SOFTWARE FOR ION KINETIC ENERGY SPECTROMETRY
and
THE METASTABLE LOSS OF NO· FROM HALO-NITROBENZENES

by

MARLIN DEAN FRIESEN

B.A., Bethel College, 1968

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1974

Approved by:

Major Professor

LD
2668
T4
1974
F75
C 2
Document

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF FLOWCHARTS

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to his major professor, Dr. Michael K. HOFFMAN, for his enthusiastic encouragement and assistance during this investigation and in the preparation of this manuscript.

Special acknowledgements are extended to Dr. Maarten van SWAAY and Bill RYAN who shared unselfishly, both of their time and of their extensive knowledge of electronics and computers. Clearly, the results of this investigation would not have been possible without the prior efforts of these dedicated individuals.

Sincere appreciation is also extended to the members of the author's graduate committee, Drs. M. Dale HAWLEY and Clifton MELOAN for their assistance throughout this study and for constructive critism of this manuscript.

Finalement, je remerci beaucoup ma femme, Christine. Son soutien et sa compréhension pendant toute la durée de cette recherche est profondément reconnu.

INTRODUCTION

In the years since HIPPLE and CONDON [1] first recognized the origin of the broad, diffuse peaks of low intensity in mass spectra, chemists have used metastable ions in numerous ways to obtain useful information about organic and inorganic compounds. In our laboratory, metastable ions have found use as a tool for elucidating the structures of gaseous ions formed in a mass spectrometer.

Our MS-9 mass spectrometer was first modified in 1972 by Dr. M. van SWAAY and W. RYAN of this department, so that refocussed metastable ions could be observed and recorded manually with high precision. It was decided that reproducibility and speed could be enhanced by interfacing the instrument to our newly acquired PDP-8E minicomputer. This thesis explains how this interfacing was accomplished and gives an example of one study obtained using this system.

PART I - THEORY

A) The origin of metastable ions

Any ion which is sufficiently stable to be accelerated out of the ionization chamber of a mass spectrometer, but which decomposes before arriving at the ion collector is know as a METASTABLE ION. Figure I-a shows the flight path followed by an ion in a mass spectrometer of NIER-JOHNSON geometry similar to the instrument employed in this study (A.E.I. MS-9). Figure I-a also summarizes the fates of daughter ions formed through metastable decompositions which take place in various sections of the flight path.

Since an ion spends a maximum of about 1 u-second in the source following ionization,[2] only those ions which decompose within 1 u-second after ionization has taken place will produce the normal fragment ion peaks observed in the conventional mass spectrum. The daughter ions of the metastable decompositions which take place in the second field-free region will be recorded in the normal ion spectrum as relatively small, diffuse (metastable) peaks. The daughter ions of all other metastable decompositions are either lost on the walls of the flight tube or collected as if they had the same mass as their parent ions.

For example, if we look at the normal ion mass spectrum of a compound which undergoes the following metastable decomposition in the second field-free region of the mass spectrometer,

$$m_1^+ \longrightarrow m_2^+ + (m_1 - m_2)$$

we should expect to see three related peaks:

THIS BOOK CONTAINS NUMEROUS PAGES WITH DIAGRAMS THAT ARE CROOKED COMPARED TO THE REST OF THE INFORMATION ON THE PAGE.

THIS IS AS RECEIVED FROM CUSTOMER.

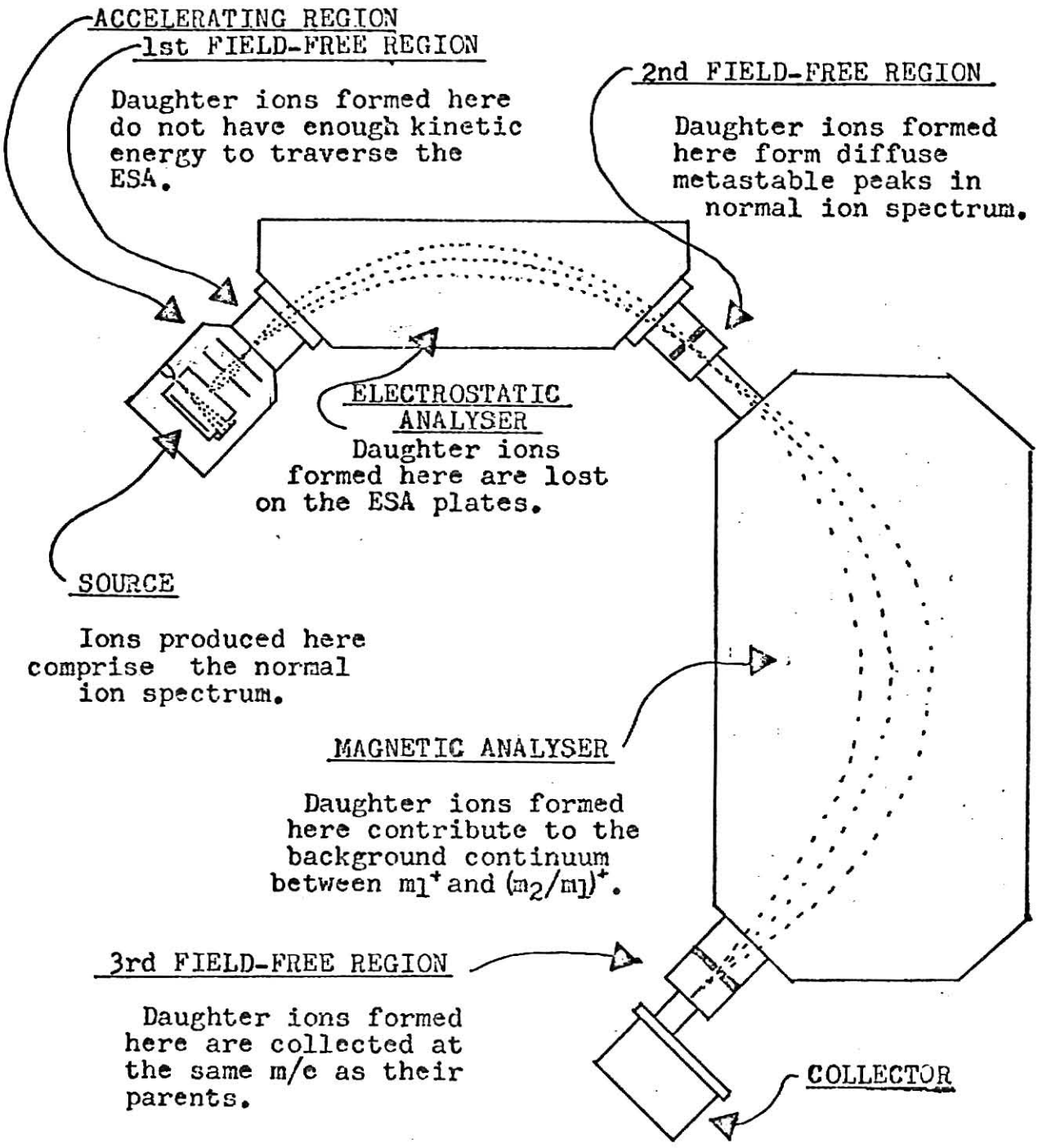


Figure I-a Flight path of ions in a mass spectrometer of NIER-JOHNSON geometry.

- the parent ion peak (m_1^+) which results from the ion's successful passage from the ion source to the ion collector without decomposition,
- the daughter ion peak (m_2^+) which results from the parent ion's decomposition in the ion source, and
- the diffuse metastable ion peak (m^*) which results from the parent ion's decomposition in the second field region.

It has long been known[1] that metastables such as m_1^+, having an actual mass m_1, will produce metastable peaks centered on the normal mass scale at:

$$m^* = \frac{m_2^2}{m_1}$$

An early successful use for metastable ions involved employing this relationship to help elucidate ion decomposition pathways by providing parent-daughter relationships.[4]

B) Methods for obtaining metastable ion peaks

Because of their relative abundances, normal ion peaks interfere badly with peaks due to metastable processes. Techniques have thus been developed to permit observation and study of pure metastable spectra.[5] This section summarizes two such techniques possible with instrumentation available in our laboratory.

