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ION MOLECULE REACTIONS: CORRELATION TIME-OF-FLIGHT ION SPECTROSCOPY AND THE $\text{CO}_2^+ - \text{H}_2$ SYSTEM

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ION MOLECULE REACTIONS:
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ABSTRACT

A time-of-flight analysis system for measurement of velocity distributions of the ionic products of gas phase ion-molecule reactions was developed. The system employed pseudorandom binary noise for ion source modulation, coupled with detector crosscorrelation for extraction of velocity distribution spectra. Crosscorrelation was accomplished by direct memory access storage of coded correlation information by a PDP 8/i minicomputer with subsequent application of a decoding algorithm for transformation of accumulated data.

Maximal length shift register sequences were utilized for ion source modulation. The modulation code sequence was transduced for beam gating by an electrostatic deflection beam chopper. Storage of the modulation sequence for later crosscorrelation was accomplished with a variable length digital delay line. The hardware options of the computer correlation interface were controlled by a software implemented, keyboard controlled system monitor computer program.

The time-of-flight system was applied to an existing ion beam apparatus for measurement of N^+ , N_2^+ , and Kr^+ ion velocity distributions. Measured N_2^+ distributions agreed well with retarding potential energy analysis measurements. The Kr^+ velocity distribution clearly resolved

mass peaks due to three naturally occurring isotopes.

In a separate series of experiments, intensity distribution maps of the products of the $\text{CO}_2^+ + \text{H}_2$ reaction were measured over an initial CO_2^+ laboratory energy range of 25-250 eV. At low energies there was strong evidence of long lived intermediate complex formation. With increasing relative energy there occurred a transition to a direct spectator stripping mechanism.

Intensity distributions for six ionic products were measured at various relative energies. DCO_2^+ product distributions reflected a large amount of direct interaction formation even at low energies, although the broad distribution at low energy suggested an intensity contribution from complex formation. With increasing energy DCO_2^+ distributions continually reflected a larger proportion of formation by direct stripping interaction up to 10 eV relative energy. Above 10 eV significant intensity loss due to product dissociation was noted accompanied by forward movement of the product intensity peak indicating product stabilization by forward recoil.

The DCO^+ product distributions displayed the symmetric behavior of complex formation at low energy. Increasing energy led to distribution asymmetry and forward peak movement. High energy distribution peaks and intensity levels were explained in terms of two stripping mechanisms. Nonreactive CO_2^+ distributions showed broad inelastic intensity even at low relative energies, in contrast with CO_2^+ scattered nonreactively by He. This was further evidence for low energy complex formation and showed significant translation to vibration energy transfer.

CO^+ and O^+ product distributions showed a collisional dissociation mechanism. OD^+ distributions showed forward scattering and low intensity.

No D_2O^+ product was noted at any energy studied.

The $CO_2^+ + H_2$ product distributions were analyzed in terms of molecular orbital correlation diagrams. There was reasonable qualitative agreement between theoretical expectations and experimental results.

INTRODUCTION

Although the majority of chemical reactions which occur naturally result from collisions between neutral molecules, for a number of years chemists have studied ion-molecule reactions in an effort to elucidate the basic dynamic mechanisms important in all chemical reactions.¹ With the aid of molecular beam apparatuses, physical chemists have been able to measure differential cross-sections for the production of ionic products in ion molecule reactions. Analysis of these intensity distribution maps have contributed much to the understanding of dynamic interactions and the effects of potential energy surfaces for intermolecular collisions.

Experimentally, product distributions for ion-molecule reactions are most often measured with energy bandpass analysis systems (energy filters). However, it is often convenient to measure product velocity distributions using a time-of-flight (TOF) principle. The first part of the thesis is devoted to the development of such a TOF system. This version of the TOF method employs an ion beam coding algorithm with a companion detector decoding system (cross correlation). The system relies on the use of a minicomputer for data information storage; it is an adaptation of a method which has been applied previously for measurement of neutron reactor response functions.²

The initial discussion deals with the construction of the TOF experimental system for study of ion-molecule reactions. It includes a presentation of the theory behind this type of experimental measurement as well as logical, electronic, and computer oriented descriptions of the actual implementation of this method.

The experimental results obtained with the computer correlation system indicate that correlation TOF analysis has a place in the study of ion-molecule reactions. In fact, it is our feeling that this type of system will find broad application in a variety of experimental disciplines including biological science. Although the principles of the method are well known in engineering circles, it is only in the last several years that dissemination of the necessary information to other disciplines has begun. It is entirely possible that in the future this method may find a degree of acceptance comparable to that achieved by Fourier transform analysis in recent years.

In contrast, the second section of the thesis (Chapter IV) presents a series of experimental measurements made with an existing energy band-pass system. The $\text{CO}_2^+ + \text{H}_2$ chemical system was studied at a variety of initial CO_2^+ energies and the product distributions for six ionic products were analyzed in terms of kinematic models (intermediate complex formation vs direct interaction), thermodynamic data and molecular orbital correlation diagrams. The experimental results were found to be amenable to such analysis and provide an example of how it is possible to visualize a more complicated reaction process in terms of basic electronic and dynamical principles. The results also provide a further understanding of the limits placed on the interpretation of reaction systems by electronic correlation diagrams.

While the two sections of the thesis are somewhat independent, each reflects an important aspect of the process of analysis of chemical reactions. The improvisation of experimental measurement systems is an integral part of the process of product analysis. There is thus an

underlying unity to the discussions presented.

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CHAPTER I

ION BEAM EXPERIMENTATION

Molecular and ion beam experiments as a class employ a collimated beam of reactant particles which are directed onto a gas phase target species with subsequent detection of reaction products as a function of product-mass, -scattering angle, and -velocity. The velocity vector of the initial beam particles serves to define a zero degree scattering angle and to scale the final distribution of product velocities. Most often, a series of experiments is conducted during which the initial laboratory energy of the projectile particles is varied, changing the amount of relative translational energy available to the reaction partners. The measured angular-velocity distributions, when viewed as a function of initial projectile energy, serve to elucidate and support some possible kinematic mechanisms for the reaction while excluding others.

Since the object of the present investigation is ion beam reactions, we will deal explicitly with this case. As ions are electronically charged, mass and energy analysis are considerably simplified over the neutral case, although the experimentally attainable energetic range is limited from below by focusing and space charge considerations.

For the purposes of describing a typical ion beam experiment^{*}, we suppose that an ion A of mass M_A and laboratory velocity $\vec{V}_A$ is directed toward a neutral target molecule BC of mass M_{BC} and thermal laboratory velocity $\vec{V}_{BC}$ and which is contained in a fixed target scattering cell.

*For a more complete description, see Chapter IV.

The most convenient method for analyzing such a reaction is the construction of an appropriate velocity vector diagram (Fig. 1). In this diagram the assumption has been made that since a typical projectile ion velocity is $\geq 10^6$ cm/sec while the target molecule has a low thermal velocity, $\vec{v}_A \gg \vec{v}_{BC}$, and we can approximate $\vec{v}_{BC}$ by C. The total momentum of the system is then $M_A \vec{v}_A$, which is of course conserved throughout the reaction.

Though experiments are carried out in a laboratory frame of reference, theoretical analysis is considerably simplified if the reaction is viewed in a center of mass (C.M.) coordinate system. The C.M. coordinate system is a frame of reference which moves with the velocity of the center of mass for the system of colliding particles; an observer in this frame of reference would say that the total net momentum for all the particles in the system was zero. In the present case the velocity of the center of mass is

$$\vec{v}_{CM} = \frac{M_A}{M_A + M_{BC}} \vec{v}_A$$

Since the relative velocity of A with respect to BC is fixed (equal to $\vec{v}_A$), in the C.M. coordinate system the laboratory velocity of A will be divided between A and BC (Fig. 1) with^{*}

$$\vec{u}_A = \frac{M_{BC}}{M_A + M_{BC}} \vec{v}_A$$

*"v" is used here to denote laboratory velocity while "u" denotes velocities measured with respect to the velocity of the center of mass. A prime (') denotes a vector after an intermolecular collision.

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Fig. 1. A velocity vector diagram for $A^+ + BC$.

$$\underline{u}_{BC} = - \frac{M_A}{M_A + M_{BC}} \underline{v}_A = - \underline{v}_{cm}$$

$$\underline{v}_{rel} = \underline{u}_A - \underline{u}_{BC} = \underline{v}_A.$$

Following a nonreactive collision, the vector $\underline{u}_A$ will be rotated about the center of mass as a result of deflecting intermolecular interactions. In general, $|\underline{u}'_A| \neq |\underline{u}_A|$ due to inelastic or superelastic collision processes. (Since only ionic products can be detected, the final vector of BC, $\underline{u}'_{BC}$, is of no fundamental interest.) The vector $\underline{u}'_A$ will describe the motion of A after the collision, A having been scattered through a C.M. angle χ . Viewed from the laboratory frame, the scattered ion will be found at an angle θ with a velocity $\underline{v}'_A$.

Experiments in the laboratory measure ion intensity as a function of $\underline{v}'_A$ and θ . Transformation of the results to a C.M. picture gives a typical scattering map (Fig. 2) which plots intensity contours in a $(\underline{u}'_A, \chi)$ representation. In a similar manner, reactive products (i.e. $A^+ + BC \rightarrow AB^+ + C$) are also mapped, the only difference being a change in the mass which is selected for detection by a quadrupole mass filter.

There are two alternative methods of constructing the two dimensional $(\underline{u}'_A, \chi)$ intensity contour map which represents relative scattering probabilities. One method, that of energy or velocity bandpass, consists of measurement of product ion intensities at a large number of discrete $(\underline{v}'_A, \theta)$ points by the use of angular and velocity (energy) filters. After coordinate transformation, the intensities are recorded in

Fig. 727-6544

Fig. 2. A typical product velocity distribution map. The center of the map corresponds to the velocity of the center of mass of the system. Angles are specified in the center of mass frame of reference. Contours represent points of equal intensity. Beam profile is full width at 20% maximum.

a (u_A^i, χ) coordinate system and contours constructed by connecting points of equal intensity by interpolation.

The angular filter used in the bandpass method consists of a mechanical aperture in front of the detector restricting the solid angle viewed by the detector. The complete detector assembly is designed to rotate through a wide range of laboratory scattering angles, viewing only an "infinitesimal" cone of scattering at each angle.

A wide variety of energy and velocity filters have been devised, including spherical and cylindrical electrostatic energy analyzers, Wien filters, retarding potential filters, or (in the case of neutral products) slotted disc velocity selectors. The advantage of the bandpass system is that its measurements are made in a nondynamic manner making them easily reproducible. Further, the system is amenable to comparatively straightforward data analysis. A disadvantage of the system is the large number of discrete measurements which are required to construct a scattering map.

A second method is that of time-of-flight (TOF) analysis. While this method also uses angular definition to restrict the solid angle of scattering viewed by the detector, it employs a different mode of energy analysis. This method measures the distribution of arrival times for pulses of ions which are admitted to the apparatus. As such, the TOF system does not explicitly employ any energy filtering system; rather, ions of all energies are detected as a function of arrival time at the detector and the arrival time used to characterize the energy distribution of detected ions (at a fixed scattering angle). Thus, a TOF measurement provides a one dimensional slice through the scattering intensity

distribution along a constant laboratory angle ray (i.e. a slice taken perpendicular to the plane of the page in Fig. 2). In contrast with the energy bandpass system then, a TOF system produces data as a "continuous" one dimensional distribution of product intensity rather than as a series of discrete points.

The TOF system employs a time domain measurement rather than one in energy domain. Using a beam chopping device (see below), a short pulse of projectile beam particles is emitted into a reaction chamber. This initial beam pulse contains ions with a narrow distribution of velocities, $f(V)$, characteristic of the initial beam composition (weighted by $N(V) \sim Vf(V)$ by flux considerations). Soon after emission, the pulse ions interact with the target molecules causing chemical reactions as well as elastic and inelastic processes, all of which alter the initial narrow velocity distribution. The resulting product ions enter an interaction-free drift region in which products with different velocities become separated spatially. A mass filter then removes all product ions except those of the desired mass. Subsequently these ions of all velocities are detected as a function of arrival time at the detector which has been stationed at a predetermined laboratory scattering angle. (The arrival time is measured with respect to the time of initial beam pulse emission.) Using the known path length through the apparatus, the distribution of product arrival times is converted to a corresponding product ion velocity distribution. By measuring this distribution for a single ion product at several laboratory scattering angles, a complete (u_A', χ) contour map is developed. The advantage of the TOF system is the relatively small number of measurements necessary to determine an

intensity distribution.* The disadvantage of the system is that the dynamic nature of the measurement makes the results susceptible to subtle dynamically induced measurement errors and more complicated data reduction schemes.

The object of our current investigation has been the analysis and construction of a modified TOF system. This method, termed "correlation time-of-flight", employs an information coding algorithm by which the initial ion beam is modulated with pseudorandom binary noise and the velocity distribution later extracted by digital cross correlation. After a brief description of the mechanics of classical TOF spectroscopy, we will examine in detail the theory and application of correlation TOF, and will describe a computer based implementation of such a system.

*Although the number of experimental measurements is smaller than that required with a bandpass system, the net number of discrete data points (data information) required to construct a scattering map is the same for both methods.

CLASSICAL TIME OF FLIGHT SPECTROSCOPY

In order to present a discussion of correlation spectroscopy, it is first necessary to discuss the classical time of flight method. Classical TOF spectroscopy has previously been applied primarily to neutral projectile systems. Beam sources are typically thermal ovens, supersonic nozzles, or slow neutron sources.¹ The electrically neutral nature of the projectiles and their relatively low velocities have encouraged the use of mechanical beam choppers, such as the slotted disc chopper, for admitting short pulses of beam particles into the reaction chamber.

In a typical neutral beam experiment, a slotted disc beam chopper consisting of a rotating disc with one or several radial slits machined on its periphery is placed in front of a beam source. As the disc rotates at high angular speed, each time a slot passes over the cross section of the beam, a short pulse of beam particles passes through the aperture and into the reaction chamber. Often, the slot is also used to trigger a photodiode which resets a time of flight clock such as a time-to-pulse height converter² (Fig. 3).

As the beam particle pulse travels through the apparatus, the pulse height of the converter ramp voltage increases linearly with time until the arrival of a particle at the detector triggers a stop pulse. The time of arrival is recorded by storing the height of the time-to-voltage pulse in a multichannel analyzer. Repetition of this process leads to accumulation of a distribution of pulse heights in the multichannel analyzer which represents the overall TOF spectrum.

There are many variations of this method. Each employs a chopper, time of flight clock, projectile interaction and projectile drift regions,

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Fig. 3. Pulse height analysis in Classical TOF spectroscopy.

and a time of flight storage device.

The theoretical analysis of the TOF system is rather straightforward.³
The steady state beam flux from the beam source is given by¹

$$I_0 = \int_0^{\infty} J(s) ds = \gamma n \int_0^{\infty} s f(s) ds$$

where I_0 = total beam flux

γ = most probable velocity

(u = molecular velocity)

$s = u/\gamma$ = dimensionless molecular velocity

n = number density of molecules in the beam

$f(s)$ = beam velocity distribution function

$J(s)$ = flux of beam molecules with velocities between s and $s+ds$.

As the beam chopper slit passes over the beam, an instantaneous cross sectional area of the beam, $A(t')$ is admitted through the slit ($t = t' = 0$ is taken when the slit first allows beam particles to pass^{*}). The resulting signal measured at the detector is given by³ (for a flux sensitive detector)

$$I(t) = \int_0^t J(s) \frac{L}{\gamma(t-t')^2} A(t') dt'$$

where L = the flight path length and the factor $L/\gamma(t-t')^2$ is a Jacobian factor between ds and dt' . The quantity of interest here is the

* t = detector time variable; t' = chopper time variable

measured velocity distribution function $f(s)$ which is contained in the differential flux, $J(s)$. Since the measured detector signal is a convolution of the gate function and the final velocity distribution, the measured TOF distribution must be deconvoluted using numerical approximation, moment analysis (Laplace Transform),⁴ Fourier Transform inversion,⁵ or integration fitting methods.⁶

The resolution of a TOF experiment is inversely proportional to the width of the shutter function.⁷ Ideally one wishes to use an extremely narrow "delta-function" gate signal for maximum resolution and to minimize the problems associated with TOF deconvolution. Unfortunately, detector signal intensity is linearly proportional to the width of the gate function and the ensuing tradeoff between intensity and resolution sets a practical maximum on the time resolution possible in any experiment.

Hagerra and Varma⁷ have calculated that for a flight time Δt and shutter function width τ , the resolution, $R = \frac{\Delta t}{\tau}$, necessary to achieve a TOF half width error of less than 2.5% is $R \geq 5$. This is readily attained in most experimental systems by choosing a flight path long enough to increase Δt sufficiently to achieve the desired resolution.

Young⁸ has recently pointed out that the measured TOF distribution also contains a convolution of a detector response function and the TOF signal arriving at the detector. The importance of the detector response depends on the relative time constants for the TOF distribution and the detector response time. In the present system, this factor is of negligible importance.

TOF systems have been used to study ion-molecule reactions as well as neutral molecule reactions. Paulson et al.⁹ have used a TOF double

mass spectrometer to study the reactions of Ar^+ , CO^+ and CO_2^+ . A similar system has been reported by Maier and Murad¹⁰ for the study of the reactions of N^+ with N_2 . A TOF system using a fast cesium ion charge exchange source has been described by Leffert.¹¹ Dittner and Datz¹² have used a TOF system for the analysis of inelastic and dissociative processes resulting from Na^+ and K^+ ions colliding with H_2 and D_2 . Toennies et al.¹³ have reported similar experiments using Li^+ over an energy range of 6-60 eV.

Though TOF has been applied to ion-neutral systems, the method has not come into general use. The single most important reason for this is the problem of chopping fast ions at a sufficiently high rate. Also, bandpass analysis systems have been highly developed in the ion beam field.

We have seen that the classical TOF system provides a useful alternative to energy bandpass systems. In the next chapter we will present a detailed discussion of the similar correlation time of flight system which is a logical refinement of the classical system.

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CHAPTER II

CORRELATION TIME-OF-FLIGHT SPECTROSCOPY

While the classical time-of-flight method is adequate for experimentation with relatively intense ion or neutral beams and with favorable signal to noise ratio (S/N), the system becomes less applicable as signal intensities decrease or as relative background levels increase. These fallibilities result from the small duty cycle (0.5-1%) necessary to achieve reasonable (<5%) experimental resolution. (The duty cycle of a beam apparatus is defined as the time fraction during which the beam is effectively turned "on.") A small duty cycle, which reduces the net particle flux by a factor of 100, accompanied by an unfavorable S/N ratio or small scattered ion intensity necessitates very long data acquisition times to accumulate a signal with acceptable statistical properties.

The use of a correlation TOF system avoids these pitfalls. The correlation method permits a duty cycle of at least 50%; this, coupled with the exclusion of uncorrelated noise, allows experimental measurements to be made in the face of adverse S/N ratios (as small as 10^{-3} or 10^{-4})¹ or in the case of small scattered ion intensities.

In this chapter, we will discuss the theory of correlation detection in detail. First, the TOF system is described in the language of linear systems analysis. There follows a discussion of random input modulation with subsequent output crosscorrelation for characterizing the response function for the TOF linear system. A description of correlation functions and their properties is given. The generation of m-sequences for experimental modulation, and the properties of such sequences are discussed. Next, the theory of the correlation method for beams is derived

and the experimental methods for applying correlation detection are reviewed. A description of our current computer based correlation system is presented along with a summary of the statistical analysis of the correlation method.

Time of Flight as a Linear System

In a time of flight experiment, a narrow, impulsive input (beam pulse) is applied to an experimental system. The molecular interactions with target molecules and the spatial distribution of product ions are, to first approximation, linear processes which act on the impulsive input to generate the measured system output (TOF function). As such, the TOF system can be analyzed as a constant parameter linear system.² Any such system is rather completely characterized by a weighting function, $h(t)$, (or impulse response function) which describes the output of the system at a time t after application of a unit impulse at the system's input (Fig. 4). In the case of the TOF system, the impulse response, $h(t)$, describes the spatial (and hence temporal) smearing of an impulsive input of source particles as the particles undergo collisions and drift toward the detector.

Using the principle of superposition, for a constant parameter linear system the output generated for any arbitrary finite system input is described by the convolution integral,

$$y(t) = \int_0^{\infty} h(t')x(t-t')dt' \quad (1)$$

The convolutional lower limit is taken as $t' = 0$ rather than $t' = -\infty$ since in order for physical causality to hold, $h(t') \equiv 0$ for $t' < 0$.

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Fig. 4. The response of a simple linear stationary system.

Some further properties of $h(t)$ have fundamental importance but are practically always satisfied. For a stable system $h(t)$ is absolutely integrable, i.e.

$$\int_0^{\infty} |h(t)| dt < \infty$$

and for a bounded system input the output will also be bounded. A necessary and sufficient condition for system stability is that the transfer function of the system defined by

$$H(p) = \int_{-\infty}^{\infty} h(t)e^{-pt} dt \quad p = a + iv$$

(the Laplace transform of the response function) have no poles in the RHP or on the imaginary axis.² For a physical system this is equivalent to a finite system frequency response (gain) at all frequencies.

Since measurement of any real system's output (including TOF) will include detection of random noise, $b(t)$, the detector output is

$$y'(t) = y(t) + b(t). \quad (2)$$

The object of our investigation is that, given $y'(t)$ as a measured detector output, we wish to remove all random noise and determine the system response function, $h(t)$, which is equivalent to the TOF spectrum.

In classical TOF experiments, the input is characterized by widely spaced narrowly shaped pulses which approximate a delta function.³ Thus

$$y(t) = \int_0^{\infty} \delta(t-t')h(t')dt' \approx h(t) \quad (3)$$

By measuring signal and noise and noise separately, $b(t)$ is calculated and subtracted:

$$h(t) = y'(t) - b(t) \quad (4)$$

and the TOF spectrum is thus determined.

Correlation Functions

As background for discussion of correlation TOF, we now review the properties of correlation functions. A correlation function is a joint moment which measures the similarity between two waveforms (functions) as a function of their relative displacement in time with respect to one another. The correlation function is calculated for each temporal displacement by integrating the product of the displaced waveforms over all time. For any given time displacement, two waveforms which are similar will have a large positive correlation, while dissimilar waveshapes will lead to a small positive or negative correlation. In general, as the displacement time is varied, both the relative similarity of the waveforms and their correlation function will change. The correlation function for repetitive waveforms will be repetitive.

There are two general types of correlation functions. An auto-correlation function of a function, $x(t)$, denoted by $R_{xx}(\tau)$, is a measure of similarity between the function $x(t)$ and a version of itself displaced

by a time τ . Mathematically,

$$\begin{aligned}
 R_{xx}(\tau) &= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T x(t) x(t+\tau) dt \\
 &= \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N x(j\Delta t) x(j\Delta t + \tau)
 \end{aligned} \tag{5}$$

where the latter description is used for a discrete parameter function and the former for the continuous parameter case.* Examples of some autocorrelation functions are shown in Fig. 5.

Some of the properties of the autocorrelation are:⁴

- (1) $R_{xx}(\tau) = R_{xx}(-\tau)$
- (2) $R_{xx}(0) \geq |R_{xx}(\tau)| \forall \tau$
- (3) $\overline{x^2} = R_{xx}(\tau=0)$

A crosscorrelation function measures the similarity between two different waveforms. For two functions $x(t)$ and $y(t)$ the crosscorrelation as a function of time displacement τ is

$$\begin{aligned}
 R_{xy}(\tau) &= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T x(t) y(t+\tau) dt \\
 &= \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N x(j\Delta t) y(j\Delta t + \tau)
 \end{aligned} \tag{6}$$

A crosscorrelation of two seemingly unrelated waveforms can be used to

*See Random Process Appendix.

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Fig. 5. Some examples of autocorrelation functions (after Bendat⁴).

determine whether they are related by a linear system; if they are related, the correlation will allow determination of the time delay between the input and output of the system.

Some properties of the crosscorrelation are:⁴

- (1) $R_{xy}(-\tau) = R_{yx}(\tau)$
- (2) $|R_{xy}(\tau)|^2 \leq R_{xx}(0)R_{yy}(0)$
- (3) $|R_{xy}(\tau)| \leq \frac{1}{2} [R_{xx}(0) + R_{yy}(0)]$

If for some delay τ , $R_{xy}(\tau) = 0$, $x(t)$ and $y(t)$ are said to be uncorrelated (assuming the means, $\mu_x = \mu_y = 0$); if $R_{xy}(\tau) = 0$ for all τ , the two functions are statistically independent.

Impulse Response Determination

Using the concept of crosscorrelation we now derive the method of extracting the impulse response function for a linear system using system input modulation with output crosscorrelation.

Recall Eq. (1)

$$y(t) = \int_0^{\infty} h(u)x(t-u)du \quad (1)$$

where $x(t)$ is the input, $y(t)$ the output, and $h(u)$ the impulse response function. To extract the function $h(u)$, we compute the crosscorrelation of input and output, $R_{xy}(\tau)$ by multiplying both sides of (1) by $x(t-\tau)$ and integrating:

$$\begin{aligned} R_{xy}(\tau) &\equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T x(t-\tau)y(t)dt & \text{(LHS) (7)} \\ &= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T x(t-\tau)dt \int_0^{\infty} h(u)x(t-u)du & \text{(RHS)} \end{aligned}$$

$$R_{xy}(\tau) = \int_0^{\infty} h(u) du \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T x(t-\tau)x(t-u) dt \quad (8)$$

when change in integration order is justified because of the finite properties of the impulse response function. Changing the variable of integration in the latter integral

$$\begin{aligned} R_{xy}(\tau) &= \int_0^{\infty} h(u) du \lim_{T \rightarrow \infty} \int_0^T x(t'+u-\tau)x(t') dt' \\ &\equiv \int_0^{\infty} h(u) R_{xx}(u-\tau) du \end{aligned} \quad (9)$$

where the limits of integration are left unchanged since the autocorrelation function is relatively independent of which time interval is used for its computation. Note the similarity between Eq. (1), the deterministic input-output relation for a linear system, and Eq. (9), the analogous stochastic input-output relation.⁵

Assume for the moment that the system input, $x(t)$ can be chosen such that its autocorrelation function is of the form, $R_{xx}(\tau) = c\delta(\tau)$ for some constant, c ($\delta(\tau)$ is the Dirac delta function.) Then

$$R_{xy}(\tau) = c \int_0^{\infty} h(u) \delta(u-\tau) du = ch(\tau) \quad (10)$$

and for this type of input modulation, the measured crosscorrelation functions will be exactly proportional to the impulse response function

of the linear system under examination (TOF). It remains to determine which type of input modulation is necessary to achieve a delta function autocorrelation.

Broadband Noise

As illustrated in Fig. 5 (c and d), the width of the autocorrelation function of a noise signal is inversely proportional to the bandwidth of the signal. In the limit of infinite bandwidth, the autocorrelation function of a noise signal becomes vanishingly narrow, approximating a delta function. Such infinite bandwidth noise is called "white noise" and has a power spectral density function* which is a constant over all frequencies.

Although white noise is unphysical (it would require infinite power to generate), in practice one can approximate white noise to any desired degree by using finite broadband noise ("pink noise"). Pink noise, with its broad bandwidth, has a relatively constant power spectral density function within this bandwidth (Fig. 6). The corresponding autocorrelation function is finitely narrow (width a bandwidth⁻¹). To approximate a delta function autocorrelation to any desired degree, a sufficiently large bandwidth of random noise is chosen for system input modulation.

*The power spectral density function is the Fourier Transform of the autocorrelation function:

$$G_{xx}(f) = 2 \int_{-\infty}^{+\infty} R_{xx}(\tau) e^{-2\pi i f \tau} d\tau$$

(The two functions are related much the same as position and momentum in quantum mechanics.) $G_{xx}(f)$ describes the frequency composition of a signal $x(t)$ in terms of the spectral density of its mean square value, (Fig. 6).

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Fig. 6. Autocorrelation and Power Spectral Density functions for broadband and white noise.

For the case of TOF, we chose the bandwidth such that the width of $B_{xx}(\tau) \ll$ width of the TOF function.

In the following section we will investigate the application of random sequences for broadband source modulation.

M-SEQUENCES

For modulation of our linear TOF system input, we turn to the class of pseudorandom linear sequences. We will discuss the generating methods for maximal length sequences and investigate some of the properties of such sequences which favor their application to correlation spectroscopy.

We are primarily interested in binary noise sequences because experimentally there are only two possible states ("on" and "off") of the ion beam which is being modulated. While there exist many methods of generating truly random noise,^{6,7} we will deal exclusively with pseudorandom noise sequences; the former methods are more difficult to construct, allow little leeway in the area of control and are not as readily reproducible as pseudorandom methods. For these reasons the use of sequences generated by linear feedback of shift registers has found wide application.⁸

Of the sequences which can be generated by shift register feedback, the maximal length sequences (m-sequences) have been used exclusively. M-sequences have well known properties, a proportionately larger bandwidth and more evenly distributed signal statistics than those sequences generated by "short-circuited" feedback.

An m-sequence can be generated by the use of an n-stage linear shift register whose input is determined by modulo 2 summation of stage n and an intermediate stage(s), k, with $k < n$ (Fig. 7). The shift register is run by an external clock of period δ and frequency $\omega = \delta^{-1}$. In theory, the feedback for generation may consist of several loops¹⁰ or of pyramided registers with separate loops.¹¹ However, in most applications, as in the present one, a single register with a single loop and two stage

Fig. 7. Shift register configuration for m-sequence generation.

		X_k	
		0	1
X_n	0	0	1
	1	1	0

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Fig. 8. Exclusive OR Truth Table.

feedback is used. Determination of the necessary feedback circuits will be discussed later.

The two stage feedback is accomplished by an "exclusive or" gate which adds modulo 2. The function of an exclusive or gate is that its output will be logical "one" if and only if the states of the two inputs are different (one is a 1, one is a 0). Otherwise, the output is logical "zero." This is the characteristic of modulo 2 addition ($0 \oplus 1 = 1 \oplus 0 = 1$; $0 \oplus 0 = 1 \oplus 1 = 0$) (see Fig. 8). We note that for practical experimental electronic purposes a binary sequence consists of {0, 1} while for mathematical and computational the sequence is considered to be composed of {+1, -1}. As long as the use is consistent, there is no contradiction; because of the manner in which data is transformed the experimental {0} has the same effect as the computational {-1}.

The mechanics of the sequence generation are simple. Initially, the state of the shift register is some nonzero binary sequence, typically 100...0. During each external clock pulse, stages n and k of the register are sampled, added modulo 2, and the result applied to the input of stage 1. Then all stages are shifted one position (to the right in our culture) and stage 1 is occupied by the result of the modulo 2 addition. The final result is a sequence with one new bit and a displaced version of n-1 bits of the original sequence.

