \(\omega t\) into equation 4.3 and get

\[
\frac{2 \cdot \pi \cdot SW}{AQ} \left( \frac{k}{N \cdot 2 \cdot \pi \cdot SW \cdot AQ} \right)^2
\]

\[
\frac{\pi k^2}{2 SW^2 AQ}
\]

which reduces to \(\frac{\pi k^2}{SW^2 AQ}\)

where \(k\) = index of array

SW = sweep width

AQ = acquisition time

It is also much simpler to use Euler's theorem to calculate the value of the exponential term. Thus the operational definition of correlation is realized as:

\[
\exp \left( -i \frac{\pi k^2}{SW^2 AQ} \right) = \cos \left( \frac{\pi k^2}{SW^2 AQ} \right) + i \sin \left( \frac{\pi k^2}{SW^2 AQ} \right)
\]

and is implemented as

\[
R_n = R_n \cos (\ ) - I_n \sin (\ )
\]

\[
I_n = R_n \sin (\ ) + I_n \cos (\ )
\]

where \(R_n\) represents the real values of the array, and \(I_n\) represents the imaginary values of the array.

This allows the new correlated values to be computed in place without increasing the memory space required. This also allows the total FFT/correlation operation to be completed in \(N + 3N \log_2(N)\) multiplications.\(^{52}\)
FAST FOURIER TRANSFORM (FFT)

The actual implementation of the Fourier transform is accomplished with a program published by Cooper. This routine is the result of much optimization and is general in its application. There are many alternatives when searching for an FT algorithm to fit an application, all based on the original work by Cooley-Tukey, varying from general improvements to specialized algorithms enhanced specifically for accuracy rather than speed. This program has seen use in an NMR environment and hence required few changes to fit turnkey-like into our system.

The program itself is written in Fortran and setup as a subroutine of NMRAN, responding to the menu solicitation for FT. There are three major subroutines internal to the FT code which process the array in three distinct steps and whose order of use determines the type of FT performed by the call. The internal subroutines act separately from each other and do no error checking to supervise the order of deployment, but this is a decision made by the programmer and not the operator. In this case there are only two possible FT calls available to the operator, a real forward FT, and a complex inverse FT, even though the code has the capability to perform all possible variations of calls.
The three subroutines, FFT, POST, and SHUFFL, will be discussed in general, but the bulk of this section must concentrate on the combined effect of all three as they operate on the array. The subroutine is available in the appendix for reference, for further detail the original source is recommended.\textsuperscript{44}

**FFT Subroutine**

This piece of code actually performs the transformation, the other two being ancillary operations concerned basically with indexing (SHUFFL) and the special treatment of real numbers (POST). The signal flow graph shown in Figure 4.5 illustrates the steps required for an array of N = 8. The array is first put into bit-inverted order such that the final sequence is uniform from 0 to 7. This bit-inversion is an artifact of the calculation regimen and is simply an index rearrangement.

In general there will be \( k \) passes required for an array of size \( N = 2^k \). Each pass constitutes a recombination of points and is indicated on the signal flow graph by each vertical column of dots. During each pass the new value is the result of the following arithmetic:

\[
x'_{1} = x_{1} + x_{2} \frac{W}{N} \quad \text{where} \quad W = \exp \left( \frac{-2\pi i}{N} \right)
\]
Figure 4.5
The calculation symmetry can also be used to advantage where

\[ x'_2 = x_1 + x_2 \omega \]

which allows the operation to be done a pair of points at a
time, and therefore calculated in place, as opposed to dupli-
cating the array space in memory.

As was done in the correlation method, the exponential
term is implemented using Euler's rule. This also allows an
elegant way of controlling the direction of the transform,
forward or inverse, by changing the state of the variable
INV, which simply changes the sign of the trigonometric
addition, shown in Figure 4.6.

**FIGURE 4.6**

\[
e^{iy} = \cos(y) + i \sin(y) \quad \text{for } INV = 1
\]
\[
e^{iy} = \cos(y) - i \sin(y) \quad \text{for } INV = -1
\]

\[ W^y = \cos\left(\frac{-2\pi y}{N}\right) + i \sin\left(\frac{-2\pi y}{N}\right) \quad \text{for } INV = 1\]

where \( y \) is the superscript of \( W \) as shown in Figure 4.5.

**SHUFFLE Subroutine**

This subroutine does exactly what the title suggests,
it SHUFFLES the array into two different orders depending
upon the state of the variable INV. This is illustrated
graphically in Figure 4.7, showing the two possible array
configurations after SHUFFLE processing in A and B for the
Figure 4.7  Action of "Shuffl"

\[ R_1 R_2 R_3 R_4 I_1 I_2 I_3 I_4 \]

INV = -1

\[ R_1 I_1 R_2 I_2 R_3 I_3 R_4 I_4 \]  

INV = 1

\[ R_1 R_2 R_3 R_4 I_1 I_2 I_3 I_4 \]
variable INV = 1 and -1, respectively. The significance of this has important implications since the FFT routine expects the data to be in a "first half real, second half imaginary" sequence and generates a complex result accordingly.

**POST Subroutine**

This routine is employed in a POST-processing function in order to complete the last step of a forward real transform. Again, depending on the sign of INV, it may be used as a pre-processing routine in an inverse real transform, but this format is superfluous to our needs.

The process is a one pass recombinatorial operation which corrects for the fact that the FFT routine acts entirely as if the array were complex. Thus the real points are calculated by trigonometrically recombining the complex points according to the relationship:

\[ X_r(n) = R_p + \cos\left(\frac{2\pi n}{N}\right) I_p - \sin\left(\frac{2\pi n}{N}\right) R_m \]
\[ X_i(n) = I_m + \sin\left(\frac{2\pi n}{N}\right) I_p - \cos\left(\frac{2\pi n}{N}\right) R_m \]

(4.6)

where \( n = 0,1,2,...,N-1 \) and \( m = N/2 \)

\[ R_p = R_n + R_{m-n} \]
\[ I_p = I_n + I_{m-n} \]
\[ R_m = R_n - R_{m-n} \]
\[ I_m = I_n - I_{m-n} \]
It is now possible to present the FT routine in its entirety. In the final state we have need to perform a forward real FT and an inverse complex FT. The calling sequence for these permutations is

\[ \text{call SHUFFLE} \quad R_1 I_1 R_2 I_2 R_3 I_3 R_4 I_4 \]
\[ \text{call FFT (INV = 1)} \quad \text{forward real} \]
\[ \text{call POST} \quad R_1 R_2 R_3 R_4 I_1 I_2 I_3 I_4 \]
\[ R_1 R_2 R_3 R_4 I_1 I_2 I_3 I_4 \]
\[ \text{call FFT (INV = -1)} \quad \text{inverse complex} \]
\[ R_1 R_2 R_3 R_4 I_1 I_2 I_3 I_4 \]

**PHASE code**

The final output from the inverse complex transform leaves the array in the "first half real, second half imaginary" order. The phase correction subroutine expects this, and performs a first order phase correction accordingly. The operator is only required to make a visual appraisal of the phase angle (in degrees) adjustment that it is estimated will result in a perfectly phased spectrum upon application. The equation used to calculate the adjustment is of the form:

\[ R_n = \cos(\text{arg}) \cdot R_n + \sin(\text{arg}) \cdot I_n \]
\[ (4.7) \]

\[ I_n = -\sin(\text{arg}) \cdot R_n + \cos(\text{arg}) \cdot I_n \]
where \( \text{arg} = \frac{\text{phz} \times \pi}{180} \)

\( \text{phz} \) = operator entered estimate in degrees.

\( R_n \) = the real points of the array.

\( n = 1, 2, \ldots N/2 \)

\( I_n \) = the imaginary points of array.

**EXponential Multiplication**

As stated earlier in the theory section, the function which described the array in the Fourier (time) domain is an exponentially decaying free induction decay (fid), and is equivalent to that which would be gathered in a pulse experiment. Consequently, the array may undergo the same manipulative techniques employed in pulse FT methods, experiencing the same trade off between resolution and sensitivity as shown in that venue. The operational difficulties of exponential multiplication can be stated simply:

1. emphasize the start of the fid \( \rightarrow \) optimum S/N

\( \rightarrow \) sacrifice resolution

2. emphasize the tail of the fid \( \rightarrow \) optimum resolution

\( \rightarrow \) expense of S/N

This translates into line width estimates, which are the required input by the operator. The equation used to model the exponential function is shown in equation 4.8, the calculation itself is done in place. A running total of all line broadening applied against a fid is kept as a book-keeping aid.
\[ R_n = R_n \times \exp \left( \frac{(n-1) \times \text{ELB}}{2 \times \text{SW}} \right) \]

(4.8)

\[ I_n = I_n \times \exp \left( \frac{(n-1) \times \text{ELB}}{2 \times \text{SW}} \right) \]

where \( n \) = index of array

\( \text{ELB} \) = operator entered line width


**SCALE code**

This routine allows scaling of the data array to a maximum value entered by the operator. This guards against overflow problems, but is used mainly before a disc file write command is exercised. This ensures that the value of the array falls within the maximum range possible to be encoded for any one value on a disc file (32767).

The operation is a simple search for the largest absolute value in the array, followed by dividing it into the scaling value entered by the operator. This is then multiplied into each array point to yield the scaled array.


**LOOKC code**

This is essentially a debugging routine which allows the operator to view the array as it is printed out on the terminal. Each value is displayed with the corresponding point number.
ZEPAK code

ZEPAK is a manipulative routine which allows any portion of the array to be zeroed to facilitate the operation of zero filling. The packing option fits a spectrum file into one half the original array size. This was originally done to enable the implementation of a processing algorithm published by Ozawa. However there was a loss of resolution by 1/2 because of the missing points, and this was no longer pursued.

ONES code

Another piece of debugging code which simply sets the entire array to the value 1. This is useful when investigating the nature of any of the multiplying functions and searching for artifacts against a reproduction of the function itself.

FIDL code

This routine lets the operator change the size of the array to facilitate debugging and to allow processing of spectra files of an unusual length.

This concludes the description of NMRAN. As previously stated, the programs are presented in the appendix for consultation if desired.
Chapter 4
Section 3

NMPLT PROGRAM

This program is straightforward, the only complexity being hidden in the cryptic format of the Zeta plotter software commands, and to this end the source is referenced. The PAKPLOT option allows the real data to be plotted without the symmetrical imaginary points. The flow chart is shown in Figure 4.8.
Chapter 5

EXPERIMENTAL

The purpose of this Chapter is to present actual spectra obtained from the instrument configured as detailed in the preceding Chapters, which illustrate operation under a variety of conditions. All Figures shown were taken directly from their Zeta-plots after being scaled to 1000.00, and all plotting dimensions are equivalent within any Figure to ensure an accurate comparison. A summary follows.