We have seen from Figure I-a that ions formed by metastable decompositions in the first field free region will possess less than the required kinetic energy necessary to be transmitted through the electric sector. The energy that the parent ion (m_1^+) possesses upon leaving the accelerating region must be divided between the two fragments, (m_2^+)

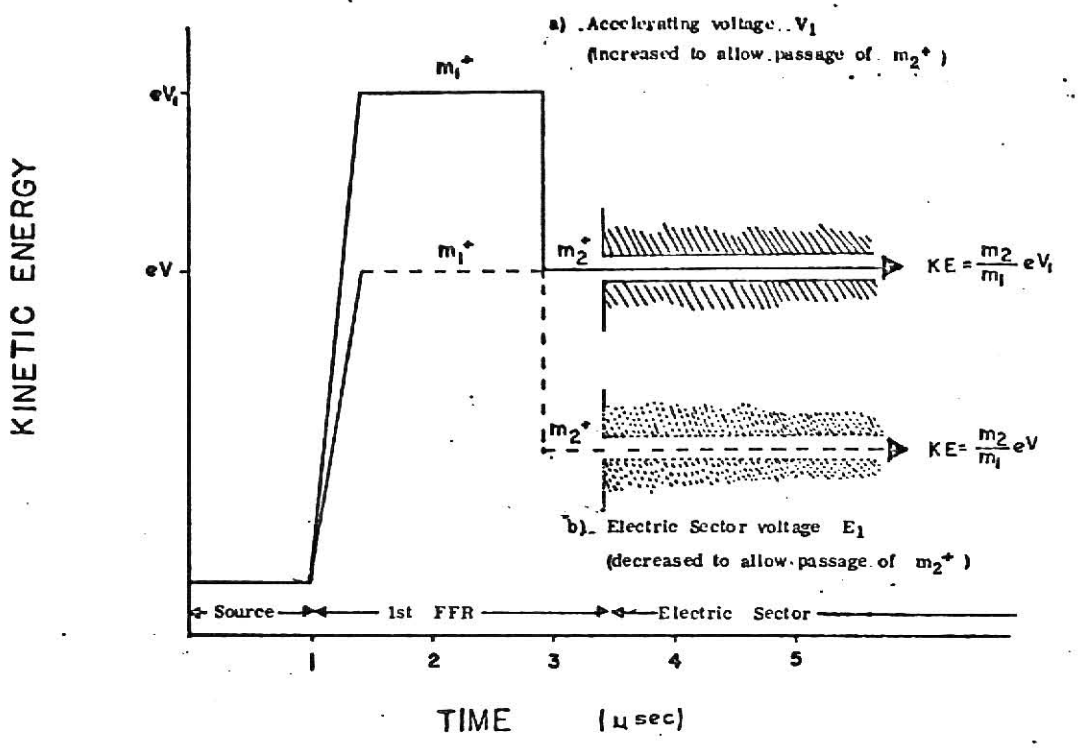


Figure I-b Schematic representations of a) the accelerating scan mode and b) the electric sector scan mode.

and (m_1-m_2), upon metastable decomposition. Modifications can be made, however, which permit the ratio of the accelerating voltage (V) to electric sector voltage (E) to be set to any value. This is usually accomplished in one of two ways,[6] as shown in Figure I-b.

a) HV or accelerating voltage scan mode.

Daughter ions (m_2^+) resulting from metastable decomposition of m_1^+ in the first field free region can be transmitted to the ion collector by first tuning the magnet to mass m_2 and then adjusting the accelerating voltage (V) to m_1/m_2 of its normal value, keeping E constant. This allows only ions of mass m_2 which have retained m_2/m_1 of the energy of m_1^+ to be transmitted. All ions from other transitions and from the

main ion beam will not have the correct energy to pass through the electric sector and will be lost on the walls of the analyser tube.

b) ESA or electric sector voltage scan mode.

The V/E ratio may also be changed by setting the magnet to transmit ions of mass m_2 while changing E to m_2/m_1 times the value used to transmit the main beam of ions, keeping V constant.

Both methods are known to possess their advantages and disadvantages.[7,8] Varying the accelerating voltage has the advantage of not affecting the mass scale but it does result in detuning in the ionization chamber. Varying the electric sector voltage does not affect the tuning of the ion source but it does alter the mass scale. In such a case, the correct mass can be obtained by multiplying the apparent mass by E/E_1, where E_1 is the new lower electric sector voltage.

Details of the modifications made in our mass spectrometer to incorporate both of these scan modes are given in PART II of this work. All experimental data obtained in this study result from use of the accelerating voltage scan mode.

C) Effect of kinetic energy release on metastable peak shapes.

Up to this point, our discussion of metastable decompositions has assumed no conversion of internal (excitation) energy into external (kinetic) energy. A study of metastable decompositions associated with any organic compound reveals that metastable peaks are invariably diffuse and may be of various shapes. (See Figure I-c) The diffuse nature of the peaks is found to be primarily due to the conversion of

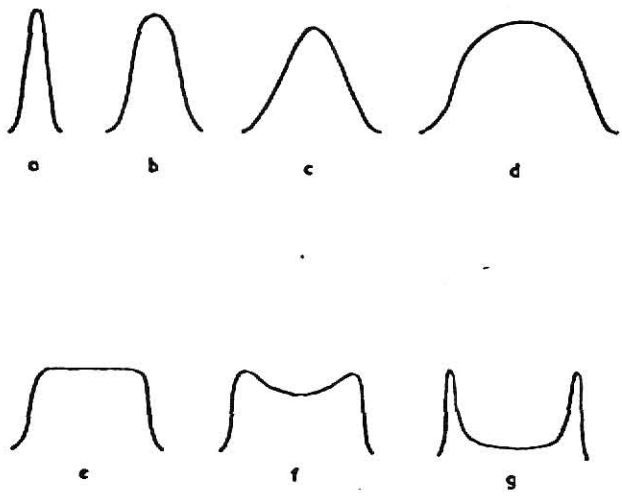


Figure I-c Variation of metastable peak shape with peak width.

the internal energy possessed by the parent ions into the kinetic energy of separation of the products. The detailed shapes of metastable peaks are much less understood, although certain features have been explained.

Metastable transitions which take place without release of kinetic energy would produce a beam of product ions having the same direction and velocity as that of the metastable ions from which they were formed. These product ions would be brought to as good a focus as the ions that had traversed the analyser tube without decomposition. If, on the other hand, each decomposition released exactly the same amount of kinetic energy in a random direction, then the beam of product ions would produce a flat-topped or dish-shaped peak. The sides of this peak would be as steeply sloped as those of a normal ion peak. However, such steeply sloped peaks are not found in practice, leading to the conclusion that the decomposition of metastable ions occurs with the release of small but varying amounts of kinetic energy. [8]

If the majority of the ions released a small amount of kinetic energy with a progressively decreasing number releasing larger amounts of energy, a GAUSSIAN-shaped peak would be formed.

If all the decomposing ions released a given energy with a small spread on both sides of this value, the resulting peak would be ROUNDED, FLAT-topped or DISH-shaped, depending on the shape of the energy distribution function as well as the average amount of energy released.

As an extreme example of this last case, we can consider a metastable decomposition which occurs with release of a significant amount of kinetic energy only in a direction parallel to the ion flight path. The effect of this directional energy release would be to increase or decrease the velocity of the daughter ion fragment (m_2^+) with respect to that of the parent ion (m_1^+), giving rise to a peak shape similar to that shown in Figure I-d. [10] In general, dish-shaped peaks result from the fact that the slit arrangement of the flight tube discriminates against ions which have appreciable energy components parallel to the slits and perpendicular to the main ion beam. Such ions will not enter the magnetic analyser due to discriminations caused by slit dimensions and geometry. In the absence of such discrimination, and with infinite energy resolution, the peaks in Figure I-d would

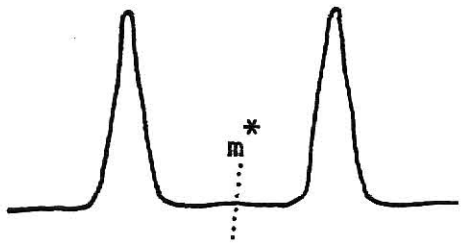


Figure I-d Peak shape produced by a metastable decomposition in which internal energy is released only in a direction parallel to the flight path of the ions.

collapse into two peaks, similar to those observed for normal ion peaks. This situation has been treated by FLOWERS.[22]

Less frequently, but as was the case for the present study, composite metastable peaks are observed.[8] Such peaks consist of overlapping or superimposed peaks of different widths. Both peaks may be due to unimolecular transitions involving parent and daughter ions of the same nominal mass, although bimolecular processes may also be involved. In many cases, these ions have the same empirical formulae and differ only in ion structure.