Each m-sequence has a well defined length. For an n-stage register there are 2^n possible states. However, one of the states 0^n forms a "kernel" of the sequence; that is, this state generates only itself and is generated only by itself. Thus once a non-zero sequence is placed in the register, it will remain nonzero throughout the sequence generation.

The $2^n - 1$ remaining states all appear once and only once during the period of the sequence leading to a nonrepetitive sequence $2^n - 1$ bits long. Thus the period of the sequence is $T = (2^n - 1)\delta \approx N\delta$ seconds long. By choosing the clock rate and the register length correctly, any "reasonable" bandwidth (determined by δ) and sequence period (N) can be achieved. The sequence is easily generated, completely reproducible and is well characterized. After the complete sequence has been generated, the initial shift register state will be repeated and the modulation will consist of repetitions of the unit sequence.

The theory of m-sequence generation has been thoroughly explored. M-sequences are part of a larger class known as "linear recurring sequences." In general, p-nary sequence (modulo p addition) generation is described by rings of primitive polynomials in an indeterminate, x, over a Galois Field of scalars. Although this general theory has contributed much to the understanding of simple binary sequences, we will not discuss it. The reader is referred to the sources in Ref. 12.

For the binary case, consider an n stage shift register which will be described by a state vector, $\vec{a} = (a_n, a_{n-1}, \dots, a_2, a_1)$ where $\{a_i\}$, contained in the set $\{0, 1\}$, are the bits of the register. The ordering of state bits is inverted because the first bit generated is contained in the last shift register stage. The mode of feedback (Boolean feedback function) is described by a weighting sequence, $(c_1, c_2, \dots, c_n)$ with $\{c_i\} \in \{0, 1\}$ where if $c_k = 1$, stage k is involved in the feedback loop.

Given an initial register sequence the state of the register at some later time is determined by the linear recurrence relation,

$$a_r = c_1 a_{r-1} \oplus c_2 a_{r-2} \oplus \dots + c_n a_{r-n} \quad (11)$$

where $\oplus$ denotes modulo 2 addition.

The operation of generating the sequence is said to be the result of an operator, T , which is the sum of a feedback operator, C , and a shift operation S .

$$\bar{T} = \bar{C} + \bar{S}$$

or in matrix notation:

$$\bar{T}_{n \times n} = \begin{bmatrix} 000 \dots 0 \\ 000 \dots 0 \\ \dots \dots \dots \\ 000 \dots 0 \\ c_1 \ c_2 \ c_3 \dots c_n \end{bmatrix} + \begin{bmatrix} 0100 \dots 0 \\ 0010 \dots 0 \\ 0001 \dots 0 \\ \dots \dots \dots \\ 0000 \dots 1 \\ 0000 \dots 0 \end{bmatrix} = \begin{bmatrix} 0100 \dots 0 \\ 0010 \dots 0 \\ \dots \dots \dots \\ 0000 \dots 0 \\ c_1 \ c_2 \ c_3 \ c_4 \dots c_n \end{bmatrix} \quad (12)$$

We represent the initial vector $\underline{a}_0$ by

$$\underline{a}_0 = \begin{bmatrix} a_n \\ a_{n-1} \\ \vdots \\ a_1 \end{bmatrix} \quad (13)$$

Then after k shift pulses the state of the register is given by:

$$\underline{a}_k = \bar{T}^k \underline{a}_0 \quad (14)$$

Since the output of the first register stage is used for experimental modulation, and since the sequential time history of stage 1 is equivalent to a state vector description, it is convenient to describe the sequence generated in terms of the stage 1 output. This output can

be associated with a generating polynomial, $G(x)$ by a one to one mapping¹³ defined by (assuming $c_n = 1$)

$$G(x) = \frac{1}{\left(1 - \sum_{r=0}^{\infty} a_r x^r\right)} = \frac{1}{\left(1 - \sum_{i=1}^n c_i x^i\right)} = \frac{1}{\left(1 + \sum_{i=1}^n c_i x^i\right)} \quad \frac{1}{\phi(x)} \quad (15)$$

where the third equality follows from the fact that in modulo 2 arithmetic, addition and subtraction are equivalent. The polynomial, $\phi(x)$ is the adjoint characteristic polynomial of the generating operator, "

$$\begin{aligned} \phi(x) &\equiv \det (T - x \cdot I) = |T - x \cdot I| \\ &= 1 \oplus c_1 x + c_2 x^2 + \dots \oplus c_n x^n = 1 + \sum_{i=1}^n c_i x^i \end{aligned} \quad (16)$$

where I is the identity matrix. The characteristic polynomial may also be represented as a series in D , an algebraic operator whose effect is to delay by one bit the variable on which it operates, each time it operates. (D can be viewed as a simple memory element with a one period delay, one input, and one output.)¹⁴

$$\phi(x) = x(1 + \sum_{j=1}^n D^j) \quad (17)$$

Thus the generating function (Eq. (15)) is given by

$$G(x) = x \left[\frac{1}{1 + \sum_{j=1}^n D^j} \right] \quad (18)$$

Equation (18) provides a prescription for determining the output sequence given the feedback coefficients $\{c_i\}$. The coefficients (1 or 0) are used to write out explicitly the generating function in terms of the Delay operator. Manual division will result in a polynomial in powers of D. The elements of the binary sequence whose sequence numbers appear as powers of D in the resultant polynomial will be ones; those whose sequence numbers do not appear as powers will be zero.

For clarification, we will use as an example the case of a four-stage shift register.¹⁴ The shift register configuration is shown in Fig. 9. The feedback is from stages 3 and 4. If we assume an initial sequence of 1000, the output of the first stage (a_k) will be (see Fig. 9 for state vectors)

$$100110101111000... \quad (N = 2^4 - 1 = 15)$$

For this configuration the characteristic polynomial is $\phi(X) = X^4 + X^2 + 1$ since $c_1 = c_2 = 0$, $c_3 = c_4 = 1$. Also $\phi(X) = x[I \oplus D^3 \oplus D^4]$. Then

$$G(X) = \frac{1}{(I \oplus D^3 \oplus D^4)} x = x [I \oplus D^3 \oplus D^4 \oplus D^6 \oplus D^8 \oplus D^9 \oplus D^{10} \oplus ...]$$

So the output sequence is

$$1(D^0), 0(D^1), 0(D^2), 1(D^3), 1(D^4) \dots$$

$$= 10011 \dots, \text{ the same as computed manually in Fig. 9.}$$

To ensure that the sequence generated by a shift register is maximal, the feedback connections must be chosen correctly. Failure to apply a proper feedback loop results in the loss of significant portions of the maximal sequence by "short cycling," that is restarting the sequence

Figure 9. A 4-stage shift register configuration

Initial state = 0000;

Enter "1" into a_1

with first shift pulse

Calculated state after k shift pulses

k = 0	a_1	a_2	a_3	a_4
1	1	0	0	0
2	0	1	0	0
3	0	0	1	0
4	1	0	0	1
5	1	1	0	0
6	0	1	1	0
7	1	0	1	1
8	0	1	0	1
9	1	0	1	0
10	1	1	0	1
11	1	1	1	0
12	1	1	1	1
13	0	1	1	1
14	0	0	1	1
15	0	0	0	1
16	1	0	0	0
:	:	:	:	:
:	:	:	:	:
:	:	:	:	:

before it has terminated. Tables of appropriate feedback connections have been published.¹⁵

The mathematical criterion for establishing maximal sequence generation is that the characteristic polynomial of the feedback configuration, $\phi(x)$, must be irreducible and primitive ($\phi(x)$ is a minimum polynomial of the m-sequence). A polynomial $p(x)$ of degree n is called irreducible if it is not divisible by any polynomial of degree less than n , providing that $p(x) > 0$. The polynomial $p(x)$ of degree n is said to be primitive if it does not divide $x^k + 1$ for $k < 2^n - 1$. (A primitive polynomial is also irreducible.)¹⁶ Since tables of primitive and irreducible polynomials are available,¹⁷ it is a simple matter to construct proper feedback connections for any reasonable length shift register.

Properties of M-Sequences

As mentioned above, an m-sequence contains $N = 2^n - 1$ bits and during the sequence each possible n -tuple (except 0^n) appears once and only once in the shift register. An m-sequence is an example of a "random telegraph wave"¹⁸ whose rate of zero crossings is described by a Poisson distribution (the m-sequence is often called a Poisson Square Wave). A picture of the m-sequence is shown in Fig. 10.

If the mean zero crossing rate for the random process is $m \text{ sec}^{-1}$, the Poisson law states that the probability of k crossings occurring during a time interval t is given by

$$P(k;t) = e^{-mt} \frac{(mt)^k}{k!} \quad (19)$$

Fig. 10. A section of a Poisson Square Wave.

This distribution describes the likelihood of the shift register output containing any given number of +1's or -1's during any interval.

The state of the m-sequence is +1 one half of the time, so the duty cycle of the sequence is 0.5. The sequence contains subsequences (runs) of all +1 or all -1 during which the shift register output remains unchanged. During the period of the sequence, one half of all runs are of length 1 (+1, -1), one quarter are of length 2 (+1 +1, -1 -1) and $1/k$ will be of length k $((+1)^k, (-1)^k)$. Furthermore, there are exactly as many runs of +1 of length k as there are runs of -1 of length k (except $(-1)^N = (0)^N$ which is excluded).

An m-sequence is closed under the operation of shift-and-add:¹⁹
for all $s \neq 0 \pmod{N}$, there exists an integer W_s such that if a_r is any bit of an m-sequence,

$$a_r \oplus a_{r+s} = a_{r+W_s} \quad (20)$$

The sequence $\{a_{r+W_s}\}$ is a shifted version of the original sequence.
(The set of sequences $\{\{a_r\}, r:1,N\}$ forms a K-module.)²⁰

The most important property of m-sequences is, for our application, the autocorrelation function. Recall that we wished to find an experimental modulation function which had an autocorrelation function which approximated a δ -function. A normalized representation of the autocorrelation function for an m-sequence of length $N = 2^n - 1$ (± 1 states) is shown in Fig. 11. This function consists of triangular peaks of height 1 and width 2δ at $\tau = 0 \pmod{N}$ and an intermittent background of height

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Fig. 11. Normalized autocorrelation function = $N = 2^n - 1$, sequence period = $N\delta$.

N^{-1} . By choosing δ small and N large, this correlation function becomes very much like a δ -function. For our application, $\delta \geq 5 \times 10^{-7}$ sec, $n = 20$, $N \approx 10^6$, so the autocorrelation function will consist of 1 μ sec wide peaks spaced 1 sec apart with a relative background level of 10^{-6} . The shape of the autocorrelation function was measured experimentally with an Hewlett-Packard 3721A Correlator and was found to conform to the expected shape. The width of the function, ~ 1 μ sec, should be easily adequate for measuring Time of Flight spectra of 30 μ sec duration and 10 μ sec total width.

Now that it is apparent that a suitable modulation sequence can be generated for extracting the TOF impulse response function, we proceed to derive explicitly how the impulse response method is applied to TOF spectroscopy.

THEORY OF CORRELATION DETECTION

Though we have discussed the general theory of impulse response determination by crosscorrelation, it remains to elucidate the theory of specific applications. To facilitate an understanding of the nature and origin of an experimentally measured correlation function and its components, we next present the mathematical theory of correlation detection as applied to beam systems. This theory provides the conceptual bridge between random experimental modulation and the computation of correlation functions.

We first suppose that the modulating m-sequence can be represented by a continuous function signifying a series of statistical pulses, x_i , placed randomly at unit time intervals, t_i :

$$x(t) = \sum_i x_i \delta(t-t_i) \quad (21)$$

The actual experimental modulation function is the convolution of this statistical function with the experimental beam pulse shape (gate function), $\phi(t)$:

$$M(t) = \int_0^{fT} x(t') \phi(t-t') dt' = \sum_i x_i \phi(t-t_i) \quad (22)$$

where T is the period of the m-sequence and fT is the total measurement interval.

Hossfeld has shown²¹ that the shape of the modulation pulse must be of a certain minimum symmetry type to ensure a proper δ -function autocorrelation and to avoid "input transducer error." This symmetry

condition is expressed (for all times, τ) as

$$\sum_j \phi_j (\tau - t_j) = 1 \quad (23)$$

Since the binary sequence always contains one more (+1) pulse than (-1) pulses, this condition requires that the trailing edge of a modulation pulse be the mirror image of the leading edge. Commonly used triangular (trapezoidal) and rectangular pulses shapes satisfy this condition inherently.

We also note that the discrete autocorrelation function for the statistical sequence can be written in terms of the duty cycle, c , and the modulation rate, m , of the sequence,²¹

$$R_{xx}(k) = \sum_{i=1}^N x_i x_{i+k} = m(1-c) \delta_k + mc \quad (24)$$

where δ_k is the Kronecker Delta.

Now we recall that the measured crosscorrelation with the linear TOF system is

$$R_{xy}(\tau) = \int_0^{FT} y'(t)x(t-\tau) dt = \sum_{j=1}^{FN} x_j y'(\tau + t_j) \quad (25)$$

where only the statistical portion of the modulation function is necessary to compute the correlation, and where

$$\begin{aligned}
 y'(t) &= \int_0^{T_h} h(\tau') M(t-\tau') d\tau' + b(t) \\
 &= \int_0^{T_h} h(\tau') \sum_{i=1}^{FN} x_i \phi(t-t_i-\tau') d\tau' + b(t)
 \end{aligned} \quad (26)$$

is the measured detector output at time t . In Eq. (26), $h(\tau)$ is the impulse response function (true TOF distribution), $b(t)$ is the uncorrelated "constant" background signal, and we have changed the upper limit of integration from $+\infty$ to T_h since the TOF signal is of finite duration ($h(\tau) = 0$ for all $\tau > T_h$). Equation (22) for the modulation function has been used to derive (26).

Putting the expression for detector output (Eq. (26)) into the correlation function (Eq. (25)) we get:

$$\begin{aligned}
 R_{xy}(\tau) &= \sum_{j=1}^{FN} x_j \int_0^{T_h} h(\tau') \sum_{i=1}^{FN} x_i \phi(\tau-t_i-\tau'+t_j) d\tau' + \sum_{j=1}^{FN} x_j b(\tau+t_j) \\
 &= \left[\sum_{i,j=1}^N x_i x_j \int_0^{T_h} h(\tau') \phi(\tau-t_i-\tau'+t_j) d\tau' + b \sum_{j=1}^N x_j \right]
 \end{aligned} \quad (28)$$

where the averaged noise included in the correlation function will be independent of τ (uncorrelated) and so can be removed from the summation.

By rewriting the double summation as

$$\begin{aligned}
 \sum_{i,j} x_i x_j &= \sum_k \sum_i x_i x_{i+k} = \sum_k R_{xx}(k) = \sum_k \{m(1-c)\delta_k - mc\} \\
 &= m(1-c) + \sum_i mc
 \end{aligned} \quad (29)$$

and by noting that

$$\sum_{j=1}^N x_j = m \quad (\text{the number of pulses per period})$$

the correlation expression becomes

$$R_{xy}(\tau) = fm \left\{ (1-c) \int_0^{T_h} h(\tau') \phi(\tau-\tau') \right. \\ \left. + c \int_0^{T_h} h(\tau') \sum_{k=1}^N \phi(\tau-\tau'+t_k) d\tau' + b \right\} \quad (30)$$

Recalling the symmetry condition (23), the sum in the second term is equal to unity. We define

$$H(\tau) = \int_0^{T_h} h(\tau') \phi(\tau-\tau') \quad (31)$$

which is the convolution of the modulating pulse shape with the true TOF function. $H(\tau)$ is exactly the TOF distribution which would be measured with a classical TOF experiment using a gate function $\phi(t)$. Thus

$$R_{xy}(\tau) = fm \left\{ (1-c)H(\tau) + c \int_0^{T_h} h(\tau') d\tau' + b \right\} \quad (32)$$

The integral in the second term of Eq. (30) may also be expressed in terms of $H(\tau)$: let

$$\theta = \int \phi(t) dt \quad (33)$$

be the total area under a unit modulation pulse. Then

$$\begin{aligned}
 \langle H \rangle &= \int_0^{T_h} H(\tau) d\tau = \int_0^{T_h} d\tau \int_0^{T_h} h(\tau') \phi(\tau - \tau') d\tau' \\
 &= \int_0^{T_h} h(\tau') d\tau' \int_0^{T_h} \phi(\tau - \tau') d\tau \\
 &= \theta \int_0^{T_h} h(\tau') d\tau' \equiv \theta \langle h \rangle
 \end{aligned} \tag{34}$$

or

$$\langle h \rangle = \theta^{-1} \langle H \rangle \tag{35}$$

Then

$$R_{xy}(\tau) = fm \{ (1-c)H(\tau) + \frac{c}{\theta} \langle H \rangle + b \} \tag{36}$$

This is the desired result. The computed crosscorrelation is proportional to the classical TOF signal superimposed on two constant background terms. The background due to the average TOF signal, $\frac{mc\langle H \rangle}{\theta}$, has been called the "background of ignorance."²² Its origin is the association of each detector pulse to m modulation pulses during the correlation, whereas physically the detected ion could have come from only one of these pulses; the detector signal is erroneously attributed to the other $m-1$ modulation pulses. However, due to the statistical properties of the modulating signal, this error becomes evenly distributed among all channels of the correlation function and assumes the identity of a constant background.

The term in Eq. (10), mb , is due to each true background pulse being attributed to m channels, the result being a constant increased background.

The method of modulation described in the above discussion was assumed to use a (1, 0) type of correlation, rather than a (+1, -1) type. Since our correlation method uses the latter type (see below), both sources of constant background are removed and the result of correlation is directly proportional to the classical TOF signal $H(\tau)$. Thus the results of the correlation experiment are equivalent to those of the classical TOF method; we now proceed to discuss how a correlation system may be implemented experimentally.

APPLYING CORRELATION TOF

Having shown how random modulation of a beam source might be used to measure the TOF spectrum and having discussed the generation and properties of the modulation signal, we now examine the mechanics of applying the correlation method to time-of-flight systems.

There are several distinct methods by which correlation spectroscopy has been applied to TOF. Each method has in common the concepts of modulation, correlation, and data storage. To our knowledge, three variations of the correlation method have been implemented. The first, used with neutral molecular beams, applies a relatively short modulation sequence which is coupled synchronously with repetitive cycling of a multichannel analyzer for data storage. Accumulated data is later transformed (correlated) by correlation of the multichannel analyzer contents with the repetitive modulation signal. The sequence of events is then modulation, data storage, and correlation, all relying on the use of the short modulation sequence. (The requirement that a short modulation sequence be used is the result of the limited number of slots which can be machined in a mechanical chopper and the finite number of multichannel analyzer channels available.)

The second method, used in neutron spectroscopy, uses a long pseudo-random signal which not only modulates the source beam, but also controls the storage of data by gating the inputs of a series of data accumulation scalars. This method does not require any limitation on the period of the modulation sequence, and filtered true random binary noise modulation could just as well be employed. The sequence of events is modulation, correlation, and data storage.

The third type of application is the one developed in our laboratory for use in ion beam experiments. This method, which is actually a hybrid of the other two, can also use long pseudorandom sequences for beam modulation. Data storage is achieved by storing detector output signal in a computer core memory by associating individual detector events with the modulation signal responsible for their genesis. Subsequent transformation of the stored data using the associated modulation signal leads to calculation of the correlation function. The sequence of events in this method is modulation, data storage, and correlation; the method thus resembles that used for neutral molecular beams, though no limits are placed on the length of the modulation sequence and synchronized data storage is not required.

Correlation with Neutral Molecular Beams

As previously described, slotted disc rotating choppers have been used to modulate neutral beam systems. Correlation modulation is achieved by machining the chopping disc with slots placed in a pseudorandom manner so that the gate function of the chopper approximates an m-sequence.²³ The resolution of the chopper is fixed by the width of the "unit beam slot" (the circumference of the chopper is divided into N unit slots which are either open or closed) and by the angular velocity of the disc. In practice both the number of unit slots and the number of multichannel analyzer slots are limited to ~1000 and this places a limit on the length, N, of the binary sequence used for modulation. (This has the effect of limiting the background height of the modulation sequence autocorrelation function to 1/1000 of the peak height. See the description of the m-sequence autocorrelation function.)

Data storage with the slotted disc system is achieved by use of a multichannel analyzer. The analyzer and the beam chopper are synchronized so that as the chopper runs through the pseudorandom sequence, the analyzer is sequentially stepped through each of its memory channels. Detector events sensed at any point in the chopping sequence are always stored in a corresponding multichannel analyzer channel associated with that particular sequence segment. Both the chopper and the analyzer are cycled repeatedly, always maintaining the synchronicity between the two.

When sufficient data (empirically determined) have been collected, the correlation function is calculated, a single point at a time, by multiplication of each of the analyzer channel contents by the corresponding value of the modulating function (± 1) and summing the result over all analyzer channels. Shifting the phase between the multichannel analyzer channels and the modulating sequence and repeating the multiplication and summation provides the value of the correlation function for different delay times. The resulting plot of net correlated signal versus phase (time) shift between modulation sequence and analyzer channels is the desired correlation function.

Correlation with Neutron Beams

A somewhat different system has been applied in the measurement of neutron beam velocity distributions²⁴ and the response function of neutron reactors.²⁵ In the former case an incident beam of polarized neutrons is chopped using a magnetic flipper chopper,²⁴ while neutron reactors are modulated by the use of electrostatic deflection plates in the Van de Graaf accelerator used for neutron generation.²⁶ (Often mechanical disc choppers have been used to measure the velocity

distributions for neutron beams in a system analogous to that described for neutral molecular beams.)

Since these methods of source modulation are electrical rather than mechanical, and since data is not stored in a finite sized multichannel analyzer, there is no physical or memory restriction on the length of the modulation sequence. Depending on the method of data storage, true filtered binary random noise (such as is produced by commercial noise generators) could be used in place of an m-sequence.

The correlation detection system employed for reactor measurements is shown in Fig. 12.²⁵ This system achieves a direct correlation between the neutron source modulation sequence and the detector output. This is accomplished by use of a series of scalars which are incremented by detector events. Each scalar is gated by one segment of the modulation sequence; though the segment of the sequence gating each scalar changes state constantly, that segment has a fixed phase with respect to the sequence segment which is currently modulating the neutron source.

The experiment is controlled by a suitable digital clock of period δ . The clock runs two shift registers; one is hooked up as a binary pseudorandom noise generator whose output is an appropriately long m-sequence; the other is a serial in/parallel out storage register which stores the sequence which has been used to modulate the source. Consider the case of an n-bit storage register. If $M(t)$ is the current modulating sequence, the nth stage of the storage register contains the segment $M(t-n\delta)$ since it requires a time $t = n\delta$ for any segment to be shifted through the storage register. Similarly, any stage k, $1 \leq k \leq n$ will contain the segment $M(t-k\delta)$. Now the parallel output of each register

Fig. 12. Crosscorrelation with gated scalars.

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stage, k , is applied to a gate, G_k , which controls the input of a scalar (counter), S_k . When a neutron is sensed by the detector, each scalar S_k whose input is gated on by the modulation signal $M(t-k\delta)$ will be incremented, indicating a positive correlation between the detector output and a +1 segment in the modulation signal at a time $(t-k\delta)$ previously. All scalars whose modulation segment was 0 rather than +1 will not be incremented. Since the system does not include the effects of negative correlation, the scalar S_0 is used to record the total detector signal for later computational correlation adjustment to include negative correlation effects. If after some period of data collection, $T_+(k\delta)$ is the contents of scalar S_k , and $T_-(k\delta)$ the total number of counts ignored by S_k , then T_0 , the contents of scalar S_0 , is equal to

$$T_0 = T_+(k\delta) + T_-(k\delta) \quad (37)$$

for any k . Then the correlation function can be calculated from

$$R_{xy}(\tau=k\delta) \propto [T_+(k\delta) - T_-(k\delta)] = [2T_+(k\delta) - T_0] \quad (38)$$

Recalling Eq. (6)

$$R_{xy}(\tau) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N x(j\Delta t) y(j\Delta t + \tau) \quad (6)$$

we see that the measured correlation function of Eq. (38) is given by summing the total number of positive correlations (T_+ is the sum of all cases where $x(j\Delta t)y(j\Delta t+k\delta) = +1$) and subtracting the total number of

negative correlations (T_- is the sum of all cases for which $x(j\Delta t)y(j\Delta t+k\delta) = -1$). The result is a net corrected value of the correlation function for $\tau = k\delta$.

The important concept of the method is that any point of the correlation function can be calculated directly by using the modulating segment (bit) corresponding to the proper delay to gate a data storage scalar. Any number of points of the correlation function could be calculated merely by increasing the number of scalars and gates and by increasing the length of the storage register. The modulating sequence need not be repetitive since the correlation is direct and immediate. Resolution is limited only by the number of scalars and the clock rate for modulation.

The drawbacks of this system are mainly those of electronic complexity and expense. The experimenter must build a complicated and dedicated single purpose correlator whose resolution is directly proportional to its complexity. For this reason, an alternative method was sought for use in ion beam experimentation.

The Present Correlation Method for Ion Beams

Prior to constructing a correlation system for ion beam analysis, we reviewed all of the techniques which had previously been applied, including commercially available correlators, multichannel analyzer, and gated scaler systems. Each system was found to have inherent disadvantages which made it difficult to apply to ion beam analysis.

Commercial correlators employ analog or digital delay lines for signal sampling followed by sequential single point correlation calculation. The comparatively low signal levels (slow repetition rate) of

an ion beam system make it infeasible to use sequential single point correlation since excessively long sampling times would be necessary.

Ion beam TOF experiments typically have a flight time of 10-50 μsec and TOF distribution widths of 2-10 μsec . This fact, coupled with the problem of synchronicity and the long access time of multi-channel analyzers (10-100 μsec) made the application of a neutral beam analysis type system impractical.

The gated scalar type of system is directly applicable; however, it is more expensive and difficult to construct. Additionally, such a system is totally dedicated and somewhat inflexible; it can only be used for specific correlation analysis without further data analysis.

A solution to the ion beam problem was found in the use of a mini-computer based system. Such a system is comparatively inexpensive (<\$6,000), requires only construction of an appropriate computer interface, and allows the use of available hardware (the computer) which can be applied to a variety of data analysis problems.

The computer used in the system is a Digital Equipment Corporation PDP 8/f which is a 12 bit minicomputer with a 1.2 μsec cycle time (see "Computer Organization" below). It was decided that simultaneous computation of 30 points of the correlation function would provide adequate experimental resolution for viewing the TOF ion spectrum in a manner similar to the gated scalar technique. Since the computer has only a single data input channel (12 data lines), and since it would require 1.2 μsec to add data to each of 30 "scalar" addresses in core memory, direct implementation of a "scalar system" would require a 40 μsec

downtime for each detector event accumulated. This is excessive considering the signal intensities ($\sim 10^5$ /sec) typically measured with an ion beam apparatus; a significant portion of the detector signal would be lost, negating the duty cycle advantages of the correlation system. The solution to this problem lies in the application of the "Data Address" concept.

The Data Address Method

While the computer has only one data input channel (even though this channel contains 12 bits), it does have multiple inputs available in the form of its 12 bit address code. The basic concept of a "data address" is that the information necessary to compute a TOF correlation function is present in the modulation sequence (which has been stored in a storage shift register) at the time of a detector event (as we saw in the gated scalar system). It is possible to retain this information while simultaneously reducing data storage time for the computer by a factor of 10 if the applicable modulation sequence is used as an address code for the computer memory. Each code sequence is uniquely associated with a core memory address in the computer. Each time a particular modulation code is contained in the storage register at the time of a detector event, the address corresponding to that code is incremented. As an experiment proceeds, the core memory addresses accumulate as their contents a distribution function representing the number of times each modulation sequence code was contained within the storage register at the time of a detector event. The connection between data addresses and the calculation of the cross correlation function will be described below.

Since we wish a 30 bit correlation function, 30 bits of the current modulation sequence must be held in a storage register. For each detector event, the 30 current bits are stored as three 10 bit segments.

The 10 bit length is suggested because of an access time-core memory size tradeoff. This tradeoff can be visualized as follows: it would take 30 computer cycles of 1.2 μ sec or 40 μ sec to store 30 independent data bits, but only 30 core memory addresses to accumulate the result. On the other hand, it would only require one memory cycle to store one data sequence 30 bits long by the data address method; however, to store a sequence k bits long by the data address method requires 2^k core addresses since there are that many possible outcomes in a k bit sequence. Thus, for one 30 bit segment it would require an astronomically large ($2^{30} \cong 10^8$ core addresses) core memory. The compromise point is the use of three 10 bit segments, requiring 5 μ sec storage time and $3 \times 2^{10} = 3 \times 1024$ addresses, both parameters tolerable for the present system.

Data transfer of a modulation code sequence is achieved through the use of a direct memory access mode of the computer. In this "data break" mode (see "Computer Organization"), the computer's central processor is disabled and program execution is temporarily stalled. The actual data transfer is controlled by the external logic of the computer interface. To increment the contents of three separate data addresses, 3 sequential data breaks must be used.

We note that one could store the modulation code just as easily by using 10 bits of the computer data lines. In this manner, a 30 bit sequence would be stored as the contents of three addresses rather than in the address itself. For each detector event, three new addresses

would be required. However, this method would allow only about 1000 detector events to occur before the memory overflowed. In contrast, the data address will allow an average of 5×10^5 detector events to occur before core memory overflow.

A block diagram of the computer system is shown in Fig. 13. A feedback shift register generates the beam modulating m-sequence. This sequence is also stored sequentially in a digital delay line and then in a storage shift register (DSMA). All registers are controlled by a variable frequency crystal generated digital clock. Detection of an ion causes the sequence in the storage register to be strobed into the data break logic, where the sequence is used to increment three addresses by direct memory access. By use of a Tektronix display terminal keyboard, the functions of the interface may be controlled by programmed commands.

Since the data address method stores correlation information in a coded manner (the code being that the binary modulation sequence specifies a 10 bit portion of a 12 bit address), a decoding transformation of the accumulated data is necessary to compute the desired correlation function.

The data transformation mimics the function of the gates used in a gated scalar system (see "Program Description") (Fig. 14). Each address is examined separately. Since the 10 least significant bits of the address contain the equivalent of the modulation sequence at the time of detector events, each bit, k , describes whether (for that particular address) the modulation segment, $M(t-k\delta)$ (where δ is the clock period), is positively or negatively correlated with the number of detector events contained within the address contents. If bit k is a "1", the

Asynchronous Units:

1. Computer
2. X-TAL Clock and Beam Modulation
3. Detector Signal

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Fig. 13. Correlation TOF Block Diagram.