The effect of sweep rate on the signal-to-noise ratio and saturation parameter was previously mentioned in Chapter 2. This artifact will be investigated using the O.D.C.B. sample employed in Chapter 4 to illustrate the operational flow chart presented there.

Example spectra of some simple organic molecules commonly used for spectrometer calibration will be discussed to demonstrate the system operation when locked on T.M.S.

Aqueous samples will then be explored with the spectrometer locked on both D.S.S. and water. This section clearly demonstrates the advantages of this configuration when investigating systems with strong solvent lines.

Finally, a study of a sparingly soluble thiazolium salt will be presented which exemplifies the type of problem where the unique capabilities of a Correlation Spectrometer find particularly useful applications.
In each case where the fast and slow passage spectra are presented on the same page, the following precautions were taken to allow rigorous comparison:

1. The same sample was used in each case.
2. Instrumental settings were equivalent.
3. Digital processing was equal except where phase correction was not required.
4. For each Figure, the fast passage spectrum was run immediately following the slow passage experiment, with no homogeneity adjustments in between. Hence if the field was to degrade over the course of the run the fast passage spectrum would represent the "worst-case" result and consequently the broadest lines.

THE EFFECT OF SWEEP RATE ABERRATIONS

The following short discourse should illustrate the principles originally discussed in Chapter 2 concerning the optimization of the S/N ratio and sensitivity, and the relationship between these parameters and the sweep rate. The O.D.C.B. spectrum has already been presented in Chapter 4. It was noted there that the resolution was not exactly equivalent to that of the slow passage spectrum, although the S/N ratio was slightly better.

The following series of Figures, 5.1 through 5.4 have equivalent scan parameters with the exception of the sweep rate, which decreases as the Figures proceed. If Figure 5.3 is compared with the slow passage spectrum in Figure 5.5 a
Figure 5.1

Uncorrelated

Correlated

Sweep rate = 70.9 Hz/sfc
Digital resolution = 8.46 FTS/Hz
True acquisition time is 2.66 sfc.
Spectral sweeps from 8.44 to 6.02 FPL.
Figure 5.2

Sweep Rate: 49.24 Hz/sec
Digital Resolution: 8.46 pts/Hz
True Acquisition Time is 4.9 sec
Spectra sweeps from 8.44 to 6.00 ppm
Figure 5.3

uncorrelated

correlated

SWEEP RATE = 9.89 Hz/sec
DIGITAL RESOLUTION = 9.46 PPM/Hz
TRUE ACQUISITION TIME IS 24.99 sec
SPECTRUM SWEEPS FROM 5.44 TO 6.02 PPM
Figure 5.4

uncorrelated

correlated

11 SWEEP RATE: 4.84 Hz/SEC
DIGITAL RESOLUTION = 8.45 PS/Hz
TRUE ACQUISITION TIME IN 49.97 SEC
SPECTRUM SWEEPS FROM 8.44 TO 6.02 PPM
Figure 5.5
Sweep Rate: 147.03 Hz/sec
Digital Resolution = 7.56 pts/Hz
True Acquisition Time is 1.64 sec
Spectra sweeps from 5.73 to 5.81 Hz

Sweep Rate: 21.56 Hz/sec
Digital Resolution = 7.56 pts/Hz
True Acquisition Time is 119.81 sec
Spectra sweeps from 8.53 to 5.61 Hz
much better correlation is perceived, with assignments becoming distinct.

The measurements were done in reverse order of presentation, Figure 5.4 being the first. Assuming a constant homogeneity contribution, there is an obvious trend with regards to resolution enhancement which nicely illustrates the line broadening effect of excessive sweep rates. This supports the conclusion that the lowest convenient sweep rate should be chosen within the limit of equation 3 of Chapter 2, to yield the greatest sensitivity for the system under investigation.

ORGANIC MOLECULES

The following sample compounds have typically been used in organic N.M.R. spectroscopy as calibration standards to establish resolution and sensitivity performance expectations. In all cases the spectrometer is locked on T.M.S. at 2500 Hz, with the actual print-out stating the scan parameters displayed in each Figure. The abscissa is calibrated by the program and output with the other spectral values.

The intention of this section is to illustrate the normal operation of the instrument using organic solvents. The results are comparable to CW spectra, and demonstrate the time saving inherent in the rapid passage experiment.
ETHYL BENZENE

The first system under scrutiny is that of a 5% ethyl benzene, 10% T.M.S., in CDCl₃. Figure 5.6 presents the spectrum of what might be an initial scan of the expected area of interest. The assignments are trivial, but if greater digital resolution is desired it is a simple task to adjust the spectral scan width to increase the number of points defining a unit Hz. This is shown in Figure 5.7, the definition of the absorbance is significantly enhanced. The wiggle in the baseline observed as the sweep approaches 0 ppm is caused by high lock modulation beating against the analytical channel as the spectrometer approaches T.M.S.

CROTONALDEHYDE (trans)

Figures 5.8 and 5.9 illustrate the absorbance spectra of trans-crotonaldehyde shown in the same format as ethyl benzene. In Figure 5.8 the methyl group signal has been truncated, presumably by the A.D.C. Interestingly, this demonstrates the fact that the information coherent to the fine structure, normally absent in the RP spectrum, must be contained in the oscillation following the main peak. Otherwise restoration by correlation multiplication would be impossible. In this case the only feature affected by the truncation is possibly the peak height. Figure 5.9 has a shorter spectral width allowing better definition of the down-field peaks.
Figure 5.6

CH₂CH₃

FAST PASSAGE

CORRELATED

SWEEP RATE: 150.62 Hz/sec
DIGITAL RESOLUTION: 2.68 Hz FID
TRUE ACQUISITION TIME: 4.5 sec
SPECTR. SWEEPS FROM 8.11 TO 5.11 FID
Figure 5.7

\[ \text{CH}_2\text{CH}_3 \]

FAST PASSAGE

CORRELATED

Sweep Rate: 20.37 Hz/sec
Digital Resolution: 5.45 Hz/sec
True Acquisition Time: 1.84 sec
Spectra: Sweeps from 3.83 to 10.67
Figure 5.8

CH₃

H

H

C=O

FAST PASSAGE

CORRELATED

11
SWEPT RATE - 176.29 HZ/SEC
DIGITAL RESOLUTION = 1.96 KHZ
TRUE ACQUISITION TIME 18.54 SEC
SPECTRAL SWEEPS FROM 10.11 TO -30.12
Figure 5.9

CH₃
H
H
C=O
H

FAST PASSAGE

CORRELATED

11
Sweep Rate = 209.1 Hz/sec
Digital Resolution = 3.9Hz/pt
True Acquisition Time is 2.4A sec
Spectrum sweeps from 10.10 to 4.9 ppm
ETHYL TOLUENE (meta)

A sample of 10% ethyl toluene, 10% T.M.S., in CDCl₃ is examined in Figures 5.10 and 5.11. The spectrum has enough resolution to enable easy assignment of the aliphatic region, and the splitting of the aromatic protons is evident.

ORTHODICHLOROBENZENE

The spectrum of O.D.C.B. should now be familiar. Figure 5.12 exhibits the original scan of the entire field to contrast the increased digital resolution available in Figure 5.13. As previously discussed in this Chapter, better sensitivity could be obtained by lowering the sweep rate.

CHLOROFORM

Finally, the trivial spectrum of chloroform is shown in Figure 5.14, the spinning side bands clearly present. The two spikes just poking out of the baseline are caused by trace ethanol added as a stabilizer at 0.7%. They are not resolved by the correlation multiplication because the ringing is hidden in the noise of the baseline.

I have been particularly brief here because the sample compounds under scrutiny are all well studied and warrant little interest other than that inherent in their presentation, as evidence of the spectrometer operation.
Figure 5.10

Sweep Rate: 163.98 Hz/sec
Digital Resolution = 2.54 HTS/Hz
True Acquisition Time is 4.90 sec
Spectra sweeps from 8.00 to 8.07 ppm

FAST PASSAGE

CORRELATED
Figure 5.11

CH₃CH₃

\[ \text{CH₃} \]

FAST PASSAGE

CORRELATED

Sweep Rate: 217.01 Hz/sec
Digital Resolution: 5.12 Hz
True Acquisition Time is 1.84 sec
Spectral Sweeps from 4.05 to 0.05 ppm
Figure 5.12

Sweep Rate = 103.98 Hz/sec
Digital Resolution = 0.04 Parts/hz
True Acquisition Time is 4.92 sec
Spectrum sweeps from 8.09 to .03 ppm
Figure 5.13
SWEEP RATE = 147.03 HZ/SEC
DIGITAL RESOLUTION = 7.56 PTS/Hz
TRUE ACQUISITION TIME IS .184 SEC
SPECTR. Sweeps from 6.73 to 5.58 Hz

FAST PASSAGE

CORRELATION

SLOW PASSAGE

SWEEP RATE = 2.26 HZ/RED
DIGITAL RESOLUTION = 7.56 PTS/Hz
TRUE ACQUISITION TIME IS 119.81 SEC
SPECTR. Sweeps from -8.73 to -5.61 Hz
Figure 5.14

CHCl₃

FAST PASSAGE

CORRELATED

Sweep Rate = 102.54 Hz/sec
Digital Resolution = 2.03 Pts/Hz
True Acquisition Time is 9.83 sec
Spectr. Sweeps from 10.04 to -0.04 ppm
AQUEOUS ENVIRONMENTS

Water has always presented a problem in the realm of proton N.M.R. spectroscopy. Where it is present as the principal solvent, it has a number of undesirable characteristics which cause problems:

1. High abundance of H$_2$O protons.
2. Wide line width relative to most absorbances.
3. Chemical shift is pH dependent.

The first point nominates water as a useful spectral feature to lock the spectrometer onto. Unfortunately points two and three oppose this since a wide line width allows the lock mechanism to drift somewhat, affecting field stability. The dependence of the chemical shift on pH means that the lock placement cannot be precalibrated in the program unless the pH of the sample was to be standardized. This is too stringent a restriction to place on sample preparation to be useful, hence D.S.S. must always be present in the sample tube for calibration purposes, if shift assignment is necessary.