It is important to note that the width of the metastable peak does not come about because of a spread of internal energies of the parent ions leaving the ion source. Metastable decompositions taking place in the first field free region are produced by a group of parent ions possessing only a small range of internal energies. This comes about because of the relatively small amount of time the metastable ion spends in the first field free region. Those molecules which receive a large excess of excitation energy upon electron bombardment decompose in the u-second which the ion spends in the ion source region. Those which receive a relatively small quantity of excess excitation energy pass through the flight tube without decomposing and are observed as molecular ions. Thus the fact that the mass spectrometer detects as metastable ions only those which fragment in a specified narrow time interval means that excess internal energies are quite closely fixed by the instrumental conditions. The widths of metastable peaks should be relatively insensitive to internal energy variations.

D) Measurement of kinetic energy release in metastable decompositions.

From the laws of conservation of energy and momentum, an equation may be derived for calculation of the kinetic energy released (T) in the decomposition of a given metastable ion, based on the width of the corresponding metastable peak. [11] This equation is applicable if decomposition occurs in the first field free region in front of the electric sector of a double focussing mass spectrometer. The kinetic energy release (T), in electron volts, is given by:

$$T = \frac{(m_2)^2 \; x^2}{16 \; m_1 \; (m_1-m_2) \; y} \; \frac{(\Delta V)^2}{V}$$

where we are considering an ion of mass m_1 carrying x positive charges, decomposing with a release of internal energy T into a daughter ion of mass m_2 with charge $+y$ and a neutral of mass (m_1-m_2). V is the initial accelerating voltage which provides sufficient kinetic energy to permit passage through the electric sector of m_1^+ but not of m_2^+, as the latter carries only a fraction of the original kinetic energy. If the accelerating voltage is then raised to a value V_1 such that:

$$V_1 = \frac{m_1 \; x}{m_2 \; y} \; (V)$$

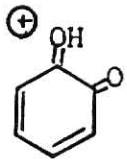
the passage of m_2^+ daughter ions through the electric sector is allowed since their kinetic energies will now be equal to y eV. ΔV represents the metastable peak width measured at half-height and corrected for the main beam width as explained in PART IV, Section C of this work.

E) Use of metastable energy release in ion structure determinations. [12]

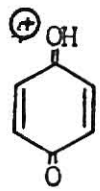
In an early study of metastable decompositions that produce wide, flat-topped metastable peaks, [13] BEYNON and FONTAINE came to the conclusion that the with of the metastable peaks, i.e., the energy released in decomposition, is related to the stability of the fragments formed and thus provides information on likely structures for the product and parent ions. For example, o-, m-, and p-nitrophenol all show the following metastable transition:

$$M^{+\bullet} \longrightarrow (M-30)^{+} + NO^{\bullet}$$

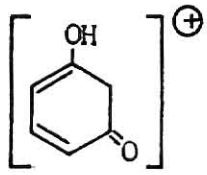
where $M^{+\bullet}$ represents the molecular ion. The mass spectra of the ortho and para compounds give rise to wide, flat-topped metastable peaks which show an energy release of approximately 750 meV. The metastable peak for the meta compound, on the other hand, is Gaussian and shows a very small energy release. This situation has been rationalized in the following manner. If the daughter ion is visualized with its remaining oxygen atom attached to the same position as the original $-NO_2$ group, then conjugated resonance-stabilized structures can be written for the ortho and para daughter ions, but not for the meta compound:



ortho



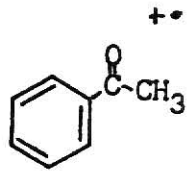
para



meta

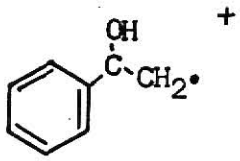
A second example [2] deals with the use of energy release values in determining the structures of metastable parent ions. The molecular ion of acetophenone loses $CH_3^{\bullet}$ with release of about 9 meV of energy.

A number of alkyl-phenyl ketones also have isobaric fragment ions (m/e=120) which result from a metastable decomposition releasing about 60 meV of energy. Clearly these differences in energy release must be due to differences in the parent ion structures. An enol structure has been suggested for the metastable fragment ion for the case of the phenyl-alkyl ketones.



keto-form

ACETOPHENONE



enol-form

Metastable energy release values have also been used to obtain ion structure information for the loss of formaldehyde from anisole and substituted anisoles,[14] and for the loss of HCN from benzaldoxime o-methyl esters.[15]

PART II - HARDWARE

A) Introduction.

Several major changes were made in our A.E.I. MS-9 mas spectrometer to permit the acquisition of refocussed metastable ion data. First, an energy resolving β-slit [12] was installed in the instrument's second field free region just after the electrostatic sector. Second, a scan box consisting of the circuitry necessary to sweep either the electrostatic sector voltage (ESA) or the ion accelerating voltage (ACC) was designed and constructed by Dr. M. van SWAAY and W. RYAN. Third, this scan box/mass spectrometer system was interfaced to a PDP-8E minicomputer to provide computer control of data acquisition.

B) Scan box circuitry.

Essentially, the scan box provides a very precise means of linearally sweeping either the electrostatic sector voltage (0 to $\pm$270 V) or the ion accelerating voltage (0 to 8000 V). As shown in Figure II-a, this choice is made by setting the ACC and ESA toggle switches to either SWEEP or MANUAL.

At the scan box's heart are two up-down decimal counters:

- a 4 BCD-digit counter called the MAIN, and
- a signed 3 BCD-digit counter called the VERNIER.

Counting pulses can be obtained from one of two sources. Under LOCAL control, an internal scan box clock, divided by a scan speed selector on the box's front panel, controls the rate of scan. Under REMOTE or computer control, scan rate depends on the computer's own real time clock which is under program control.

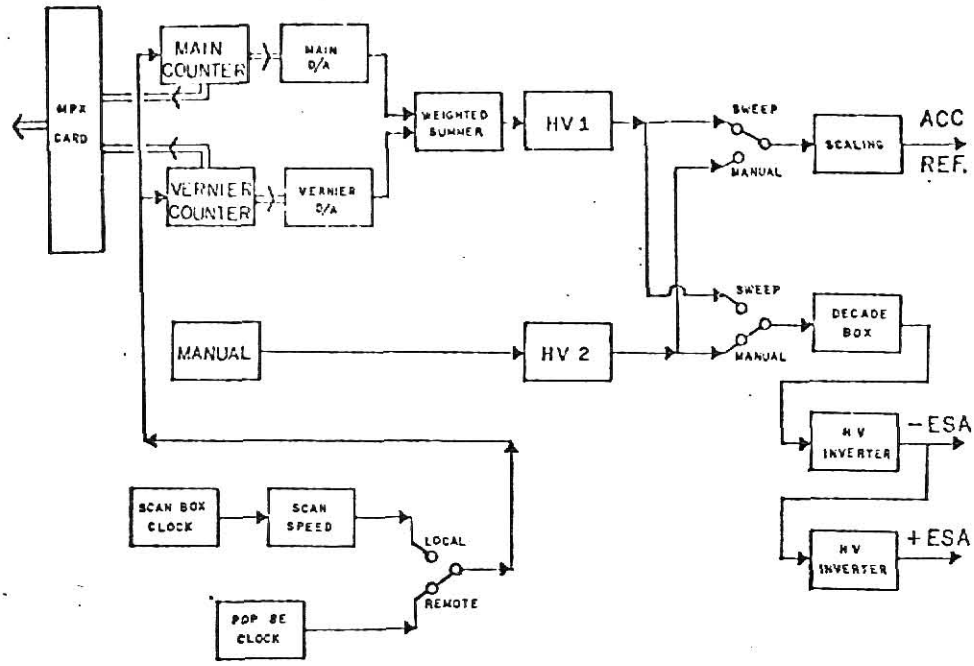


Figure II-a Scan box circuitry.

The digital signals coming from both the MAIN and VERNIER counters are first transformed into corresponding analog signals by two separate digital to analog converters. These two signals are then summed such that the least significant digit in the VERNIER counter's display has a value of 1/10 of the value of the corresponding digit in the MAIN display. In effect, this means that a full scale scan of the MAIN is from 0 to 9999 units while a full scale scan of the VERNIER is from −99.9 to +99.9 units. The digitally swept signal is then sent to the high voltage amplifier (HV 1). The voltage chosen to be held constant (MANUAL) is selected via a 4-digit thumb-wheel switch. This signal is amplified by a similar high voltage amplifier (HV 2).