Figure 14. Data transformation for the data
Transformation of addresses 1325₈ and 0723₈
(10 significant bits to be transformed)

1325₈:

Bit position	1	2	3	4	5	6	7	8	9	10
Data address	1	0	1	1	0	1	0	1	0	1

Contents: 34

Result:

Add to signal scalar:	34	-	34	34	-	34	-	34	-	34
Add to noise scalar:	-	34	-	-	34	-	34	-	34	-

Next address for example:

0723₈:

Bit position	1	2	3	4	5	6	7	8	9	10
Data address	0	1	1	1	0	1	0	0	1	1

Contents: 21

Result:

Add to signal scalar:	-	21	21	21	-	21	-	-	21	21
Add to noise scalar:	21	-	-	-	21	-	21	21	-	-

Cumulative result:

Signal scalars	34	21	55	55	-	55	-	34	21	55
Noise scalars	21	34	-	-	55	-	55	21	34	
Net (≤ 0)	13	-	55	55	-	55	-	13	-	55

contents of the address are added to signal accumulation scalar k ; otherwise the contents are added to noise scalar k . This process is carried out for each of the 10 bits of each address. There are three sets of signal and noise accumulators in the computer memory, corresponding to the three 10 bit segments of the modulation sequence used as independent data addresses. When each of the $3K$ possible addresses have been transformed in this manner, the resulting contents of each of the 30 noise scalars is subtracted from the contents of the companion signal scalar. The result is the TOF correlation function.

We have seen how the correlation TOF system can be applied in several ways. In the following section we will discuss a somewhat more abstract picture of the correlation method applications.

VECTOR SPACE PICTURE

Having explained in detail the mechanism by which the crosscorrelation function is calculated, we now present a more theoretical consideration of this process with the hope that it will clarify how the correlation is accomplished. This description is couched in the language of vector space theory.

We mentioned previously that the bits contained in random noise generator shift register can be represented by a state vector, $\underline{a}$. It is only natural then to define a vector space, U , which is spanned by the cyclicly generated state vectors. We call U the state or sample space. For an n -stage shift register, this space is identical to R^n . The points in U which are accessible to the state vector form the vertices of an n -dimensional hyperspace cube. Since the state vector is represented by a binary n -tuple, $\underline{a} = (a_n, a_{n-1} \dots a_1)$, there are 2^n vertices of this cube, all of which are accessible except the all zero n -tuple. This is consistent with the number, $2^n - 1$, of states which are generated during the modulation sequence.

We also noted earlier (see "M-sequences") that the generated sequence is said to be the result of an operator T operating on an initial state vector. T is the sum of a feedback operator, C , and a shift operator, S . Given an initial state vector, $\underline{a}_0$, the vector space U is generated by T . Because of the shift and add property of m -sequences,²⁷ the operator T is a linear operator, although this is by no means obvious. If $T^k \underline{a}_0$ represents the k^{th} state vector in the sequence after k operations by T , because of the shift and add property it is also true that

$$\underline{a}_0 + T^k \underline{a}_0 \in U, \quad k \in I, \underline{a}_0 \in U \quad (39)$$

where modulo 2 addition is assumed. Thus the vector space U is closed under operation by T .

Because R^n is complete, if we define a scalar product on U , U is a separable Hilbert space²⁸ (Euclidean). This scalar product can be defined by the modulo 2 addition:

$$\langle \underline{x}, \underline{y} \rangle = \sum_{i=1}^A x_i y_i \pmod{2} \quad (40)$$

Thus we are dealing with a separable Hilbert space and a 1:1 linear operator for describing the process of sequence generation.

The picture of operation is thus given by specifying an initial state vector, $\underline{a}_0$, which is then repeatedly acted upon by the generating operator, T . This operation moves the state vector about the vertices of the hyperspace cube in a fixed cyclic manner. The all zero vector, $\underline{0}$, is excluded because it is in the kernel of the operator T . Since each n -tuple appears only once during the sequence, the state vector passes through each vertex once and only once during the period of the sequence.

Because of the nice properties of the state vector space, it is possible to define projection operators²⁸ which act on the state vectors. One such projection operator, G , can be used to represent the generating polynomial, $G(x)$, which describes the output of the first stage of the shift register. The n -tuple which represents this one dimensional

projector is simply $G = (1, 0, \dots, 0)$ and we can make the association,

$$G(x) \approx \sum_{k=0}^{2^n-1} G^k_{\underline{a}_0} \quad (41)$$

We will now describe how the use of projection operators can be viewed as a method of calculating the TOF correlation function.

The point of this vector space picture is to gain a better understanding of how the crosscorrelation function is generated by the data address method. In the vector space representation, the crosscorrelation is a measure of the correlation between the position of the state vector and the occurrence of detector events. We can associate with each point in the state phase space a density in phase; this density in phase associates with each state vector the number of occasions on which a detector event occurred while that state vector represented the contents of the modulation generating shift register.

This representation is especially applicable to the data address method. In this method the addresses in the computer core memory are used to represent the phase space points, while the contents of each address represent the associated density in phase. In contrast with methods such as the gated scalar scheme (see "Application of Correlation TOF") the data address method accumulates the density in phase and later computes the correlation function, as we now describe.

In the data address method, the crosscorrelation function is computed from untransformed raw data by the use of a binary mask (test bit) and a series of associated signal and background accumulators (see "Program Description"). The process of using a masking bit for testing

the bits of each address is equivalent to defining a series of one dimensional projection operators which act sequentially on each relevant phase space state vector. A background and signal accumulator are associated with each projector; if the result of the projection operation with any projector acting on a state vector is a non-zero vector, the density in phase associated with the state vector is added to the signal accumulator (i.e. there was a positive correlation between the position of that state vector and the associated detector events). A zero vector result of the same projection operation results in the associated density in phase being added to the background accumulator (negative correlation between the state vector and the associated detector events). The complete calculation of the correlation function then involves the action of n projection operators on each of the 2^n-1 state vectors (assuming n points of correlation function are being calculated).

If we define the projection operator for a delay time τ as R_τ , and if $\underline{a}$ is the state vector and $\rho(\underline{a})$ the associated density in phase, then

$$R_{xy}(\tau) = \int_{\substack{\text{all} \\ \text{space}}} R_{\tau} \underline{a} \rho(\underline{a}) d\underline{a} \quad (42)$$

The form of each one dimensional projection operator is a n -tuple with a "1" in a position determined by τ and the remaining bits zero. For a modulation clock period δ , if $\tau = k\delta$, the n -tuple will contain a "1" in the k^{th} place. For a (1, 0) type of correlation (background not subtracted) the discrete correlation function is then

$$R_{xy}(\tau) = \sum_{k=1}^{2^n-1} R_{\tau} a_{\sim k} \rho(a_{\sim k}). \quad (43)$$

For a (+1, -1) correlation, as is used in the data address method to account for negative correlation effects (background subtracted)

$$R_{xy}(\tau) = \sum_{k=1}^{2^n-1} \{R_{\tau} a_{\sim k} - (1-R_{\tau}) a_{\sim k}\} \rho(a_{\sim k}) \quad (44)$$

We note that the effect of the projection operation is really equivalent to the use of a series of phase density weighted inner products.

Similarly the autocorrelation function for the modulation sequence can be represented by an inner product sum which is unweighted. If we denote the n-tuple representing each projector $R_{\tau}(k)$ by $a_{\sim k}$, then

$$R_{xx}(\tau) = \langle a(t) | a(t+\tau) \rangle = \sum_{k=1}^{2^n-1} \langle a(t) | a_{\sim k} \rangle \langle a_{\sim k} | a(t+\tau) \rangle \quad (45)$$

where $a(t)$ is the true state vector at time t .

This view of the calculation of the correlation function calculation is a convenient vehicle for displaying the conceptual difference between the gated scalar system of correlation and the data address system. While, as we have shown, the latter method accumulates the density in phase before the sequential operation by projection operators, the scalar system works by immediate and simultaneous projection. Each time a detector event is noted by the scalar system, each of the gates in the scalar system essentially performs the projection operation on the current

state vector. All n projection operations are accomplished simultaneously because of the extensive hardware of the system. Thus, rather than using a single series of weighted projections, this system uses repeated unweighted projections.

Summarizing, we see that the vector space picture of correlation analysis provides a simple view of the operation of the data address method. Although the formalism is readily suggested by the framework of the system, to our knowledge this is the first time this formalism has been explicitly developed.

In the next section we will discuss the statistical analysis of the system we have described in an effort to see how the unique method of data address must be constructed to avoid data transduction error.

STATISTICAL ANALYSIS

Now that we have examined the theory of the correlation method, it is relevant to discuss the statistical evaluation of the method to see how it may compare in accuracy with others.

There are several points of view from which the correlation system may be analyzed. First, ignoring experimental questions, we inquire how closely the measured estimate of the correlation function corresponds to the true TOF signal. Secondly, we analyze the sources of experimental distortion and compare the general results of correlation measurement to those obtained with classical TOF systems. We then proceed to examine the problems associated with our own computer based correlation system and discuss the general problem of detector paralysis. Finally we view the correlation system in light of the Shannon sampling theorem in an effort to explain the relative efficacy of the method.

System Optimization

There has been a good deal of discussion in the literature pertaining to the optimization of correlation analysis systems.²⁹ This discussion centers about defining the variables available within the system and choosing their values so as to make correlation analysis broadly applicable in an accurate manner. The optimization problem is beyond the scope of this thesis since the principal parameters (duty cycle, method of sequence generation, modulation sequence symmetry) are fixed by the experimental electronic methods which have been used in implementing the present correlation system.

Correlation Measurement Variance

In the process of making a measurement of a correlation function, one is actually making an experimental estimate of the function by repeated single correlations. Stern et al.²⁵ have derived a detailed statistical analysis of the correlation function "estimator" using the fundamental laws of conditional probability, the accumulated single correlations and a simple assumption about the net steady state particle flux as the modulation bandwidth is increased to ∞ . They have showed that in fact the measured estimator of the correlation function is equivalent to the "true" correlation function. Hence we may have some confidence that the accumulation of single correlations will reveal the true shape of a TOF distribution.

Given that we are indeed measuring the shape of the TOF distribution, the next question to be dealt with is how good is the measurement. That is, given that an accumulation of single correlations will converge toward the true correlation function, how fast will that convergence be?

A measure of the reproducibility and (in the absence of systematic error) accuracy of any experimental measurement is its variance. In general, any set of measurements of a process can be represented by a mean value and a variance.* We recall that the mean of a set of measurements, $\{x_k\}$ is defined as

$$\mu_x = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N x_k = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T x(t) dt. \quad (46)$$

*See "Random Process Appendix".

The variance describes the mean square deviation of the measurements from the mean value:

$$\text{Var}(x) \equiv \sigma_x^2 \equiv \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N [x_k - \mu_x]^2 = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T [x(t) - \mu_x]^2 dt \quad (47)$$

The variance of the correlation estimator has been evaluated by various means of different authors; the most fundamental method is to work from single correlations using simple, joint, and conditional probabilities to evaluate explicitly the factors of the correlation estimator variance. This has been accomplished by Stern²⁵ who has shown that basically the expected relative error (dimensionless variance) is attributable to three sources: finite counting times, finite counting rates, and spontaneous source fluctuations:

$$E_{\text{rel}}^2 = \frac{\sigma_R^2}{R_{xy}^2(\tau_0)} = R_T^2 + R_C^2 + R_r^2 \quad (48)$$

where $R_{xy}(\tau_0)$ is an average value of the correlation estimator and the three terms refer to errors (variance) due to measurement time, counting rate and source fluctuations, respectively. The last term is not applicable in the present case; the relatively large numbers of ions (10^3 - 10^4) released with each beam pulse make statistical fluctuations in the source output negligible (<1%). For the present system, we will evaluate the magnitudes of the remaining terms.

The remaining terms have been shown to be represented by:

$$R_T^2 = (2\alpha T)^{-1} \quad (49)$$

$$R_c^2 = \left(\frac{W}{2\eta}\right)^2 (\bar{r}T)^{-1} \quad (50)$$

where α = TOF bandwidth, T = total measurement time, η = the modulation index (1 in this case), and $\bar{r}$ = the average counting rate. The factor W is defined by

$$W = \frac{2\pi}{\alpha} = \frac{\text{modulation bandwidth}}{\text{TOF bandwidth}}$$

For the present system, we can evaluate the magnitude of these variance terms using:

$$\alpha = \frac{1}{10} \mu\text{sec} = 10^{-5} \text{ sec}^{-1}$$

$$T = 30 \text{ seconds}$$

$$W = 10$$

$$\eta = 1$$

for the cases of $\bar{r} = 10^2, 10^3, 10^4$ counts/sec. We then find that the error due to counting rate is $R_c^2 \sim (\bar{r})^{-1} = 10^{-2}, 10^{-3}, 10^{-4}$ for the above counting rates, while $R_T^2 < 10^{-6}$.

Thus we conclude that for the present wideband modulation used and the relatively intense signal expected, the experimentally generated variances will be of the order of 1% of the mean correlation estimator value, an entirely tolerable level.

The fact that these experimental considerations do not lead to

significant variance does not imply that variance is a negligible problem. We have yet to consider the problem of signal/noise ratio (S/N) and the effects of random or correlated noise; this will be discussed next.

In a correlation measurement system, there is no practical method of removing correlated noise. For instance, crosstalk between source modulation and signal detection will remain invisible to the correlator and yet could contribute significantly to the measured TOF distribution, possibly leading to false peaks in the correlation function. The experimenter's only recourse is careful design to eliminate any possibility of correlated noise. One hopeful note is provided by the fact that correlated noise will most probably be measured with a very short correlation time ($\tau \approx 0$) since electronic signals from modulation are transmitted at high speed. This has the effect of separating any correlated noise peak from the TOF correlation peak since ion time of flight is finite. We note that as yet we have seen no evidence of correlated noise in the TOF distributions which have been measured.

The variance due to uncorrelated noise has been dealt with by Von Jan and Scherm²² and by Hossfeld and Amadori.²¹ They have derived the following expression for correlation variance as a function of delay time (single point correlation variance):

$$\sigma_R^2(\tau) = \left\{ \frac{R_c + b}{f N/L} \right\} \left\{ \frac{\frac{1}{L} + c\sigma_\tau^{-1}}{(1-c)(c + \frac{1}{N})} \right\} \quad (51)$$

where $\sigma_\tau \approx \frac{R_c + b}{R}$ and

$R_{\tau} = R_{xy}(\tau)$ (single point of correlation function)

b = average background per channel

L = number of channels needed to span the measured TOF function

$N = 2^n - 1$ = length of the modulation sequence

f = the number of times the modulation sequence repeats during the measurement

c = duty cycle = 0.5

$\bar{R} = \frac{1}{L} \sum_{\tau=1}^L R_{\tau}$ = the average TOF signal.

The first factor is identical to the error which would be measured in a classical TOF experiment with a pulse repetition rate N^{-1} . The factor fN is a measure of the total measurement time and thus for fixed signal levels, the relative error decreases in an inverse manner as the measurement time is increased.

In order to compare the results for classical and correlation measurements, the "classical" term is often divided out to give a relative gain factor:

$$g^2 = \frac{\{\sigma_R^2(\tau)\}_{\text{classical}}}{\{\sigma_R^2(\tau)\}_{\text{correlation}}} = \frac{(1-c)(c+\frac{1}{N})}{L^{-1} + \frac{c\bar{R}}{R_{\tau}+b}} \quad (52)$$

This gain factor expresses the gain in accuracy which is achieved by use of the correlation method. It is primarily a function of the relative size of the correlation function at any point,

$$\frac{R_{\tau}+b}{\bar{R}} = G_{\tau}$$

since the duty cycle, c , modulation length N , and TOF width, L , are relatively fixed. For a duty cycle of $c = 0.5$ both Von Jan and Hossfeld have calculated that the correlation method will provide superior results ($g^2 > 1$) if $\sigma_s \geq 2$; this implies that the correlation method will always give a more accurate measurement of the shape of correlation peaks in the presence of low background levels (large S/N), and will give higher accuracy for the entire correlation spectrum in the presence of large relative background levels ($b > 2\bar{R}$). An example of this effect is shown in Fig. 15 (after Von Jan and Scherm²²). In Fig. 15A a measurement is made in the presence of a low background level. For portions of the spectrum below $\sigma_t = 2$ the correlation method is less effective than the classical method while for viewing the peak the correlation method is better. In Fig. 15B a measurement is made in the presence of a high relative background level. In this case, all of the spectrum lies above $\sigma_t = 2$, so the correlation method is better for the entire spectrum.

We note that all of the above discussion has assumed a stationary experimental system. This is often not the case; experimentally a system is rarely stable in a long term sense since beam energy fluctuates a finite amount as does beam intensity. Also the vacuum system may undergo pressure fluctuations as may the pressure of target gas contained within a scattering cell. This experimental reality provides further support for the use of the correlation method since if in some experimental measurement classical and correlation methods were to have identical accuracies (gain factor equal to one), data collection by the classical method would require a time interval at least 10 times as long as that required by a correlation measurement, making the classical method much more susceptible

a. Small Background Case

b. Large Background Case

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Fig. 15. Relative efficiency of the correlation method for small and large S/N cases.

to experimental drift. This advantage, which is entirely due to duty cycle considerations, has been widely overlooked.

In summary then, the correlation method is superior under adverse S/N conditions and for examining correlation peaks. In both methods, the examination of less intense portions of the TOF spectrum is accomplished with lower efficiency, and this fact often determines the time necessary to measure the TOF spectrum with sufficient accuracy; for this case the bandpass system of measurement has definite advantages.

Detector Paralysis

We turn now to the discussion of measurement accuracy problems which are particularly associated with the present computer based system. By far the most important aspect is the problem of data transduction errors or detector paralysis.

TOF spectroscopy is a dynamic method of measurement. Consequently, it is susceptible to dynamic errors inherent in the measurement process which are much less amenable to analysis and correction than the errors of a non-dynamic energy bandpass system.

The most significant type of dynamic error to which a TOF system may be subjected is the error of data transduction. Any particle detection system has a finite bandwidth capability; hence each detector has a finite period of time (deadtime) after it has detected a particle event during which it is unable to register the appearance of subsequently arriving particles. This phenomenon, known as detector paralysis, may have profound effects on a dynamic measurement system.

Detectors of events are generally classified as being one of two types.³⁰ A Type I (non-paralyzable) counter which registers a particle

arriving at time t , will then lock out any further particles arriving during a (random) period, τ (the deadtime). Particles arriving in the locking interval $(t, t+\tau)$ are not registered, nor do they affect the counter in any way. A scintillation counter is an example of a Type I Counter.

In contrast, a Type II (paralyzable) Counter does not lock out particles which arrive during the deadtime associated with initial particle detection. As each particle arrives, it locks the counter for a random locking time, τ , regardless of whether it was counted or not. For a sufficiently large particle flux, a Type II Counter can be completely paralyzed, the first particle being counted and all further particles merely extending the deadtime. A "non-self quenching Geiger-Müller counter with a high impedance preamplifier"¹⁸ is an example of a Type II Counter.

The computer based data acquisition method of the current correlation TOF system is basically a Type I counter. Since the actual particle detector is much faster than the computer data storage part of the system, the bandwidth (200kHz) of the interface data storage system effectively limits the bandwidth of the counting system. This bandwidth limitation is due to the necessity of three 1.2 μ sec memory access cycles to acknowledge the arrival of a single detected ion. Since the computer and the detector are asynchronous, a 5-7 μ sec deadtime can be considered as a reasonable worst case estimate of the limit on data storage bandwidth.

The question we must deal with is whether the typical 5 μ sec counter deadtime will prejudice the shape of the measured TOF distribution in

favor of faster particles which may arrive first at the detector, locking out the slower particles which arrive later.

In general for classical TOF, the effects of Type I Counter deadtime depend on the relative bandwidths of the detector (B_{Det}) and the dynamic signal being measured (B_{TOF}). As we now describe, at each extreme ($B_{Det} \gg B_{TOF}$, $B_{TOF} \gg B_{Det}$), the measured TOF signal will be measured accurately, while the intermediate case ($B_{Det} \sim B_{TOF}$) may lead to data storage prejudice.

The case of a very fast detector ($B_{Det} \gg B_{TOF}$) is the simplest. In this case the deadtime of the counter is negligibly small and all relevant signal data will be stored. The opposite case ($B_{TOF} \gg B_{Det}$) is that of random phase sampling where the detector is locked most of the time and randomly samples the TOF signal in a "Monte Carlo" type of detection. Note that the random phase assumption is of prime importance. The case of detector downtime being correlated with the TOF signal may lead to severe distortion.

The median case ($B_{Det} \sim B_{TOF}$) contains the greatest possibility of data prejudicing. In this case, given a suitable particle flux, the TOF signal and the detector are matched in phase in a resonant manner. The fast particles of any beam pulse are registered and the slow particles are locked out. The detector becomes unlocked in time to register a fast particle from the next TOF pulse, and the scheme is repeated. While a distribution of arrival times will be measured, it is conceivable that the prejudice of the distribution may be so great as to display periodic structure within the TOF waveform, the period being characteristic of the detector deadtime.

Of course this discussion depends strongly on the net particle flux and the signal repetition rate. In a classical TOF experiment, the repetition rate is always relatively slow so that given a minimum flux of particles at the detector (say 5-10 ions/beam pulse) data transduction would be far from perfect, favoring the high velocity portion of the distribution.

In the case of correlation analysis, depending on the path length of the TOF analyzer, it may often be the case that $B_{\text{Det}} \sim B_{\text{TOF}}$. However, we maintain that this method avoids prejudice because of its inherently large repetition rate. The beam pulse rate on the average is great enough so that several or many pulses are produced within a time characteristic of the TOF function (Fig. 16). As these pulses travel through the TOF system, they will overlap spatially leading to a net steady state beam flux. Since the ion flux arriving at the detector is approximately constant in time, the detector does not differentiate between fast and slow ions; the distribution of ions causing detector counts will be distributed numerically in proportion to their velocity characterized number density in the ion beam. Similarly, ions which are rejected due to detector downtime will also be rejected in proportion to the velocity distribution ("counts neglected and not detected can be rejected"). This is another example of random phase sampling.

As an illustration, consider a measured TOF distribution of 6 μsec width at the detector generated by a mean modulation frequency of 1 megahertz. Since the modulation bandwidth is greater than the TOF bandwidth (as it must be for reasonable resolution), on the average, unit beam pulses will overlap spatially before they approach the detector. Now

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Fig. 16. The high relative repetition rate for the correlation method.

since there are runs of consecutive "1's" and "0's" in the modulation sequence, there is the possibility of negligible pulse overlap if a sufficiently long run of "0's" were present in the sequence. We recall from the discussion of *m*-sequences that the probability of having *n* consecutive "1's" or "0's" is 2^{-n} . For the 6 μ sec wide TOF signal, it would require a run of at least 6 zeroes to eliminate beam pulse overlap; thus runs of length *k*, $k < 6$, will not be subject to causing distortion. The total probability of having a run of zeroes greater than 6 is

$$P(n \geq 6) = \frac{1}{2} \left(1 - \sum_{k=1}^5 2^{-k} \right) = \frac{1}{64}$$

where the factor of $\frac{1}{2}$ is a result of only one half of the modulation sequence being comprised of zeroes. Thus, for this case, only 1.5% of the modulation pulses will allow the possibility of TOF distortion.

This necessity for beam pulse overlap puts another critical constraint on the length of the TOF flight path. Let's assume that one wishes to allow only a small fraction, ϵ , of the beam pulses not to overlap. Further assume that the TOF distribution has a maximum velocity, V_2 , minimum velocity, V_1 , and velocity bandwidth $\Delta V = V_2 - V_1$. To achieve overlap in a fraction of pulses $1 - \epsilon$ we determine *n* from the following inequality:

$$\epsilon \leq \frac{1}{2} \left(1 - \sum_{k=1}^n 2^{-k} \right) \quad (53)$$

The width of the TOF function at a detector placed *L* cm away from the source is

$$\tau_{\text{TOF}} = \frac{L}{v_1} - \frac{L}{v_2} = \frac{L\Delta v}{v_1 v_2} \quad (54)$$

To achieve the necessary overlap then,

$$\tau_{\text{TOF}} \geq n \tau_{\text{Mod}} \geq \frac{n}{B_{\text{Mod}}} \quad (55)$$

where τ_{Mod} and B_{Mod} are the modulation period and bandwidth, respectively. Equating (2) and (3) we find

$$L \geq \frac{n v_1 v_2}{\Delta v B_{\text{Mod}}} \quad (56)$$

Practically speaking, this inequality will practically always be satisfied since choosing L sufficiently large to give reasonable resolution will eliminate any beam overlap problem. However, this constraint warns us that if the TOF flight path is not sufficiently great, not only will there be poor resolution, but there may also be signal distortion.

We have included as an appendix a more rigorous derivation of the detector paralysis problem using a mathematical derivation based on the autocorrelation function of the modulation sequence. For further discussion, please see this appendix.

Shannon's Sampling Theorem

In viewing the correlation system, it seems somewhat like an experimenter is "getting something for nothing" by using such a system to gain increased signal detection capability. The answer to this allegation is contained in the well known Shannon Sampling Theorem.³¹

Shannon's theorem tells us that any information channel can be characterized as having a maximal information transfer capacity, and that any desired level of accuracy in information transfer through the channel can be achieved by error correcting codes³² at the expense of lowering the information transfer rate.

The TOF system can be viewed as an information transfer channel. The classical TOF method is an extremely inefficient mode of data transfer; it's somewhat reminiscent of a trans-Atlantic telephone conversation in which each word spoken must reach the other end of the line before the next word is uttered. Thus it is this tremendous inefficiency which makes the correlation method look efficient.

The classical method makes no explicit use of any error correcting code for information transfer. However, the use of single beam pulses is in reality a very simple transmission code. The correlation method on the other hand explicitly uses an error correcting code (random modulation) which is much more efficient. Whereas the classical method simply includes signal errors (noise) with the detected signal and later subtracts it, the error correcting property of random modulation is used explicitly to remove uncorrelated noise in the correlation method.

Although the correlation method makes much fuller use of the information capacity of the TOF channel, one can only wonder whether still more efficient methods might be found, further enhancing experimental accuracy and speed.

In summary, we have discussed the sources of experimental variance and found them not overly important. The correlation and classical methods were compared for accuracy and the former method shown to be

superior in many instances. The problem of detector par 'lysis was shown not to apply to the correlation system providing that the system is designed with a sufficiently large flight path. Finally, we have reviewed the information transfer aspects of the two systems and saw how coding led to increased information handling capability.

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CHAPTER III.

COMPUTER ORGANIZATION

This section is the first of several which discuss the electronic and informational techniques which have been used to implement a computer based TOF correlation system. Since the computer interface, the main object of the discussion which follows, is intimately connected with the internal hardware structure of the computer itself, we will first describe some of the pertinent organization within the computer. This discussion is admittedly brief; since many of the details of the computer's operation are beyond the scope of this thesis, the reader is referred to the DEC PDP8/e Small Computer Handbook.

The PDP 8/f is a 12 bit minicomputer with a 1.2 μ sec cycle time.

Overall, the basic computer organization can be described as follows:¹

"The PDP-8/E system consists of a central processor, core memory, and input/output facilities; all of which interrelate by means of a common bus called 'Omnibus.'

"All arithmetic, logic, and system control operations are performed by the central processor. Information storage and retrieval operations are performed by the core memory. The memory is continuously cycling, automatically performing a read and write operation during each computer cycle. Input and output address and data buffering of the core memory are performed by registers in the central processor, and the operation of the core memory is under control of timing signals produced by the central processor."

In essence, the central processor, via programmed control, manipulates the contents of the core memory in the process of performing arithmetic and logical operations in a logically ordered temporal sequence.

The computer's core memory consists of 8 K addresses ($1\text{ K} \equiv 1024_{10}$) divided into two 4 K fields. Each field is labeled by a three bit Extended Memory Address code (EMA), allowing up to 32 K of core memory to be employed. Each core address is capable of storing a 12 bit binary number. Within each 4 K field, memory addresses are divided into blocks of 200_8^* , denoted as "pages." Thus addresses 0, 200, 400, etc. each denote the start of a new core page. All programming operations are page relative; that is, when an address is named as an operand, it is specified relative to the beginning of the page on which the computer is currently operating. (For example, if the computer is operating on the page starting with address 1200, the address 1302 is specified as 102.) This type of addressing is a result of the 12 bit configuration of the computer's central processor. To specify an address in a 4 K field uniquely would require a 12 bit code; page relative addressing requires only 7 of the possible 12 bits contained as the contents of an address, leaving 5 bits available for actual operational instructions. It must be remembered that there are two 12 bit numbers associated with each address: the address code itself and its contents.

A simplified picture of the computer operation may be described as follows: the Central Processor (CPU) determines an operator address whose contents will determine the next operation to be carried out. The contents of the operator address contain both the operation to be carried out and an operand address whose contents will be the subject of the

*Octal notation will be used for describing the operations of the computer.

operation. The operation is performed on the operand contents and the result stored either in the operand address or in a storage register called the accumulator (AC). Next, the CPU looks in a Program Counter (PC) register to determine the next operator address, and the process then continues. A program consists of a series of such operations designed to achieve a mathematical calculation or logical core memory manipulation.

The Central Processor (CPU) of the computer consists of a timing sequence generator, an Instruction Register for programming operations, parallel adders, an Accumulator (AC) for recording the results of arithmetic and logical operations, and several 12 bit registers utilized in programming control. There are also gating networks for multiplexing input to and output from the CPU and the core memory. Most important of the control registers are the Central Processor Memory Address Register (CPMA) which stores the Memory Address (MA) which is currently being used by the CPU as an operand address, and the Program Counter Register which stores the memory address from which the next instruction will be taken at the completion of the current programming operation. During a programmed operation, the operand part of an instruction is stored in the CPMA, while the operational instruction is stored in the Instruction Register.

Normally, the Program Counter limits core address manipulation to one 4 K field of memory until the EMA is explicitly changed. In the absence of "jump" commands, programming is sequential; the CPU accesses the memory location contained in the Program Counter, performs the required operation(s), increments the Program Counter by one and continues

the processing. However, manipulation of the contents of the Program Counter allows non-sequential programming using JMP (jump) operation codes and allows the CPU to make transitions between the current core page and any other page.

Operations Codes

There are 8 operations codes which are employed in programming sequences. Of these, five are "memory reference instructions" which store and retrieve data from core memory, and one is the so-called "house-keeping" JMP operation which transfers program control to any memory address unconditionally (not a subroutine-type transfer). A list of the Memory Reference Instructions, their operations, and octal operation codes are given in Table A. The AND function is the only logical operation. The TAD and DCA instructions are used for arithmetic manipulations, while the ISZ instruction is used for program looping. JMS transfers control to a subroutine with an option for exit from the subroutine returning program control to the program location requesting the subroutine entry.

The remaining two operations codes are called "augmented instructions." Code 6XXn is used for input/output transfer (IOT) between the computer and its peripherals, each peripheral being assigned a six bit (2 digit) octal code (XX) which it alone recognizes. Code 7nnn is an operations code which allows manipulations of the contents of the AC and logical checking of the contents of the AC.