In the following spectra, no digital massaging was done other than phase correction where required. All samples were run with a 20 Hz hardware filter in place. Since the exact position of the water resonance cannot be predicted a priori, the chemical shift scales are calculated after the experiment using D.S.S. as a reference, where the spectrometer was locked on the water signal.
ETHANOL IN WATER

The first example presented is a spectrum of 5% ethanol in water with 5% D.S.S. added to calibrate the abscissa. Figure 5.15 is organized such that the RP response along with scan parameters is shown on top, followed by the correlated result. The slow passage spectrum is given at the bottom for comparison. Again, instrumental settings were equal, the rapid passage experiment run immediately after the slow passage run.

In both final spectra the well known triplet/quartet features are easily identifiable. Contrasting the results, the S/N ratio is significantly better in the correlated spectrum, but the line width is perhaps narrower in the SP example. In the rapid passage result the quartet is much clearer than in the equivalent slow passage response.

The time required for each scan is also notable since the rapid passage spectrum was gathered in only 42.79 sec, while the slow passage experiment took 2hrs 13min. This is a significant saving realized and is what makes the technique superior to pulse methods when the dynamic range problem avoided is taken into account.

PROLINE AND IMIDAZOLE

The object of the next series of spectra is to demonstrate the usefulness of a correlation spectrometer in biochemical applications. One molar solutions of proline and imidazole were studied in D₂O and H₂O with 10% D.S.S.
Figure 5.15

SWITCH RATE: 126.44 Hz/sec
DIGITAL RESOLUTION: 6.17 Hz/sec
TRUE ACQUISITION TIME: 3.00 sec
SPECTRAL SWITCH FROM: 4.14 to -0.75 Hz

CH$_2$CH$_2$OH

FAST PASSAGE

CORRELATED

SLOW PASSAGE

SWITCH RATE: 1.23 Hz/sec
DIGITAL RESOLUTION: 4.17 Hz/sec
TRUE ACQUISITION TIME: 369.57 sec
SPECTRAL SWITCH FROM: 4.14 to -0.75 Hz
Figure 5.16

- Resolution: 3.51 kHz
- Fast passage
- Slow passage
- Correlated
- HOD

**Chemical Shifts**
- H: 5.77 to 7.97 ppm
- COOH: 0.12 to 0.53 ppm

**Spectrum Details**
- Acquisition time: 1.90 kHz
- Digital resolution: 7.13 kHz
- Spectrum sweep from 0.77 to 8.17 kHz
Figure 5.17

H
\[ \text{H} \]

\[ \text{N} \]

\[ \text{COOH} \]

in \( \text{H}_2\text{O} \)

FAST PASSAGE

CORRELATED

- Sweep rate: 40.64 Hz/65
- Digital resolution: 1.20 ppm Hz
- True acquisition time: 1.00 min
- Spectral width from 4.67 to 16.71 ppm
Figure 5.18

Sample Rate = 10.29 Hz/sec
Digital Resolution = 3.58 pts/Hz
Total Acquisition Time is 7.33 sec

Spectra sweeps from 8.04 to 0.0 Hz

Fast Passage

HOD

Correlated

Slow Passage
present for calibration. In D₂O the spectrometer can easily be locked on the D.S.S. signal, the residual water is small enough not to knock the lock box off the D.S.S. at 10%.

In Figure 5.16, the slow and rapid passage spectra of proline in D₂O are compared. The presence of the D.S.S. complicates the example a little by overlapping with the proline lines, the proton sitting on the nitrogen has exchanged with D₂O and is not seen. The slow passage result exhibits better resolution but the S/N ratio is not equal to that of the correlated spectrum.

The fast passage spectrum run in water, presented in Figure 5.17, has better resolution. This is probably a consequence of the slower sweep rate and resulting optimization of the saturation parameter. The time difference between the two sweep rates indicates a substantial saving, with the rapid passage taking only 25 sec while the equivalent slow passage experiment required 7 minutes.

The spectrum of imidazole was run in D₂O with the resolution easily comparable between the slow and rapid passage results. Spinning side bands are observed in both spectra, the slow passage result exhibits a slight ringing even at 4 Hz/sec. The time difference for the two is similar to the proline result.
STUDY OF A THIAZOLE

The labile exchange of the C-2 proton in the thiazolium ion has been shown to be requisite to the catalytic ability of thiamin.\textsuperscript{55} The soluble thiazole (III) has been isolated as the result of cleavage of thiamin (I) in the presence of $\text{SO}_3^-\text{H}$.\textsuperscript{56} (Figure 5.22)

Figure 5.22

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.22.png}
\end{figure}

The mechanism of this reaction has received attention kinetically\textsuperscript{57} and corroborative evidence has been furnished by N.M.R.\textsuperscript{58} The study of the mechanism of the base catalyzed opening of the thiazole ring in thiamin has previously been studied using stopped-flow N.M.R. at 60 MHz on a C.W. instrument.\textsuperscript{59}
Figure 5.19

**TIME RESOLUTION** 1000 HZ

**DIGITAL RESOLUTION** 25.6 KHZ

**TIME ACQUISITION TIME** 4.0 sec

**SPECTRA SWEPT FROM** 4.9 to 2.9

**CH_{3}c**

**CH_{3}b**

**HOCH_{2}CH_{2}**

**S**

**H_{e}**

FAST PASSAGE

HOD

b
c
d

CORRELATED

SLOW PASSAGE

5 4 3 2 1 0

**TIME RESOLUTION** 25.6 KHZ

**DIGITAL RESOLUTION** 25.6 KHZ

**TIME ACQUISITION TIME** 4.0 sec

**SPECTRA SWEPT FROM** 4.9 to 2.9
Figure 5.20

CH₃
\[\text{HOCH}_2\text{CH}_2\]

FAST PASSAGE

CORRELATED

A

B

Sweep Rate: 125.72 Hz/sec
Digital Resolution: 8.49 kHz/sec
True Acquisition Time: 1.5 s
Spectral Sweeps from: 11001 to 11010

Sweep Rate: 125.72 Hz/sec
Digital Resolution: 8.49 kHz/sec
True Acquisition Time: 4.99 sec
Spectral Sweeps from: 4181 to 4191
Work progressing in this department was involved in the investigation of the kinetic properties of the isolable thiazolium ring (III). This study deals with the application of correlation N.M.R. as a corroborative tool to supply evidence supporting a previous mechanistic hypothesis.⁶⁰

Figure 5.19 illustrates comparable fast and slow passage spectra run in D₂O of the iodide salt of the ring(III). Nothing is observed to low field of HOD, the proton Hₐ is assumed exchanged with the solvent D₂O.

Figure 5.20 is a spectrum of the same salt (IV), this time run in water. The Hₐ proton is clearly visible at 9.8 ppm unexchanged. The contribution from the non-bonding electrons on the nitrogen atom has shifted the peak significantly downfield, as expected.⁶¹

Figure 5.21 gives positive evidence that the base catalyzed ring opening does, in fact, end in the structure shown(V). The formyl proton, Hₐ', is found where we would expect an equivalent system⁶², at 8.1 ppm.

Figure 5.23
The Experimental section has demonstrated that the instrument does in fact function in a variety of operating conditions and has furnished useful results that would not have been possible by pulse methods because of the severe dynamic range problems caused by the solvent, water.
Chapter 6

FUTURE APPLICATIONS AND CONCLUSIONS

It has taken the duration of this thesis to bring this project to the point where it is a viable research grade spectrometer in the chosen configuration. The more interesting potential of system development and evolution has just become realizable. The areas of development lie in two obvious sectors:

1. General enhancement of instrument capabilities on existing features.

2. Extension of facility to new experiments.

Under the first heading there are a number of published advanced software programs which would benefit the system. Cooper has published a peak-picking routine, and there has been continuous development in the literature of digital methods for handling dynamic range problems, correlation development, and truncation artifacts. The entire range of traditional pulse data massageing techniques such as Gaussian multiplication and trigonometric multiplication are available. Further, a wing processing method enabling extraction of data out of the shoulder of the water signal has been published specifically for a correlation system. The software at hand currently has no baseline correction routine, this should warrant attention.
Unfortunately, before any further software development should progress to any extent, serious thought should be given to increasing the HP-4000 memory capabilities. The existing software runs as three separate programs by necessity because of memory protect errors issued when attempting to load too large a program. One alternative is the rather complicated procedure of writing overlays which allow an extremely efficient use of memory and disc.

With regards to new experiments, it should be plain that the forte of this spectrometer configuration is in the study of aqueous systems. To this end, it compliments the pulse spectrometer already resident in the Department in providing a more extensive range of capabilities to the users.

Specifically, the study of chemical exchange by rapid scan FT NMR has already been dealt with theoretically in the literature.\textsuperscript{77} Flow,\textsuperscript{78} and stopped-flow NMR\textsuperscript{79} have been well demonstrated as perfectly viable as corroborative evidence and in kinetic studies as well. As of yet, the advantages of Rapid Scan Correlation FT NMR have not been brought to bear on kinetic problems in aqueous systems, a perfectly viable and possibly superior method of investigation. Less obvious is the development of already existing variable temperature capabilities to run non-isothermal kinetics.\textsuperscript{80} Spin lattice relaxation measurements have also been demonstrated, with potential advantages over pulse techniques.\textsuperscript{81}
CONCLUSION

In conclusion the following statements can safely be made with respect to the objectives of this thesis:

1. The configuration detailed in this text does function successfully as a Rapid-Scan Correlation FT NMR spectrometer.

2. The instrument operation has been demonstrated in a variety of experimental conditions and returned respectable results.

3. The system has proven useful in elucidating the solution to a problem unobtainable or difficult to obtain by pulse techniques.

4. The spectrometer has very promising prospects with regards to further developments and provides an important compliment to the NMR facilities of the department.

5. What has for most universities become scrap metal has been transformed here into a viable research spectrometer.
REFERENCES


26. IBID, pg.18


42. IBID pg.668
    Cambridge Univ. Press, 1974
44. Cooper, J.W., Intro. to Pascal for Scientists pg.211
    J.Wiley 1981
47. Singleton, R.C., IEEE Trans. Audio. and Elec.,
49. Cooper, J.W., Spect. Tech. for Organic Chemists
    J.Wiley, NY, 1981
    Prentice Hall, N.J., 1978
51. Nicolet Zeta Corp., Fundamental Plotting Subroutines
52. Cooper, J.W., The Minicomputer in the Lab. pg.278
    Wiley Interscience, 1978
54. Rowader, S.B.W., Fukushima, E., Exptl. Pulse NMR, A Nuts
    and Bolts Approach, pg.88, Addison-Welsly, 1981
58. Jordan, F., IBID, pg.17
61. Jackman, L.M., Sternhall, S., Appl. of NMR in Organic
62. IBID pg.191
64. Varian Instruments Canada, HA-100 Operating Manual.