The ACC high voltage signal, whether swept or manual, is then scaled upward before presentation to the mass spectrometer itself. The ESA high

voltage, whether swept or manual, is first fed through the mass spectrometer's decade box to retain high-resolution peak matching capability. It is then inverted twice to produce the voltage needed to supply the positive and negative electrostatic sector plates.

C) Interfacing the computer to the scan box.

The scan box described in the previous section was designed such that all scanning operations can be digitally controlled to allow interfacing of the scan box to the computer. There are several reasons for taking this course of action. Most importantly, the quality of data obtained can be greatly improved with signal averaging. The computer can also speed up considerably the rate at which data can be obtained, evaluated and displayed. Reproducibility should also be improved as the computer takes and evaluates its data in the same way for each acquisition.

Figure II-b shows the relationship of the computer to the mass spectrometer, to the scan box, and to the computer's various peripherals. The mass spectrometer is controlled by the scan box which is itself controlled by the computer via a set of 24 digital (DIGIO) signals: 12 into the computer and 12 out from the computer.

The 12 output signals, which correspond to the 12 bits of the PDP-8E's 12 bit word are assigned as follows:

Bit Ø .....Not assigned
Bit 1 .....Not assigned
Bit 2 .....Activate DOWN scan
Bit 3 .....SEL Ø for multiplexer card
Bit 4 .....SEL 1 for multiplexer card
Bit 5 .....Set VERNIER to ZERO
Bit 6 .....Set VERNIER sign to +
Bit 7 .....Activate UP scan
Bit 8 .....Activate VERNIER scan
Bit 9 .....Activate MAIN scan
Bit 10 .....Set VERNIER sign to -
Bit 11 .....Clock pulse

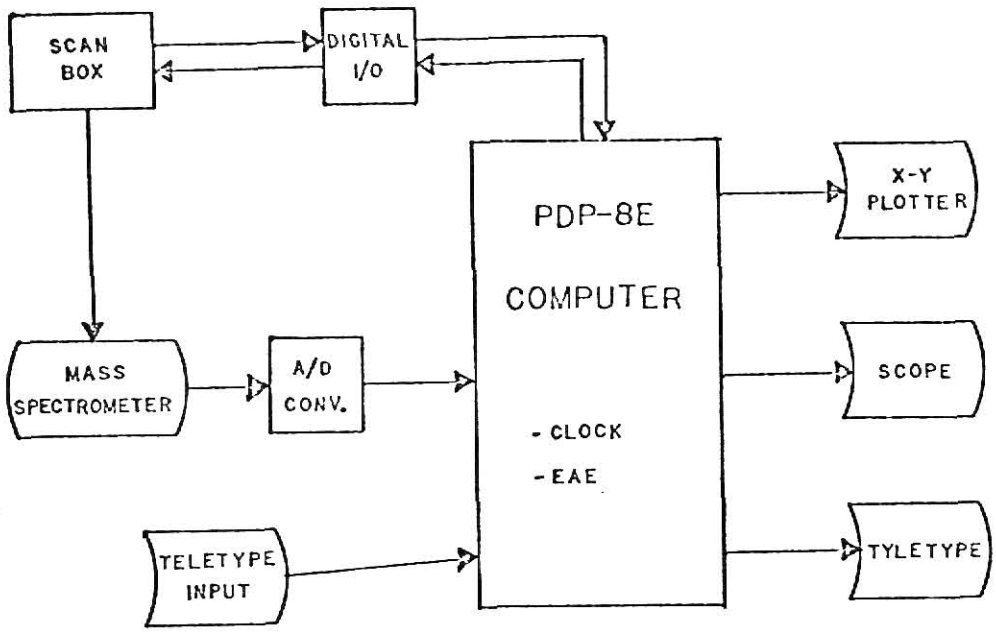


Figure II-b Relationship of computer to mass spectrometer, scan box, and peripherals.

The 12 input signals inform the computer of the status of the MAIN and VERNIER counters. To initialize these counters, the computer compares a chosen value to the value currently displayed by the counter. The difference between these two values represents the number of clock pulses needed to set the counter to the chosen value. Input of the MAIN counter's 16 bits and the VERNIER counter's 12 bits means that the DIGIO's 12 available input bits are not sufficient. This problem is overcome by employing a multiplexer circuit (Figure II-c) whereby 2 output bits (bits 3 and 4) control which of 4 buffered 12-bit words will be input to the computer. Bit assignments are given in Figures II-c and II-d.

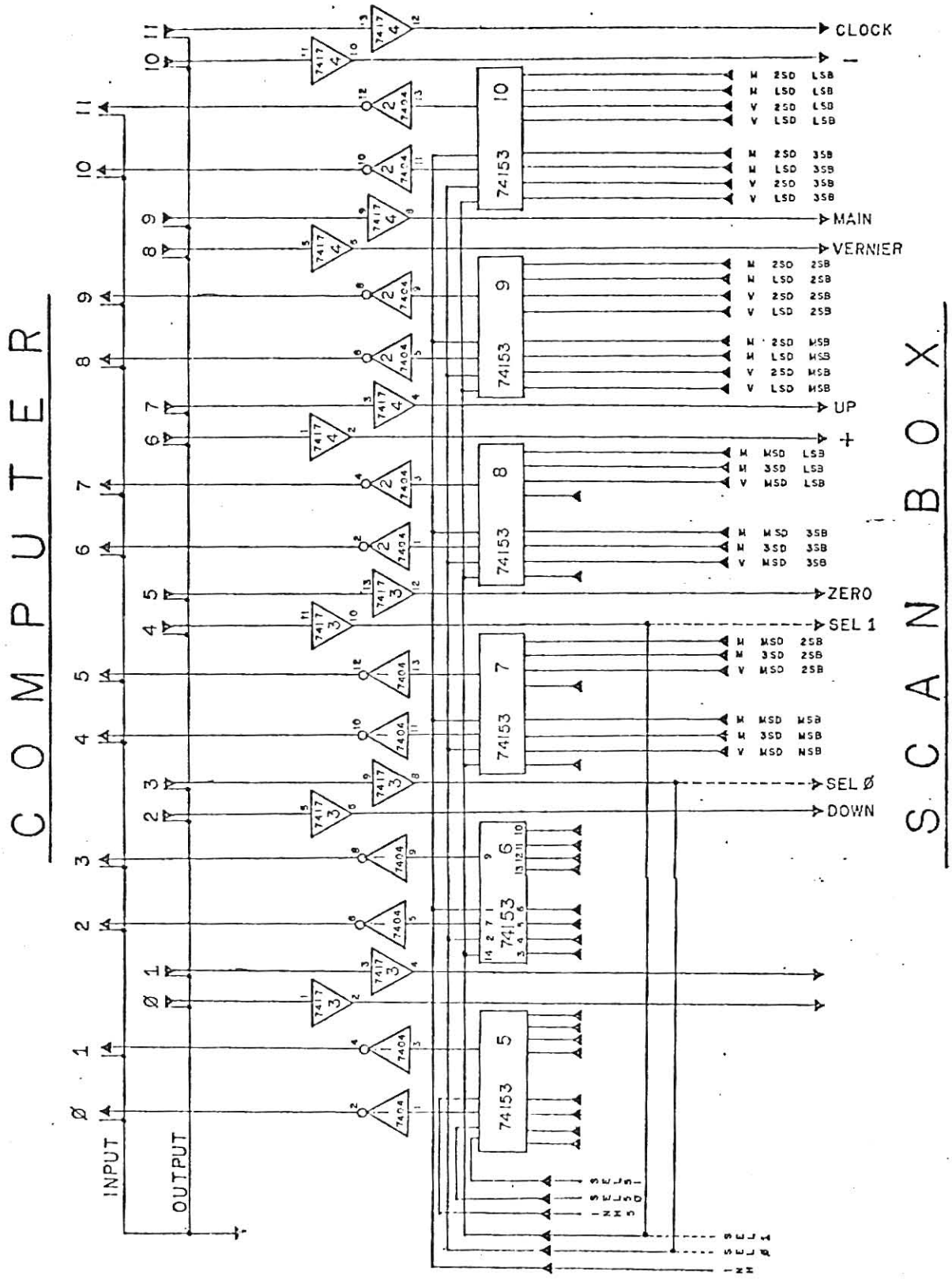


Figure II-c Multiplexer / Buffer card circuitry.

			BITS		
	SEL Ø	SEL 1	Ø - 3	4 - 7	8 - 11
MAIN	L	L	xxxx	MSD	2SD
	L	H	xxxx	3SD	LSD
VERNIER	H	L	xxxx	MSD	2SD
	H	H	xxxx	xxxx	LSD

Figure II-d Bit assignments for input to multiplexers.