In the PDP 8, the octal numbers 0000-3777 are positive while the numbers 4000-7777 are negative. This allows twos complement addition as well as program looping by incrementing negative numbers (or positive

Table A. Memory reference instructions
for DPD 8/f

Mnemonic	Operation	Op. Code (Octal)
(1) AND	Logical $\oplus$ between AC and memory	0nnn
(2) TAD	Two's complement addition between AC and memory	1nnn
(3) ISZ	Increment memory, skip next instruc- tion if the result is zero; for program looping	2nnn
(4) DCA	Deposit AC in memory, clear AC	3nnn
(5) JMS	Jump to subroutine	4nnn
(c) JHP (housekeeping)	Unconditional jump	5nnn

numbers) until a zero result is obtained.

The Omnibus

The computer bus (OMNIBUS) is available to all of the computer's peripherals, as well as the CPU, and transports 96 different signals. Some of the more pertinent bus lines are as follows: The memory address lines (MA 0-11) which carry the MA being accessed currently by the CPU; memory data lines (MD 0-11) which transfer the contents of the address carried on the MA lines back and forth between core memory and the CPU; data lines (DATA 0-11) which carry the contents of the AC; and the timing pulses which are used to gate all operations both within the CPU and in the computer-peripheral interfaces.

Programmed Operation

We are now in a position to give a more detailed description of the sequence of events which occurs in programmed operation. Initially the computer is balted and the first address of the program is entered on the programmer's console. We assume that a correctly coded program has previously been stored in the core memory starting at this initial address. When the computer is started, the CPU examines the contents of the program counter, which now contains the initial address. Since the contents of the initial address are the first operation and operand in the programming sequence, the CPU gates on the MA lines to access this address (the operator). The operations code of the operator address is loaded into the 3 bit Instruction Register and the operand address is placed in the CPMA register. Using the memory data lines to access the contents of the operand address, the CPU carries out the specified operation on either the operand or the accumulator contents, or both.

The results of the operation are then either stored in the AC or gated back to the operand address via the Memory Buffer lines. The Program Counter is then incremented and the process continues. We have assumed here that a Memory Reference Instruction was being implemented. In the case of a jump or augmented instruction, the operation is rather a manipulation of the Program Counter, the accumulator or a peripheral device.

Data Transfers

Besides the augmented 6XXn instruction used for communicating with a peripheral device labeled XX, there are two additional modes of operation which are used for data transfer between the computer and its peripherals: interrupt transfer and direct memory access (DMA) or "data break" modes. Both of these modes of operation rely on an interrupting signal being generated by the peripheral itself; both modes provide for data transfer at the request of the peripheral device.

In an interrupt transfer, the peripheral raises a "flag" (pulls down the "interrupt line" on the OMNIBUS) telling the CPU that it wants access. The raising of a flag causes the CPU to interrupt its normal program routine and to jump to absolute location 0000 (within the current EMA field). Previously a program has been placed starting at location zero; this program acknowledges the interrupt, tests to determine which peripheral has made the request, and jumps to an appropriate subroutine which services the peripheral, using IOT's (6XXn) to complete the data transfer. Upon completion of the transfer, the subroutine returns program control to the point of operation in effect prior to the interrupt. Interrupt programming is used for servicing peripherals which do not have a critically short access time.

In comparison with interrupt transfers which modify normal program operation and require relatively little in the way of peripheral control logic, the data break (DMA) transfer is a "cycle stealing" technique which requires a complicated arrangement of control logic to disable the normal computer functions and to make the CPU a slave of the peripheral. With this type of transfer the normal operations of the CPU are temporarily suspended; the operational components of the CPU (i.e. the Program Counter, CPMA Register, Instruction Register and gating logic) are disabled and substituted for by a parallel set of logic in the peripheral device. The peripheral supplies the memory address, controls the operation to be carried out by the CPU arithmetic and logical elements and supplies its own data (for transfer into memory). Thus the Direct Memory Access mode can occur at any time and can transfer large blocks of data into or out of memory without disturbing (except temporally) the normal programming operation. The DMA mode effects data transfer at high speed and is used to service peripheral (such as a high speed disc file) which have a critical access time. It is this DMA mode which has been employed in data acquisition for our correlation TOF system.

Having examined the framework of the computer's operation, we next discuss the computer interface which allows the computer to acquire data from an ion beam apparatus, and which forms the heart of the correlation system.

THE CORRELATION SYSTEM COMPUTER INTERFACE

In any computer based data acquisition system, a central role is played by the computer interface logic. By itself a computer exists in an information vacuum. The interface provides the link between the computer and the outside world. The interface accepts information from external sources and is responsible for transduction of computer generated commands and calculations for application to peripheral output devices and the experimental apparatus. The interface is also responsible for synchronizing the asynchronous units involved in the experimental system.

In the present computer system, the interface has the central role in implementing the correlation method. It is the interface which modulates the ion beam apparatus, and which plays the command role in storing correlation information extracted from the experimental system. A general picture of the central role of the interface is presented in Fig. 17.

Overall, the interface resides on three printed circuit boards which fit directly into the computer and have access to all of the computer bus lines including timing signals, memory address lines and data lines. The Bin Time Clock Board contains a crystal oscillator and frequency dividing network, a pseudorandom binary sequence generator (PRNG), variable length shift register delay lines, detector output sensing device, and appropriate control logic.

The Data Break Board contains all of the data break logic, a device priority network, an input/output transfer (IOT) decoding network and a shift register storage line for retaining the delayed PRNG output for data correlation. Additionally this board contains a PRNG sequence sample and hold network connected in parallel with multiplexers used to gate

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Fig. 17. The central role of the computer correlation interface.

the memory address lines for storing data addresses during a data break.

The Digital to Analog Conversion Board (DAC) contains two 12 bit digital to analog converters used to display accumulated transformed data graphically on an oscilloscope, as well as a separate IOT decoding network and control logic.

Overview of Interface Operation

A block diagram of the functions contained on the Clock and Data Break boards is shown in Fig. 18. The time scale of interface operation is provided by the digital clock frequency dividing network, one of whose outputs is chosen to fit the required time scale of the experiment. The clock frequency is used to run all the registers contained in the interface including the random sequence generator (PRNG). The PRNG output is used to modulate the ion beam experiment; this output is also contained in a variable length digital delay line and stored dynamically in the shift register storage line. When a detector event is sensed, the delayed code contained in the storage line is stored in the computer core memory by the data address method (see "Application of Correlation TOF") through three sequential data breaks to three 1 K quadrants of the upper 4 K of the computer's memory. The sequential storage in each of the three quadrants is directed by the memory quadrant generator.

In the following sections we will describe in detail the design and implementation of the electronic circuitry which comprises the interface.

I. Bin Time Clock Board

1. Interface Bin Time Clock (Figure 19)

The computer interface design using a pseudorandom experimental modulation requires a stable, reproducible, variable rate clock signal

Fig. 18. Correlation interface block diagram.

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Fig. 19. Clockrate dividing network. (Times noted are the clock pulsewidth.)

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since it is this clock signal which determines the absolute time scale for the time domain measurement of the TOF distribution. The basic clock rate is produced by an X-tron 10 MHz crystal oscillator which is stable to within 0.001% (10 ppm). This base rate is divided by a digital dividing network (Fig. 19). The outputs from the dividing network are connected to the input of a digital multiplexer (Texas Instruments SN74151). Using the multiplexer, one of the available clock rates is selected via four data select lines, which are enabled by use of a "command word" decoding network (see "Command Word Control and IOT's" below) which allows programmed control of the desired clock rate.

The clock rate and period were measured using a calibrated Tektronix Type 555 Dual Time Base/Dual Beam Oscilloscope and a pulse generator for comparison. The rate was also measured using a frequency counter; the measured clock rate was equal to that expected, within experimental error.

2. Pseudorandom Binary Noise Sequence Generator (PRNG)

As was described in the theory of the correlation experiment, a linear shift register with modulo-2 summing feedback is used for generating an m-sequence to be used in experimental modulation.² The PRNG used in this case is constructed from two 10 bit serial in/parallel out static shift registers (Signetics 8273) (Fig. 20). To achieve maximal sequence generation with a 20 bit shift register, feedback from stages 3 and 20 are employed.³ As previously noted, the modulo-2 feedback is achieved by use of an "exclusive" or gate whose truth table for the present application is shown in Fig. 20. The output of stage 1 of the 20 bit register is connected to both the input of the digital delay line (see

20 3	1	0
1	0	1
0	1	0

Exclusive OR
Truth Table

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Fig. 20. PRNG configuration for maximal sequence generation: $N = 20$ stages.

below) and to a coaxial cable line driver (ST13) which drives a coaxial cable to the ion beam chopping circuit (see below).

Since the PRNG shift registers are run by the Bin Time Clock, the clock frequency establishes the base frequency for the PRNG output, thereby determining the band width of the experimental modulation.

Since the all-zero state of the shift register PRNG excludes generation of the desired m-sequence, the input of the PRNG (Stage 1) is ORed with the "Initialize" bus signal which is generated each time the computer is turned on. Additionally, the clock input of the PRNG is also ORed with the "Initialize" signal except that the application of the pulse to the clock input is delayed by a monostable multivibrator ("one shot"). This circuitry insures that each time the power for the interface is turned on, a "1" will be applied to the input of the PRNG and strobed into Stage 1 by the delayed initialize pulse; the initial state of the PRNG is always nonzero.

3. Classical TOF Capability

Although the normal operation of the data acquisition system will be in a correlation mode using PRNG output for beam modulation, the capability for operation in a classical TOF mode has been built into the interface. This mode of operation allows calibration of the time scale of the TOF spectrum and provides a means of corroborating the results of correlation TOF measurements.

For classical TOF operation, an external pulse generator (Tektronix PG501) is employed. The pulse width of the generator is adjusted to give a tolerable detector output rate while maintaining the greatest possible TOF resolution (pulse widths of ~ 2 μ sec). The pulse repetition rate is

adjusted until there is no overlap of individual beam pulses at the detector (typically 10 kHz). The pulse generator output is connected simultaneously to the beam chopping circuit and the input of the digital delay line (via an optical coupler). The output of the PRNG is turned off using command word I (see below). Beam pulses then travel through the ion path of the experimental apparatus as the corresponding digitized generator pulses travel through the shift registers of the digital delay line and the sequence storage register (see "Data Break Board" description below). The mode of data storage is identical to that used in the correlation mode of operation; using the data address method, detection of an ion at the end of the ion drift region causes three data breaks to record the length of the storage registers traversed by the digitized generator pulse responsible for admitting the ion to the beam path. The only operational change in data acquisition comes during the process of transforming the data stored in the core memory. Since there are only "positive correlations" between detector events and digitized generator pulses, it is unnecessary to subtract the negatively correlated transformed data (see "Program Description"). This positive correlation property is the result of the non-overlapping nature of the ion (and digital) pulse train.

4. Digital Delay Line

Since the interface will be used to examine the TOF spectrum of a variety of ion reaction products and may be applied to several apparatuses with quite different ion flight paths, the mean time of flight expected may vary from 10 μ sec to over 100 μ sec depending on the ion product mass and energy and the flight path of the apparatus. It is

thus important to have some measure of control over which particular time segment of the possible TOF spectrum is to be viewed by the correlator. For long flight times one could always reduce the Bin Time Clock rate such that no delay between beam modulation and detector signal would be required. However, this would entail a large loss in spectrum resolution and the measurement of narrow TOF distributions with long flight times would be fruitless (Fig. 21). By using a delay line to store the experimental modulation sequence during a long flight time, short duration TOF distributions with long flight times can be examined without a loss of resolution.

To be of use, a delay line must retain a faithful representation of the output of the PRNG; otherwise spurious noise is introduced into the correlation calculation. For this reason a shift register delay line has been applied in this case. The delay line is constructed in two parts (Fig. 22). One, the "short delay" is composed of two dual 8 bit serial in/serial out static shift registers (Signetics 8277) hooked in a head to tail configuration (Fig. 22). The output of each 8 bit register is connected to a one of eight multiplexer ("Short Delay") whose output is selected via three bits of the "Delay Command Word" (Command Word II - see below).

The "long delay" is constructed from a single hex-32 bit static shift register (Fairchild 3349), also hooked in a head to tail configuration (Fig. 22). The outputs are connected to a second one of eight multiplexer ("Long Delay") whose output is selected by three separate bits of the delay command word.

Possible "true" TOF spectrum

$\tau = \text{bin No.}$

Measured correlation function with
no delay, clock period = $3 \mu\text{sec}$

$\tau = \text{bin No.}$

Measured correlation function with
delay = $72 \mu\text{sec}$, clock rate = $1 \mu\text{sec}$

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Fig. 21. Increased resolution possible using digital delay line.

Fig. 22. Digital delay line construction.

XBL 748-6914

All of the delay line shift registers are clocked by the output of the Bin Time Clock. Thus the real time delay through any series of registers is a direct function of the clock rate; only the number of clock pulses needed to shift a pulse sequence through this series of registers is constant. To calculate the real time delay, one must multiply the delay length by the clock period. The total delay is the sum of the long and short delays. Any delay of from zero bins (clock pulses) to 224 bins, in steps of 8 bins, is possible by selection of the appropriate delay command word code.

The combined use of variable clock period and delay length allows great flexibility in viewing the TOF correlation function. Normally, a quick low resolution scan using a comparatively large clock period and no delay serves to determine the mean time of flight and its approximate width. Then, by using an appropriate delay and shorter clock period, the TOF correlation function can be expanded to fill the 30 channels of the correlator in a high resolution scan (assuming a sufficiently long flight path to establish a 30 μ sec wide realtime distribution). In some cases it may be desirable to examine only a portion of the TOF distribution using very high resolution. Practically, however, this would only be applicable to high mass ion products if a reasonable length (100-200 cm) drift path were being employed.

The delay line precision was examined as a function of delay time and clock rate by direct cross correlation of the PRNG output (delay input) with the delay output using a Hewlett-Packard 3721A Correlator. Since the period of the autocorrelation function of the PRNG output for 20 stage feedback is longer than any of the possible delay period, the

peak of the measured cross correlation function represented a direct measure of the delay time. The measured delay was consistently within 2% of that expected, and typically was within 0.5%. A picture of a typical delay cross correlation measurement is shown in Fig. 23.

5. Command Word Control and IOT's

The operation of the computer interface for data acquisition requires that the user maintain explicit control over the hardware generated options of the interface. This control ability is provided by a software mediated, hardware implemented decoding network by which the user chooses from a variety of modes of hardware operation.

As has been previously mentioned (see "Computer Organization"), computer peripherals, including the correlation interface, are controlled from the central processing unit of the computer by use of input/output transfer commands (IOT). Each peripheral device is assigned one or more six bit binary identification codes which it alone recognizes. In octal notation, IOT commands are of the format $6XXn$, where the 6 denotes that this is an IOT command, XX is the six bit device code, and n represents the particular (one of 8) command to the peripheral device. Since the recognition of each device code requires an independent decoding network, it is advantageous to restrict each peripheral device to one or two device codes. However, since there are at most 8 independent commands (3 bit code; $2^3 = 8$) which can be executed with a single device code, in using IOT's alone a hardware designer is faced with a trade-off between the needed programmable hardware flexibility and the size of the decoding network needed to implement it.

Fig. 23. Crosscorrelation measurement for experimental m-sequence (delayed autocorrelation).

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This tradeoff can be avoided by the use of a "command word" structure.⁴ In this method the information contained in many (up to 12 with the present computer) bits can be transferred for hardware execution by the use of a single IOT. The informational bits originate in the accumulator of the computer, having been loaded previously into the accumulator by a program control sequence. On IOT command, the informational bits which are present on the 12 data lines (on the OMNIBUS) leading from the accumulator are strobed into a series of one bit latches (D flip flop) which are contained within the peripheral device. The latches record the information contained in the computer code and execute the coded commands by enabling gates controlling the hardware options or by selecting the inputs of multiplexers. Using a command word structure as many as 96 bits of information for hardware control can be transferred using a single IOT decoding network.

In the present interface, one IOT decoding system (code = 33) is used. A summary of the IOT commands is shown in Table I; 3 IOT's are used for the control of 3 command words (Command Word I, Delay, Clock), 2 IOT's are used for control of the data overflow facility, and two others are applied to hardware testing procedures. Command Word I is a general purpose control word which exclusively executes hardware options by enabling AND gates on the interface boards (Table II); these gates are primarily used for turning on or off several logical units of the interface hardware such as the Bin Time Clock, the Data Break facility, the detector input, or the hardware test facilities.

Command Word II (Delay) is used to control the length of the digital delay line (Table III), while Command Word III (Table IV) allows selection

TABLE I

INTERFACE BOARDS IOT INSTRUCTION SET

DEVICE CODE = 33

Code	Interface Action
6330	Not used
6331	Load command word I from AC
6332	Load delay (command word II)
6333	(Software sequence entry)
6334	Skip on overflow
6335	Imitate detector pulse input
6336	Load bin time clock (command word III)
6337	Reset overflow

TABLE II

COMMAND WORD I; LOAD WITH 6331													
Data Bit		0	1	2	3	4	5	6	7	8	9	10	11
<u>Gate</u>		<hr/> not used											
Data Break	On	1											
	Off	0											
Clock	On		1										
	Off		0										
Overflow	On			1									
	Off			0									
EMA Field	On				1								
	Off				0								
TOF	Classical					1							
	Correlation					0							
Detector	On						1						
	Off						0						

Normal operation code: Correlation = 7500

Classical = 7700

TABLE III

COMMAND WORD II DELAY; LOAD WITH 6332							
Data Bit	0	1	2	3	4	5	6-11 not used
<u>Long Delay</u>							<u>Code</u>
0 bits	0	0	0				0000
32 bits	0	0	1				1000
64 bits	0	1	0				2000
96 bits	0	1	1				3000
128 bits	1	0	0				4000
160 bits	1	0	1				5000
192 bits	1	1	0				6000
<u>Short Delay</u>							
0 bits				0	0	0	0000
8 bits				0	0	1	0100
16 bits				0	1	0	0200
24 bits				0	1	1	0300
32 bits				1	0	0	0400
All zero out				1	1	0	0600
All ones out				1	1	1	0700

Long delay + short delay $\approx$ long code + short code = total code $\approx$ total delay (i.e. 64 bits + 8 bits $\approx$ 2000 + 100 = 2100 $\approx$ 72 bits).

TABLE IV

COMMAND WORD III		BIN TIME CLOCK; LOAD WITH 6336					
Data Bit (0-7 not used)		8	9	10	11		
<u>Frequency</u>		<u>Code (101)</u>					<u>Bin time (μsec)</u>
2000	KHz	0	0	0	0	0	.5
1000		1	0	0	0	1	1
500		2	0	0	1	0	2
250		3	0	0	1	1	4
200		4	0	1	0	0	5
125		5	0	1	0	1	8
100		6	0	1	1	0	10
50		7	0	1	1	1	20
25		10	1	0	0	0	40
12.5		11	1	0	0	1	80
10		12	1	0	1	0	100
5	KHz	13	1	0	1	1	200

of the rate for the Bin Time Clock. Both of these command words are executed by multiplexer selection from multiple inputs to give a single desired output.

6. Detector Input

Since all of the interface hardware employs TTL^{*}, all signals coming into the interface must be digitized to the proper voltage levels before they can be utilized. The ion detectors currently used in our laboratory for TOF are of the electron multiplier type (Channeltron or Bendix Magnetic Multiplier) which, when coupled with an output pre-amplifier, produce negative output pulses approximately one volt in amplitude and 500 nanoseconds in duration. To conform with the TTL logic of the interface, a comparator circuit with a variable discriminator lower level and variable width output pulse is used to convert the (0, -1 volt), detector output signal into a TTL compatible (0, +4 volts) waveform (see below for complete comparator description). The comparator output is connected by a 50 Ω BNC cable to the input of an optically coupled TTL gate (Motorola MOC 1000 or 4N25). The optical coupler eliminates the possibility of external noise pulses overloading the interface TTL logic causing damage to the hardware.

The output of the optical coupler is used to initiate the data break cycle of the interface for storing correlation data in the computer's core memory. (A similar optical coupling scheme is employed for inputting pulses from the external pulse generator when the interface is operated in a classical TOF mode.)

^{*}Transistor-Transistor Logic Defines logical "0" as a voltage less than +0.8V. and logical "1" as a voltage greater than +2.8V.

11. Data Break Board

1. The Data Break Hardware

Within the correlation interface, the data break facility fulfills the important function of transferring correlation data from the interface to the core memory of the computer, where it is stored for later analysis. The data break sequence is triggered into action by the arrival of pulses from the ion detector; once this triggering has been effected, a rapid series of hardware events takes place in an orderly manner with each event being synchronized by the internal computer bus timing signals. As previously noted, during a data break data transfer the functions of the central processor registers are taken over by the external logic hardware of the interface while the CPU registers are disabled. Since the description of the data break event sequence is intimately involved with the computer's hardware structure, we suggest that at this point the reader should review the "Computer Organization" section presented earlier.

A schematic diagram of the basic data break hardware is shown in Fig. 24. With reference to this figure, we now describe the sequence of events which comprise a data break transfer.

The data break is initiated when a Break Request latch is triggered by an incoming detector pulse. At an appropriate sampling time, the New Break flip flop is clocked by the Internal Strobe pulse from the Omnibus, requesting a device priority check, disabling the central processor Memory Address register and signaling the CPU that a data break is in progress.

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Fig. 24. Basic data break hardware system (DEC Small Computer Handbook).

The device priority system provides a means for causing the computer to service peripheral devices requesting a data break according to which device has been assigned the higher priority. Such a system is necessitated by the fact that often two or more devices may simultaneously (within a single computer memory cycle of 1.2 μ sec) request a data break. In such a case, one wishes to allow data transfer from the fastest (hence highest priority) peripheral first (such as a disc). The priority network of the correlation interface checks, by use of the data lines of the Omnibus, whether any higher priority device is also requesting a data break. If so, the interface must await completion of the data transfer from the other device before its own data break proceeds. As a practical matter, there are currently no other data breaking devices presently incorporated in the computer system and the interface will be permitted to continue its requested data break immediately. However, later addition of a disc or tape file to the system would require the priority system to be installed in all data break devices, so it has been included in the present design as a matter of course. The correlation interface has been assigned a priority of 3 (out of a possible 12; top priority is 1).

Once the device priority has been established, the CPU Instruction Register and the Major State Register (which controls read and write operations) are disabled and the CPU Memory Address (CPMA) loading from the Program Counter is inhibited. The direction of data transfer (into the core memory in this case) is established and the contents of the Break Memory Address Register of the interface (denoting the core address to be accessed during the data break - see below) are gated onto the Memory Address line of the Omnibus (which are also connected to the CPU).

At this point the contents of the object address (on the Memory Address lines) are gated onto the Memory Data lines, pass through the CPU parallel adders where the contents are incremented by one ("add-to-memory"), and the result returned via the Memory Data and Memory Buffer lines to the object memory address. The net result is that the contents of the address contained in the Break Memory Address Register have been incremented by one. This completes the task of the originally requested data break. However, in the case of the correlation interface, we recall that since three separate addresses must be incremented to store the information contained in the 30 bits of the modulation sequence, two further data breaks will be immediately requested and carried out.

In reality, there are many additional gating and directional signals which must be generated for the successful completion of the data break. However, they are not conceptually important in understanding the method and will not be discussed. The reader is again referred to the discussion in the PDP8 Small Computer Handbook

2. Generation and Storage of the Break Memory Address

In the description of the correlation method ("Application of the Correlation Method"), we noted that the correlation function is accumulated by incrementing three core memory addresses contained in the delayed PRNG output sequence present at the time a detector output pulse arrives at the interface. The conversion of the PRNG output sequence into usable memory addresses is accomplished in the following manner (see Fig. 25).

The modulation sequence emerges from the digital delay line on the Bin Time Clock Board and is transferred via one line of a 16 line board

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Fig. 25. Generating data break memory addresses.

interconnect cable to the Data Break Board. The sequence is input to a shift register storage line comprised of three 10 bit serial in/parallel out registers (Signetics 8273) hooked in series and clocked by the Bin Clock output (also transferred by the board interconnect cable). The parallel output of the storage line is connected to the input of five hex-latches (Texas Instruments SN74174). Using a monostable multivibrator (TI SN74123), each clock pulse is delayed and then used to strobe the contents of the storage line into the latches after the storage line contents have been shifted (sample and hold). (This strobe pulse is inhibited by the arrival of a detector pulse until the currently stored sequence in the latches has been used as the Break Memory Address for the three resulting data breaks.) The storage line is necessary to maintain the continuity of the PRNG output sequence while data breaks are being completed.

With each detector output pulse, the three data breaks necessary to record the 30 bits of correlation information use a 10 bit segment of the modulation sequence which has been stored in the sample and hold latches. During each break, 10 bits of the sequence are concatenated by a data multiplexing system with a 2 bit "quadrant code" which supplies the two most significant bits of the Break Memory Address and hence determines which 1 K portion of the upper 4 K field of memory the least significant 10 bits pertain to (Fig. 26). The quadrant code also provides the data multiplexer data selection code necessary to choose which ten address bits (of 30) will be gated onto the Memory Address lines during each data break. The Memory Quadrant Generator is a 2 bit binary counter (TI SN 7490) which is reset to the first quadrant (01) by the incoming detector

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Fig. 26. A sample of break memory address formation.

pulse and incremented (to 10 and 11) before each of the two subsequent data breaks. Thus if the 30 bit modulation code can be represented by three 10 bit numbers, N_1 , N_2 , N_3 , the addresses which will have their contents incremented by one during the three data breaks will be $01N_1$, $10N_2$, and $11N_3$.

We have now completed the connection between the delayed modulation sequence and the storage of correlation information by the data address method.

3. Data Overflow

As data is accumulated through repeated data breaks, eventually the 12 bit capacity of the core memory addresses will be exceeded causing data overflow. The effect of an overflow is to change the contents of a memory data address from 7777_8 to 0000_8 since $7777_8 + 0001_8 = 10000_8 \equiv 0000$. This is a totally undesirable effect since overflow will be correlated with addresses whose address bits are representative of sequence segments which are highly correlated with measured detector pulses. Preferential overflow and subsequent zeroing of some addresses will cause distortion of the shape of the transformed TOF correlation distribution favoring buildup of signal in those channels with smaller net signal heights.

To avoid this overflow condition, the data break logic is equipped with an overflow sense line connected to an overflow flip flop. During a data break, when the contents of a data storage address have been incremented, the incremented contents are gated back to the Break Memory Address on the Memory Data lines; it is at this point that a data overflow is sensed. When the two most significant bits of the Memory Data

lines are both in a "1" state (6000₈ detector counts in the Break Memory Address) during a data break, the overflow latch is set raising a flag which, by interrupt programming routine, causes the computer to cease data acquisition and initiate the data transformation routines. Since the contents of the core memory data storage addresses never exceed 6000₈ (maximum capacity is 7777₈), there is never any real data overflow which can occur.

This concludes the description of the Data Break Board Hardware.

III. Hardware Test Facilities and Checkout Procedures

To facilitate testing of the interface, several software controlled testing facilities were built into the interface. We will describe these and the testing procedures briefly.

Two of the available eight device IOT's have been dedicated to testing procedures. The first, IOT3, enables the user to design a software program for entering a given binary test sequence into the digital delay line and subsequently into the Break Memory Address, mimicing the function of the random sequence generator in a known, predetermined manner. This IOT loads the least significant bit of the accumulator (Data 11) into the delay line by gating Data 11 onto the delay line input and then clocking the delay line shift registers to enter the data bit using the IOT3 pulse delayed by a monostable multivibrator. One need only load the accumulator bit 11 and then apply IOT3 to load each bit of the desired testing sequence into the delay line registers. By this method a known sequence can be generated by software for use as a Break Memory Address. To employ this procedure, both the Bin Time Clock and the PRNG output must be defeated using Command Word I (Table II).

Once a test sequence has been entered, the second test IOT, IOT5, which simulates an incoming detector pulse, is used to cause one or more data breaks to the known core memory address contained in the software test sequence. Subsequent examination of the contents of this address reveals whether the data break system is functioning correctly.

It should be noted that the connection between Data 11 of the accumulator and the delay line input was removed after initial testing and the input employed for classical TOF pulse sequence entry. (To re-establish this facility, the connections E10-7 → E26-9 and E31-3 → E26-10 must be made on the Clock Board.)

Some further test procedures which have been used are as follows:

1. Clear the memory data storage block, defeat the Bin Time Clock and use an external pulse generator for repeated data breaks to the three frozen Break Memory Addresses by simulating detector input. (The three addresses can be seen on the programmer's console by single stepping the computer operation). This process allowed estimation of the maximum detector input rate which can be tolerated by the data break system (about 100 kHz) and was used to check the overflow facility. IOT5 can also be used in place of the pulse generator for the latter test.

2. Rather than using the frozen Break Memory Address in the tests described above, by selecting the proper short delay code (Table III), all ones or all zeroes can be loaded into the Break Memory Address for testing as above.

3. To check both the function of the data break and the accuracy of the data transformation, the PRNG is allowed to supply random Break Memory Addresses while the unrelated asynchronous output of an external

pulse generator is used to simulate detector output. (IOT5 can also be used.) Since the "detector output" is uncorrelated with the "modulation signal" of the PRNG output, the net transformed correlation function should be zero everywhere (except for small statistical fluctuations), as was found to be the case.

4. The Classical TOF distribution provides an additional check on the operation of the data break system.

All of the above procedures were found helpful for electronic debugging of the correlation interface. While constant interface testing should be unnecessary, periodic checks of the interface functions are certainly in order.

IV. Board Interconnect Cable

Since signals are generated on each of the two main interface boards which are required for use on the companion board, a 16 line interconnect cable is used to transfer signals between the two boards. A list of these signals is shown in Table V.

The potential user is cautioned that both of the two main boards must be emplaced in the computer bus and the interconnect cable must be connected between the two if either is to be put into the bus. Failure to follow this rule will cause destruction of core memory software and generally will make the computer nonfunctional. It is also quite important to ensure the proper connection of the interconnect cable on both ends, or damage to the interface may result.

V. D/A Converter Board

The Digital to Analog Converter Board is used to display accumulated transformed data. Two 12 bit DAC's (11 signal bits + sign bit; Hybrid

TABLE V

INTERCONNECT CABLE		(CLOCK BOARD ↔ DATA BREAK BOARD)	
		E10 ↔ C7	
Pin	Line	Pin	Line
1	Clock output	9	NC
2	Delayed PRNG sequence	10	NC
3	NC	11	IOT 6 [10-7]
4	NC	12	My device [14-3]
5	IOT 1 [10-2]	13	EMA field [E19-10]
6	IOT 2 [10-3]	14	Break on/off [E14-2] [E19-7]
7	IOT 3 [10-4]	15	Overflow on/off
8	NC	16	Detector on/off [E26-3]

Systems DAC372-11 with 0.025% linearity, 2 volt/ μ sec slew rate, and 5 μ sec maximum settling time) were chosen which were sufficiently fast and reasonably inexpensive. One DAC is used for converting the X-axis of the display (TOF distribution Bin number) and the other for converting the Y-axis (relative correlation function height). The conversion of each axis is accomplished by clearing the accumulator of the CPU and giving an appropriate IOT causing the proper DAC to be loaded from the data lines. The board has its own device codes (05, 06; see Table VI) and IOT decoding networks. The display of data is controlled by a software subroutine of the main program monitor (see "Computer Program" below) which automatically scales the X-axis to allow 30 TOF channels to span the entire voltage range of the X-axis DAC. The resulting analog X-Y plot of the data is displayed on a Tektronix 545B oscilloscope.