PROGRAM NMRUN

SOURCE FILE IS GRUN:11
BINARY FILE IS RRUN
PROGRAM COMES UP ON RU,NMRUN.
PROGRAM LOADS ON TR,TRUN
BINARY FILE IS RRUN
THIS PROGRAM Responds AT TERMINAL #7 (REMOTE)

THIS IS THE MAIN PROGRAM FOR CONTROL OF THE HA-100
IN THIS CONFIGURATION THE INSTRUMENT IS RUN AS A
RAPID PASSAGE ADIABATIC CONTINUOUS WAVE SPECTROMETER.
THE WAVETEK IS DRIVEN BY THE SWEEP SUBROUTINE

INITIALIZE THE VARIABLES

COMMON XDATA(2048), NN
COMMON SW, AQ, SWFRT
EQUIVALENCE (XDATA(1),IDATA(1))
INTEGER IDATA(4096)
ISTR=0
KLOK=0
IRATE=1
NSCAN=10
NN=2048
DO 4 I=1,4096
4 CONTINUE
WDOH=10.00
WDOL=2.00

THE ARRAY HAS BEEN ZERODED!!!

DECIDE WHICH OF THREE MAIN FUNCTIONS TO PERFORM

1
100 WRITE(7,100)
100 FORMAT("READ,WRITE,RUN, OR STOP??")
READ(7,101)IRES

101 FORMAT(A2)
IF (IRES.EQ.2HRU) GO TO 108
IF (IRES.EQ.2HWR) GO TO 550
IF (IRES.EQ.2HRE) GO TO 500
IF (IRES.EQ.2HST) STOP
GO TO 1

FIRST FUNCTION IS RUNNING THE EXPERIMENT

108 WRITE(7,109)
109 FORMAT("ZERO, SET-UP, SWEEP, OR EXIT??")
READ(7,110)IREP
IF (IREP.EQ.2HSE) GO TO 120
IF (IREP.EQ.2HSW) GO TO 170
IF (IREP.EQ.2HZE) GO TO 180
IF (IREP.EQ.2HEX) GO TO 1
GO TO 108

C***************
120 WRITE (7,121)
121 FORMAT ("ENTER SPECTRAL RANGE OF INTEREST")
122 WRITE (7,122)
123 FORMAT ("ENTER DESIRED HIGH FIELD LIMIT IN PPM")
124 READ (7,*) WDOL
125 WRITE (7,123)
126 FORMAT ("ENTER DESIRED LOW FIELD LIMIT IN PPM")
127 WRITE (7,124)
128 DOH = (WDOL*100.0)+2500.00
129 WRITE (7,125)
130 FORMAT ("ENTER EXACT VALUE IN HZ, OFF FREQ. CNTR")
131 CALL RMIN
132 READ (7,*) DOH
133 WRITE (7,126)
134 FORMAT ("SET WAVTEK MIN. TO ",F7.2," HZ")
135 WRITE (7,127)
136 CALL RMAX
137 READ (7,*) DOL
138 WRITE (7,128)
139 FORMAT ("ENTER EST. AQUISITION TIME")
140 READ (7,*) AQEST
141 WRITE (7,129)
142 CALL RMIN
143 READ (7,*) NSCAN
144 FORMAT ("ENTER THE NUMBER OF SCANS WISHED")
145 WRITE (7,130)
146 WDOH = (DOH-2500.00)/100.00
147 SW = ABS (DOL-DOH)
148 NRES = 2048.00 / SW
149 DWLEST = AQEST/NRES
150 RATE = DWLEST/0.000100
151 WRITE (7,131)
152 IF (IRATE.LT.1) GO TO 137
153 DELL = FLOAT(IRATE)*0.000100
154 AQ = DELL*2048.00
155 WRITE (7,132)
156 SWPRT = SW/AQ
157 WRITE (7,133) SWPRT
WRITE(7,131) RES
FORMAT("DIGITAL RESOLUTION = ",F7.2," PTS/HZ")
WRITE(7,132) AQ
FORMAT("TRUE ACQISITION TIME IS ",F7.2," SEC")
WRITE(7,133) WDOH,WDOI
FORMAT("SPECTR. SWEEPS FROM ",F7.2," TO ",F7.2," PPM")
WRITE(7,135)
FORMAT("CHANGE PARAMETERS??, YES,NO, OR JUST AQ. TIME?")
READ(7,136) IHRU
FORMAT(A2)
IF (IHRU.EQ.2HYES) GO TO 120
IF (IHRU.EQ.2HNO) GO TO 108
IF (IHRU.EQ.2HAQ) GO TO 139
GO TO 134
WRITE(7,138)
FORMAT("ERROR -- DWELL TIME TOO SMALL/")
GO TO 134

*******************************************************************************

170 DO 171 I=1,4096
IDATA(I)=0
171 CONTINUE
ISTRT=0
NON=2047

*******************************************************************************

CALL SWEEP(ISTRT,NON ,KLOK,IRATE,NSCAN)
*******************************************************************************

C FLOT IS DONE ON PREMISE THAT IDATA IS PACKED USING C
C EVERY SECOND DATA LOCATION VIA THE ASSEMBLR ROUTINE SWEEP C
WRITE(7,173)
173 FORMAT("SWEEP DATA FLOATING")
J=1
DO 172 I=1,2048
XDATA(I)=FLOAT(IDATA(J))
J=J+2
172 CONTINUE
GO TO 134

C ZERO ARRAY
180 DO 181 I=1,4096
IDATA(I)=0
181 CONTINUE
GO TO 108

*******************************************************************************

C
500 CALL DSCRD
GO TO 1
C*****************************************************************************
C
550 CALL DSCRT
GO TO 1
END

C*****************************************************************************
C
SUBROUTINE DSCRD
DIMENSION IDCB(144), IBUF(1), NAME(3)
COMMON XDATA(2048), NN
COMMON SW, AQ, SWPRT

C WRITE(7,505)
505 FORMAT("ENTER NAME OF FILE YOU WISH TO BE READ")
READ(7,510)NAME
510 FORMAT(3A2)
C
CALL OPEN(IDCB, IERR, NAME, 0, 0, 0)
IF (IERR.LT.0) GO TO 540
C
CALL READF(IDCB, IERR, IBUF, 1)
IF (IERR.LT.0) GO TO 540
C
NN=IBUF(1)
MN=2*NN
C
CALL READF(IDCB, IERR, XDATA, NN)
IF (IERR.LT.0) GO TO 540

)
C
CALL CLOSE(IDCB, IERR)
IF (IERR.GE.0) GO TO 545

C 540 WRITE(7,541)
541 FORMAT("ERROR IN FILE HANDLING(IERR)!")
C
545 WRITE(7,546)
546 FORMAT("FILE READ COMPLETED")
C
RETURN
END

C*****************************************************************************
C
SUBROUTINE DSCRT
DIMENSION IDCB(144), IBUF(1), NAME(3)
COMMON IDATA(2048), NN
COMMON SW, AQ, SWPRT
REAL IDATA
C
WRITE(7,555)
555 FORMAT("ENTER NAME OF FILE TO BE WRITTEN ")
560 FORMAT(3A2)
   C
   ISIZE=-1
   ITYPE=3
   IERR=0
   ICR=11
   C
   CALL CREAT(IDCB, IERR, NAME, ISIZE, ITYPE, 0, ICR)
   IF (IERR.LT.0) GO TO 590
   C
   IL=1
   IBUF(1)=NN
   C
   CALL OPEN(IDCBL,IERR,NAME)
   IF (IERR.LT.0) GO TO 590
   C
   CALL WRITF(IDCBL, IERR, IBUF; IL)
   IF (IERR.LT.0) GO TO 590
   C
   IL=2*NN
   CALL WRITF(IDCBL, IERR, IDATA, IL)
   IF (IERR.LT.0) GO TO 590
   C
   IL=2
   CALL WRITF(IDCBL, IERR, AQ, IL)
   IF(IERR.LT.0) GO TO 590
   CALL WRITF(IDCBL, IERR, SW, IL)
   IF(IERR.LT.0) GO TO 590
   C
   CALL LOCF(IDCBL,IERR,IREC,IRB,IOFF,JSEC)
   IF (IERR.LT.0) GO TO 590
   C
   ITRUN=JSEC/2-IRB-1
   C
   CALL CLOSE(IDCBL, IERR, ITRUN)
   IF (IERR.GE.0) GO TO 595
   C
590 WRITE(7,591)
591 FORMAT("FILE HANDLING ERROR(IERR)"")
   C
595 WRITE(7,596)
596 FORMAT("FILE WRITE COMPLETED!!")
   RETURN
      END
C
C*******************************************************************************
END$  
C
THAT'S ALL FOLKS!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
C*************************************************************************
  PROGRAM NMRAN
C*************************************************************************
C
C SOURCE FILE IS GRAN::11
C BINARY FILE IS RAN
C PROGRAM COMES UP ON RU,NMRAN
C PROGRAM LOADS ON TR,TRAN
C THIS PROGRAM Responds AT TERMINAL #6 (REMOTE)
C
C THE DSCRT AND DSCRD ROUTINES PROVIDE HARD COPY
C STORAGE AND RETRIEVAL FOR THE SPEC. FILES ON THE
C REMOVABLE DISC.
C THE DSHAP SUBROUTINE PERFORMS THE CORRELATION MULTI-
C PLICATION AND ACCESS TO THE FOURIER TRANSFORM ROUTINE
C AND ALL OTHER DATA MANIPULATION ROUTINES.
C
C INITIALIZE THE VARIABLES
C
    COMMON XDATA(2048), NN
    COMMON SW, AQ, SWPRT
    EQUIVALENCE (XDATA(1),IDATA(1))
    INTEGER IDATA(4096)
    NN=2048
    TLB=0.00
    DO 4 I=1,4096
    IDATA(I)=0
    4 CONTINUE
    WDOH=10.00
    WDOL=2.00
    AQ=0.0
    SW=0.0

C DECIDE WHICH OF THREE MAIN FUNCTIONS TO PERFORM
C*************************************************************************
C
1   WRITE(6,100)
100  FORMAT("READ,WRITE,SHAPE, OR STOP??")
    READ(5,101)IRES
101  FORMAT(A2)
    IF (IRES.EQ.2HSHA) GO TO 200
    IF (IRES.EQ.2HWR) GO TO 550
    IF (IRES.EQ.2HRE) GO TO 500
    IF (IRES.EQ.2HST) STOP
    GO TO 1

C FIRST FUNCTION IS RUNNING THE EXPERIMENT
C*************************************************************************
C
C SHAPE SUBROUTINE CALL
C*************************************************************************
C
200  CALL DSHAP
    GO TO 1
C 500 CALL DSCRD
   GO TO 1