D) Usage of the scan box.

A diagram of the scan box's frontpanel is given in figure II-e. To acquire refocussed metastable ion data, either the accelerating voltage (ACC) or the electrostatic analyser voltage (ESA) must be swept while the other of the two is held constant. This choice of scan mode is made via switches (22) and (23) .*

For all data acquisition in this study, switch (23) is kept in the up position (to sweep the ACC voltage) while switch (22) is kept in the down position (to hold ESA voltage constant).

The voltage to be held constant is set by the 4-digit thumb-switch labelled MANUAL.* This value can be incremented by up to 2 units with potentiometer (16) . The voltage to be swept is displayed by a 4-digit counter (2) labelled MAIN. Under manual control, an initial value for the swept voltage may be loaded by setting the MAIN preset thumb-switch (25) to the

---

* Mode switches (22) and (23) , as well as the MANUAL value (15) must be set manually by the operator whether under LOCAL or REMOTE (computer) control. (Chosen by switch (14))

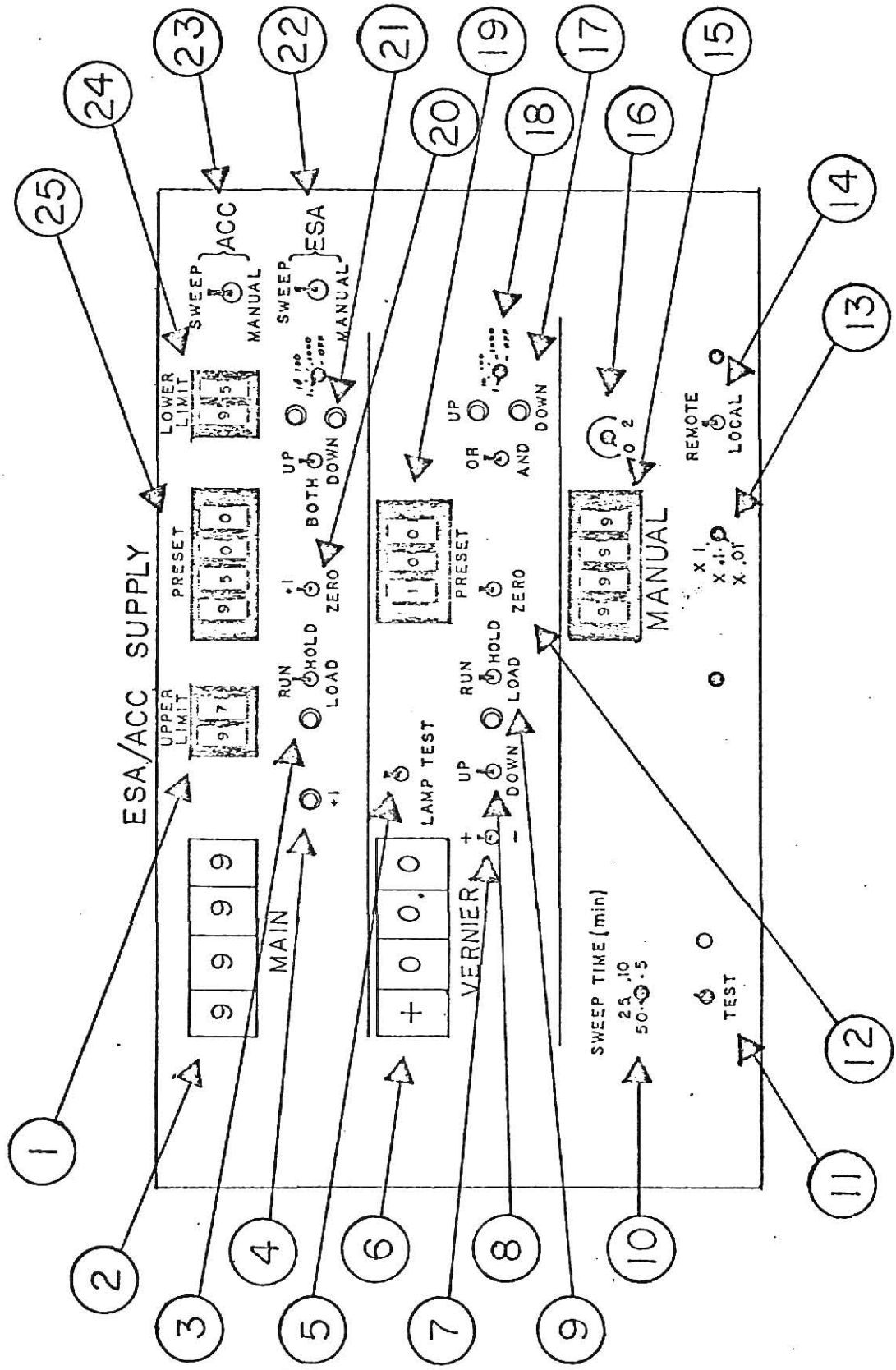


Figure II-e Scan box front panel.

desired value and by depressing the LOAD switch (3) . As set up in Figure II-e, depressing the LOAD switch would load 9500 into the MAIN display (2) . Lifting the +1/zero switch (20) would increment this value by one unit and would light the +1 indicator light (4) . Depressing this switch (20) would reset the MAIN display to 0000 .

Upper and lower limits for the desired scan are defined by the 2-digit thumb-switches (1) and (24) , which represent only the 2 most significant digits of the MAIN display. Under local control, the MAIN counter scans from the MAIN-preset value to the upperlimit (UP only), to the lower limit (DOWN only) or between both limits (BOTH).

Under computer control, the MAIN display is initialized by answering question (E) :

E) MAIN SET TO ?

The computer controlled scan box always begins its scan from this initial value while the scan's upper or lower limits depend on questions (C), (G) and (H) :

C) SCAN UP(UP) OR DOWN(DOWN) ?
G) NO. OF POINTS ?
H) HOW MANY STEPS PER POINT ?

Under local control, the MAIN direction switch (21) allows for three direction modes: UP only , DOWN only , or BOTH up and down . Direction of the MAIN scan is indicated by the UP-DOWN lights (21) both under local and remote control. Under local control, a scan is begun by raising switch (3) to the run position. Scanning under computer control is explained in PART III.

A higher degree of resolution can be obtained by sweeping the VERNIER display (6) . As with the MAIN, an initial value is set into the

3-digit VERNIER thumb-switch (19) and is loaded by depressing the LOAD switch (9) . Initial VERNIER sign is set by raising or depressing the sign switch (7) . Depressing switch (12) zeroes the VERNIER display. VERNIER sweep direction is chosen by setting switches (8) and (17) to either UP, DOWN or UP AND DOWN. A single scan on the VERNIER goes from the + or - preset value, through zero, to the corresponding value with the opposite sign. For example, with -10.0 set in the VERNIER display, with switch (8) set to UP, and with switch (17) set to OR, the VERNIER would repeatedly scan upwards from -10.0 to +10.0.

Under computer control, the sign and value for the VERNIER display are set by answering question (F) :

F) VERNIER STARTING POINT ?

The computer controlled scan box begins its scan from this value, with the upper or lower limit of the scan depending on the responses to questions (C), (G) and (H).

Switches (10) , (13) and (18) are used only when the scan box is under LOCAL control. Switch (10) controls the scan rate for both the MAIN and VERNIER displays. Switch (18) provides a marker on the strip-chart recorder output every 1, 10, 100 or 1000 units on the VERNIER display. A similar switch is provided for the MAIN display. Switch (13) controls the strip-chart recorder's speed.

Finally, switch (11) provides a method of checking to see if various scan box check-points give correct outputs. Switch (5) lights all lamps on the scan box front panel to test them.

PART III - SOFTWARE

A) Peripheral requirements.

The program was designed to facilitate and improve the acquisition of refocussed metastable ion data from an A.E.I. MS-9 mass spectrometer. It was written for the PDP-8E minicomputer (Digital Equipment Corporation, Maynard, MASS.) with 12 K of core in PAL-8 assembly language. [16] Necessary peripherals are:

a) DK8-EP Programmable real-time clock

b) AD8-EA Analog to digital converter

c) DR8-EA 12 channel buffered digital I/O

d) VC8-E CRT display (modified to allow software selection of scope or x-y plotter output)

e) ASR-33 Teletype with low speed punch

f) KE8-E Extended arithmetic element.

B) Source.