VI. Voltage Comparator

As noted above, a voltage comparator circuit is employed to convert the preamplified electron multiplier detector signal into a TTL-Compatible Waveform. This circuit* (see Fig. 27) employs a voltage comparator (National Semiconductor LM306) to determine when the output voltage of the ion detector circuit becomes more negative than a variable reference threshold voltage which is controlled by a potentiometer. The comparator circuit has the ability to use either positive or negative going pulses as its input.

When the comparator is turned on by the magnitude of the detector output voltage surpassing that of the reference threshold, a variable

*Originally designed by the U.C. Berkeley Dept. of Chemistry Electronics Shop.

TABLE VI

D/A CONVERTER BOARD IOT INSTRUCTION SET

DEVICE CODES = 05, 06

Code	Action
6051	Clear X
6053	Clear X and load X
6054	Intensify X
6057	Clear X, load X and intensify
6061	Clear Y
6063	Clear Y and load Y
6064	Intensify Y
6067	Clear Y, load Y and intensify
MD 11 → load registers	
MD 10 → enable data lines	
MD 9 → intensify sequence	

width output pulse is generated by a monostable multivibrator (TI SN74121). The width of the output pulse is controlled by a potentiometer which varies the RC time constant of the multivibrator. Finally, the output pulse is driven from the comparator circuit to the computer interface on a BNC cable by a Dual Differential Line Driver (National Semiconductor DM 8830).

VII. Ion Beam Chopping

In ion beam TOF experiments, a central problem is the construction of an adequate beam chopping mechanism. In this section we will define the chopping problem and describe the simple electronic circuitry which we have applied to the correlation TOF system for beam modulation.

There are two types of problems associated with ion beam chopping: the effects of modulation bandwidth on signal resolution and the electronic problem of implementing wide bandwidth modulation of an ion beam using large amplitude voltages. The first problem is more subtle and arises from the intimate connection between modulation and detection. The second problem is an obvious one whose basis is technological. Together they require careful design of a beam chopping system to ensure successful measurement.

In part, the difficulty in chopping an ion beam arises from the large ion velocities which are typically found in ion beam experiments. While neutral molecular beam projectiles typically have thermal velocities of $\sim 10^4$ cm/sec, slow enough to permit mechanical chopping, the projectiles in an ion beam have velocities of the order of 10^6 cm/sec. This higher velocity makes mechanical chopping of ion beams impossible. However, since ions are charged particles, electrostatic deflection methods

are readily applicable to an ion beam system.

In an electrostatic chopping system, one or more metal deflecting plates (grids) are positioned parallel to the path of the ion beam in close proximity to it. An electronically generated chopping signal is used to apply voltages to the grids. Depending on the voltage applied to the grids, the beam is either allowed to pass into the TOF apparatus undeflected (beam "on") or deflected away from the apparatus so that no ions reach the detector. Thus the problems associated with actual beam chopping are basically electronic.

Even with the fast electronic components available currently, the problems associated with chopping an ion beam are nontrivial. As has been previously noted, a TOF experiment has its resolution limited by the width and precision with which pulses of ions are admitted to the apparatus. With electrostatic chopping, the maximum chopping rate is determined by several experimental variables: the ion mass, the deflection required to remove ions from the beam path, the ion velocity, the rise time of the deflecting pulses and the width of the chopping region. All of these variables bear on the problem of adequate deflection while ion velocity and the width of the chopping region are responsible for signal resolution.

The signal resolution question can be summarized in the following way: for any TOF experiment there are two natural time periods whose dimensionless ratio serves to scale the experiment. These are the overall time of flight and the width of the TOF distribution, denoted by τ_{TOF} and τ_w , respectively. Of course, each of these is a function of the length of the flight path; however, for any given experiment the ratio,

$\alpha \equiv \tau_w / \tau_{TOF}$, will be invariant. Typically this ratio is less than 0.10, i.e. the width of the distribution is less than 10% of the total flight time. This fact by itself presents no problem. However, as we will discuss below, there exists a fundamental limitation on the modulation bandwidth which can be applied with a beam chopper. Since the modulation bandwidth fixes the time resolution with which the TOF signal is viewed, to achieve a given resolution a severe limitation is placed on the minimum flight path that must be used for experiments.

More explicitly, consider that one wishes to view a TOF distribution with a resolution R . R is determined by the number of discrete time channels which span the TOF distribution as it is measured at the detector. If the bandwidth of the source modulation is such that each channel is of width τ_{mod} , then

$$R \sim \tau_w / \tau_{mod}$$

Recalling that $\tau_w = \alpha \tau_{TOF}$,

$$R = \frac{\alpha \tau_{TOF}}{\tau_{mod}} \quad \text{or} \quad \tau_{TOF} = \frac{R \tau_{mod}}{\alpha}$$

where again, α is the dimensionless time scale which fixes the relative width of the TOF distribution in terms of the total time of flight.

A typical limit on the modulation band width is 1 megahertz so that the minimum $\tau_{mod} = 1 \mu\text{sec}$. To see how this poses a restriction on the time of flight (path length), let's suppose that we desire a resolution of 20 (i.e. 20 points of the calculated correlation function will define the shape of the TOF distribution) and that α has the value 0.05, not an unrealistic value. Then

$$\tau_{\text{TOF}} = \frac{(20)(1 \text{ } \mu\text{sec})}{0.05} = 400 \text{ } \mu\text{sec} !$$

For a typical ion of mass 30 at an energy of 5eV, the velocity is approximately 5×10^5 cm/sec.

Therefore, to achieve a resolution of 20 for such an ion in a TOF experiment a 200 cm flight path would be required. This is a somewhat large figure; it becomes apparent how important the limitation on modulation bandwidth is.

This limitation on bandwidth arises in the following manner: the time width of an ion beam pulse cannot be made shorter than the time it takes for an ion of minimum velocity (for whatever experiment is at hand) to traverse the chopping region. As ions pass through the chopping region, only those deflected less than a minimum amount (discussed below) will pass unhindered into the TOF analysis system. If the pulse repetition rate for modulation were large enough so that several deflecting pulses were applied to the deflecting grids during the time each ion traversed the grid region, every ion would be partially deflected as it passed through. (Here we are assuming the use of correlation modulation which consists of a rapid train of modulating pulses. For classical modulation the analogous statement concerning ion transmission is that the deflection voltage is never turned off long enough to allow ions to pass through the chopper.)

For correlation modulation, only those ions which enter the deflection region at a time when a series of consecutive "beam on" pulses were applied to the chopper (a run of "1's" in the chopping sequence) would be

allowed to pass through unhindered. Depending on the actual modulation bandwidth, all single "beam on" pulses which were contained in runs of one or two (or more) would be ineffective for causing ions to enter the TOF analysis system; the net result is that no matter how large a modulation bandwidth was applied to the beam chopper, the effective modulation bandwidth would be limited by the ion passage time through the chopper. (The problem of ions passing through the beam chopper is somewhat reminiscent to the following physics problem: An electromagnetic wave of a single frequency (photon) is propagating through space. Being of a single frequency, of course its position is completely indeterminate. If the wave passes through an open door and you proceed to close the door, which side is the photon on?)

A separate problem which must be overcome in ion beam chopping is that of achieving fast risetime chopping pulses sufficient to provide a good approximation to a square wave modulation signal using short (0.5 cm) chopping grids. A schematic diagram defining the system is shown in Fig. 28. A pair of deflecting grids separated by a width d and of length l are placed in a region of total length L . A deflecting voltage of magnitude $\pm V/2$ is applied to the grids to turn the beam off. We assume here that the ion beam is of negligible width, that all beam ions are moving parallel to the beam axis, and that a potential of $V = 0$ is applied to the grids when the beam is turned "on." The exit of the chopping region is defined by an aperture of diameter b ; a collimated ion beam enters the chopping region from the left and in the absence of deflecting voltages, passes through the exit aperture and into the TOF analysis region. When the deflecting voltage is applied, a uniform

Fig. 28. Deflection geometry for beam chopping.

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transverse electric field of strength V/d is present between the deflecting plates. For simplicity, we will assume that the most efficient space utilization ($l = L$) is being employed.

The object of our investigation is now to determine the voltage necessary to be applied to the grids to cause sufficient ion deflection. An ion of mass m , longitudinal velocity u and charge e entering the chopping region will traverse that region in a time $\tau = l/u$. Using Newton's laws, the total deflection caused by the ion when the grids are charged will be

$$\Delta x = 1/2 a_1 \tau^2 = 1/2 e V/d (l/u)^2$$

For successful deflection $\Delta x > b/2$ so the required voltage is

$$V \geq \frac{bd}{e} (u/l)^2$$

Note the l^2 term in the denominator. Since we wish to make the chopping region as short as possible, it is easy to see how the voltage required for deflection can increase rapidly as l is diminished.

The above discussion has assumed that the deflecting voltage has been applied before the ion enters the chopping region. For a more general analysis we assume the modulating pulse has the rising shape shown in Fig. 29. The total grid voltage, V , is a linear function of time until it reaches its "steady state" value, V_0 :

$$V = ktV_0 \quad 0 \leq t \leq t_0; \quad kt_0 \equiv 1 \text{ (linear approx.)}$$

$$= V_0 \quad t_0 < t \leq t_1$$

where t_1 is the time the ion either exits from the region or is deflected

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Fig. 29. Voltage character of the deflection pulse.

onto the plate of the collimator. If the deflecting pulse is initiated at $t = 0$ when the ion has already traversed a distance ϵ into the deflecting region there are two possible cases to consider:

$$(1) \quad \frac{(l-\epsilon)}{u} < t_0 : \Delta x = 1/4 a_0 k \left(\frac{l-\epsilon}{u} \right)^3$$

$$(2) \quad \frac{(l-t)}{u} > t_0 : \Delta x = 1/4 a_0 t_0^2 + 1/2 a_0 \left(\frac{(l-\epsilon)}{u} - t_0 \right)^2$$

where $a_0 = \frac{eV}{d}$ and the results come from simply integrating $F = ma$. A similar set of equations will hold for the case of an ion being present in the chopping region when the deflecting pulse is turned off. These expressions allow the calculation of the maximum distance, ϵ , which the ion can traverse before the deflecting pulse is applied and still be deflected out of the beam path sufficiently. In practice there will always be some ions in the chopping region which will not be deflected sufficiently. These ions will be negligible in number (compared to the total flux in a beam pulse) provided that the deflecting voltage is sufficiently large and if the risetime of the chopping pulse is small enough.

It has been recently pointed out that such sampling of a continuous ion source may lead to distortions in the TOF spectrum.⁵ We have noted some broadening of the TOF spectrum when a single deflection grid is used. In this case the potential along the ion path becomes nonzero when the deflecting voltage is applied, allowing both fringing field effects and risetime and falltime accelerating effects to affect the TOF spectrum. The use of a symmetrical grid system removes the possibility of such

effects.

For our current TOF system, we have determined that for a 1 megahertz chopping rate, a deflection voltage of $\pm 30V$ will be sufficient to deflect ions with a 0.5 cm grid length. The application of a 30 volt signal at 1 megahertz leads to restrictions on the RC time constant for the system. We have achieved a 100 nanosecond risetime using the chopping circuit described below by mounting the chopper as close to the chopping grids (v1 foot) as possible in order to cut down stray capacitance.

We note that there are two methods by which chopping might be improved. One is to reduce the space between the chopping grids as well as the diameter of the exit aperture. This, however, will be limited by the increasing capacitance of the parallel grids as they are moved closer, and by the loss of ion flux due to the smaller aperture size. The other means by which chopping might be improved would involve deceleration of the ions after they have passed through the target interaction region of the TOF analysis system. This has the effect of increasing the effective flight time and hence the relative resolution which can be achieved with a given beam chopping modulation bandwidth.

The Present Beam Chopping System

The beam chopping system which we are currently using is shown in Fig. 30. The circuit is essentially composed of two transistors which control the grid voltages. When the transistors are turned off (beam off) the grids float at ± 30 volts. When the transistors are turned on, current passes through the emitters, causing a voltage drop across the voltage adjustment potentiometers. Thus by adjusting the potentiometers, the grid voltages are selected to pass a maximum amount of the ion beam

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Fig. 30. Beam chopping circuit.

through the deflection region when the beam is turned on.

The input of the chopping system can be chosen from two modes. In the "adjust" mode, the input to the DM8830 line receiver is held high so that the transistors are turned on and the potentiometers can be adjusted for maximum detector signal. In the "run" mode, the line receiver input is switched so that the output of the random noise generator is applied to the chopping circuit, turning the beam on and off randomly. The chopper is mounted as close to the beam apparatus as is possible to reduce the capacitance of the input to the grids (<100 pf) to reduce the RC time constant of the grid circuit.

Because of limitations on the interface electronics, a maximum modulation band width of 1 MHz has been used with this system. For the 5mm length of the deflecting grids this is close to the maximum chopping rate which can be tolerated for most ions. We have determined empirically that pulse widths of less than $1/2$ μ sec lead to severe attenuation of the transmitted ion signal, so that the 1 MHz limitation is pretty much applicable to each of the components within the system.

The chopping system has worked more than adequately at the 1 MHz bandwidth for both classical and correlation TOF measurements. We note that the chopping circuit in its final form was designed by Mr. Paul Salz of Lawrence Berkeley Laboratory. It is remarkably effective considering its simplicity.

This concludes our discussion of the conceptual and electronic methods which together comprise the correlation TOF interfacing system. We have shown how the use of an electronically generated modulation system coupled with a direct memory address data storage system can be

used to extract the correlation information which describes a TOF distribution.

In the following section we will describe the computer program which controls this experimental system and which is used for data reduction.

Fig. 12. Crosscorrelation with gated scalars.

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from a peripheral device causes program control to be transferred to a service routine appropriate to the particular device. A sample skip chain program is shown in Fig. 31.

The keyboard monitor is the primary control facility for the computer system. This monitor is a keyboard service routine which responds to the ASR33 Teletype or the keyboard of a Tektronix 4010 Display Terminal. When an alphabetic key on either keyboard is struck, the service routine determines which letter was sent from the peripheral and searches through an alphabetically coded table of subroutine addresses. Once the alphabetically coded address is found, the computer jumps to the start of the corresponding subroutine. With this method, as many as 26 independent entry points into system monitor subroutines can be accessed at any time when the interrupt system of the computer is enabled. To add a new entry point for a subroutine, the user has only to place the subroutine's starting address in the coded table position corresponding to the (previously unused) desired code letter. The keyboard monitor rejects all numerical and punctuation characters by typing a "?" and returning to a wait loop where program control normally resides. The same rejection procedure is also applied to unused alphabetic codes.

II. The Operational Subroutines

We will now describe the subroutines which actually control the computer interface and data acquisition. Each is accessed by a separate alphabetic code.

An important "subroutine" which is used is the Octal Debugging Technique (ODT) program which is a standard DEC program (access code = A). This program allows communication with and alteration of any other source

Figure 31. A skip chain

Location	Command
0000	Turn off interrupt
0001	Skip if TTY flag set
0002	Skip (unconditionally)
0003	Jump to TTY service routine
0004	Skip if overflow flag set
0005	Skip
0006	Jump to overflow service routine
0007	Skip if printer flag set
0010	Skip
0011	Jump to printer service routine
'	'
'	'
'	'

program in the lower 4 K field of memory. It is used in the system monitor because it facilitates program statement modification (changing the contents of addresses which contain other programs). This statement modification is used for inserting different command word options (see "Interface Description"), for entering new subroutines and modifying them. ODT also contains a breakpoint facility* which is useful for debugging new subroutines.

The "Start" subroutine (access code = S) is used for interface initialization and to clear the data acquisition portion of the core memory (2000₈-7777₈ of the upper 4 K field). This routine resets all interface command words to zero and clears all interrupt flags. It zeroes the data addresses in the upper 4 K field of core memory and then sequentially loads each of the three command word codes into the accumulator and strobes them into the interface latches using the proper IOT's. The interrupt facility is enabled, the data break system is turned on to initiate data acquisition and program command is then transferred to the keyboard monitor wait loop.

The "Classical TOF" subroutine (access code = B) is used when a classical TOF mode of operation is desired. This routine alters the command word I code to enable classical TOF operation and makes a minor change in the data transformation routine (see below) by program address modification. It then jumps to the "start" subroutine which carries on as before, except that a different command word I code is loaded.

*The breakpoint facility allows the user to run a program up to any pre-determined internal point (breakpoint) at which time program control is returned to ODT for program analysis and modification.

The "Correlation TOP" subroutine (access code = C) is used for correlation TOP measurements. As with the classical mode, this routine modifies the Command Word I code and the data transformation subroutine and then enters the "start" procedure.

The "Data Transformation" routine (access code = U) is exceedingly important, as it halts further data acquisition and extracts the correlation function information from the data stored in the "data addresses" of the upper 4 K of core. Since this routine is fundamental to the computer correlation method, we will describe it in some detail.

We first recall that the correlation information is stored within the configuration of each address and that the contents of each address merely denotes the number of times that address code was stored in the Break Memory Address Register at the time a detector event occurred. What we wish to compute is the total number of times a particular bit was equal to "1" during a detector event; this corresponds to a positive correlation between a one being in that bit position and a detector event occurring. Similarly, the number of times a bit was "0" at the time of a detector event provides the number of negative correlation between the bit position and detector events. The net value of the correlation function associated with any bit position is the number of positive correlations minus the number of negative correlations.

Since the data is stored as three 10 bit sequence representing 30 bits of the correlation function, we will require 30 double precision signal (+ correlation) accumulators and 30 double precision background (- correlation) accumulators. Since the information was stored in 10 bit segments, one 1 K portion of the uppermost 3 K of the core memory is

transformed at a time, leading to accumulation of signal and background in 20 different signal and noise accumulators at once (10 signal, 10 background).

The accumulation of signal and background is accomplished by using a single masking bit ("1") in a 10 bit binary mask in conjunction with the logical AND function (code 0nnn) of the computer. To start the transformation, the first address of the lowest 1 K section of data addresses (2000₈) is generated. The masking bit is placed in the most significant bit position of the 10 bit mask (corresponding to the third most significant bit of the address—the first two bits being the quadrant code). The address code and the mask are then ANDed together. If the third bit of the address was 1, the resulting number left in the accumulator will be nonzero; otherwise the result will be zero. Depending on this result, the contents are added to either the first signal or first background accumulator (see Fig. 31A).

Next, the masking bit is shifted right one place and the next bit of the address (fourth most significant) is tested in the same manner, the result being stored (added) to either signal or background accumulator number 2. The process then continues until all 10 bits of interest in the address have been tested and the contents of that address have been added to exactly 10 signal or noise accumulators depending on the state of the bits of the address. Then the address is incremented and the process is repeated starting with the masking bit in the third significant bit of the address. The same 20 signal and background accumulators are used.

Figure 31A. Masking addresses for data transformation

Example: A 4 Bit address, 0010 has contents = 0042

Address:	0010	→	0010	→	0010	→	0010
Mask:	$\oplus$ 1000		$\oplus$ 0100		$\oplus$ 0010		$\oplus$ 0001
Result:	0000		0000		0010		0000
	↓		↓		↓		↓
	Add 42 to background accum, #1		Add 42 to background accum, #2		Add 42 to signal accum #3		Add 42 to background accum #4

Test address 0010 next.

When the first 2000₈ (2000-3777) addresses have been transformed, a second group of 10 signal and 10 background accumulators are then used to transform the second 2000₈ (4000-5777) addresses, and a third set is then used for addresses 6000-7777. The overall net result is that the contents of each of the 3 K addresses have been added to 10 signal or background accumulators depending on the particular configuration of the bits of each address.

Once the transform is complete, the contents of each background accumulator are subtracted from the contents of the companion signal accumulator, and the result is stored in the signal accumulator. Next a display setup routine compresses the most significant portion of the 24 bit signal accumulators into a 12 bit format and stores the result in a 36₈ address display buffer. (This action scales the Y axis for the display.) When this has been completed, the program clears the data acquisition section of the core memory, reloads the proper command word codes, and resumes taking data via the data break system.

The above discussion relates to the transformation of correlation data. In the case of classical TOF operation, only positive correlations between address bits and detector events is possible. This is the result of a slow repetition rate which unambiguously associates each detector event with the modulation pulse responsible for its genesis. Since there are no negative correlations, background accumulators are not used in transforming classical TOF data; the formatted signal accumulator contents are rather displayed directly.

The "Display" subroutine (access code = D) is used to display transformed data on a Tektronix Type 545B oscilloscope using the D/A Board

(see "Interface Description"). The routine automatically scales the X axis of the display so that the 36₈ addresses of the display buffer will span the entire range of the X axis D/A converter. The routine then sequentially loads the X and Y D/A converters using the computer's accumulator and intensifies each display point. This process is repetitively cycled so that the display is maintained even on a non-storage oscilloscope until the routine is interrupted by a keyboard command or a data overflow flag. The display is of the form of a histogram whose height is the value of the correlation function.

Data storage was initially achieved by taking a Polaroid picture of the displayed data. However, all future data storage will be in the form of punched paper tape which can be used to transmit data to a CDC 6600 computer over a telephone line for further data analysis.

III. Data Overflow Service

As we noted in the "Interface Description," the correlation interface is equipped with a data overflow facility which pulls down the computer interrupt bus line when the data addresses have been filled sufficiently. A data overflow interrupt will be serviced by checking the interrupt skip chain of the computer program and jumping to a data overflow service routine.

This routine immediately turns off the data break system, turns off the computer's interrupt facility and jumps to the data transformation subroutine. The use of the overflow system thus allows repeated filling of the memory with raw data followed by automatic transformation of the data. The only restriction on the amount of data accumulated is the capacity of the double precision signal accumulators which store the

accumulated transformed data.

In summary, the system monitor provides a versatile means of controlling the functions of the correlation interface and of accumulating and transforming data. In the interest of saving core memory for storage, the monitor has been kept comparatively simple. However, it will be easy to add new subroutine blocks in the future if additional programming functions are deemed necessary.

EXPERIMENTAL MEASUREMENTS USING THE TOF CORRELATOR

In order to demonstrate the application of the TOF correlation system, we have measured the velocity distributions of several ion beam species. Although there is no existing beam apparatus in our laboratory with a sufficiently long ion drift path for TOF experiments, these low resolution measurements were made to demonstrate the operation of the correlator for viewing ion velocity distributions.

The apparatus employed (which was constructed by James Fair) is similar to the one described in Chapter IV. An electron bombardment ion source is used to generate an ion beam which is then momentum selected with a sector electromagnet. Two beam deflection plates normally used for beam alignment were connected to the ion beam chopper in a symmetric ($\pm$) voltage configuration. Ion scattering takes place in a fixed scattering cell mounted immediately forward of the beam chopping region. (No scattering gas was employed since measurements of primary beam velocity distributions were made.) Product ions are mass selected using a radio frequency quadrupole mass filter. In normal operation of the apparatus in a bandpass mode, a Wien filter (crossed electric and magnetic fields) is employed for velocity analysis of the mass selected products. During TOF experiments, the Wien filter was disabled so that ions of all velocities were transmitted to the detector, a Bendix magnetic electron multiplier.

The apparatus, including the detector train, is in a linear configuration appropriate for use in TOF measurements. The total ion flight distance between chopping region and detector was estimated to be 40 cm.

To measure the effective path length of the apparatus (taking into account the voltage distribution along the flight path due to focusing elements), a 10 eV beam of N^+ was observed by both classical and correlation TOF methods. The measurement confirmed the approximate figure of 40 cm for effective flight path and both TOF methods measured similar flight times (30 μ sec) and TOF distribution widths (2 μ sec). Since the mass of N^+ is comparatively small, no analysis of the beam velocity distribution was possible (short flight path + fast ion + low resolution).

To study the velocity distribution of a primary ion beam, an N_2^+ beam approximately 12 eV in energy was employed. Correlation TOF spectra were measured and compared with the velocity distribution measured by an accurate retarding potential analysis. Measurement of an entire N_2^+ spectrum required only 20 seconds. When the correlation spectra were scaled to account for beam intensity fluctuations, the points of each measured spectrum were consistently reproducible within a 10% range, although most spectrum points fell within a 5% range of the mean intensity measured for each TOF channel.

The shape of the TOF spectrum was quite similar to that measured by retarding potential analysis (Fig. 32). For purposes of comparison, the velocity distribution measured with the retarding potential were converted to a TOF spectrum by consideration of the potential distribution along the ion flight path and integration of the total time of flight (Fig. 32a). The TOF measurement had a FWHM width of 2.5 μ sec while the retarding potential measurement corresponded to a FWHM of 1.6 μ sec. The low resolution of the TOF spectrum ($\tau_{TOF}/\tau_{modulation} = 4$) and the flatness of the correlation peak suggest that the additional width of the

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Fig. 32. N_2^+ velocity distributions measured by retarding potential analysis (A) and TOF correlation (1 μsec channel width) (B).

TOF measurement can be attributed to counting of ions at the peak of the velocity distribution by more than one TOF channel (the peak velocity lies between two channels so that each accounts for half of the peak intensity). This results in an apparent flattening (and increased FWHM dimension) of the velocity distribution.

To overcome the resolution problem associated with short ion drift path, a measurement of the TOF spectrum of Kr^+ was made. Krypton gas contains several naturally occurring isotopes: Kr^{82} (11%), Kr^{84} (57%), and Kr^{86} (17%). While formation and momentum analysis of a Kr^+ beam will cause distortion of these relative isotopic abundances from those of natural krypton, it was expected that due to the large mass of Kr^+ (~84 amu) compared to the isotopic mass differences (2 amu) some of each isotope would be transmitted by both the momentum analyzer and quadrupole mass filter. Measurement of the Kr^+ velocity distribution should thus reveal three mass peaks in the form of one major peak bracketed by two satellites.

As with N_2^+ , several spectra of a 10 eV Kr^+ beam were measured and the results averaged (again the spectrum shape was consistent). A complete spectrum required 20-30 seconds to accumulate. The results are shown in Fig. 33. There is clear resolution of the three mass peaks (beam intensity was maximized at a QPMS setting of 84). The intensities of the peaks are approximately equal to the expected isotopic abundance, although the mass 86 peak was both somewhat smaller than expected and positioned closer to the mass 84 peak than expected.

While it is not possible to make any definitive statement about the efficacy of the computer correlation system on the basis of these results,

Fig. 33. 10% correlation spectrum of Kr^+ ion beam showing peaks due to isotopes Kr-82 , Kr-84 , Kr-86 .

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they do demonstrate that the correlation method can be applied to an ion beam system. In large part, the need for an adequate flight path (>100 cm) to increase resolution places a severe constraint on measurements which can be made with the apparatus in its present form. In the near future, the flight path of the apparatus will be enlarged with a drift tube and AC quadrupole lens system. After this modification, it will be feasible to study the TOF spectra of ionic products of ion-molecule reactions in greater detail and provide a clearer indication of the capabilities of the correlation system.

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CHAPTER IV

REACTION OF CO_2^+ WITH H_2 ISOTOPES

The second section of this thesis deals with experimental elucidation of the reactions of CO_2^+ ions with the isotopes of H_2 , primarily D_2 . This system with five atoms and 17 valence electrons is somewhat more complicated than those previously studied;¹ hence it provides insight into how multiatom complexes might be visualized and how molecular orbital correlation diagrams can be applied to predicting the shape of multicenter potential surfaces and their effect on the formation of reaction products. After presenting in more detail the motivation for this work, we will discuss the system in detail and outline the experimental apparatus which was used to acquire data. We then present the experimental results and a discussion of the pertinent correlation diagrams along with an interpretation of the results from both kinematic and potential surface points of view.

Models for Ion-Molecule Reactions

For purposes of discussion, we will assume that the hydrogen isotope, D_2 , has been used for study of the reactions of CO_2^+ . (In fact, D_2 was employed in most experiments.) Our study of $\text{CO}_2^+ + \text{D}_2$ has been aimed at understanding the elementary dynamics of the reaction through the evaluation of experimentally determined product velocity vector distributions.

Chemical reactions have generally been classified as belonging to one of the two broad categories: those proceeding through the formation of a long-lived intermediate collision complex and those proceeding via a short lived direct interaction mechanism. The time scale of the reaction is provided by the period, τ , required for a complete rotation of

the collision intermediate formed as the reactant molecules approach each other closely (with a distance comparable to that of a chemical bond). If the time of this close interaction is less than τ , the reaction is said to occur by a direct mechanism, while if this interaction time is greater than τ the collision is said to proceed through intermediate complex formation. Whether a reaction is direct or proceeds through a complex is determined by the potential energy surface representing the total electronic energy of the reactants as they interact and form products, and by the initial relative translational energy of the system.

Most ion-molecule reactions previously studied have been found to evolve by a direct mechanism. The simplest and most often applied model of direct interactions is that of spectator stripping. For the reaction $A + BC \rightarrow AB + C$, the spectator stripping model assumes that A interacts with B, while C remains unaffected (a spectator). The model assumes that as A approaches BC, the BC bond is dissolved so that when A hits B, C has no momentum imparted to it. By the conservation of momentum, the velocity of AB formed by spectator stripping is

$$v_{SS}(AB) = \frac{M_A}{M_A + M_B} v_A$$

where M_A and M_B are the masses of A and B and v_A is the initial velocity of A. Products formed by spectator stripping are most often forward scattered (relative to the center of mass) and appear at a 0° scattering angle relative to the direction of v_A . This follows again from the conservation of momentum; since no transverse momentum is imparted to C, the same must hold for AB.

In the spectator stripping model the internal energy of the AB product is the relative energy of A with respect to B (E_a) less the exothermicity of the reaction:

$$U_{AB}' = E_a - \Delta E_o^o,$$

where

$$E_a = \frac{1}{2} \mu v_A^2 = \frac{m_B}{m_A + m_B} E_L$$

and

$$\mu = \frac{m_A m_B}{m_A + m_B} = \text{initial reduced mass of A on B}$$

E_L = initial laboratory energy of A.

As E_L is increased, U_{AB}' increases until eventually the internal energy of AB exceeds its dissociation energy. At this point AB formed by spectator stripping is no longer stable, and any product intensity peak due to a strict spectator interaction is expected to disappear. In fact, the disappearance of product formed by spectator stripping is often reflected by apparent movement of peak intensity forward to a velocity greater than v_{SS} .