C 550 CALL DSCRT
   GO TO 1
END

C SUBROUTINE DSHAP
COMMON IDATA(2048), NN
COMMON SW, AQ, SWPRT
REAL IDATA, ISRG, ICRG
INTEGER HWDO
RDTN=0.00
PHZ=90.00

C PRESENT THE MAIN MENU
C 201 WRITE(6,202)
202 FORMAT("CORX, EXPX, FT, PHASE, SCALE, LOOKC, ZEPK, ONES, FIDL, QUIT")
   READ(6,203) IRAP
203 FORMAT(A2)
   IF (IRAP.EQ.2HPH) GO TO 210
   IF (IRAP.EQ.2HCO) GO TO 220
   IF (IRAP.EQ.2HON) GO TO 230
   IF (IRAP.EQ.2HEX) GO TO 240
   IF (IRAP.EQ.2HZE) GO TO 250
   IF (IRAP.EQ.2HFT) GO TO 260
   IF (IRAP.EQ.2HSC) GO TO 270
   IF (IRAP.EQ.2HLO) GO TO 280
   IF (IRAP.EQ.2HFI) GO TO 290
   IF (IRAP.EQ.2HQU) GO TO 299
   GO TO 201

C PHASE ADJUSTMENT AND RECONSTRUCTION
C 210 WRITE(6,211) PHZ
211 FORMAT("CURRENT PHASE ANGLE = ",F7.2," DEG. ENTER NEW VALUE")
   READ(6,*) PHZ
   NO2=NN/2
   RG=(PHZ/180.00)*3.141592654
   CRG=COS(RG)
   SRG=SIN(RG)

C J=NO2+1
   DO 212 I=1,NO2
ISRG=SRG*IDATA(J)
RSG=SRG*IDATA(I)
ICRG=CRG*IDATA(J)
IDATA(I)=RCRG+ISRG
IDATA(J)=-RSG+ICRG
J=J+1
212 CONTINUE
WRITE(6,213)PHZ
213 FORMAT("FINISHED PHASE ADJUST TO ",F7.2," DEG.")
GO TO 201
C**************************************************************************************
C****************************************************************************************
C . CORRELATION MULTIPLICATION
C EXPECTS ARRAY IN FORM
CRRR/III
C**************************************************************************************
C**************************************************************************************
C 220 CONTINUE
C NO2=NN/2
WRITE(6,222)SW,AQ
222 FORMAT("SW= ",F7.3," Hz. AQ= ",F7.3," Sec.")
C
JDX=NO2+1
AR=3.141592654/(AQ*SW)
IDATA(1)=0.00
IDATA(JDX)=0.00
C
DO 229 IDX=1,NO2
RDX=FLOAT(IDX)
ARG=AR*RDX**2
ARGC=COS(ARG)
ARGS=SIN(ARG)
HOLDI=IDATA(IDX)
HOLDJ=IDATA(JDX)
IDATA(IDX)=(HOLDI*ARGC)-(HOLDJ*ARGS)
IDATA(JDX)=(HOLDI*ARGS)+(HOLDJ*ARGC)
JDX=JDX+1
229 CONTINUE
GO TO 201
C**************************************************************************************
C**************************************************************************************
C 240 CONTINUE
C EXPONENTIAL MULTIPLICATION
C**************************************************************************************
C**************************************************************************************
C ELB=0.00
NO2=NN/2
J=NO2+1
WRITE(6,241)TLB
241 FORMAT("TOTAL LB IS ",F7.2," -ENTER ADDITIONAL LB")
READ(6,*)ELB
TLB=TLB+ELB
DO 242 I=1,NN
BRKT= -((I-1)*ELB)/(2*SW)
PNT= EXP(BRKT)
IDATA(J) = IDATA(J) * PNT
J = J + 1
242 CONTINUE
WRITE(6, 243) TLB
243 FORMAT("FID HAS TOTAL OF ", F7.2, " Hz LB BY EXP ")
GO TO 201
C
C***********************************************************************
C JUMP TO FOURIER TRANSFORM SUBROUTINE
C
260 CONTINUE
CALL FFTN
GO TO 201
C
C***********************************************************************
C
230 CONTINUE
WRITE(6, 231)
231 FORMAT("THE ARRAY HAS BEEN 11111111'D")
DO 232 I = 1, NN
IDATA(I) = 1.0
232 CONTINUE
GO TO 201
C
C***********************************************************************
C
250 CONTINUE
LWDO = 0
HWDO = NN
ISKP = 1
WRITE(6, 256)
256 FORMAT("ZERO, PACK OR QUIT??")
READ(6, 257) IREP
257 FORMAT(A2)
IF(IREP.EQ.2HZE) GO TO 258
IF(IREP.EQ.2HPA) GO TO 259
IF(IREP.EQ.2HQU) GO TO 201
GO TO 250
258 CONTINUE
WRITE(6, 251)
251 FORMAT("ENTER THE ZEROING WINDOW PARAMETERS BY POINT NUMBER")
WRITE(6, 252) LWDO
252 FORMAT("THE LOWER WINDOW IS POINT NUMBER ", I5).
READ(6, *) LWDO
WRITE(6, 253) HWDO
253 FORMAT("THE HIGH WINDOW IS POINT NUMBER ", I5)
READ(6, *) HWDO
WRITE(6, 263) ISKP
263 FORMAT("ZERO BY EVERY ", I5, " PTS??")
READ(6, *) ISKP
DO 254 I = LWDO, HWDO, ISKP
IDATA(I) = 0
254 CONTINUE.
255 FORMAT("ARRAY HAS BEEN ZEROFED FROM ",I5," TO ",I5," BY ",I5)

C
C    GO TO 201
C
259 CONTINUE
C    NO2=NN/2
C    J=2
C    DO 261 I=1,NO2
C    IDATA(I)=IDATA(J)
C    J=J+2
C
261 CONTINUE
C
WRITE(6,262)
C
262 FORMAT("ARRAY PACKED: RRRR/GBGE")
C
C    GO TO 250
C
270 CONTINUE
C
C    THIS ROUTINE DOES A SCALING FUNCTION
C
C    SORT FOR THE MAX VALUE OF THE ARRAY
C
C    YMAX=ABS(IDATA(1))
C    DO 271 I=1,NN
C    VABS=ABS(IDATA(I))
C    IF (YMAX.GE.VABS) GO TO 271
C    YMAX=ABS(IDATA(I))
C
271 CONTINUE
C
WRITE(6,272)YMAX
C
272 FORMAT("THE MAX. VALUE OF THE ARRAY IS ",F7.2)
C
WRITE(6,273)
C
273 FORMAT("ENTER SCALING VALUE(32767 IS MAX)")
C
READ(6,*),SKL
C
C    SCALE THE ARRAY
C
C    DO 274 I=1,NN
C    IDATA(I)=(IDATA(I)/YMAX)*SKL
C
274 CONTINUE
C
WRITE(6,275)SKL
C
275 FORMAT("THE ARRAY HAS BEEN SCAL ED TO ",F7.2)
C
GO TO 201
C
C
280 CONTINUE
C
C
WRITE(6,281)NN
C
281 FORMAT("CURRENT # OF PTS IN ARRAY= ",I5)
C
C
WRITE THE ARRAY
C
C    DO 283 I=1,NN
C    WRITE(6,282)I,IDATA(I)
C
282 FORMAT("PT NMBR ",I5," HAS THE VALUE ",F7.2)
C
283 CONTINUE
WRITE(6,284)
FORMAT("THE END OF THE ARRAY")
GO TO 201

CONTINUE
WRITE(6,291)NN
FORMAT("CURRENT # OF PTS = ",I5," -ENTER NEW VALUE!")
READ(6,*)NN
WRITE(6,292)NN
FORMAT("ARRAY NOW CONTAINS ",I5," PTS!")
GO TO 201

CONTINUE
RETURN
END

SUBROUTINE DSCRD
DIMENSION IDCBD(144), IBUF(1), NAME(3)
COMMON XDATA(2048), NN
COMMON SW, AQ, SWPRT
WRITE(6,505)
FORMAT("ENTER NAME OF FILE YOU WISH TO BE READ")
READ(6,510)NAME
FORMAT(3A2)
CALL OPEN(IDCBD, IERR, NAME, 0, 0, 0)
IF (IERR.LT.0) GO TO 540
CALL READF(IDCBD, IERR, IBUF, 1)
IF (IERR.LT.0) GO TO 540

NN=IBUF(1)
MN=2*NN
READ TOTAL # OF PTS; NN IS # OF REAL PTS
CALL READF(IDCBD, IERR, XDATA, MN)
IF (IERR.LT.0) GO TO 540

MN=2
CALL READF(IDCBD, IERR, AQ, MN)
IF (IERR.LT.0) GO TO 540
CALL READF(IDCBD, IERR, SW, MN)
IF (IERR.LT.0) GO TO 540

CALL CLOSE(IDCBD, IERR)
C WRITE(6,541)
C FORMAT("ERROR IN FILE HANDLING(IERR)!")
C WRITE(6,546)
C FORMAT("FILE READ COMPLETED")
C RETURN
END

******************************************************************************
C SUBROUTINE DSCRT
C DIMENSION IDCB(144), IBUF(1), NAME(3)
C COMMON IDATA(2048), MN
C COMMON SW, AQ, SWPRT
C REAL IDATA
C
C WRITE(6,555)
C FORMAT("ENTER NAME OF FILE TO BE WRITEN (REMOVABLE DISC)")
C READ(6,560)NAME
C FORMAT(3A2)
C
C ISIZE=-1
C ITYPE=3
C IERR=0
C ICR=11
C
C CALL CREAT( IDCB, IERR, NAME, ISIZE, ITYPE, 0, ICR)
C IF (IERR.LT.0) GO TO 590
C
C IL=1
C IBUF(1)=MN
C
C CALL OPEN(IDCB,IERR,NAME)
C IF (IERR.LT.0) GO TO 590
C
C CALL WRITF(IDCB, IERR, IBUF, IL)
C IF (IERR.LT.0) GO TO 590
C
C IL=2*MN
C CALL WRITF(IDCB, IERR, IDATA, IL)
C IF (IERR.LT.0) GO TO 590
C
C IL=2
C CALL WRITF(IDCB, IERR, AQ, IL)
C IF (IERR.LT.0) GO TO 590
C CALL WRITF(IDCB, IERR, SW, IL)
C IF (IERR.LT.0) GO TO 590
C
C CALL LOCDF(IDCB,IERR,IREC,IRB,IOFF,JSEC)
C IF (IERR.LT.0) GO TO 590
C
C ITRUN=JSEC/2-IRB-1
IF (IERR.GE.0) GO TO 595

590 WRITE(6,591) —
591 FORMAT("FILE HANDLING ERROR(IERR)")

595 WRITE(6,596)
596 FORMAT("FILE WRITE COMPLETED!!")
RETURN
END

-------------------------------------------------------------

THIS PROGRAM PERFORMS A FAST FOURIER TRANSFORM
SIMILAR TO THE COOLEY-TOOKEY ALGORITHM.
THE CODE WAS TRANSLATED INTO FORTRAN FROM A
PASCAL LISTING WRITTEN BY JAMES COOPER WITH
SOME MODIFICATIONS.