The main program is made up from five source subprograms:

METSTB.SY (SYMBOL)

METSTB.DL (DIALOG)

METSTB.DT (DATA)

METSTB.OT (OUTPUT)

METSTB.SR (SUBROUTINES)

These subprograms are assembled (PAL-8) into two binary subprograms:

METDLR.BN

METDOT.BN

These are loaded (ABSLDR) together with a teletype driver (TLTPE4.SV) and an energy-release calculation subprogram (METEGY.SV) to produce the final core image file:

METSTB.SV

Note that METEGY.SV must be loaded into field 2. Specific instructions for the above operations are given in the descriptions program: METSTB.DS. (See appendix B)

Each of the program's five source subprograms entails a specific function or a related group of functions.

METSTB.SY (SYMBOL)

This sub-program contains all the octal-code information and definitions required for the computer's various peripherals. Also contained in this sub-program are the base-page storage allocations.

METSTB.DL (DIALOG)

This sub-program allows the operator to input, via the teletype, chosen values for a series of 10 variables which define computer or mass spectrometer operations. (See appendix A - Flowcharts #1 and #2) The following is a list of the 10 questions asked to obtain these variables: (See METSTB.DS for acceptable responses to these questions.)

A) TITLE:
B) SCAN MAIN(MA) OR VERNIER(VE) ?
C) SCAN UP(UP) OR DOWN(DO) ?
D) MANUAL SET TO ?
E) MAIN SET TO ?
F) VERNIER STARTING POINT ?
G) NO. OF POINTS ?
H) HOW MANY STEPS PER POINT ?
I) NO. OF SCANS ?
J) MAXIMUM DATA SPREAD ACCEPTED ?

The computer then signals that is has entered the CORRECTION MODE by typing the question:

ALL OK ?

on the teletype. Acceptable responses for the CORRECTION MODE follow:

[A-J]

After the initial, sequential input of responses to the 10 questions, an individual variable can be altered by recall of a single question. This is accomplished by responding to the question "ALL OK?" with the letter of the desired question and then answering it as before.

[P]

Typing a "P" provides teletype output of all ten questions along with their respective, current responses. This option is useful if the operator wishes to know the current values for all the variables or if he wishes to have a clean copy of this information for future reference.

[Y]

Typing a "Y" indicates to the computer that all ten responses are acceptable to the operator and an on-the-fly scope data display commences (See below). Program control goes from the CORRECTION MODE to the INSTRUCTION MODE.

[CTRL/C]

Typing "CTRL/C" returns the computer to the keyboard monitor.

METSTB.DT (DATA)

This sub-program provides two data acquisition subroutines:

-an on-the-fly scope data display in which the scope display is updated every 1 or 2 seconds (See flowchart #4a), and

-the main data acquisition subroutine in which data is collected, inspected and stored. (See flowchart #5)

In addition, this sub-program contains the subroutines which reset the MAIN and VERNIER counters.

As explained above, typing a "Y" in the CORRECTION MODE passes control to the on-the-fly scope data display. This display is organized

as follows: A scan position is sampled every 10 milliseconds as controlled by the computer's real-time clock. Between each pair of such data samplings, there is sufficient time to display the complete stored scan. Thus for a scan of 100 scan positions, a new scan is displayed every 1000 msec. or every 1 second. This display is useful to verify that the chosen variables produce the desired spectrum and also to provide a real-time display necessary for making adjustments in mass spectrometer controls: β-slit, multiplier, etc.

The on-the-fly scope display continues until some key on the teletype is struck. Acceptable responses, making up the INSTRUCTION MODE, come from both the DATA and OUTPUT source sub-programs. The DATA options are discussed here; OUTPUT options are discussed in the following sections.

(O)

Typing an "O" transfers program control back to the CORRECTION MODE. Acceptable responses in this mode were listed in the DIALOG section.

(H)

Typing an "H" provides a list and explanation of the responses which are acceptable in the INSTRUCTION MODE. Program control remains in the INSTRUCTION MODE.

(D)

Typing a "D" transfers program control to the main data acquisition routine. Typing any character on the teletype keyboard during acquisition transfers program control back to the INSTRUCTION MODE.

The main data acquisition routine is set up such that 16 values for a given scan position are sampled during 4 cycles of the 60 cycle A-C line voltage, ie., 16 values per 66.6 msec. At the outset, 16 values are sampled for the first scan position and are stored in the Raw Data Buffer in field 1. (See Figure III-a) During the next 4.16 msec., these 16 values are moved to the Ranking Buffer where they are ranked by magnitude, from

FIELD 1 Data Storage

Raw Data Buffer		Ranking Buffer		
Address	Pt. no.	Address	Pt. no.	
		220	-	
200	1	221	1	Smallest
201	2	222	2	
202	3	223	3	
203	4	224	4	
204	5	225	5	
205	6	226	6	
206	7	227	7	
207	8	230	8	8 inner values
210	9	231	9	
211	10	232	10	
212	11	233	11	
213	12	234	12	
214	13	235	13	
215	14	236	14	
216	15	237	15	
217	16	240	16	Largest

Figure III-a Temporary data storage allocations.

smallest to largest. If none of the values are full scale and if the difference between points #12 and #5 is less than the maximum data spread acceptable (Question J), the inner eight points are added to a running sum for that particular data point. The program then moves the mass spectrometer to the next scan position.

If these conditions are not met, another value is obtained for the original scan position and stored as point #1 in the Raw Data Buffer. These 16 values are then inspected as before and, if found unacceptable, are replaced sequentially, one at a time, until an acceptable set is obtained or until 150 additional values have been sampled and rejected. The program then moves on to the next scan position.

If the move-inspect-reject/accept sequence for a given set of 16 data values requires more than the allotted 4.16 msec., a timing error is indicated by the teletype bell (optional) and data acquisition for that scan position is restarted. When the specified number of points and scans has been completed, the average value for each individual scan position of the scan is calculated and stored in field 1. These data points are then scaled such that the maximum point of the scan is set equal to the full scale value of the scope and x-y plotter displays. Upon completion of acquisition, the recorded unscaled peak is displayed on the scope and program control returns to the INSTRUCTION MODE.

METSTB.OT (OUTPUT)

This sub-program provides for the output of the acquired data via:

a) the oscilloscope,

b) the x-y plotter (See flowchart #6a) and

c) the teletype/paper tape punch (See flowchart #6b).

In addition, a subroutine which calculates and outputs the width of the recorded peak at half-height is included. (See flowchart #7) Access to the OUTPUT routines, like the DATA routines, is via the INSTRUCTION MODE.

(U)

Typing a "U" provides a scope display of the unscaled data collected during data acquisition. Program control remains in the INSTRUCTION MODE.

(S)

Typing an "S" provides a scope display of the scaled data collected during data acquisition. Program control remains in the INSTRUCTION MODE.

(P)

Typing a "P" transfers program control to the x-y plotter subroutines. (See flowchart #6a)

Upon entry, the plotting subroutine requires input of responses for the following two questions:

SCALED(S) OR UNSCALED(U) DATA?
LINE PLOT(L) OR POINT PLOT(P)?

The word CALIBRATE: is then typed out on the teletype. The following 7 instructions are available for calibrating the plotter and for plotting the actual peak.

O - Move the pen to the plot's x-y origin.

X - Move the pen to the plotter's x-maximum.

Y - Move the pen to the plotter's y-maximum.

C - Move the pen to the center of the plot.

R - READY ! Move the pen to the plot's first point.

G - GO ! Exit the calibration routines and commence plotting.

NOTE: Striking any key during the actual plotting of the peak will abort the plot and return program control to the INSTRUCTION MODE.

(T)

Typing a "T" provides for teletype/punch output of both the input parameters (Questions A-J) amd the individual digital data points obtained by the main data acquisition routine. (See flowchart #6b)

Upon entry, the program provides output of 10 inches of leader/trailer punched paper tape. The paper tape punch must be switched to "on" during this time. The program then asks the operator if he wants to output the scaled or the unscaled data. This is followed by output of the 10 questions (A-J) and responses giving the input parameter conditions under which the data were obtained. The data follow, set off from the previous text by an additional 10 inches of leader/trailer. Data output consists of the required number of lines of 10 octal data point values each. The paper tape punch should be switched to "off" during final leader/trailer output.