The intermediate complex model assumes the existence of a strong chemical attraction between the reactant molecules which binds them together into a transitory unit of unspecified geometry which lives for several rotational periods. During this time the complex rotates, finally dissociating into products which are symmetrically distributed in angle (the angular distribution of products is uncorrelated with the

initial relative velocity vector). This random dissociation leads to the measurement of product intensity distributions which are symmetric about the $\pm 90^\circ$ axis in the center of mass coordinate system.

As a rule, complex formation occurs when the internal energy of the incipient complex is primarily due to reactant attraction ($E_{\text{rel}} < \text{well depth}$; $U_{\text{ABC}} \approx -\Delta E_0^0$). Thus, although the presence of a potential well may allow the possibility of complex formation, at high relative energies temporary disposition of large amounts of $(\text{ABC})^*$ internal energy may preclude complex formation. It should also be noted that though a potential energy well for complex formation may exist, there are cases where this surface is inaccessible to the reactants leading to reaction by a direct interaction mechanism or no reaction at all.²

The formation of a long lived complex suggests that it should be possible to predict the relative frequency of formation for competing product channels using unimolecular decomposition (RRKM) theory³ or a statistical phase space model.⁴

For the $\text{CO}_2^+ - \text{D}_2$ system there exists the possibility of forming a bound intermediate, D_2CO_2^+ . This species is the molecular ion of formic acid and is known from photoionization measurements⁵ to be bound by approximately 1.75 eV. Especially at low relative energies, one might expect that there is a sizeable probability of forming D_2CO_2^+ during $\text{CO}_2^+ - \text{D}_2$ collisions, and that such intermediate formation will be reflected in the distribution of product intensities as a function of barycentric velocity and scattering angle.

The conceivable products of the $\text{CO}_2^+ + \text{D}_2$ reaction are numerous and include CO_2^+ , DCO_2^+ , DCO^+ , OD^+ , D_2O^+ , D_2^+ , O^+ , CO^+ and O_2^+ . As such we have

been interested not only in the distributions of products as a function of initial translational energy, but also in the relative cross sections for formation of each product. In measuring product intensity distributions there are several questions which we have sought to answer:

- (1) At low relative energies does intermediate complex formation occur? If so, at what relative energies does the complex persist?
- (2) How important is the large number of internal degrees of freedom in the $\text{CO}_2^+ - \text{D}_2$ system? Does this fact influence the amount of translational + vibrational energy transfer or complex formation?
- (3) If complex formation occurs are relative product intensities explainable in terms of RRKM or phase space theories?
- (4) If reaction proceeds by direct interaction, is a spectator stripping model applicable?
- (5) Are the attractive forces associated with a potential energy well displayed in product intensity distributions; if not, is it possible to explain the result by use of molecular orbital and state correlation diagrams? (See below.)

We have found that the $\text{CO}_2^+ - \text{D}_2$ system appears to interact by way of complex formation at low relative energies (<1.5 eV) and that the reaction mechanism gradually becomes more direct at higher energies. After describing the apparatus used for experimental measurement, we will discuss the thermodynamics of the $\text{CO}_2^+ + \text{H}_2$ system, the pertinent correlation diagrams, before detailing the experimental results which support the above mechanistic description.

Experimental

The experimental apparatus used to study the $\text{CO}_2^+ + \text{D}_2$ system has been applied to the study of a large number of ion molecule reactions¹ and has been described in detail previously.⁶ It basically consists of three independent regions: an ion source for preparing a narrow beam of incident ions of known mass and energy, a scattering cell where the incident ions undergo intermolecular collisions, and a product analysis region where ionic products are counted as a function of their mass, final energy and laboratory scattering angle.

The apparatus itself is composed of two connecting vacuum chambers: a small source chamber pumped by a single 6" oil diffusion pump, and a much larger (4 ft³) reaction chamber containing the scattering region and the initial stages of the detector train, pumped by two 6" oil diffusion pumps. Each diffusion pump is mounted on a liquid nitrogen cooled baffle to reduce oil backstreaming and increase effective pumping speed. The main chamber typically has a pressure of 3×10^{-7} Torr (in the absence of scattering gas).

Ion Source Assembly

For the current experiments, a Broida type⁷ microwave discharge source was used. This source consists of a 1 cm diameter quartz tube mounted on one side of the source chamber surrounded by a microwave cavity. Microwave radiation supplied by a 3GHz commercial diathermy source maintains a steady discharge through a desired source gas once the discharge has been initiated by a spark from a tesla coil. The discharge is confined to a 2 cm length by a piece of platinum mesh placed within the discharge tube.

For producing CO_2^+ ions a mixture of CO_2 and helium is used. While the actual pressure within the discharge tube is uncertain, it is approximately 50 μ . The ratio of CO_2/He in the discharge, as measured by an ionization gauge is 30/1; however, the relative efficiency for ionization of these gases suggests that the actual ratio is closer to 2/1. From this discharge mixture not only CO_2^+ ions, but also CO^+ , O^+ , and C^+ ions may be extracted. In most cases, larger fluxes of ions can be achieved if the CO_2 gas pressure in the tube is kept just above the minimum pressure necessary to maintain the discharge.

As has been noted previously,⁸ a primary advantage of the microwave discharge source over electron bombardment sources is the relatively low electron temperature of the discharge. While electrons in a bombardment source typically have energies of 50-100 eV, the electron temperature in the microwave discharge is of the order of 5 eV. The result of the low electron temperature is that CO_2^+ ions will be formed almost exclusively in the ground ionic state ($\Delta E = 13.78$ eV) rather than in excited $^2\eta_u$, $^2\Sigma_u^+$ or $^2\Sigma_g^+$ states ($\Delta E \geq 17.3$ eV).

Once a steady discharge is achieved, ions are extracted from the discharge region by a 700 volt extraction potential. They then pass through a series of electrostatic focusing lenses and into the entrance of a magnetic mass spectrometer. As the ions enter the spectrometer, the beam passes through an electrostatic quadrupole lens which converts the beam from one of circular cross section to one of rectangular cross section and focuses the beam on the entrance to the analyzer; after momentum analysis, a second quadrupole forms the ions again into a beam of circular cross section. This maneuver increases the effectiveness of

the momentum analyzer by causing all ions in the beam to traverse the analyzer in a single horizontal plane. The quadrupole lenses also aid in focusing and shaping the ion beam before it enters the scattering region. The momentum analyzer itself is a 66° sector electromagnet. By varying the energy at which ions traverse the analyzer and the strength of the magnetic field (by adjustment of the current through the magnet) any of the ions produced by the source discharge may be selected for use.

The momentum analyzer has a resolution of 2% of the energy at which the ions are analyzed. This fact coupled with the natural isotopic abundances relevant to CO_2^+ ($\text{C}^{13} = 1.11\%$; $\text{O}^{17} = 0.037\%$; $\text{O}^{18} = 0.20\%$) supports the experimental observation that $^{45}\text{CO}_2^+$ and $^{46}\text{CO}_2^+$ from the ion source do not play a significant role in interfering with intensity distribution measurements. Any such interference would be removed by measurement of relative background levels.

Scattering Cell

As the beam of the momentum selected ions exits from the momentum analyzer, it is again refocused by electrostatic lenses onto the fixed entrance to the target gas scattering cell. This target cell basically consists of two tightly fitted concentric cylinders, capped at both ends. The interior cylinder is fixed in position relative to the ion source train and contains a 2 mm x 2 mm square entrance aperture for the cell. The outer cylinder is fixed to a rotatable lid mounted on top of the main vacuum chamber. The complete detection train, as well as the scattering cell exit rotate with the movable lid, allowing analysis of ionic products at a wide range of laboratory scattering angles. The exit slit of

the collision cell is a 2 mm diameter round hole.

The path length through the scattering cell is 3.8 mm. Target gas pressures of approximately 10^{-3} Torr are maintained within the scattering cell and lead to beam attenuations of 15-20% during passage of the beam through the cell. This ensures that only single scattering events are responsible for the final distribution of reaction products. The scattering cell pressure is measured with a capacitance bridge manometer (MKS Baratron) whose advantage over an ion gauge is that it is insensitive to the ionization efficiency of the gas which is being monitored.

For the reactions of CO_2^+ , He, H_2 , HD, and D_2 gases were used in the scattering cell. The small size of the cell apertures allowed the use of intracell pressures 1000 times greater than the background chamber pressure; a 10^{-3} Torr cell pressure typically caused a two-fold increase in chamber pressure, an entirely tolerable figure. Since only relative cross sections for reactions were measured, no effort to calibrate the absolute pressure within the collision cell was required.

Detector Train

As mentioned above, the entire detector train is mounted on the 20 inch diameter rotatable lid (which is mounted on a differentially pumped double tec-ring seal). Product ions emerging from the collision cell enter a 90° spherical electrostatic energy analyzer which passes ions of the desired final energy into the vertical plane of the detector train. The energy analyzer has an angular resolution of 2.5° full width and energy resolution of 3% FWHM. The transmitted ions are focused by a series of electrostatic lenses onto the entrance of a quadrupole mass filter and then into the ion detector.

The detector itself consists of a polished aluminum plate which is maintained at a potential of -25 kilovolts. As the highly accelerated product ions strike the plate, they cause ejection of secondary electrons which are then accelerated by a +28 kilovolt potential and impinge on a lithium-drifted silicon semiconductor wafer which transduces the pulses of secondary electrons into electrical pulses which are amplified by an FET preamp and linear amplifier and counted with a Hamner NS-11 10 Mc scalar. Using a Teletype Scanner, the resulting scalar counts are typed out on ASR33 teletype along with the counting time and collision cell pressure for later analysis.

Experimental Procedure and Data Analysis

In undertaking an experiment on this apparatus, the first order is to achieve a steady gaseous discharge. The appropriate momentum analysis energy is chosen so as to guide extracted ions to a beam flag positioned at the scattering cell. The ion current at the beam flag (10^{-11} - 10^{-10} A) is monitored using a Keithley electrometer. The gas pressure, quadrupole lens voltages and microwave power are used in a concerted manner to achieve a steady discharge which yields maximum ion beam intensity. At this point the beam flag is rotated out of the beam path and the beam current monitored using a Cary 31 electrometer connected to one of the lens elements of the detector train. This allows monitoring and optimization of the angular and energy widths of the beam. When this final beam is determined to be stable, it is characterized as to energy and angular distribution. Liquid nitrogen is then added to a reservoir which cools the semiconductor detector, and after a 20 minute cooling period, the detector is turned on.

Measurements of product intensity are commonly made according to one of two schemes: the detector is positioned at a constant laboratory angle and the energy of the product energy analyzer is scanned, or the product energy is left fixed and the laboratory angular distribution is scanned. The former method is termed as a "scan" while the latter is referred to as a "cut". Typically one scan is taken at the initial laboratory angle corresponding to the incident ion beam (centerline) to give an idea as to the extent of the energy distribution and subsequently between 10 and 20 cuts in angle are taken to span that energy distribution. Using the teletype, the intensity at each energy-angle point is recorded until a complete map of the product intensity distribution is accumulated consisting of between 200-300 intensity measurements. This process takes from 3-6 hours and requires frequent monitoring of the primary beam intensity and energy-angular position. Changes in these parameters are automatically taken into account by linear interpolation during data analysis. We note that though the time required for each intensity measurement is a function of relative product intensity, each measurement is typically made over a 15-20 second interval to average out any instantaneous beam fluctuations.

The information printed on the teletype is transferred to computer data cards which are then analyzed on the LBL CDC 5600 computer.

At each energy-angle point for which product intensity is measured, the signal and background counts are normalized using the intensity conversion

$$\bar{I} = \frac{10^7(S-B)}{T_i P_g(\theta) E_f^{3/2}}$$

where

S = signal counts

B = background

T = counting time in seconds

i_o = peak incident beam intensity (in units of 10^{-12} A)

P = scattering gas pressure (in units of 10^{-6} Torr)

$g(\theta)$ = detector angular viewing factor through the scattering cell
(a function of scattering angle)

E_f = electrostatic energy analyzer setting

The $E^{3/2}$ factor normalizes the measured intensity to the detector volume in velocity space.

Calculated intensities are plotted by a Calcomp plotter as a function of barycentric velocity and scattering angle. Using the plotted intensity points, contours of equal intensity are drawn onto the array and the result is an intensity contour map of the final product distribution. One such map is required for each individual product of the reaction at each initial relative energy for the reactants. Comparison of the maps for any product as a function of initial relative energy yields information as to the mechanism(s) important for the reaction.

The resolution of each experiment is a function of the angular and energy distribution of the incident beam, as well as the thermal motion of the gaseous target molecules. This coupled with incident beam intensity fluctuations makes the resultant intensity maps something less than a high resolution picture, yet there is a surprising amount of information which can be inferred solely from the general shape of the distributions. Put another way, the detail of the information provided is at

least as great as our knowledge of the appropriate potential energy surfaces (often much greater) so that the tests which might be applied to the experimental data are pretty much possible with current velocity and angular resolution.

Kinematics and Intensity Distributions

Though we briefly alluded to the interpretation of scattering diagrams in Chapter I (see Fig. 1), there are a broad range of scattering processes which may be interpreted with the aid of velocity vector diagrams. Figure 1 dealt with the general case of an ion A which is incident on a neutral molecule, BC, whose thermal velocity was considered negligible. The results of such a collision can be classified into several broad categories:

- (1) Elastic scattering: $A^+ + BC \rightarrow A^+ + BC$
- (2) Inelastic scattering: $A^+ + BC \rightarrow A^{++} + BC$
 $\rightarrow A^+ + BC^*$
 $\rightarrow A^+ + B+C$
- (3) Reactive scattering: $A^+ + BC \rightarrow AB^+ + C$
 $\rightarrow AC^+ + B$
 $\rightarrow AB + C^+$
 $\rightarrow A + BC^+$ etc.

The velocity vector diagrams pertinent to each of these classes are shown in Fig. 34.

In an elastic scattering event, no chemical reaction occurs, and translational energy representing relative motion of the particles is strictly conserved (i.e. remains within the translational mode). Only the angle of motion relative to the initial velocity vector is changed,

a. Elastic collision: $A^+ + BC \rightarrow A^+ + BC$

b. Inelastic collision: $A^+ + BC \rightarrow A^+ + BC^*$

c. Reactive collision: $A^+ + BC \rightarrow AB^+ + C$
(exothermic)

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Fig. 34. Velocity vector diagrams for elastic, inelastic and reactive collision processes.

the amount of change depending on the strength of the elastic interaction and the impact parameter (aiming error) of the collision. This type of collision is often represented as the type occurring between colliding billiard balls.

For all three classes of collisions, it is possible to define a quantity, Q , which denotes the amount of relative translational energy which is converted from translational to internal modes during the collision process. If E_{rel} denotes the initial relative translational energy ($E_{rel} = \frac{1}{2} \mu g^2$; μ = initial reduced mass, g = initial relative velocity) and E'_{rel} denotes the final relative translational energy of the products ($E'_{rel} = \frac{1}{2} \mu' g'^2$) we define

$$Q = E'_{rel} - E_{rel}.$$

If Q is negative, this implies that some initial relative translational energy has been converted to electronic, vibrational, or rotational internal modes of the products. If $Q > 0$, initial internal energy has been converted into the translational energy mode (superelastic collision).

Since the elastic collision process by definition assumes $E'_{rel} = E_{rel}$, elastically scattered projectiles will be found at the $Q = 0$ locus of points (Fig. 34a) which forms a circle about the center of mass in the appropriate velocity vector diagram. This circle represents all points at which a projectile, A^+ , may be found after simple rotation of the relative velocity vectors about the center of mass following an elastic collision.

By conservation of total energy, all relative translational energy lost during a collision must be found in internal modes (electronic, vibrational, rotational or heat of formation). If U_{int} and U'_{int} represent, respectively, the energy contained in internal modes before and after a collision, then

$$E_{rel} + U_{int} = E'_{rel} + U'_{int}$$

or

$$-Q = U'_{int} - U_{int}$$

and the elastic case ($Q = 0$) is consistent with a zero net change in internal product energy.

For the inelastic class of collisions, $Q < 0$ and

$$E'_{rel} < E_{rel}, \quad U'_{int} > U_{int}$$

since translational energy is converted into internal modes. This case is represented in Fig. 34b. For this type of collision there is again no chemical transfer, only a rearrangement of the available translational energy among translational and internal modes.

The reactive case (Fig. 34c) is a further extension of these concepts. The only additional complications arise because the reaction may fail to be thermoneutral, and because the product masses differ from those of the reactants ($\mu' \neq \mu$). In this case the change in energy of formation (exo- or endo-thermicity) must be taken into account in balancing the distribution of energy before and after the reaction. Conservation of energy is then represented by

$$E_{\text{rel}} + U_{\text{int}} = E'_{\text{rel}} + U'_{\text{int}} + \Delta E^{\circ}_0$$

or

$$Q = U_{\text{int}} - U'_{\text{int}} - \Delta E^{\circ}_0$$

if ΔE°_0 is defined as negative for exothermic reactions following the normal convention.

For a reactive process, it is apparent that if $U_{\text{int}} = U'_{\text{int}}$ that $Q = -\Delta E^{\circ}_0$. Thus, even if the internal modes of the products remain in their initial energy states (though of course different modes are available before and after the collision since chemical transfer has occurred) there must be a net conversion of energy into (from) bond energy from (into) translation in the case of an endoergic (exergic) reaction. This is represented by the $Q = -\Delta E^{\circ}_0$ circle in Fig. 32c.

Thus we can begin to see how a particular collision may be visualized. The vector scattering diagram for reactants (initial vectors) and products (final vectors) is constructed. At any point on the diagram, Q may be calculated knowing $E_{\text{rel}} = \frac{1}{2} \mu g^2$, $E'_{\text{rel}} = \frac{1}{2} \mu' g'^2$. Using a known value of ΔE°_0 , it is then possible to compute the amount of internal energy converted into internal modes. This quantity provides information as to the chemical state of undetected products (whether they are dissociated) and provides some clues as to the nature of the reaction mechanism (see below). In reality, for a multiatom system such as $\text{CO}_2^+ + \text{D}_2$ there are many fewer inferences which can be made concerning energy disposal in internal modes as compared with systems of two or three atoms.⁹ Nevertheless, such analysis does yield some limits on which products can be

formed at any initial relative energy and maintains some usefulness in a more complicated system.

States and Energetics

Before discussing the distributions of reaction products, it is appropriate to present the energetics of the CO_2^+-H_2 system. We begin with a discussion of the formation of CO_2^+ .

Neutral CO_2 has been thoroughly studied previously.¹⁰ Its ground electronic state is $^1\Sigma_g^+$ and has the molecular orbital population shown in Table 7. CO_2 is linear and has an equilibrium internuclear distance $r_0 = 1.16\text{\AA}$. Formation of ground state $\text{CO}_2^+ (^2\Pi_g)$ occurs when one of the nonbonding π_g electrons is removed. The $1\pi_g$ orbitals essentially represent the lone pair oxygen electrons; the nonbonding character of the $1\pi_g$ orbitals is supported by the fact that the rotational constants for $\text{CO}_2^+ (^2\Pi_g)$ and $\text{CO}_3 (^1\Sigma_g^+)$ are almost equal, both species being linear.¹¹ Formation of $\text{CO}_2^+ (^2\Pi_g)$ requires 13.78 eV.

The excited states of CO_2^+ are also listed in Table 7. The $^2\Pi_u$ results from removal of an electron from the bonding $1\pi_u$ orbital of CO_2 and requires 17.32 eV. While the $^2\Pi_u$ state is also linear, both excited Σ states are known to be bent.

The vibrational frequencies for $\text{CO}_2 (^1\Sigma_g^+)$ and $\text{CO}_2^+ (^2\Pi_g)$ have been determined from photoelectron spectroscopy (PES) to be¹² (in cm^{-1})

	CO_2^+	CO_2	
ν_1	1250	1388	(symmetric stretch)
ν_2	530	667	(bend)
ν_3	1469	2349	(asymmetric stretch)

TABLE 7. Electronic States of CO_2 and CO_2^+ 6,10

Species	State	Orbital Configuration	r_e^0 (Å)	Geometry	E^*
CO_2	1E_g^+	$(1\sigma_g 1\sigma_u 2\sigma_g 3\sigma_g 2\sigma_u 4\sigma_g 3\sigma_u)^2 1\pi_u^4 1\pi_g^4$	1.16	linear	0
CO_2^+	$2\pi_g$	$1\pi_u^4 1\pi_g^3$	1.17	linear	13.78
	$2\pi_u$	$1\pi_u^3 1\pi_g^4$		linear	17.32
	2E_u^+			bent	18.08
	2E_g^+			bent	19.4

*Relative to CO_2 (1E_g^+)

and the Franck-Condon factors for transitions $\text{CO}_2(000) \rightarrow \text{CO}_2^+(^2\Pi_g)$ have been measured:¹²

$\text{CO}_2(v_1, v_2, v_3)$		$\text{CO}_2^+(v_1, v_2, v_3)$	F.C. factor
(0,0,0)	→	(0,0,0)	(.82)
	→	(1,0,0)	(.15)
	→	(2,0,0)	(.02)

Thus, one expects that in the case of vertical ionization, predominantly unexcited (vibrationally) CO_2^+ will be formed. Of course, the conditions present in the microwave discharge source may indeed lead to adiabatic rather than vertical transitions, and neutral CO_2 may be vibrationally excited within the discharge. However, since the equilibrium geometries of CO_2 and CO_2^+ are quite similar, one expects that similar F.C. factors will pertain to ionization of vibrationally excited CO_2 and that CO_2^+ produced in the discharge will approximately reflect the vibrational energy distribution of neutral CO_2 . Moran and Friedman¹³ have discussed the problem of vibrational excitation and determined that an upper limit of 1 eV for the internal vibrational energy of CO_2^+ is likely.

As has been reported previously, the electron temperature of the CO_2 discharge is approximately 5 eV.⁸ This makes it unlikely that the excited states of CO_2^+ are produced in any quantity. Moran and Friedman¹³ have reported that $\text{CO}_2^+(^2\Pi_u)$ (the excited state of CO_2^+ most likely to be produced) decays to $\text{CO}_2^+(X^2\Pi_g)$ in 10^{-6} seconds. The result is that we may assume with some certainty that the CO_2^+ ions undergoing reaction are almost exclusively in the ground $^2\Pi_g$ state.

The thermodynamics of the $\text{CO}_2^+ - \text{H}_2$ system are presented in Table 8. The heats of reaction have been derived using predominantly the heats of formation tabulated in Ref. 5. Formation of H_2CO_2^+ is 2.5 eV exothermic. The value for formation of $\text{H} + \text{HCO}_2^+$ is derived using the measured proton affinity of CO_2 .^{15,16} A value for the proton affinity of 5.1 eV (used in subsequent calculations) reported in Ref. 15 represents the average value of those reported. The resulting value for the well depth with respect to dissociation of H_2CO_2^+ to HCO_2^+ or HCO^+ ¹⁴ is approximately 1.7 eV.

Although not all of the processes listed in Table 8 are expected to occur in $\text{H}_2 + \text{CO}_2^+$ collisions, the exhaustive listing is helpful for evaluating the energetic limitations placed on the formation of the actual reaction products (CO_2^+ , HCO_2^+ , HCO^+ , OH^+ , CO^+ , O^+). As the experimental results are evaluated below, frequent reference to Table 8 will be made.

TABLE 8

Primary Reactions		ΔH_{298}^0 (eV)
$\text{CO}_2^+ + \text{H}_2$	$\rightarrow \text{H}_2\text{CO}_2^+$	-2.56
	$\rightarrow \text{H} + \text{HCO}_2^+$	- .75
	$\rightarrow \text{HCO}^+ + \text{OH}$	- .77
	$\rightarrow \text{HCO} + \text{OH}^+$	+3.7
	$\rightarrow \text{HCO}^+ + \text{O} + \text{H}$	+4.4
	$\rightarrow \text{CO}^+ + \text{H}_2\text{O}$	+0.7
	$\rightarrow \text{CO} + \text{H}_2\text{O}^+$	+1.58
	$\rightarrow \text{CO}^+ + \text{H}_2 + \text{O}$	+5.79
	$\rightarrow \text{CO}^+ + 2\text{H} + \text{H}$	+5.9
	$\rightarrow \text{O}^+ + \text{H}_2\text{CO}$	+5.33
	$\rightarrow \text{O} + \text{H}_2\text{CO}^+$	+2.58
	$\rightarrow \text{O}^+ + \text{H}_2 + \text{CO}$	+5.4
	$\rightarrow 2\text{H} + \text{CO}_2^+$	+4.5
	$\rightarrow \text{H}_2^+ + \text{CO}_2$	+1.66
Secondary Reactions		ΔH_{298}^0 (eV)
HCO_2^+	$\rightarrow \text{H} + \text{CO}_2^+$	+5.25
	$\rightarrow \text{H}^+ + \text{CO}_2$	+5.13
	$\rightarrow \text{HCO}^+ + \text{O}$	+4.4
	$\rightarrow \text{HCO} + \text{O}^+$	+9.4
	$\rightarrow \text{CO}^+ + \text{OH}$	+6.6
	$\rightarrow \text{CO} + \text{OH}^+$	5.7
HCO^+	$\rightarrow \text{CO}^+ + \text{H}$	6.65
CO^+	$\rightarrow \text{C}^+ + \text{O}$	8.4
	$\rightarrow \text{C} + \text{O}^+$	3.35

MOLECULAR ORBITAL CORRELATION DIAGRAMS

While it is known from the thermodynamics of the CO_2^+-H_2 system that the existence of a bound intermediate (H_2CO_2^+) is possible, it is by no means certain that the potential surface which originates from the ground electronic states of the reactants leads to the formation of the ground state intermediate. For a number of ion-molecule reactions previously studied, a qualitative description of the real potential surfaces for the reaction has been achieved by the use of molecular orbital and electronic state correlation diagrams.² For the CO_2^+-H_2 system, we have constructed such diagrams, which will now be described.

For any chemical reaction the dynamics of the colliding reactants are determined by the electronic potential energy surface of the reaction (within the framework of the Born-Oppenheimer approximation). However, for all but the simplest reactions, the potential energy surfaces are not known in detail; calculation of these surfaces is most often an expensive and complicated proposition, especially for the multidimensional surfaces appropriate to reactions involving many atomic centers.

Without knowing the details of the potential surface, it is still possible to visualize the qualitative features of the surface for a reaction using molecular orbital (M.O.) correlation diagrams. As a chemical reaction progresses, the molecular orbitals of the reactants evolve into those of an intermediate collision complex and finally into those of the reaction products. By following the evolution of these orbitals, it is possible to ascertain the overall electronic energy throughout the reaction in order to decide whether formation of a long lived collision intermediate is possible.

To construct an M.O. correlation diagram, one first assumes a "dynamically reasonable" collision geometry with one or more symmetry elements. The orbitals of the reactants, intermediate, and products are then identified and resolved in the point group corresponding to the symmetry elements for the assumed geometry. Especially in a low symmetry intermediate case, such as H_2CO_2^+ , the nodal structure of the various M.O.'s provides useful clues to the evolution of each orbital as the reaction progresses.²⁰ The orbital energy of each orbital is estimated using SCF calculations, electron affinities, appearance potentials and photoelectron and ultraviolet spectroscopy. After each orbital for reactants, intermediate and products has been identified and placed according to energy, orbitals of the same symmetry species are connected (orbital correlation). The mixing of orbitals of the same species by nonsymmetric nuclear motions and spin-orbit interactions is considered and potentially avoided crossings of surfaces are identified.

When the M.O. correlation has been completed, by placing the electrons of the reactants in the orbitals, the identification of electronic states for each of the species found during the evolution of the reaction is made. By correlating the electronic states of like symmetry for reactants, intermediate and products, a state correlation diagram is constructed which is a rough approximation to the potential surfaces appropriate to the reaction.

In general there is more than one collision geometry appropriate to the reaction (or several narrowly constrained ranges of collision geometries) or more than one possible set of products. For each possible

geometry range or set of products, a separate set of correlations is required.

For the CO_2^+-H_2 system the intermediate, H_2CO_2^+ , can be formed in one of two basic ways (Fig. 35). Parallel approach by H_2 and CO_2^+ leads to the C_g symmetry intermediate favoring the formation of HCO_2^+ or HCO^+ (Fig. 35a), while perpendicular approach of H_2 toward CO_2^+ leads to an intermediate of C_{2v} symmetry (Fig. 35b). Figure 1c shows a third possible mode of approach, but this geometry does not lead to formation of a stable H_2CO_2^+ molecular configuration. These geometries of course represent idealizations; any relative geometry of approach is possible, but these examples provide a first approximation useful for constructing correlation diagrams. Once the diagram has been constructed, it is possible to consider the effects of geometric perturbation on the stability of the complex.

We begin with H_2CO_2^+ formation as a C_g symmetry intermediate. The molecular orbital correlation diagram for this case is shown in Fig. 36. The D_{eth} point group of CO_2^+ and H_2 is used to classify the reactant molecular orbitals, while the orbitals for the HCO_2^+ product are classified according to C_{2v} symmetry. The important elements of the orbital correlation are the combination of the H_2 σ_g and σ_u^* orbitals taken in bonding-antibonding combinations with the in-plane π_u and π_u^* orbitals of CO_2 (Fig. 37) in a manner similar to the prototype $\text{H}_2 + \text{ethylene}$ case.²⁰ In each case the in-phase combination leads to the low energy bonding orbital while the out-of-phase combination leads to the high energy antibonding orbital containing an additional node. The correlation which follows leads to association of the in-plane $\pi_u(\text{CO}_2^+)$ with the $6a'$ orbital

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Fig. 35. Collision geometries for the $\text{H}_2\text{-CO}_2^+$ intermediate complex.

- a) C_s symmetry intermediate; b) C_{2v} symmetry intermediate;
- c) a perpendicular approach leading to direct interaction.

XBL 749-7236

Fig. 36. Molecular orbital correlation diagram for formation of HCO_2^+ from $CO_2 + H_2$, parallel internuclear axis approach.

Basis Orbitals

Bonding Combinations

Antibonding Combinations

XBL 749-7227

Fig. 37. Bonding and antibonding combinations of H_2 and CO_2^+ orbitals to form $H_2CO_2^+$ molecular orbitals (labeled in parentheses).

of H_2CO_2^+ , $\sigma_g(\text{H}_2)$ with the $11a'$, $\pi_u^*(\text{CO}_2)$ with $7a'$ and $\sigma_u^*(\text{H}_2)$ with the $12a'$ orbital of the intermediate. This correlation leads to an avoided crossing of the $11a'$ and $7a'$ orbitals as the intermediate is formed. The mixing of these orbitals can be visualized as due to formation geometry less than parallel, or as due to the asymmetrizing presence of the non-participating oxygen atom. In the latter case, one can see that the node between the O atom and the closest H atom (Fig. 37) contains geometric components both parallel and perpendicular to the CO_2^+ internuclear axis which perturb an otherwise symmetric (approximately C_{2v}) situation, mixing the $7a'$ and $11a'$ orbitals and leading to an avoided crossing. The exact point of the avoided crossing and the height of any resulting potential energy barrier in the entrance channel are open to speculation. The significant point is that there theoretically exists a route by which reactants in the ground state may adiabatically evolve to the ground state of the intermediate, suggesting that the potential well for formation of an intermediate complex may be accessible.