THIS PROGRAM HAS THREE SUBROUTINES WITH IN IT, EACH
OF WHICH PERFORM AN ENTIRELY SEPERATE FUNCTION.
WHAT FOLLOWS IS A FLOW CHART OF THE INDEXING SYSTEM
USED FOR THIS APPLICATION TO CORRELATION PROCESSING.

REAL ARRAY----- RRRRRRRR--------FREQ. DOMAIN

RIRIRIRI

(REAL) SHUFL-------
(FWD) FFT-------- TO
(TRFRM) POST------

COMPLEX ARRAY-- RRRRIII--------TIME DOMAIN

(COMPLX) FFT------- TO
(INV) (TRFRM)

COMPLEX ARRAY-- RRRRIII--------FREQ. DOMAIN

-------------------------------------------------------------

SUBROUTINE FFTN
COMMON X(2048), N
COMMON SW, AQ, SWPRT
INTEGER CMBK
DATA PI2/1.570796327/

INV=1

106 WRITE(6,101)
READ(6,102) CMBK
FORMAT(A2)
IF(CMBK.EQ.2HP0) GO TO 104
IF(CMBK.EQ.2HIN) GO TO 103
IF(CMBK.EQ.2HST) GO TO 108
GO TO 106

C
INV=-1
CALL FFT(INV,PI2)
GO TO 107
C
CONTINUE
C
CALL SHUFL(INV)
CALL FFT(INV,PI2)
CALL POST(NU,INV,PI2)
WRITE(6,109)

C
FORMAT("TRANSFORM COMPLETED")
RETURN
END

C
SUBROUTINES BEGIN
C
FIRST A FUNCTION WHICH PERFORMS "BIT INVERSION"
C
FUNCTION IBITR(J,NU)
IB=0
DO 25 IN=1,NU
J2=J/2
IB=IB*2+(J-2*J2)
25 J=J2
IBITR=IB
RETURN
END

C
NEXT SUBROUTINE IS DEBUG
C
OUTPUTS THE DATA ARRAY DURING PROGRAM DEVELOPMENT
C
SUBROUTINE DEBUG
COMMON X(2048), N
COMMON SW, AQ, SWPRT
DO 15 I3=1, N
15 WRITE(6,105) X(I3)
FORMAT(57,2)
RETURN
END

C
NEXT SUBROUTINE IS POST
C
ACTION IS PENDANT ON THE STATE OF "INV"
C
IF INV=1 THEN DO POST PROCESSING FOR FORWARD REAL TRANSFORM
C
IF INV=-1 THEN DO PRE PROCESSING FOR INVERSE REAL TRANSFORM
C
THIS SUBROUTINE WORKS THROUGH THE ARRAY BY CUTTING IT IN
C
HALF AND PROCESSING FROM THE ENDS TO THE MIDDLE.
C
THE INDEX I AND M WORK THE FIRST HALF OF THE ARRAY.
C
THE INDEX IPN2 AND MPN2 WORK THE 2ND HALF OF THE ARRAY.
SUBROUTINE POST ( NU, INV ,PI2)
COMMON X(2048), N
COMMON SW, AQ, SWPRT
REAL IPCOS, IPSIN, IC, IS1, IP, IM
NN2=N/2
NN4=N/4
DO 35 L=1,NN4
  I=L+1
  M=NN2-I+2
  IPN2=I+NN2
  MPN2=M +NN2
  RP= X(I)+X(M)
  RM= X(I)-X(M)
  IP= X(IPN2)+ X(MPN2)
  IM= X(IPN2)- X(MPN2)
C TAKING COSINE OF PI/2N
  ARG=(PI2 / NN4)*(I-1)
  IC= COS (ARG)
C THE COSINE WILL BE -VE IF DOING INV. FT.
  IF (INV.EQ.-1) IC=-IC
  IS1= SIN(ARG)
  IPCOS= IP*IC
  IPSIN= IP*IS1
  RMSIN= RM*IS1
  RM COS= RM*IC
C PROCESSING REAL(R__) AND IM AGINARY(I__) POINTS
  X(I)= RP + IPCOS - RMSIN
  X(IPN2)= IM-IPS IN-RMCOS
  X(M)= RP- IPCOS+ RMSIN
  X(MPN2)= -IM-IPSIN-RMCOS
35 CONTINUE
RETURN
END
C
C NEXT SUBROUTINE IS SHUFFL ***********
C RIRIRIRI
C TO
C RRRIII
C
C IN PREPARATION FOR FORWARD TRANSFORM, OTHERWISE REVERSE
C
C THE DIRECTION OF SHUFFLE DEPENDS ON STATUS OF INV.
C
C INV IS 1 THEN: LARGE CELLS AND WORK DOWN ARRAY
C INV IS -1 THEN: SMALL CELLS AND WORK UP ARRAY.
C
SUBROUTINE SHUFL (INV)
COMMON X(2048), N
COMMON SW, AQ, SWPRT
INTEGER CELNUM, CELDIS, PASS, PARNUM
C
IF (INV.EQ.-1) GOTO 43
C EL DIS = N/2
CEL NUM= 1
GOTO 47
CONTINUE
CELDIS= 2
CELMUN= N/4
PARNUM= 1
CONTINUE

PERFORM THE FIRST PASS

I= 2
DO 45 J= 1, CELNUM
  DO 41 K= 1, PARNUM
    XTEMP= X(I)
    IPCM1= I+ CELDIS -1
    X(I)=X(IPCM1)
    X(IPCM1)=XTEMP
    I=I+2
  CONTINUE
  I=I+ CELDIS
45 CONTINUE

CHANGE VALUES FOR 2ND PASS

IF (INV. EQ. -1) GOTO 42
CELDIS= CELDIS/2
CELMUN= CELNUM/2
PARNUM= PARNUM/2
GOTO 44
CONTINUE

CELDIS= CELDIS*2
CELMUN= CELNUM/2
PARNUM= PARNUM/2
CONTINUE

IF((CELDIS.LT.2.AND.INV.EQ.1).OR.(CELMUN.EQ.0.AND.INV.EQ.-1))
  1 GOTO 49
GOTO 47
49 RETURN
END

NEXT SUBROUTINE IS FFT

SUBROUTINE FFT( INV, PI2 )
COMMON X(2048), N
COMMON SW, AQ, SWPR
REAL I2COSY, I2SINY, K1, K2
INTEGER CELNUM, CELDIS, PASS, PARNUM

NU=0
N1=N/2
N2=N1
CONTINUE
NU=NU+1
N1=N1/2
DO 51 I=1, N2
II=I-1
K=IBITR(II,NU)+1
IF (I.LE.K) GOTO 51
IPN2= I+ N2
KPN2= K+ N2
TR= X(K)
TI= X(KPN2)
X(K)= X(I)
X(KPN2)= X(IPN2)
X(I)= TR
X(IPN2)= TI
51 CONTINUE
I=1
C THE FIRST PASS IS DONE ALONE.
52 IF (I.GT.N2) GOTO 53
K= I+ 1
KPN2= K+ N2
IPN2= I+ N2
K1 = X(I) + X(K)
X(K) = X(I) - X(K)
X(I) = K1
K1 = X(IPN2) + X(KPN2)
X(KPN2)= X(IPN2) - X(KPN2)
X(IPN2) = K1
I = I + 2
GOTO 52
53 CONTINUE
CELNUM = N2/4
PARNUM = 2
CELDIS = 2
PASS = 2
DELTAY=PI2
C EACH NEW CELL STARTS HERE.
59 INDEX = 1
Y=0
DO 58 I2=1, PARNUM
IF (Y.EQ.0) GOTO 54
COSY = COS(Y)
SINY = INV*SIN(Y)
54 CONTINUE
DO 57 L = 1, CELNUM
I = CELDIS * 2 * (L-1) + INDEX
J = I + CELDIS
IPN2= I+ N2
JPN2= J+ N2
IF (Y.NE.0) GOTO 55
K1 = X(I) + X(J)
K2 = X(IPN2) + X(JPN2)
X(J) = X(I) - X(J)
X(JPN2) = X(IPN2) - X(JPN2)
GOTO 56
55 CONTINUE
R2COSY = X(J)*COSY
I2COSY = X(JPN2)*COSY
I2SINY = X(JPN2)*SINY
K1 = X(I) + R2COSY + I2SINY.
K2 = X(IPN2) - R2SINY + I2COSY
X(J) = X(I) - R2COSY - I2SINY
X(JPN2) = X(IPN2) + R2SINY - I2COSY
56 CONTINUE
   X(I) = K1
   X(IPN2) = K2
57 CONTINUE
   Y = Y + DELTAY
   INDEX = INDEX + 1
58 CONTINUE
   CELNUM = CELNUM/2
   PARNUM = PARNUM*2
   CELDIS = CELDIS*2
   DELTAY = DELTAY/2
   PASS = PASS+1
   IF (CELNUM.NE.0) GO TO 59
   RETURN
END
END$
C THAT'S ALL FOLKS!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
C**********************************************************
PROGRAM NMPLT
C
C SOURCE FILE: GPLT
C BINARY FILE: RPLT
C
C THIS PROGRAM READS A DISC FILE (6 CHARACTERS)
C AND PLOTS THE FILE ON THE ZETA PLOTTER.
C THE COMMAND RU,NMPLT BRINGS THE PROGRAM UP.
C THE TRANSFER FILE TR,TPLT LOADS THE PROGRAM.
C THIS PROG. RUNS ON THE AXISM CALL FROM RZETA4.
C
C LOADER REQUIRES BINARY ZETA PLOTTER FILES 'PLOTS', 'SYMBO',
C 'NUMBE', 'AXISM', 'PLOT', 'PON', AND 'ZZZ'.
C
C THIS PROGRAM ALSO HAS THE CAPABILITY OF PLOTTING
C ABSORPTION AXIS WHEN LOOKING AT TIME DOMAIN SPECTRA
C
C
COMMON IZETA(1500)
COMMON IDATA(2048), NN
COMMON SW,AQ
REAL IDATA
1 CONTINUE
IERR=0
LEN=0
70 FREQL=0.0
FREQH=10.0
TIKI=100.0
XL=20.0
YL=15.0
FINCX=1.0
FINCY=1.0
C
101 WRITE(6,102)
102 FORMAT("READ, PLOT, PAKPLT, OR STOP??")
READ(6,103)IRES
103 FORMAT(A2)
IF (IRES.EQ.2HRE) GO TO 400
IF (IRES.EQ.2HPL) GO TO 300
IF (IRES.EQ.2HPA) GO TO 250
IF (IRES.EQ.2HST) STOP
GO TO 101
400 CONTINUE
CALL RDSPC
GO TO 101
250 CONTINUE
NN=NN/2
300 CONTINUE
WRITE(6,500)XL
500 FORMAT("LENGTH OF PLOT (CM) = ",F7.2)
READ(1,*)XL
WRITE(6,510)YL
510 FORMAT("PLOT HEIGHT (CM) = ",F7.2)
READ(1,*)YL
YLI=YL/2.54
C CALCULATE THE MAGNITUDE OF THE SCALING FACTOR
C YYMAX=IDATA(1)
DO 301 I=1,NN
IF(YYMAX.GT.IDATA(I)) GO TO 301
YYMAX=IDATA(I)
301 CONTINUE
WRITE(6,888)YYMAX
888 FORMAT("MAX. Y VALUE = ",F7.2)
C CALCULATE THE INCREMENT ON THE X AXIS
C FINCX=(XLI)/FLOAT(NN)
C CALCULATE THE INCREMENT ON THE Y AXIS
C FINCY=YLI/(YYMAX*2)
WRITE(6,889)FINCY
889 FORMAT("Y INC. = ",F10.3," IN/PT")
C PLOT THE AXIS
C X=0.0
Y=0.0
CALL PLOTS(53,0,-1)
CALL AXISM(0.0,0.0,XLI,1.0,0.0,1.0,0.2)
C Y=-(YLI/2)
C CALL AXISM(0.0,Y,YLI,1.0,1.0,1.0,0.2)
C THE Y AXIS HAS BEEN REMOVED
CALL PLOT(0.0,0.5,3)
C CONTINUE
WRITE(6,890)
890 FORMAT("TRANSFERRING DATA TO ZETA PLOTTER")
C PLOT SPECTRUM
DO 28 I=1,NN
SUM=FINCY*IDATA(I)
YY=SUM
XX=X
CALL PLOT(XX,YY,2)
X=X+FINCX
28 CONTINUE
X=XLI/2.0-3.0
Y=YLI+0.8
X=XLI+1.0
CALL PLOT(X,0.0,999)
GO TO 101
END
SUBROUTINE RDSPC
DIMENSION IDCB(144), IBUF(1), NAME(3)
COMMON IZETA(1500)
COMMON IDATA(2048), NPTS
COMMON SW,AQ
REAL IDATA