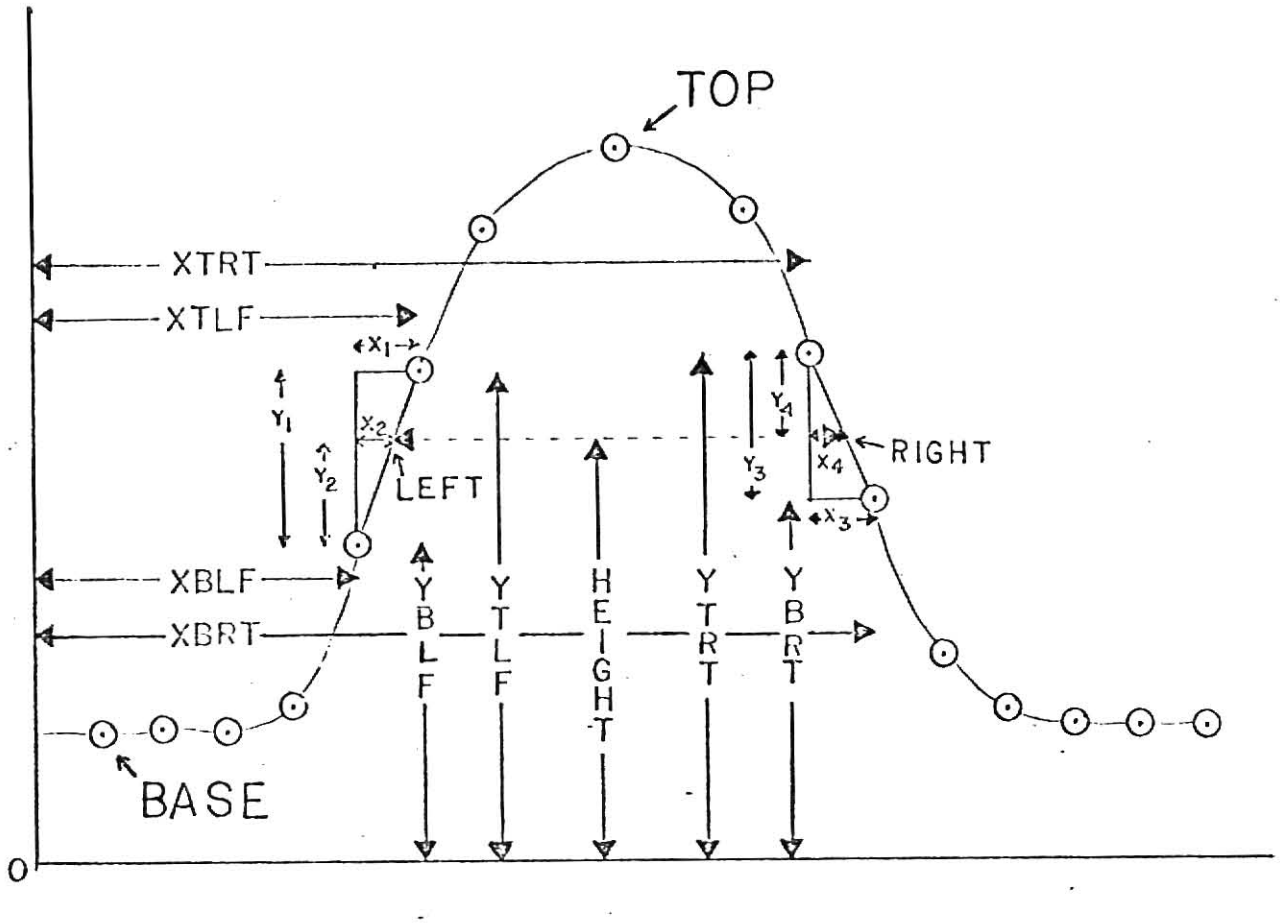


Figure III-b Definitions needed to calculate the width of the metastable peak at half-height.

(W)

Typing a "W" provides output of a calculated value for the width of the metastable peak at half-height. (See flowchart #7 and Figure III-b)

Initially, the point of maximum intensity (TOP) and the point of minimum intensity (BASE) are subtracted to provide the half-height of the recorded peak.(HEIGHT) Since the calculated half-height does not necessarily coincide with a recorded data point, the exact positions, parallel to the x-axis, where the plot crosses the half-height (LEFT and RIGHT) must be found by trigonometric interpolation. Subtracting LEFT from RIGHT gives the value of the peak's width at half-height which is printed out on the teletype.

If for some reason the subroutine cannot calculate a value for this width, the error message:

ERROR SOMEWHERE ! TRY ANOTHER PEAK !

is printed and program control returns to the INSTRUCTION MODE.

Sometimes, for very noisy scans, the subroutine will find a value for the width at half-height which corresponds to the distance between two neighboring points on the left side of the peak. This results in the width at half-height being reported as zero or as some very small value. Typing a (>) causes the program to search for the second occurence of a data point lower in magnitude than the half-height. This option is also intended for use when the center of a dish-shaped peak dips below the value of the half-height, resulting in an apparently small value.

NOTE: The (>) option whould be used only when use of the (W) option fails to produce a good value.

METSTB.SR (SUBROUTINES)

This sub-program contains the two subroutines which are used at various places throughout the program:

BCDBIN - a subroutine which changes a string of 6-bit ASCII digits (TEXT pseudo-op) into a double precision number, and

BINBCD - a subroutine which changes a double precision binary word (up to 9999 decimal) into a string of 6-bit ASCII digits (TEXT pseudo-op).

METEGY.SV (ENERGY)

This sub-program is used to calculate (T), the kinetic energy release value, for a given metastable decomposition from the observed metastable and main beam peak widths. It uses the Digital Extended Arithmetic Element-Floating Point Package (EAEFPP.BN). As this program occupies nearly half a field of core space (locs. 5000-7577), it was necessary that METEGY.SV reside in field 2. The teletype driver (See next section) must also reside in field 2 but its core locations (locs 7200-7577) overlap those of EAEFPP.BN. A relocated teletype driver (TLTP44.SV) was created from TLTPE4.PA by revision of origin statements.

The calculation source program (METSTB.EN) is outlined in flowchart #8. Program execution is initiated by typing (E) while in the INSTRUCTION MODE. The 4 parameters needed for the calculation are typed out as follows:

M1= +Ø.ØØØØØ-- M2= +Ø.ØØØØØ M* WIDTH= +Ø.ØØØØØ MB WIDTH= +Ø.ØØØØØ

where:

M1 = the molecular weight of the metastable parent ion.

M2 = the molecular weight of the resulting daughter ion.

M* = the width (ΔV) of the recorded metastable peak.

MB = the width of the recorded main beam peak.

The values for these parameters can be altered by typing (1), (2), (*), or (B) respectively. Legal inputs consist of a decimal floating-point number, terminated by a carriage return. For example, the following are equivalent and acceptable:

726.7
.7267E3
.7267E Ø3
+7267E-1

NOTE: Input of numbers larger than ±999.99999 causes overflow resulting in a string of asterisks.

Typing a (C) initiates calculation of T, the energy release value. The program first obtains a corrected value for the metastable peak width from the following formula:

$$m^*_{(corr)} = \left[(m^*)^2 - \left(MB \cdot \frac{M2}{M1} \right)^2 \right]^{\frac{1}{2}}$$

This value is stored and can be recalled at a later time by typing W .

The kinetic energy release value (T) is then calculated by means of the corresponding formula given in PART I.

$$T = \frac{(M2)^2 \quad (Const) \quad (1)}{(M1) \quad (M1 - M2) \quad (1)} \quad \frac{(m^*_{corr})^2}{V}$$

where Const is a combined constant equal to 0.8/16 = 0.05 . The 0.8 comes about because the scan box's 10,000 scale positions correspond to the full scale scan of 0 to 8000 volts.

As we saw in PART I, V represents the initial accelerating voltage which provides sufficient kinetic energy to permit passage through the electric sector of m_1^+ but not of m_2^+. In this work, we assume that the accelerating voltage which passes m_2^+ through the electric sector is equal to 9500 scan positions or 7600 volts. V is thus calculated from:

$$V = \frac{M2}{M1} \times 9500$$

The calculated value for T is then printed on the teletype.

Typing a (T) causes output of current values for the 4 stored parameters: M1, M2, M*, and MB.

Typing an (O) returns program control to the CORRECTION MODE to permit recording a new metastable peak.

TLTPE4.SV (TELETYPE DRIVER)

A teletype driver is a series of subroutines which facilitates utilization of the teletype. TLTPE4.SV entails eight functions which are explained in Appendix D.