The formation of HCO_2^+ proceeds via the ground state intermediate in a simple way when the $\sigma_g(\text{H}_2)$ electrons evolve through the $7a'$ state of H_2CO_2^+ . The final assignment of an electron to the $1s(\text{H})$ orbital occurs through the transfer of a nonbonding $10a'$ electron which may involve a second avoided crossing (Fig. 36).

The M.O. correlation diagram for formation of $\text{HCO}^+ + \text{OH}$ is shown in Fig. 38. The formation of ground electronic state products from the ground state intermediate is readily apparent. In this case, the formation of HCO^+ over OH^+ (see below) is explainable both on the basis of thermodynamics ($\text{HCO}^+ + \text{OH}$ lies some 4 eV below $\text{HCO} + \text{OH}^+$; see Table 8)

and on the basis of the molecular orbital correlation. The alternate set of products, $\text{HCO} + \text{OH}^+$, are adiabatically inaccessible, and the total energy of the filled molecular orbitals in the $\text{HCO} + \text{OH}^+$ case is well separated in energy from that of $\text{HCO}^+ + \text{OH}$.

The formation of $\text{C}_{2v} \text{H}_2\text{CO}_2^+$ by a perpendicular approach of H_2 and CO_2^+ leads to the M.O. correlation diagram shown in Fig. 39. The in- and out-of-phase combination of the terminal 2S oxygen orbital and the $\text{H}_2\sigma_g$ orbital lead respectively to the bonding $2a_1$ and antibonding $4a_1^*$ orbitals of H_2O (since the symmetry of the intermediate and the H_2O^+ product are identical, identification of the intermediate orbitals has been dispensed with). In a similar manner, combination of the in-plane $\pi_u(\text{CO}_2^+)$ and $\sigma_u^*(\text{H}_2)$ orbitals leads to the formation of a $1b_2-2b_2^*$ bonding-antibonding pair. Combination of the $\text{CO}_2^+ \sigma_g$ and σ_u bonding orbitals forms the bonding and nonbonding orbitals of CO (combination leads to the localization of the orbitals).

Starting with the ground state reactants, one finds again that the $\sigma(\text{H}_2)$ electrons initially correlate to a high energy orbital ($4a_1^*$). A crossing of the $4a_1^*$ orbital surface by that of the $3a_1$ orbital again provides a path to ground state products. However, in this case it is likely that the energies of the adiabatic surfaces (noncrossing path) are closely spaced in energy since the $3a_1$ and $4a_1^*$ orbitals are largely in different regions of space. The experimental observation that no H_2O^+ is formed in the reaction (see below) may provide support for the conclusion that the close orbital spacing at the avoided crossing allows the reactants to follow a non-adiabatic path in a large fraction of $\text{CO}_2^+ + \text{H}_2$ collisions occurring in a nearly perpendicular geometry.

XBL 749-7234

Fig. 39. Molecular orbital correlation diagram for formation of $H_2O^+ + CO$ from $CO_2^+ + H_2$.

We note parenthetically that a crossing of the $3a_1$ and $4a_1^*$ orbitals is likely to occur at a high energy. This is suggested by the fact that the molecule OCF is bent (OCF can be correlated with OCOH which should have a geometry similar to OCOH₂). This suggests that an H₂OCO intermediate would also be bent in a low energy configuration. It may be that formation of H₂O⁺ requires achievement of a lower energy bent intermediate. Formation of such an intermediate would require some destruction of the CO₂⁺ π bonding system, entailing a significant energy of activation.

Throughout our discussion of correlation diagrams we have dealt only with the orbital correlations, neglecting the state diagrams which actually describe the electronic potential energy surfaces. This omission is motivated by the fact that the orbital energies of the intermediates are very poorly characterized. Additionally, especially in the case of the C_s intermediate geometry, the low symmetry of the intermediate leads to labeling of the electronic states as being of only two types (A', A''). Thus in any state correlation diagram there will be a very large number of closely spaced states of the same symmetry (especially in the A' case), and it is impossible to draw any meaningful conclusion. This is a problem that will persist throughout the further study of reactions involving many atoms and low symmetry intermediate geometries.

In summary, we have seen how the molecular orbital correlation diagrams for the CO₂⁺ + H₂ system describe a possible low energy path to product formation. The importance of lowered symmetry in the reaction intermediate may determine whether mixing of orbitals of like symmetry leads to avoided crossings with a significant energy gap allowing the

formation of a ground state intermediate. In the following section the experimental measurements of product intensities are presented. In view of the preceding discussion it is possible to rationalize the appearance of HCO_2^+ and HCO^+ as major products while little or no H_2O^+ or OH^+ are found.

CO_2^+ RESULTS AND DISCUSSION

The experimentally determined product velocity distributions for the CO_2^+-H_2 system illustrate a reaction in which both the formation of a long-lived intermediate complex and a direct interaction mechanism are displayed. At all the initial relative energies studied, there was evidence of strong chemical coupling between the reactant species. Consistent with the moderate depth of the electronic potential well, low energy results display the symmetric behavior associated with complex formation while higher energy distributions support a spectator stripping mechanism. Intermediate complex formation and lifetime appear to be governed by the effectiveness with which initial relative translational energy is disposed among the active vibrational modes of the incipient complex.

DCO_2^+

Previous studies of CO_2^+ have provided a limited amount of information about this product, which is the major reactive channel. Ding¹⁷ has published a brief description of the zero degree energy distribution of DCO_2^+ as a function of initial relative energy. He found that at very low relative energy ($E_{\text{rel}} < 0.5$ eV) there is some suggestion that complex formation may occur, while at low and intermediate relative energies (1-8 eV), velocity distributions reflect a spectator stripping mechanism.* However, the experimental error reported for the low energy results make it unclear whether there is indeed complex formation occurring.

*There is some ambiguity in these results since the reported energy scales (laboratory and relative) are inconsistently labeled.

Smith and Futrell¹⁸ have reported the results of ion cyclotron resonance studies of CO_2^+ in which they measured the specific rate constant for H atom transfer at low translational energies (<10 eV). These authors report a value of $k = 4 \times 10^{10} \text{ cm}^3/\text{molecule-second}$ for the HCO_2^+ formation rate constant; this value was found to be independent of incident ion kinetic energy for $E < 6 \text{ eV}$. The fact that this rate constant is approximately one-fourth of the typical value ($k = 15\text{-}20 \times 10^{10} \text{ cm}^3/\text{molecule-second}$) expected from Langevin polarization theory¹⁹ raises a question about the nature of the potential surface for the reactants at impact parameters somewhat smaller than the critical impact parameter for Langevin collisions. While this might be viewed as evidence supporting a moderately sized barrier to complex formation in the entrance channel of the potential surface, such a proposition would be entirely speculative.

The examination of HCO_2^+ and DCO_2^+ product velocity distributions in our laboratory is complicated by problems of mass analysis. There are several distinct aspects of this problem. The incident CO_2^+ ion beam contains approximately 1% $\text{C}^{13}\text{O}_2^+$ (mass 45) which is transmitted by the momentum analyzer of the ion source train, though this was not found to provide significant interference. A more significant problem encountered was transmission of nonreactively scattered CO_2^+ (mass 44) by the quadrupole mass filter. Although each measurement of product intensity includes a background measurement which removes mass 44 whose source is primary beam transmission, background measurements are incapable of correcting intensities for nonreactively scattered CO_2^+ which is transmitted at a QPMS setting of mass 45 or 46. Since there is a relatively large

amount of inelastic nonreactively scattered CO_2^+ at all initial relative energies studied, and since resolution of mass 45 from mass 44 is very limited with the apparatus used in these studies, DCO_2^+ was chosen for study at most relative energies. HCO_2^+ was studied only at low relative energies since use of an H_2 target rather than D_2 decreases the initial relative translational energy of the reactants by a factor of one-half.

Figure 40 displays the HCO_2^+ product velocity distribution measured in our laboratory for $E_{\text{rel}} = 1.5$ eV, the lowest relative energy studied. The distribution appears quite symmetric. However, in view of the relatively large initial beam velocity distribution (20% Beam Profile), one cannot state categorically that there is no asymmetric component to the map. In this figure, as well as subsequent ones, the velocity expected for a spectator stripping (SS) model is marked with an X. This low energy result unquestionably contains a large symmetric component suggestive of complex formation. The intensity of the product distribution ($\bar{I}$ units) is quite large and in fact is somewhat larger than the intensity of nonreactively scattered CO_2^+ at the same relative energy (see below). This suggests that a large fraction of ion-molecule collisions in this system are influenced by the chemical forces represented by a potential energy well.

The DCO_2^+ distribution for $E_{\text{rel}} = 2$ eV is shown in Fig. 41. While this map also shows a sizeable symmetric component, its basic nature is asymmetric. The peak intensity falls very near to the velocity expected from a spectator stripping collision.

In order to establish unequivocally the stripping nature of the product distribution at this low translational energy, a similar map of

the DCO_2^+ resulting from collisions with HD was constructed (Fig. 42). Again, the velocity distribution is quite broad with a product intensity peak at the spectator stripping velocity. For each of these cases the Q value of the spectator velocity is given by the negative of the relative energy between CO_2^+ and the D atom. Since the D atom comprises a larger fraction of the total target mass in the HD case, Q_{ss} appears closer to the center of mass in the HD map, although Q_{ss} is approximately equal in both cases.

The comparison of these two distributions provides firm evidence for a direct interaction mechanism at relative energies as low as 1.5-2 eV. However, the broad extent of the product distribution suggests the continued influence of a long lived complex. One possible explanation of these results is that small impact parameter collisions lead to complex formation while more grazing collisions could lead to DCO_2^+ formation by a stripping mechanism.

Figures 43 and 44 are DCO_2^+ intensity maps (from D_2) for relative energies of 2.9 eV and 5 eV respectively. As the relative energy is increased the distributions become increasingly asymmetric and more highly peaked about the stripping velocity. This is in keeping with the assumption that as relative translational energy is increased much above the well depth, it becomes more difficult to form a long lived complex and the direct interaction predominates.

As mentioned above, the internal energy associated with formation of DCO_2^+ by a stripping mechanism is a function of the relative energy of D and CO_2^+ since the spectator D atom is incapable of removing this relative energy. As translational energy is increased, eventually this internal

energy will exceed the dissociation energy for DCO_2^+ . The thermodynamics for this process are:

Thus ΔE_0^0 for dissociation of DCO_2^+ is +5.1 eV which lies +4.4 eV (or 102 Kcal/mole) in energy above the initial reactants.

The DCO_2^+ product will be unstable if $Q_{ss} \geq -\Delta E_0^0$ or

$$E_{\text{rel}} - E'_{\text{rel}} \geq 4.4 \text{ eV}$$

If E_a denotes the energy of CO_2^+ relative to the D atom,

$$-Q_{ss} = E_a = \frac{M_D}{M_D + M_{\text{CO}_2}} E_{\text{LAB}} \quad \text{or}$$

$$E_{\text{LAB}} = -\frac{M_D + M_{\text{CO}_2}}{M_D} Q_{ss}$$

Dissociation of DCO_2^+ occurs then when $E_L > \frac{2+4.4}{2} \text{ (4.4 eV)} \approx 100 \text{ eV}$ and the spectator stripping peak is expected to be greatly attenuated (and show forward movement due to loss of more highly excited product) for initial CO_2^+ energies greater than 100 eV.

Product intensity distributions for DCO_2^+ were examined at laboratory energies of 100 and 125 eV. At 100 eV (8.3 eV relative energy - Fig. 45) the stripping peak persisted, but showed a little forward movement. At 125 eV the peak intensity had moved farther forward and intensity of the DCO_2^+ product dropped by a factor of 10. This is consistent with loss of

DCO_2^+ formed by a strict spectator stripping mechanism and stabilization of the detected product by forward recoil. This is consistent with the results of Ding.¹⁷

At initial laboratory energy of 150 eV no significant amount of DCO_2^+ was detected. At this and higher energies, product stabilization by forward recoil becomes improbable and formation of products in competing reactive channels is likely.

XBL 748-7117

Fig. 40. HCO_2^+ intensity distribution for 1.5 eV relative energy (H_2 target).

Relative Energy = 2.03 eV

XBL 749-7208

Fig. 41. DCO_2^+ intensity distribution for 2 eV relative energy (D_2 target). X marks spectator stripping velocity.

XBL 749-7210

Fig. 42. DCO_2^+ intensity distribution from HD at 1.5 eV relative energy. X marks spectator stripping velocity.

Fig. 43. DCO_2^+ intensity distribution from D_2 at 2.9 eV relative energy.

Relative Energy = 5.0 eV

XBL 749-7207

Fig. 44. DCO_2^+ intensity distribution from D_2 at 5 eV relative energy. 2 Spectator stripping peak is becoming more pronounced.

Relative Energy = 8.3 eV

XBL 749-7238

Fig. 45. DCO_2^+ intensity distribution from D_2 at 8.3 eV relative energy.

1194

Relative Energy = 10.4 eV

XBL 749-7237

Fig. 46. DCO_2^+ intensity distribution from D_2 at 10.4 eV relative energy. Intensity peak has moved forward of the spectator stripping velocity showing forward recoil product stabilization.

DCO⁺ (HCO⁺)

The DCO⁺ product forms a second important reactive channel in the CO₂⁺-H₂ system. While DCO⁺ intensities are typically lower than DCO₂⁺ intensities by a factor of 50, there is a sizeable amount of this product produced in the reaction.

The DCO⁺ product distributions provide further evidence for low energy complex formation giving way to a direct mechanism at higher energies. The reaction forming DCO⁺ + OD is 0.7 eV exothermic, very close to the value for formation of DCO₂⁺.

Figures 47-51 show HCO⁺ and DCO⁺ product intensity maps over a range of initial relative energies. The HCO⁺ distribution in Fig. 47 is very close to being symmetric while Fig. 48 showing the analogous DCO⁺ distribution shows somewhat greater forward emphasis. In both cases the distribution is peaked at the center of mass. As the relative energy increases to 8.3 eV (Fig. 49) this asymmetry becomes more marked and a forward peak is present. The distribution for E_{rel} = 10.4 eV (Fig. 50) is quite similar. The position of the peak moves steadily forward with increasing energy until the distribution lies entirely in the forward direction (Fig. 51).

The movement of the product distribution with increasing energy is most clearly viewed by examination of the zero degree scattering (center lines) with a normalized velocity scale as shown in Fig. 52. At low energies the distribution is quite symmetric about the center of mass and steadily progresses toward forward scattering as the initial energy is increased. This is further evidence of complex formation at low

energies with a more direct interaction at higher energies.

To investigate whether there is any isotope effect with regard to HCO^+ and DCO^+ formation, both HCO^+ and DCO^+ product intensities at low relative energies were measured using HD as a target. The results, shown in Fig. 53, show that in both velocity distribution and intensity there is no discernible isotope effect.

To verify presence of a symmetric distribution peaked at the center of mass at low energies, HCO^+ centerline distributions from H_2 were measured (Fig. 54). These zero degree scattering profiles generally display the symmetric behavior expected from long lived complex formation.

The exact mechanism of formation of the DCO^+ product has not yet been clearly defined. Using the velocity and intensity distributions for DCO^+ (Fig. 52) it is possible to make some inferences. At low energy ($E_{\text{rel}} < 4 \text{ eV}$) a peak of intensity 1000 is positioned about the center of mass velocity. The intensity and position of the peak along with the low internal energy associated with complex formation support the contention that at low relative energy, DCO^+ is formed directly from decay of the D_2CO_2^+ intermediate complex.

At somewhat higher energies the peak intensity increases and moves forward. In this intermediate energy regime ($E_{\text{rel}} = 4\text{--}8 \text{ eV}$), the DCO^+ product appears near a velocity consistent with a "double stripping" mechanism ($v_{\text{gs}}(\text{CO}^+)$ in Fig. 52). The picture of the interaction is of CO^+ interacting solely with a single D atom while O interacts with the other D atom. While such a process requires a rather severely constrained range of collision geometries, it is not entirely unlikely that such an interaction may occur.

As initial relative energy is further increased, the intensity peak for DCO^+ moves further forward until ($E_{\text{rel}} \sim 10 \text{ eV}$) it appears near the velocity corresponding to stripping formation of DCO_2^+ ($v_{\text{ss}}(\text{DCO}_2^+)$ in Fig. 52). In this case one imagines that DCO_2^+ is formed by a direct interaction and later decays to form $\text{DCO}^+ + \text{O}$ ($\Delta E_{\text{O}}^0 = 4.5 \text{ eV}$) or $\text{CO}_2^+ + \text{H}$ ($\Delta E_{\text{O}}^0 = 5.2 \text{ eV}$). Since the relative energy (10 eV) lies above that at which DCO_2^+ formed by a strict stripping mechanism remains stable and since the DCO^+ product is thermodynamically favored, it is easy to rationalize the production of DCO^+ from stripped DCO_2^+ .

As relative energy is increased further, there is a dramatic drop in DCO^+ peak intensity at high relative energy, DCO^+ formed both by a double stripping mechanism and by decay of DCO_2^+ is expected to be unstable. For the double stripping case, the energy of the CO^+ moiety is 28/44 of the CO_2^+ energy and relative to the D atom.

$$-E_a = Q = -28/44 \times 2/30 E_{\text{LAB}} = .0424 E_{\text{LAB}}$$

At $E_{\text{LAB}} = 150 \text{ eV}$ DCO^+ formed by double stripping will be found at $Q = -6.4 \text{ eV}$. If we add to this one-half the exoergicity of the reaction ($\text{CO}_2^+ + \text{D}_2 \rightarrow \text{DCO}^+ + \text{OD}$ $\Delta E_{\text{O}}^0 = .7 \text{ eV}$) then the internal energy of DCO^+ is

$$U = -Q - \Delta E_{\text{O}}^0 \approx 6.7 \text{ eV}.$$

This is equal to the dissociation energy of DCO^+ (6.7 eV) and one expects that DCO^+ formed by a double stripping mechanism will disappear for $E_{\text{LAB}} > 150 \text{ eV}$.

For the case of formation of DCO^+ from DCO_2^+ , the Q value for formation of DCO_2^+ ($E_a = -Q_{\text{ss}} = 2/46 E_{\text{LAB}}$) is equal to 6.5 eV at $E_{\text{LAB}} = 150 \text{ eV}$. However, the formation of $\text{DCO}^+ + \text{O}$ from DCO_2^+ requires 4.5 eV energy. Since this endothermicity must be subtracted from the final internal

energy of DCO^+ , at 150 eV in the laboratory,

$$U = -Q - \Delta E_0^0 \approx 2 \text{ eV.}$$

This internal energy is less than the dissociation energy of DCO^+ by a considerable amount. We thus expect that at 150 eV DCO^+ formed by double stripping will be unstable while DCO^+ formed from decay of DCO_2^+ will remain undissociated (dissociation in the latter case occurs for $E_{\text{LAB}} > 250 \text{ eV}$). The drop in peak intensity of DCO^+ for $E_{\text{LAB}} > 150 \text{ eV}$ thus provides evidence for formation of a significant amount of DCO^+ by a double stripping mechanism at intermediate energies. It appears that at high energies this component of the DCO^+ intensity distribution disappears with the remaining DCO^+ being that formed by decay of DCO_2^+ . It is unclear whether the forward movement of the DCO^+ peak intensity toward v_{as} for DCO_2^+ is actually due to DCO_2^+ stripping followed by DCO^+ formation, or if the peak movement is due to a forward recoil effect. The above discussion tends to support the latter hypothesis.

In any case, DCO^+ formation appears to be the result of several types of interaction mechanisms within the energy range studied. It is possible that several mechanisms may work simultaneously at any given energy. The transition between mechanisms of DCO^+ formation is likely a gradual one.

XBL 749-7205

Fig. 47. HCO^+ intensity distribution from H_2 at 4.4 eV relative energy.

XBL 749-7206

Fig. 48. DCO^+ intensity distribution from D_2 at 4.4 eV relative energy.

XBL 749-7204

Fig. 49. DCO^+ intensity distribution from D_2 at 8.3 eV relative energy; X marks spectator stripping velocity of DCO^+ (double stripping).

XBL 749-7231

Fig. 50. DCO^+ intensity distribution from D_2 at 10.4 eV relative energy; X marks spectator stripping velocity of DCO_2^+ .

XBL 749-7203

Fig. 51. DCO^+ intensity distribution from D_2 at 16.7 eV relative energy.

XBL 749-7229

Fig. 52. DCO^+ centerline distributions from D_2 as a function from long lived complex to direct interaction mechanisms.

XBL 749-7228

Fig. 53. HCO^+ and DCO^+ centerline distributions from HD showing no significant isotope effect at low relative energy.

XBL 749-7230

Fig. 54. HCO^+ centerline distributions from H_2 at low initial relative energy.

Nonreactive CO_2^+

The nonreactively scattered CO_2^+ distributions contribute further evidence for strong chemical interaction between CO_2^+ and D_2 . At all initial relative energies there is a large amount of inelastically scattered CO_2^+ . The distributions suggest that scattering occurs by simultaneous direct interaction and long lived complex mechanisms.

A product map of CO_2^+ from D_2 is shown in Fig. 55 for $E_{\text{rel}} = 1.86$ eV. There is a large component of elastic scattering which follows the $Q = 0$ circle, yet in the forward hemisphere there is a significant amount of inelasticity displayed, even at this low relative energy. For comparison, Fig. 56 shows the analogous experiment with He target gas. While there is again a large elastic component to the map, near the center of mass the intensity drops, suggesting a much less inelastic type of interaction. Comparison of these two distributions leads to the conclusion that even though much nonreactive scattering occurs by a direct mechanism, the formation of a long lived complex in collisions of CO_2^+ with D_2 is likely responsible for the highly inelastic CO_2^+ intensity.

The CO_2^+ distribution from D_2 at $E_{\text{rel}} = 3.0$ eV is shown in Fig. 57. The relative inelasticity has increased and now contributes to the formation of a ridge projecting back toward the center of mass. The existence of such high inelasticity at this relative energy is significant because for $E_{\text{rel}} = 3.0$ eV electronic excitation or dissociation of D_2 ($E_0^0 = 4.5$ eV) are not possible; thus all inelasticity must be due to excitation of either D_2 or CO_2^+ vibrational modes. The CO_2^+ results are more inelastic than the Ar^+-D_2 results²¹ at a similar energy. This

suggests either that complex formation is occurring or that the large number of additional vibrational degrees of freedom in the CO_2^+ case are important.

Figures 58-60 are maps of CO_2^+ from D_2 at relative energies of 5, 8.3, and 10.4 eV respectively. They continue to display large inelastic components although the overall intensity of the maps drops off as collisions occur with greater relative energy. This intensity change is consistent with an expected drop in total cross section for CO_2^+-D collisions as the relative energy is increased.

XBL 748-7118

Fig. 55. Nonreactive CO_2^+ intensity distribution from D_2 at 1.9 eV relative energy showing broad inelasticity at the center of mass velocity.

XBL 748-7116

Fig. 56. Nonreactive CO_2^+ intensity distribution from He at 1.9 eV relative energy. There is a significant lack of intensity due to inelastic collisions near the center of mass velocity.

XBL 746-7115

Fig. 57. Nonreactive CO_2^+ intensity distribution from D_2 at 3 eV relative energy.

XBL 749-7209

Fig. 58. Nonreactive CO_2^+ intensity distribution from D_2 at 5 eV relative energy.

XBL 749-7202

Fig. 59. Nonreactive CO_2^+ intensity distribution from D_2 at 8.4 eV relative energy.

XBL 749-7235

Fig. 60. Nonreactive CO_2^+ intensity distribution from D_2 at 12.3 eV relative energy.

CO⁺

The CO⁺ product is a third reactive channel which was studied at several energies. At initial energies below 100 eV, no significant amount of CO⁺ was detected. For energies above this level, in general the CO⁺ distributions are very similar to products of collisionally induced dissociation which have been measured in other ion-molecule systems.²² The CO⁺ product lies forward of the center of mass and has a broad angular distribution. The overall intensity remains approximately constant as a function of relative energy.

One question which arises is whether the formation of CO⁺ occurs by an impulsive dissociation, or whether the chemical interaction between CO₂⁺ and D₂ plays a role in the dissociation. The distribution of CO⁺ formed in collisions with He (Fig. 61) are quite similar to those from D₂ (Fig. 62-64). This suggests that in both cases the dissociation occurs by an impulsive collision in which the chemical nature of the product plays a very small role. The large Q figures for the CO⁺ distribution peaks (Figures 62-64) make it highly unlikely that any H₂O target is formed. It is more probable that (H₂ + O), (H + OH) or (H + H + O) are formed, with each neutral product leaving the scene of the collision taking with it a sizeable amount of translational energy, consistent with the large -Q values of the CO⁺ distribution. Another possible source of CO⁺ intensity might be dissociation of highly excited HCO⁺ formed by a stripping mechanism for Q_{ss} > D_{HCO⁺}. However, it is impossible to confirm this mechanism for CO⁺ production.

XBL 749-7232

Fig. 61. CO^+ intensity distribution from He at 10.4 eV relative energy.

Relative Energy = 12.5 eV

XBL 749-7200

Fig. 62. CO^+ intensity distribution from D_2 at 12.5 eV relative energy.

Relative Energy = 16.7 eV

XBL 748-7112

Fig. 63. CO^+ intensity distribution from D_2 at 16.7 eV relative energy.

XBL 748-7114

Fig. 64. CO^+ intensity distribution from D_2 at 20.8 eV relative energy.

OD⁺, O⁺, and H₂O⁺

Both OH⁺ and O⁺ were noted as minor products of CO₂⁺ + H₂ collisions. H₂O⁺ was not detected at any of the relative energies studied, which is consistent with a possible energy barrier in the entrance channel suggested by the H₂O⁺ correlation diagram.

Figure 65 shows the distribution of OD⁺ from D₂ at a relative energy of 16.7 eV and Fig. 66 the distribution for O⁺ from D₂. Neither product was detected for E < 100 eV. Because of the very low intensity associated with each of these reaction products, they were not investigated to any extent. It is assumed that O⁺ is the product of collisional dissociation while OH⁺ may be formed either directly from the H₂CO₂⁺ intermediate or from dissociation of highly excited HCO₂⁺ or HCO⁺. In any case, neither of these products has contributed to our understanding of the overall reaction system.

It should be noted, however, that OD⁺ is clearly not the product of a double stripping mechanism in which DCO and OD⁺ are simultaneously formed by independent collisions of CO and O⁺ (in the form of CO₂⁺) with separate D atoms. This possibility is ruled out by the position of the OD⁺ distribution. In the event of a double stripping mode of OD⁺ formation, one would expect an intensity peak at $v = \frac{16}{18} v_0$ where v_0 is the velocity of the incident CO₂⁺. This velocity lies behind the center of mass where there is in fact negligible intensity.

By similar reasoning the formation of O⁺ from excited (D₂O⁺)^{*} may be ruled out since such a mechanism in which an O⁺ ion is stripped from CO₂ as it passes by would also lead to O⁺ backscattering.

Fig. 65. OD^+ intensity distribution from D_2 at 16.7 eV relative energy.

XBL 748-7113

XBL 749-7201

Fig. 66. O^+ intensity distribution from D_2 at 8.3 eV relative energy.

Summary of Results

As we have emphasized previously, the $\text{CO}_2^+ - \text{H}_2$ system can be characterized as a reaction evolving through both a long lived complex and a direct spectator stripping mechanism. The DCO_2^+ product is predominantly the result of the stripping process although complex formation apparently plays a role for $E_{\text{rel}} < 2$ eV. The HCO^+ product is formed by a complex at low energies, and its formation at higher energies can be rationalized using two competing stripping processes. The CO_2^+ which is nonreactively scattered shows large inelasticity due to vibrational mode excitation. CO^+ and O^+ appear to be formed by collisional dissociation while no H_2O^+ was found at any relative energy. All of these results can be rationalized in terms of the pertinent molecular orbital correlation diagrams.

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APPENDIX A

THE MATHEMATICAL DESCRIPTION OF RANDOM PROCESSES

In support of the discussion of pseudorandom modulation presented in Chapter II, we have collected a brief introduction/review of the description of random processes. This discussion is by no means cyclopedic, but is aimed at defining the terms used to describe random processes.

A random process describes a system whose output is not deterministic; given a sample record (time history) of the results of a random phenomenon, it is only possible to make probabilistic statements concerning the nature of future sample records. The collection of all possible sample records from a random phenomenon is called a stochastic process (random process). Thus, in stochastic theory no distinction is drawn between the phenomenon responsible for sample record generation and the collection of all such records; the phenomenon and its results are from a statistical point of view identical.

The events of a stochastic process are described by a random variable, X , and the process itself is denoted by $\{X(t), t \in T\}$ where $\{T\}$ is an index set describing the time variable. $\{T\}$ can be either a discrete or continuous set, describing respectively discrete or continuous parameter processes.

The space of all possible outcomes of the process is called the sample space, S :

$$X(t) \in S, t \in T$$

The collection of all sets of events (partial sample records) is denoted by F , the family of events.¹ For many physical processes the sample space is R^1 and the family of events is B , the Borel sets.² The random variable X is real, finite valued and defined on all of S .

A collection of sample records of a stochastic process is an ensemble. In general, ensemble averages of process properties (simple and joint moments) are not necessarily equal to the corresponding time averaged properties.

The output of a stochastic process can be described by a probability law (distribution function). This characterization may be presented in one of several ways (ensemble averages):

(1) By the probability density function,

$$P_{t_1}(x_1) = \lim_{\Delta x \rightarrow 0} \frac{x_1 < X(t_1) < x_1 + \Delta x}{\Delta x} \quad x_1 \in S$$

which describes the probability that the stochastic output in a small range surrounding the value $x_1 \in S$.

(2) By the moments of the distribution, including the mean value and autocorrelation function:

$$\mu_x(t_1) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N X_k(t_1)$$

$$R_{xx}(t_1, t_1 + \tau) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{k=1}^N X_k(t_1) X_k(t_1 + \tau)$$

These are, respectively, the first simple and joint moments. Complete characterization of a stochastic process requires specification of higher moments as well.

(3) By spectral density functions which are the Fourier transforms of simple and joint moments (i.e. the power spectral density function).

In general, each of these measures varies with time. If this is the case, the process is said to be nonstationary. If μ_x and R_{xx} are time invariant the process is said to be weakly stationary, while if all higher moments are also time invariant the process (and hence the distribution function) are said to be strongly stationary.³ From a practical standpoint, proof of weak stationarity is often used to justify an assumption of strong stationarity.