WRITE(6,405)
405 FORMAT("ENTER NAME OF FILE YOU WISH READ")
READ(6,410)NAME
410 FORMAT(3A2)

CALL OPEN(IDCB, IERR, NAME, 0, 0, 0)
IF (IERR.LT.0) GO TO 440

CALL READF(IDCB, IERR, IBUF, 1)
IF (IERR.LT.0) GO TO 440

NPTS=IBUF(1)
NPT=2*NPTS

CALL READF(IDCB, IERR, IDATA, NPT)
IF (IERR.LT.0) GO TO 440

MN=2
CALL READF(IDCB, IERR, AQ, MN)
IF (IERR.LT.0) GO TO 440
CALL READF(IDCB, IERR, SW, MN)
IF (IERR.LT.0) GO TO 440

CALL CLOSE(IDCB, IERR)
IF (IERR.GE.0) GO TO 445

WRITE(6,441)
441 FORMAT("ERROR RETURNED WHILE HANDLING FILE (IERR)")

WRITE(6,446)
446 FORMAT("DISC FILE READ COMPLETED!!")

RETURN
END

END$
NAM SWEEP,7

17/ 6/83

FORTRAN CALLABLE DATA ACQUISITION ROUTINE:

THE ROUTINE PROVIDES A SWEEP RAMP (UP TO 2048 STEPS), WITH DATA
ACQUISITION AT EACH STEP.
DATA ARE STORED IN INTEGER FORM IN THE VECTOR "STOR". THE DIMENS:
OF "STOR" IS SET BY THE CALLING PROGRAM (<= 2048).

FORTRAN CALLS:

CALL RMIN
CALL RMAX
CALL SWEEP(ISTRT,NPTS,KLOK,IRATE,NSCAN)

ISTRT = RELATIVE START ADDRESS ON RAMP
NPTS = NUMBER OF POINTS ON RAMP
(ISTRT + NPTS <= 2048)
KLOK = CLOCK (TIME BASE GENERATOR) PERIOD
(0 = 100 MICROSEC, 1 = 1 MSEC, 2 = 10 MSEC, ETC)
IRATE = CLOCK TICK COUNTER
(I.E. MULTIPLES OF CLOCK PERIOD)
NSCAN = NUMBER OF SCANS (SWEEPS)

HP 21MX-E OPERATING UNDER RTE-II
MEMORY PROTECT IS DISABLED AT THE FIRST INTERRUPT
(FROM THE TBG OR THE ADC), & IS RESTORED
WHEN SWEEP EXITS, I.E. SWEEP OPERATES WITH
MEMORY PROTECT DISABLED.

THE SYSTEM CLOCK IS DISABLED DURING ACQUISITION OF DATA.
IT IS RESTORED WHEN PRIVILEGED INTERRUPTS ARE
NO LONGER PENDING.

USES THE DUAL 12-BIT DAC.
THE SCAN COUNT IS WRITTEN ON THE TERMINAL DISPLAY.

THIS ROUTINE DOES NO ERROR CHECKING.

ENT RMIN,RMAX,SWEEP
EXT $CVT,LIBR,LIBX,EXEC,OPEN,CLOS,PRTK,RINT
EXT .ENTR,MESSS
COM IZETA(1500)
COM STOR(1)
TBG EQU.11B
ADC EQU 13B
TTY EQU 21B
SKLOK EQU 15B

* RAMP MINIMUM FOR CALIBRATION
RMIN NOP
    LDA RMIN, I
    STA RETRN
    JSB #OPEN
    LDA =B10000
    OTA DAC X-AXIS ZERO
    CLA
    OTA DAC Y-AXIS ZERO
    JSB #CLOS
    JMP RETRN, I

* RAMP MAXIMUM FOR CALIBRATION
RMAX NOP
    LDA RMAX, I
    STA RETRN
    JSB #OPEN
    LDA =B7777
    OTA DAC Y-AXIS FULL SCALE
    LDA =B13777
    OTA DAC X-AXIS FULL SCALE
    JSB #CLOS
    JMP RETRN, I

* SWEEP AND DIGITIZATION ROUTINE
ISTRT BSS 1 RELATIVE START ADDRESS
NPTS BSS 1 NUMBER OF POINTS ON RAMP
IKLKO BSS 1 CLOCK PERIOD
IRATE BSS 1 CLOCK TICK COUNTER
NSCAN BSS 1 NUMBER OF SCANS

* SWEEP NOP
    JSB .ENTR ENTRY POINT
    TRANSFER FORTRAN DUMMY ARGUMENTS
    DEF ISTRT
    JSB UNBUF UNBUFFER TERMINAL
    LDA ISTRT, I START INITIALIZATION
    ALS
    ADA #STOR
    STA ASTRT
    SARA, I
    STA DCNT COUNTER
    LDX =D-10
    CLA
    STA NOVER
    STA SCNT
    STA MIN1
    STA MAX1
    STA SHFTS
    STA SHFTS+
    JSB #OPEN LOWER MEMORY PROTECT FENCE & DISABLE INTERRUPT
LDA =B40000  ADC MODE
OTA ADC
LDA INTBG  SET INTERRUPT CELL CONTENTS
STA TBG  CLOCK INTERRUPT
LDA INTTY
STA TTY  TTY INTERRUPT
LDA INADC
STA ADC  ADC INTERRUPT
CLA
STA SCNT  ZERO SCAN COUNTER
OTA 1,C  CLEAR SWITCH REGISTER

START SCAN
START LDA SCNT  CHECK NO. OF SCANS
CPA NSCAN,I
JMP FINIS
ISZ SCNT
JSB INIT  INITIALIZE ADDRESS INDEX & POINT COUNTER
LDA =B160000  PREPARE TO READ TTY
OTA TTY
STC TTY,C  ENABLE TTY INTERRUPT
LDA =B10000
ADA ISTRT,I
STA XVAL  SET DAC X-AXIS TO START VALUE
OTA DAC  AND OUTPUT TO DAC
CLA
OTA DAC  SET DAC Y-AXIS TO ZERO
LDA =B3
OTA TBG
STC TBG,C  SET 0.1 SEC. DELAY
SFS TBG  AND TURN ON TBG
JMP #-1
CLC TBG,C  TO ALLOW FOR SETTLING TIME
DISABLE TBG
LDA IKL0K,I  SET TBG PERIOD FOR SWEEP
OTA TBG
LDY DCNTR  INITIALIZE TBG DELAY COUNTER
LIA 1,C  LOAD SWITCH REGISTER INTO "A"
SSA  CHECK SWITCH REGISTER
JMP OUT  EXIT IF S15 SET
CLC SKL0K,C  DISABLE SYSTEM CLOCK
STF 0  ENABLE INTERRUPT SYSTEM
STC TBG,C  START TBG
STC ADC,C  SWITCH ON ADC
LDB SCNT
OTB 1,C  DISPLAY SCAN NO. IN SWITCH REGISTER
JMP WAIT

PROC CMA,INA  PROCEED AFTER TBG INTERRUPT
SHFTS NOP
-NOP
-NOP
CLO
ADA ADDR,I
SOC C  LOCATIONS FOR "ARS"

IS THERE AN OVERFLOW?
STA ADDR,I NO, THEN STORE NEW SUM
ARS,ARS DIVIDE INTENSITY TO FIT DAC
ARS,ARS
ADA =B1777 ADD 1/4 OF DAC RANGE
OTA DAC DISPLAY INTENSITY (Y-AXIS)
ISZ ADDR INCREMENT ADDRESS INDEX
ISZ ADDR **SKIP ONE ADDRESS
ISZ XVAL INCREMENT DAC INDEX
LDA XVAL
OTA DAC STEP X-AXIS SWEEP
ISZ PCNT IS SCAN COMPLETE?