For a stationary (meaning strongly stationary henceforth) stochastic process, if the corresponding time averaged properties of the mean and autocorrelation,

$$\mu_x(k) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T X_k(t) dt$$

$$R_{xx}(\tau; k) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T X_k(t) X_k(t+\tau) dt$$

are equal to the corresponding ensemble averaged (over index k) properties, the process is said to be ergodic. This is an important requirement for characterizing the properties of a stochastic process since it is rarely practical to compute ensemble averaged properties. Ergodicity is difficult to prove. However, if a process is self-stationary, i.e.

properties computed over short time intervals are relatively invariant with respect to interval choice, then an assumption of stationarity and ergodicity is justified.³

An equivalent way of specifying the probability density function for a process is to use its probability law (or cumulative probability density function):

$$P_X(x_1) = \text{Prob } [X(t) \leq x_1]$$

$$= \int_{-\infty}^{x_1} P(x') dx'.$$

Two stochastic processes are said to be identically distributed if they have the same probability law.

The importance of the above mentioned terminology is this: random processes (such as m-sequences or detector outputs) are generally assumed to be stationary and ergodic. As statistical methods are applied to more complicated physical systems, the systems designer must remain acutely aware of the assumptions of stationarity and ergodicity as well as the often made assumption of system linearity. Thus an understanding of the description of random processes becomes more important as more sophisticated analytical systems of measurement (such as impulse response determination) are employed. During our initial evaluation of the correlation TOF system we found the above concepts important and hence their presentation here.

APPENDIX B

DETECTOR COINCIDENCE ANALYSIS

In presenting the statistical analysis of the correlation method in Chapter II, a discussion of the problem of detector paralysis required the estimation of the probability that two ions are detected during a short interval. We present here a derivation of this probability under the assumption of a Gaussian TOF distribution.

We recall that the output of the TOF system, $y(\tau')$ is given by the convolution of the TOF response function, $h(t)$ and the input modulation, $g(t-\tau)$:

$$y(\tau) = h * g = \int_{-\infty}^{\infty} h(t) g(t-\tau) dt \quad (B-1)$$

The probability of coincident detection of two particles during any time interval τ is described by the autocorrelation function, $R_{yy}(\tau)$, of the system output:

$$R_{yy}(\tau) = \frac{1}{2T} \int_{-T}^T y(\tau') y(\tau'+\tau) d\tau' \quad (B-2)$$

By using Eq. (B-1) in (B-2),

$$\begin{aligned} R_{yy}(\tau) &= \frac{1}{2T} \int_{-T}^T d\tau' \int_{-\infty}^{\infty} h(t') g(t'-\tau') dt' \int_{-\infty}^{\infty} h(t) g(t-\tau'+\tau) dt \\ &= \frac{1}{2T} \int_{-\infty}^{\infty} h(t') dt' \int_{-\infty}^{\infty} h(t) dt \int_{-T}^T g(t'-\tau') g(t-\tau'+\tau) d\tau' \end{aligned}$$

$$R_{yy}(\tau) = \int_{-\infty}^{\infty} h(t') dt' \int_{-\infty}^{\infty} h(t) dt R_{gg}(t-t'+\tau) \quad (B-3)$$

where the third equality follows from changing the variable of integration ($\tau' \rightarrow \tau'' + t'$) and the definition of the autocorrelation function for the input modulation,

$$R_{gg}(t-t'+\tau) \equiv \frac{1}{2T} \int_{-T}^T g(-\tau'') g(t-t'+\tau-\tau'') d\tau'' \quad (B-4)$$

Stern and coworkers^{*} have evaluated this autocorrelation function as:

$$R_{gg}(\tau) = e^{-2m|\tau|} \quad (B-5)$$

where m is the average zero crossing rate of the modulation function.

Using this expression and an assumption of a Gaussian response function (not an unreasonable approximation),

$$h(t) = A e^{-(t-t_0)^2/a^2} \quad (B-6)$$

we can evaluate the output autocorrelation function as:

$$R_{yy}(\tau) = A^2 \int_{-\infty}^{\infty} e^{-(t-t_0)^2/a^2} dt' \int_{-\infty}^{\infty} e^{-(t-t_0)^2/a^2} e^{-2m|t-t'+\tau|} dt \quad (B-7)$$

^{*}T. E. Stern, A. Blaquiere and J. Valat, J. Nuclear Energy A/B 16 499 (1962).

In a typical TOF correlation experiment the width of the TOF function is generally much greater than the width of a unit modulation pulse (typically by a factor of 10-25 for a reasonable length flight path):

$$a \gg \frac{1}{2m}$$

Using this assumption, we approximate the overlap integral

$$\int_{-\infty}^{\infty} h(t) e^{-2m|t-t'\tau|} dt \quad (B-8)$$

by $h(t'-\tau) \cdot 1/m$. This approximation follows from the fact that the smoothly varying response function, $h(t)$, will have an approximately constant value, $h(t'-\tau)$ over the time interval where the modulation autocorrelation function is nonzero; the autocorrelation function is approximated as a rectangle of height 1 and width $1/m$ (Fig. B-1).

Thus

$$\begin{aligned} R_{yy}(\tau) &\cong \frac{A^2}{m} \int_{-\infty}^{\infty} e^{-(t'-t_0)^2/a^2} e^{-(t'-\tau-t_0)^2/a^2} dt' \\ &\cong \frac{A^2}{m} \int e^{-1/a^2(2y^2-2y\tau+\tau^2)} dy \quad (y = t' - t_0) \\ &\cong \frac{A^2}{m} e^{-\tau^2/2a^2} \int_{-\infty}^{\infty} e^{-2/a^2(y-\tau/2)^2} dy \end{aligned}$$

XBL 749-7313

Fig. B-1. Estimating the overlap integral of the TOF distribution function, $h(t)$, and the modulation autocorrelation function, $R_{gg}(t)$.

$$R_{yy}(\tau) \equiv \frac{A^2}{m} e^{-\tau^2/2a^2} \sqrt{\pi/2} a \quad (B-9)$$

which is the desired result for the output autocorrelation. As expected, this expression is proportional to the square of the scattered signal, A, and depends exponentially on the coincidence interval, τ .

Using the values,

$$\begin{aligned} a &= 10^{-5} \text{ sec} \\ m &= 10^{+6} \text{ sec}^{-1}; m^{-1} = 10^{-6} \text{ sec} \\ A &= 10^7 \text{ molecules/sec scattered} \end{aligned}$$

$$R_{yy}(\tau) = 10^3 e^{-(\tau/10^{-5} \text{ sec})^2} \quad (B-10)$$

Evaluating the probability of 2 detector events occurring in 5 μsec (the approximate detector deadtime), we note that the exponent in Eq. (B-10) will be small (~ 0.05) so that the exponential factor is $\approx$ equal to 1.

To measure the total probability we integrate Eq. (B-10),

$$\begin{aligned} P &= 10^3 \int_0^{5 \mu\text{sec}} e^{-(\tau/10^{-5} \mu\text{sec})^2} d\tau \approx 10^3 \int_0^{5 \mu\text{sec}} d\tau \\ &= 5 \times 10^{-3} \end{aligned}$$

Thus the probability of coincident detection occurring within a 5 μsec interval is 0.5%. This shows that, given a sufficiently long flight path

and broad modulation bandwidth, deadtime losses of detector signal should not pose a significant problem in TOF impulse response measurements by the correlation method.

APPENDIX C

```

    /*** IOF CORRELATION PROGRAM MONITOR
    /   EDITOR LISTING COMPILED BY
    /   MACRO-8 COMPILER
  
```

CAF=6007

*0

```

00000 0000      0000
00001 3040      DCA SAVEAC
00002 7004      RAL
00003 5005      JMP *+2
00004 0000      0000      / SAVE FOR ODT LINK
00005 3041      DCA SAVEL
00006 5577      JMP I (400
  
```

*20

```

00020 7300  BACK,  CLA CLL /RECOVER VALUES BEFORE INTERRUPT
00021 1041      TAD SAVEL      /AND PROCEED FROM THERE
00022 7010      RAR
00023 1040      TAD SAVEAC
00024 6001      ION
00025 5400      JMP I 0

00026 7000  WAIT,  NOP
00027 5026      JMP .-1
00030 1000  BIN1A, 1000      / ADDRESS OF BIN1
00031 1074  NBIN1A, 1074    / ADDRESS OF NBIN1
00032 0000  TH1RD, 0
00033 0000  NBINNO, 0000
00034 0000  BINNO, 0000
00035 0000  COUNT, 0000
00036 0000  INDEX, 0000
00037 0000  ADDR, 0000
00040 0000  SAVEAC, 0000
00041 0000  SAVEL, 0000
00042 0000  SCANNO, 0
00043 0000  SEGNO, 0
00044 0000  INSTR, 0
00045 0000  HOLDL, 0
00046 0000  HOLDS, 0
00047 0000  CURADD, 0
  
```

*101

00101	0001	0001	/ CLOCK CODE HERE
00102	0000	0000	/ DELAY CODE HERE
00103	0006	0006	/ # PLACES ROTATE FOR DISPLAY
			/ SETUP (*300) HERE

*200

00200	6007	START1,	CAF	
00201	7300		CLA CLL	
00202	4777		JMS	DOZERO
00203	3000		3000	/ CLEAR DISPLAY BUFFER
00204	3035		3035	
00205	4777		JMS	DOZERO
00206	1000		1000	/ CLEAR ACCUMULATORS
00207	1167		1167	
00210	6337		6337	/ CLEAR OVERFLOW FLAG
00211	4776		JMS TYPX	
00212	0233		MESS1	
00213	4775		JMS ZDATA	
00214	7300		CLA CLL	
00215	1101		TAD	101 / SET CLOCK
00216	6336		6336	
00217	7300		CLA CLL	
00220	1102		TAD	102 / SET DELAY
00221	6332		6332	
00222	7300		CLA CLL	
00223	1270		TAD	A / LOAD CwI
00224	6331		6331	
00225	4774		JMS WAITR	
00226	7300		CLA CLL	
00227	1271		TAD B	
00230	6331		6331	
00231	6001		10N	
00232	5026		JMP WAIT	
00233	4007	MESS1,	TEXT ' G	
00234	1737	Q-		
00235	4000	'		

*270

00270	3500	A,	3500	/CwI CODE
00271	7500	B,	7500	/ CwI CODE...TURN ON DATA BREAK

*300	/ SETUP FOR DISPLAY ROUTINE
00300 7300 SETUP,	CLA CLL
00301 1356	TAD BUF
00302 3360	DCA DEP
00303 1030	TAD BIN1A
00304 3361	DCA GET
00305 1372	TAD KX
00306 3362	DCA SETX
00307 1103	TAD 103
00310 7041	CIA
00311 3363	DCA RAT1
00312 1363	TAD RAT1
00313 1367	TAD TWELV
00314 7041	CIA
00315 7100	CLL
00316 3364	DCA RAT2
00317 1363	TAD RAT1
00320 3365	DCA ROT1
00321 1364	TAD RAT2
00322 3366	DCA ROT2
00323 1761	TAD 1 GET
00324 0371	AND X1
00325 7010	RAR
00326 2365	ISZ ROT1
00327 5325	JMP *-2
00330 3370	DCA TEMP1
00331 2361	ISZ GET
00332 1761	TAD 1
00333 0373	AND NEG
00334 7440	SZA
00335 5345	JMP ZERO
00336 1761	TAD 1 GET
00337 0357	AND K2
00340 7004	RAL
00341 2366	ISZ ROT2
00342 5340	JMP *-2
00343 1370	TAD TEMP1
00344 5346	JMP *-2
00345 7300	CLA CLL
00346 3760	DCA 1 DEP
00347 2360	ISZ DEP
00350 2361	ISZ GET
00351 2362	ISZ SETX
00352 5317	JMP SAX
00353 6001	ION
00354 5755	JMP 1
00355 2700	2700 / CLEAR NBINS

00356	3000	BUFF,	3000
00357	0077	X2,	0077
00360	0000	DEP,	0000
00361	0000	GET,	0000
00362	0000	SETX,	0000
00363	0000	RAT1,	0000
00364	0000	RAT2,	0000
00365	0000	ROT1,	0000
00366	0000	ROT2,	0000
00367	0014	TWELV,	0014
00370	0000	TEMP1,	0000
00371	7700	X1,	7700
00372	7742	KX,	7742
00373	4000	NEG,	4000

/ THE DAISY CHAIN INTERRUPT PROCESSOR

00374	0513
00375	2400
00376	1200
00377	2407

*400

00400	6031	KSF	/ KEYBOARD FLAG?
00401	7410	SKP	/ NO
00402	5215	JMP KEYFLG	/ YES; SERVICE IT
00403	6334		/ GO TO OVERFLOW SERVICE ROUTINE
00404	7410	SKP	
00405	5325	JMP	525
00406	5207	JMP UNDEF	/ UNDEFINED FLAG
00407	6041	UNDEF, TSF	/ CHECK PRINTER FLAG
00410	5213	JMP	..+3
00411	6042		6042 .# / TCF
00412	5020	JMP	BACK
00413	7300	CLA	CLL
00414	5024	JMP	24
00415	6036	KEYFLG, KRB	/ ACCEPT INPUT CHARACTER AND ECHO
00416	6046	TLS	
00417	6041	TSF	
00420	5217	JMP	..-1
00421	6042	TCF	
00422	1377	TAD (-301	/ TRIM CHAR.
00423	7510	SPA	
00424	5242	JMP QM	/ NOT A VALID CHARACTER
00425	3240	DCA	OFFSET
00426	1240	TAD	OFFSET
00427	1376	TAD (-32	/ VALID CHARACTER?
00430	7700	SMA	CLA

00431	5242	JMP QM / NOT VALID
00432	1260	TAD SLIST
00433	1240	TAD OFFSET / CALCULATE ACTION LIST
00434	3241	DCA INSTRR
00435	1241	TAD INSTRR
00436	3241	DCA INSTRR
00437	5641	JMP I INSTRR
00440	0000	OFFSET, 0000
00441	0000	INSTRR, 0000
00442	7300	CLA CLL
00443	4775	JMS TYPX
00444	0446	MQM
00445	5020	JMP BACK
00446	4077	MQM, TEXT ' ?
00447	3740	
00450	0000	

*460

00460	0461	SLIST, 0461	/ ADDRESS OF FIRST POINTER
00461	7000	7000	/ ODT
00462	2600	2600	/ CLASSICAL TOF
00463	2620	2620	/ CORRELATION TOF
00464	2760	2760	/ DISPLAY
00465	0442	QM	/ E
00466	0442	QM	/ F
00467	0442	QM	/ G
00470	0442	QM	/ H
00471	0442	QM	/ I
00472	0442	QM	/ J
00473	0442	QM	/ K
00474	0442	QM	/ L
00475	0442	QM	/ M
00476	0442	QM	/ N
00477	0442	QM	/ O
00500	0442	QM	/ P
00501	0442	QM	/ Q
00502	0442	QM	/ R
00503	0200	START1	/ S
00504	0442	QM	/ T
00505	0622	SCAN	/ U
00506	0442	QM	/ V
00507	0442	QM	/ W
00510	0442	QM	/ X
00511	0442	QM	/ Y
00512	0442	QM	/ Z

/ WAITS FOR PRNG CODE TO MOVE
/ THROUGH THE DELAY LINE

00513	0000	WAITER,	0000
00514	7300		CLA CLL
00515	3321		DCA TOAD
00516	2321		ISZ TOAD
00517	5316		JMP -1
00520	5713		JMP I WAITER
00521	0000	TOAD,	0000

*525 / OVERFLOW SERVICE ROUTINE

00525	6002		IOF
00526	7300		CLA CLL
00527	1335		TAD EX
00530	6331		6331
00531	6337		6337
00532	7300		CLA CLL
00533	5734		JMP I .+1
00534	0622		SCAN
00535	2400	EA,	2400

00575	1200
00576	7746
00577	7477

*600

00600	0000	NTOTAL,	0000
00601	7300		CLA CLL
00602	1031		TAD NBIN1A
00603	1035		TAD COUNT
00604	1432		TAD I THIRD
00605	3033		DCA NBINNO
00606	1037		TAD ADDR
00607	6211		6211
00610	3100		DCA 100
00611	1500		TAD I 100
00612	6201		6201
00613	1433		TAD I NBINNO
00614	3433		DCA I NBINNO
00615	2033		ISZ NBINNO
00616	7004		RAL
00617	1433		TAD I NBINNO
00620	3433		DCA I NBINNO
00621	5600		JMP I NTOTAL

00622	7300	SCAN,	CLA CLL	/ TRANSFORMATION ROUTINE
00623	1777		TAD	EX
00624	6331		6331	
00625	7300		CLA CLL	
00626	1267		TAD	F
00627	3032		DCA	THIRD
00630	1256		TAD	DUD
00631	3257		DCA	DUM
00632	1265		TAD	K4
00633	3263		DCA	INDX
00634	3255	NEXTK,	DCA	TEMP
00635	1264		TAD	K3
00636	3266		DCA	TIMES
00637	1657		TAD I	DUM
00640	3255		DCA	TEMP
00641	1255	GENER,	TAD	TEMP
00642	4273		JMS	TEST
00643	2255		ISZ	TEMP
00644	2266		ISZ	TIMES
00645	5241		JMP	GENER
00646	7000		NOP	
00647	2032		ISZ	THIRD
00650	2257		ISZ	DUM
00651	2263		ISZ	INDX
00652	5234		JMP	NEXTK
00653	4776		JMS	SIGNAL
00654	5775		JMP	SETUP
00655	0000	TEMP,	0000	
00656	0660	DUD,	LO1K	
00657	0000	DUM,	0000	
00660	2000	LO1K,	2000	
00661	4000	MID1K,	4000	
00662	6000	HI1K,	6000	
00663	0000	INDX,	0000	
00664	6000	K3,	6000	
00665	7775	K4,	-3	
00666	0000	TIMES,	0000	
00667	0670	F,	A0	
00670	0000	A0,	0	
00671	0024	A1,	24	
00672	0050	A2,	50	
00673	0000	TEST,	0000	
00674	3037		DCA	ADDR
00675	1320		TAD	BITSTR
00676	3321		DCA	BIT
00677	3035		DCA	COUNT
00700	1317		TAD	K1
00701	3036		DCA	INDEX

00702	1037	TEST1,	TAD	ADDR
00703	0321		AND	BIT
00704	7740		SZA	CLA CLL
00705	4774		JMS	TOTAL
00706	4200		JMS	NTOTAL
00707	2035		ISZ	COUNT
00710	2035		ISZ	COUNT
00711	1321		TAD	BIT
00712	7010		RAR	
00713	3321		DCA	BIT
00714	2036		ISZ	INDEX
00715	5302		JMP	TEST1
00716	5673		JMP I	TEST

00717	7766	K1,	7766
00720	1000	BITSTR,	1000
00721	0000	BIT,	0000

00774	2200
00775	0300
00776	2223
00777	0535

*1000

01000	0000	BIN1,	0	/DP AC
01001	0000		0	
01002	0000		0	
01003	0000		0	

/BIN3 TO BIN30 AND NBIN1 TO NBIN30 FOLLOW

*1200

01200	0000	TYPX,	0
01201	7300		CLA CLL
01202	1600		TAD I TYPX
01203	3214		DCA TYPNT
01204	2200		ISZ TYPX
01205	1614	TYPX1,	TAD I TYPNT
01206	7002		7002
01207	4215		JMS TYPY
01210	1614		TAD I TYPNT
01211	2214		ISZ TYPNT
01212	4215		JMS TYPY
01213	5205		JMP TYPX1
01214	0000	TYPNT,	0

```

01215 0000 TYPY, 0
01216 0234 AND TK77
01217 7450 SNA
01220 5600 JMP I TYPX
01221 1235 TAD TKM37
01222 7440 SZA
01223 5227 JMP TYPY1
01224 1236 TAD TK215
01225 4242 JMS TLSX
01226 1237 TAD TKM125

```

```

01227 7510 TYPY1, SPA
01230 1240 TAD TK100
01231 1241 TAD TK237
01232 4242 JMS TLSX
01233 5615 JMP I TYPY
01234 0077 TK77, 77
01235 7741 TKM37, -37
01236 0215 TK215, 215
01237 7653 TKM125, -125
01240 0100 TK100, 100
01241 0237 TK237, 237

```

```

01242 0000 TLSX, 0
01243 6046 TLS
01244 6041 TSF
01245 5244 JMP *-1
01246 6042 TCF
01247 7200 CLA
01250 5642 JMP I TLSX

```

/ D/A DISPLAY CONTROL; X AXIS AUTOMATICALLY SCALED
DYL=6063
DXL=6053
DLX=6054

*1600

```

01600 7300 DISPLA, CLA CLL
01601 3266 DCA N
01602 1264 TAD START2
01603 7041 CIA
01604 1265 TAD STOP2
01605 3272 DCA DIFF
01606 1272 TAD DIFF
01607 7004 RAL

```

01610	7430		SZL	
01611	5214		JMP	+3
01612	2266		ISZ	N
01613	5207		JMP	+4
01614	7200		CLA	
01615	1264	STAR,	FAD	START2
01616	3267		DCA	XN
01617	7200	RET,	CLA	
01620	1667		TAD	1 XN
01621	6063		DYL	/ (6063) LOAD Y AXIS WITH CONTENTS OF XN
01622	7800		CLA	
01623	1264		TAD	START2
01624	7041		CIA	
01625	1267		TAD	XN
01626	3270		DCA	XAXFS
01627	7100		CLL	
01630	1266		TAD	N
01631	7040		CMA	
01632	3271		DCA	NN
01633	1270		TAD	XAXFS
01634	2271	SKIP,	ISZ	NN
01635	5261		JMP	ROT
01636	6053		DXL	/ (6053) LOAD X WITH SCALED LOCATION #
01637	6054		DIK	/ (6054) INTENSIFY
01640	5242		JMP	+2
01641	7760		7760	
01642	7200		CLA	
01643	1241		TAD	+2
01644	3251		DCA	+5
01645	2251		ISZ	+4
01646	5245		JMP	+1
01647	7200		CLA	
01650	5252		JMP	+2
01651	0000		0000	/ INDEX
01652	1265		TAD	STOP2
01653	7041		CIA	
01654	1267		TAD	XN
01655	2267		ISZ	XN
01656	7440		SZA	
01657	5217		JMP	RET
01660	5215		JMP	STAR
01661	7100	ROT,	CLL	
01662	7004		RAL	
01663	5234		JMP	SKIP
01664	3000	START2,	3000	
01665	3035	STOP2,	3035	
01666	0000	N,	0000	
01667	0000	XN,	0000	
01670	0000	XAXFS,	0000	
01671	0000	NN,	0000	
01672	0000	DIFF,	0000	

*2200

02200	0000	TOTAL,	0000
02201	7300		CLA CLL
02202	2200		ISZ TOTAL
02203	1030		TAD BIN1A
02204	1035		TAD COUNT
02205	1432		TAD I THIR
02206	3034		DCA BINNO
02207	1037		TAD ADDR
02210	6211		6211
02211	3100		DCA 100
02212	1500		TAD I 100
02213	6201		6201
02214	1434		TAD I BINNO
02215	3434		DCA I BINNO
02216	2034		ISZ BINNO
02217	7004		RAL
02220	1434		TAD I BINNO
02221	3434		DCA I BINNO
02222	5600		JMP I TOTAL

02223	0000	SIGNAL,	0000
02224	7300		CLA CLL
02225	1377		TAD (-36
02226	3036		DCA INDEX
02227	1030		TAD BIN1A
02230	3034		DCA BINNO
02231	1031		TAD NBIN1A
02232	3033		DCA NBINNO
02233	1433	DSUB,	TAD I NBINNO
02234	7041		CIA
02235	1434		TAD I BINNO
02236	3434		DCA I BINNO
02237	7004		RAL
02240	3257		DCA KEEP
02241	2033		ISZ NBINNO
02242	2034		ISZ BINNO
02243	1433		TAD I NBINNO
02244	7040		CIA
02245	1434		TAD I BINNO
02246	1257		TAD KEEP
02247	3434		DCA I BINNO
02250	7100		CLL
02251	3257		DCA KEEP
02252	2033		ISZ NBINNO
02253	2034		ISZ BINNO
02254	2036		ISZ INDEX
02255	5233		JMP DSUB
02256	5623		JMP I SIGNAL
02257	0000	KEEP,	0000

02377	7742		
		*2400	
02400	0000	ZDATA,	0000
02401	6211		6211
02402	4207	JMS	DOZERO
02403	2000		2000
02404	7777		7777
02405	6201		6201
02406	5600	JMP I	ZDATA
02407	0000	DOZERO,	0000
02410	7300	CLA CLL	
02411	6214		/RDF
02412	3242	DCA	DATAF
02413	6201		6201
02414	1607	TAD I	DOZERO
02415	3237	DCA	FIRST
02416	2207	ISZ	DOZERO
02417	1607	TAD I	DOZERO
02420	3240	DCA	LAST
02421	1240	TAD	LAST
02422	7040	CMA	
02423	1237	TAD	FIRST
02424	3241	DCA	INDEXZ
02425	1242	TAD	DATAF
02426	7640	SCA CLA	
02427	6211		6211
02430	3637	DCA I	FIRST
02431	2237	ISZ	FIRST
02432	7000	NOP	
02433	2241	ISZ	INDEXZ
02434	5230	JMP	--4
02435	2207	ISZ	DOZERO
02436	5607	JMP I	DOZERO
02437	0000	FIRST,	0000
02440	0000	LAST,	0000
02441	0000	INDEXZ,	0000
02442	0000	DATAF,	0000

*2600 / CLASSICAL TOF MODE

02600	7300		CLA CLL
02601	1210		TAD XK1
02602	3611		DCA I XA1
02603	1212		TAD XK2
02604	3613		DCA I XA2
02605	1212		TAD XK2
02606	3614		DCA I XA3
02607	5777		JMP START1
02610	7700	XK1,	7700
02611	0271	XA1,	0271
02612	7000	XK2,	7000
02613	0653	XA2,	TEMP-2
02614	0706	XA3,	TEST1+4

*2620 / CORRELATION TOF MODE

02620	7300		CLA CLL
02621	1230		TAD YK1
02622	3631		DCA I YA1
02623	1232		TAD YK2
02624	3633		DCA I YA2
02625	1234		TAD YK3
02626	3635		DCA I YA3
02627	5777		JMP START1
02630	7500	YK1,	7500
02631	0271	YA1,	271
02632	4776	YK2,	4776
02633	0653	YA2,	TEMP-2
02634	4200	YK3,	4200
02635	0706	YA3,	TEST1+4

*2700 / CLEAR NBINS

02700	4776	JMS	DOZERO
02701	1074		1074
02702	1167		1167
02703	5704	JMP I	+.1
02704	0212		0212

*2760 / ION BEFORE DISPLAY

02760	6001	ION	
02761	5762	JMP I	+.1
02762	1600		1600
02776	2407		
02777	0200		
00177	0400		

Variable Address Assignments

A	0270	LAST	2440	TK237	1241
ADDR	0037	LOIK	0660	TK77	1234
A0	0670	MESS1	0233	TL5X	1242
A1	0671	MIDIK	0661	TOAD	0521
A2	0672	MEM	0446	TOTAL	2200
B	0271	N	1666	TwELV	0367
BACK	0020	BINNO	0033	TYPNT	1214
BINNO	0034	BINIA	0031	TPX	1200
BIN1	1000	NEG	0000	TPX1	1205
BINIA	0030	NEXTK	0634	TPY	1215
BIT	0721	NN	1671	TPY1	1227
BITSTK	0720	NTOTAL	0600	UNDEF	0407
BUFF	0356	OFFSET	0440	WAIT	0026
COUNT	0035	GM	0442	WAITER	0513
CURADD	0047	RAT1	0363	XAAXFS	1670
DATAF	2442	RAT2	0364	XA1	2611
DEP	0360	RET	1617	XA2	2613
DIFF	1672	ROT	1661	XA3	2614
DISPLA	1600	ROT1	0365	XK1	2610
DIX	6054	ROT2	0366	XK2	2612
DOZERO	2407	SAVEAC	0040	XN	1667
DSUB	2233	SAVEL	0041	X1	0371
DUD	0656	SAX	0317	X2	0357
DUM	0657	SCAN	0622	YA1	2631
DAL	6053	SCANNO	0042	YA2	2633
DYL	6063	SEGNO	0043	YA3	2635
EX	0535	SETUP	0300	YK1	2630
F	0667	SETX	0362	YK2	2632
FIRST	2437	SIGNAL	2225	YK3	2634
GENEK	0641	SRIP	1634	ZDATA	2400
GET	0361	SLIST	0460	ZERO	0345
HI1K	0662	STAR	1615		
HOLDL	0045	START1	0200		
HOLDS	0046	START2	1664		
INDEX	0036	STOP2	1665		
INDEXZ	2441	TEMP	0655		
INDX	0663	TEMP1	0370		
INSTR	0044	TEST	0673		
INSTIR	0441	TEST1	0702		
KEEP	2257	THIRD	0032		
KEYFLG	0415	TIMES	0666		
KX	0372	TKM125	1237		
K1	0717	TKM37	1235		
K3	0664	TK100	1240		
K4	0665	TK215	1236		

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ACKNOWLEDGMENTS

There have been many people who have contributed to the work described within this thesis. It is a pleasure to acknowledge their contributions.

It has been a priveledge to work with Professor Bruce Mahan. His thorough scientific knowledge, independent thought, and resourcefulness were a constant source of support. While fostering independence in the work of his associates, he was a leader in the true sense, providing invaluable advice and taking an active part in the formulation of both theoretical and experimental ideas.

Thanks to Dr. Keith Gillen and Dr. John Winn for their experimental insights and frequent discussions. To Jim Fair, thanks for assistance in measuring time of flight distributions with his hard won beam apparatus. To Ralph Terkowitz, thanks for assistance in implementation of minicomputer programs.

Thanks to the folks in the Electronics Shops for invaluable discussion and electronic construction. Most prominent were Tom Merrick, Steve Smirega and Phil Eggars.

Thanks to Shirley Ashley for her superior organizational abilities in preparing the thesis and to Kelly Ramilovic for an excellent typing job. Thanks also to Nancy Monroe for her unexcelled figure design and execution.

Special thanks to Professor Howard Shngart for his careful reading and comments on the thesis, and to all those in the Department of Chemistry and the Inorganic Materials Research Division who

provided so much support.

This thesis is dedicated to my wife, Patte, whose continual support and encouragement were so vital in oft-occurring times of adversity when the easy answer was "throw in the towel".

We gratefully acknowledge the financial support of the U. S. Atomic Energy Commission (through LBL) under whose sponsorship this work was undertaken, and support from a National Science Foundation Traineeship.

This thesis is dedicated with the hope that science may continue to find a place for generalists within its ever expanding and more specialized framework.