WAIT JMP * NO, WAIT FOR TBG INTERRUPT

* PROCEED IF SCAN COMPLETED
CLF 0 YES, DISABLE INTERRUPT SYSTEM
CLC TBG,C DISABLE TBG
CLC ADC,C DISABLE ADC
JSB #PRTK RESTORE MEMORY PROTECT
LDA =B10000
OTA DAC X-AXIS TO ZERO
CLA
OTA DAC Y-AXIS TO ZERO

* OUTPUT SCAN NO. TO VIDEO TERMINAL
ISX SHOULD SCAN NO. BE OUTPUT?
JMP SKIP NO, SKIP
LDX D-10 YES, PREPARE TO OUTPUT EVERY 10TH SCAN COUNT
JSB #CLOS
JSB DECOD SCNT TO ASCII
JSB #OPEN
LDA =B120000 PREPARE TO WRITE ON TERMINAL
OTA TTY
LDA =B15 CARRIAGE RETURN
OTA TTY
STC TTY,C
SFS TTY
JMP #-1
LDA =D-3
STA CPCNT

NUMB LDA CADDR,I
ALF,ALF ROTATE.BYTES
AND =B377 MASK
OTA TTY OUTPUT NUMERAL
STC TTY,C
SFS TTY
JMP #-1
CLC TTY,C
LDA CADDR,I
AND =B377 MASK
OTA TTY OUTPUT NUMERAL
STC TTY,C
SFS TTY
JMP #-1
ISZ CADDR
ISZ CPCNT
JMP NUMB

* SKIP NOP
STF 0
* CHECK FOR POSSIBILITY OF OVER FLOW ON NEXT SCAN
JSB INIT
CLA
STA MIN2
STA MAX2
LM
LDA ADDR,I FIND MAXIMUM
SSA
IS NO. NEGATIVE?
JMP NEG
YES
ADA MAX2
NO, ADD CURRENT +VE MAXIMUM
SSA
JMP NEXT
LDA ADDR,I
CMA,INA
STA MAX2
JMP NEXT
NEG, CMA,INA
ADA MIN2
SSA
JMP NEXT
LDA ADDR,I
STA MIN2
NEXT
ISZ ADDR
ISZ ADDR
ISZ PCNT
JMP LM
LDA MAX1
CMA,INA
ADA MAX2
CLO
ALS,ALS
ADA MAX2
SOS C
IS AN OVERFLOW LIKELY?
JMP *+2
NO, PROCEED
JMP OVER
YES, GO TO DIVIDE ROUTINE
LDA MIN1
CMA,INA
ADA MIN2
CLO
ALS,ALS
ADA MIN2
SOS C
JMP 02
OVER
ISZ NOVER
CCA
ADA NOVER
LDB ARSE
SLA
LDB ARSES

**SKIP ONE ADDRESS

START DIVIDE ROUTINE

SKIP IF "A" EVEN
ADA SHFTA
STB OB, I
JSB INIT
01
LDA ADDR, I
ARS
STA ADDR, I
ISZ ADDR
ISZ ADDR
ISZ PCNT
JMP 01
LDA MAX2
LDB MIN2
ARS
BRS
JMP *+3
02
LDA MAX2
LDB MIN2
STB MIN1
STA MAX1
OLD MAXIMUM
LDB NOVER
ADB EXOV
SSB
OVERFLOW LIMIT REACHED?

* START NEW SCAN
JMP START

NO, START NEW SCAN

* OVERFLOW LIMIT
CLO
YES, STOP SCANNING
STC SKLOK, C
ENABLE SYSTEM CLOCK
LDA =B120000
OTA TTY
PREPARE TO WRITE ON TTY
JSB #PRINT
RESTORE INTERRUPT CELL CONTENTS
JSB REBUF
RE-BUFFER TERMINAL
JSB EXEC
MESSAGE TO TERMINAL
DEF *+5
DEF .2
DEF .7
DEF LIM
(OVERFLOW LIMIT)
DEF .8
JMP TERM

* INTERRUPT ROUTINES

TTYR NOP
TTY INTERRUPT
CLC TTY, C
JSB #PRTK
STA SAVE
LDA =B100000
OTA 1, C
LDA SAVE
JMP TTYR, I

TBGR CLF TBG
TBG INTERRUPT
ISY
LIA ADC
STC ADC,C  RE-START ADC
LDY DCNTR
JMP PROC

ADCR NOP   ADC INTERRUPT
CLC ADC,C
JMP ADCR,I

* BINARY TO DECIMAL CONVERSION ROUTINE *

DECOD NOP
JSB $LIBR
NOP
LDA SCNT
CCE
JSB $CVT3
STA CADDR
JSB $LIBX
DEF DECOD

* NORMAL EXIT *

FINIS CLC TTY,C
CLC ADC,C
CLC TBG,C
STC SKLOK,C  ENABLE SYSTEM CLOCK
LDA #20000  PREPARE TO WRITE ON TERMINAL
OTA TTY
JSB #RINT  RESTORE RTE INTERRUPTS
JSB REBUF  RE-BUFFER TERMINALS
JSB EXEC   MESSAGE TO TERMINAL
DEF *.5
DEF .2
DEF .7
DEF FIN   (FINISHED)
DEF .5
JMP TERM

* OVERFLOW EXIT *

OVERF CLF 0
CLC TTY,C
CLC ADC,C
CLC TBG,C
STC SKLOK,C  ENABLE SYSTEM CLOCK
LDA =B120000  PREPARE TO WRITE ON TERMINAL
OTA TTY
JSB #RINT
JSB REBUF  RE-BUFFER TERMINAL
JSB EXEC   MESSAGE TO TERMINAL
DEF *.5
DEF .2
DEF .7
DEF .4
JMP SWEEP,I EXIT

* ABORT EXIT *

OUT JSB #OPEN
CLC TBC,C
CLC ADC,C
CLC TTY,C
STC SKLOK,C
LDA =B120000 PREPARE TO WRITE ON TERMINAL
OTA TTY
JSB #RINT RESTORE RTE INTERRUPTS
CGA
ADA SCNT
STA SCNT
OTA .1,C
JSB REBUF REBUFFER TERMINAL
JSB EXEC
DEF .4+5
DEF .2
DEF .7
DEF ABORT (ABORTED)
DEF .5
JMP TEND EXIT

* MAXIMIZE ARRAY BEFORE EXITING *

TERM NOP
NLP1 JSB INIT
LDA PCNT
ALS
STA PCNT POINT COUNT x 2.
CLO
NLP2 LDA ADDR,I GET DATUM
ADA ADDR,I DOUBLE IT
SOC IS THERE AN OVERFLOW ?
JMP NMAX YES, JUMP TO PROCESSING ROUTINE
STA ADDR,I NO, SO STORE DOUBLED DATUM
ISZ ADDR SET NEXT ADDRESS
ISZ PCNT END OF THE ARRAY ?
JMP NLP2 NO, SO PROCESS NEXT NUMBER
JMP NLP1 YES, START NEXT PASS
NMAX LDA ADDR FIND ADDRESS
CMA;INA AT WHICH
ADA ASTRT OVERFLOW OCCURRED
SZA,RS EXTRA AT FIRST POINT ?
JMP TEND YES, SO EXIT
STA PCNT NO, SO STORE POINT NO.
LDA ASTRT SET START ADDRESS
STA ADDR OF ARRAY
NLP3 LDA ADDR,I GET DATUM
STA ADDR,I       AND REPLACE
ISZ ADDR       NEXT ADDRESS
ISZ PCNT       END OF PARTIAL ARRAY ?
JMP NLP3
TEND JSB DECOD   DECODE NO. OF SCANS
LDA CADDR,I
STA ACNT
ISZ CADDR
LDA CADDR,I
STA ACNT+1
ISZ CADDR
LDA CADDR,I
STA ACNT+2
JSB EXEC       MESSAGE TO TERMINAL
DEF *+5
DEF .2
DEF .7
DEF ACNT       (NO. OF SCANS)
DEF .6
JMP SWEEP,I


*      *      *      *
INITIALIZATION ROUTINE
*      *      *      *
INIT NOP
LDA NPTS,I
CMA,INA
STA PCNT       POINT COUNTER
LDA ASTRT
STA ADDR       ADDRESS INDEX
JMP INIT,I


*      *      *      *
UNBUFFER CONSOLE & TERMINAL
UNBUF NOP
LDA UBUFR
STA UBUFR
LDA UBUFR+1
STA UBUFR1
LDA UBUFR+2
STA UBUFR1+1
LDA UBUFR+3
STA UBUFR1+2
JSB MESSS
DEF *+3
DEF UBUFR1
DEF .9
JSB MESSS
DEF *+3
DEF UBUFR7
DEF .7
JMP UNBUF,I


REBUF NOP
JSB MESSS
DEF #+3
DEF RBUF1
DEF .9
JSB MESSS
DEF #+3
DEF RBUF7
DEF .7
JMP REBUF,I

* INTERRUPT STATEMENTS *

ORB
INTBG JMP INT1,I
INT1 DEF TBGR
INADC JSB INT2,I
INT2 DEF ADCR
INTTY JSB INT4,I
INT4 DEF TTYR
ORR

* CONSTANTS *

UBUF5 ASC 5,EQ,2,0,UN
UBUF1 BSS 6
UBUF7 ASC 4,EQ,3,UN
RBUF1 ASC 5,EQ,2,0,BU
RBUF7 ASC 4,EQ,3,BU
FIN OCT 6412
ASC 4,FINISHED
XOVER ASC 4,OVERFLOW
LIM OCT 6412
ASC 4,OVERFLOW LIMIT
ABORT OCT 6412
ASC 4, ABORTED
ACNT BSS 3
ASC 3, SCANS
ASTOR DEF 'STOR'
SHFTA DEF SHFTS
ARSE ARS
ARSES ARS,ARS
EXOV DEC -6
.1 DEC 1
.2 DEC 2
.3 DEC 3
.4 DEC 4
.5 DEC 5
.6 DEC 6
.7 DEC 7
.8 DEC 8
.9 DEC 9
STORAGE

NOVER BSS 1
RETRN BSS 1
ASTRT BSS 1
PCHR BSS 1
DCNTR BSS 1
MIN1 BSS 1
MIN2 BSS 1
ADDR BSS 1
XVAL BSS 1
MAX1 BSS 1
MAX2 BSS 1
SAVE BSS 1
SCNT BSS 1
CPCNT BSS 1
CADDR BSS 1

END
END$