GASCAP.SV (GAUSSIAN DECONVOLUTION)

GASCAP.SV is a general purpose data reduction program which was used to deconvolute the composite metastable peaks obtained by METSTB.SV. The program was obtained from DECUS. (DECUS program no. 8-237, MADCAP IV) Complete instructions for the use of this program can be found in the program description published by DECUS. A short summary of those sections utilized in our work is given in flowchart #9 and in the description program (GASCAP.DS). (See Appendix C)

Useful data operations available in GASCAP.SV include:

DI: Accept raw data from paper tape reader (PTR).

CO: Compute a new plot and display it on the scope.

AL: Alter peak parameters; then compute a new plot.

SW: Swap block Ø and block 1 data.

SU: Subtract block 1 data from block Ø data.

SM: Smooth the data using an 11-point function.

IN: Integrate data after subtracting value of pivot line.

OU: Output data via TTY or PTP.

PL: Plot data on x-y plotter as a line or point plot.

Our metastable peaks were deconvoluted as follows: The recorded metastable data were first input to data buffer Ø via the paper tape reader. The data were then scaled such that the y-data range was equal to 500 units.

A similar peak was then generated in data buffer 1, assuming 3 overlapping Gaussian peaks. (See Figure IV-g) The peak parameters of height, width at half-height and position were then varied by trial and error until an acceptable fit for the two curves was obtained. Individual peaks were then measured, plotted and output digitally for future reference.

PART IV - AN EXPERIMENTAL STUDY

A) Background.

Our purpose in measuring the kinetic energy release (T) values for various mass spectral relations is to see whether T is a characteristic of ion structure. We have approached this problem by looking at the effect or non-effect of substituents on T as a function of structure. This study involves a series of mono- and di-substituted halo-nitrobenzenes.

The loss of NO• is a characteristic reaction of aromatic nitro compounds and has been the subject of many studies.[17] Recently, BEYNON et al.[18] looked specifically at the metastable peaks resulting from the loss of NO• from para-substituted nitrobenzenes. They observed composite metastable peaks and attributed the two overlapping peaks to two distinct unimolecular fragmentation pathways from the molecular ion. Collision-induced ions were ruled out by taking measurements over a large range of pressures (2×10^{-7} to 5×10^{-5} Torr). The possibility of forming an excited neutral was dismissed since the first excited state of the neutral NO• lies some 4.7 eV above the ground state.

The high energy release process, T_ℓ , resulting in a wide dish-shaped metastable peak was postulated to involve a three membered cyclic transition state.

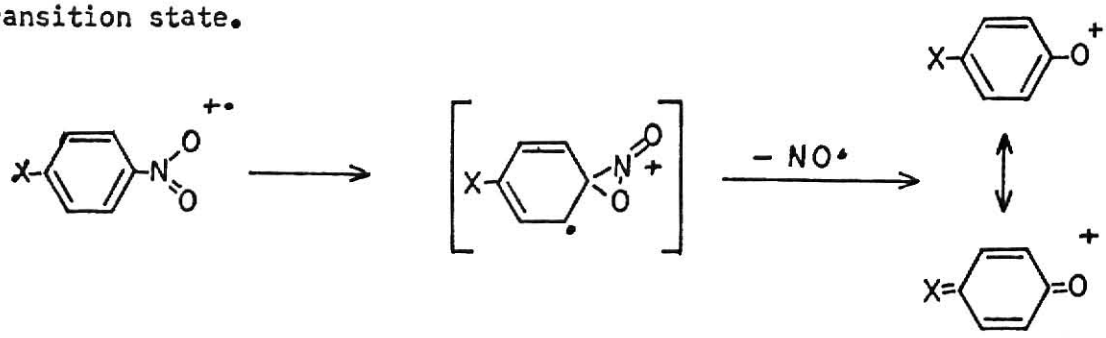


Figure IV-a Postulated decomposition pathway involved with T_ℓ .

In this mechanism, the transition state involves a structure in which the ring and the nitro group are in orthogonal planes and are bonded in a spiro type of arrangement. This daughter ion should be resonance stabilized by electron-donating substituents in the para positions.

The smaller energy release process, T_s , resulting in a Gaussian-shaped peak, was postulated to involve some sort of four-membered transition state, leading to a product ion with the oxygen atom attached to some carbon other than C_1 .

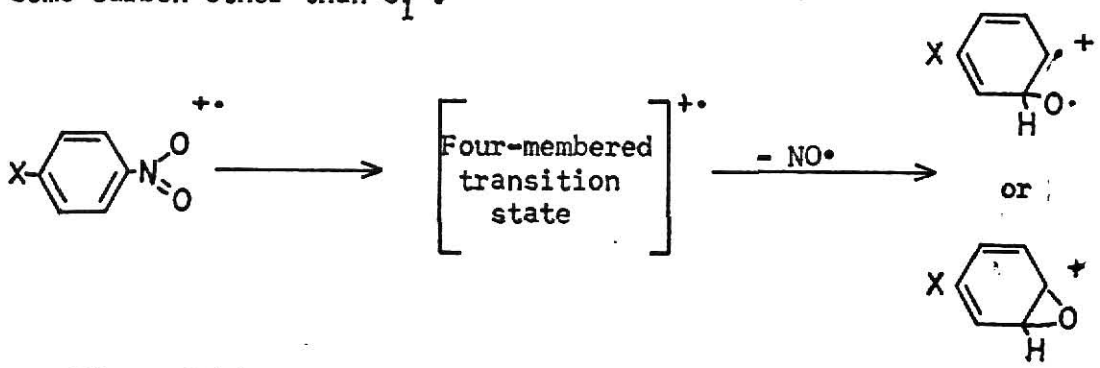


Figure IV-b Postulated decomposition pathway involved with T_s .

In this mechanism, the transition state involves a structure in which the ring and the nitro group must be in the same plane. The low stability of the product ions resulting from this decomposition leads to its choice as the low energy release process.

An alternative possibility [17a] is that the small energy release process, T_s , results from a simple cleavage and that a nitro-nitrite isomerism precedes the NO• loss.

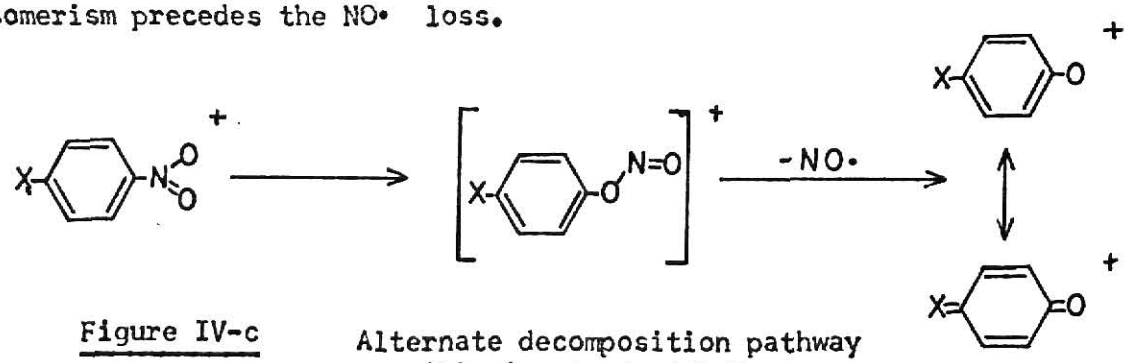


Figure IV-c Alternate decomposition pathway possibly involved with T_s .

A recent ^{13}C study [19] has provided more insight into these processes. A metastable is observed for the loss of CO• from the product ion in the above reactions.

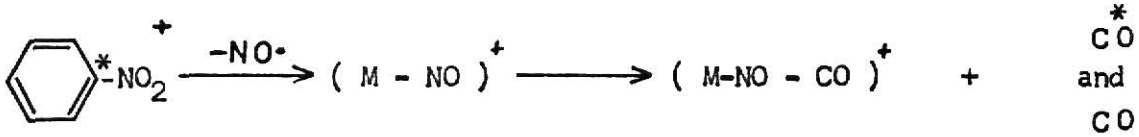


Figure IV-d Loss of CO following loss of NO• from nitrobenbene.

COOKS and HOLMES have shown that the CO lost from nitrobenzene labelled with carbon-13 in the 1-position contains both labelled and non-labelled carbon. This reinforces the hypothesis that two unimolecular processes are involved in the loss of NO from the molecular ion.

B) Experimental.

All measurements of kinetic energy release values were performed on an A.E.I. MS-9 mass spectrometer, modified as described in the HARDWARE section (PART II).

Standard operating conditions were:

- Ionizing electron energy.....70 eV
- Electron current (total emission).....0.1 mA
- Ion source temperature.....140 °C
- Indicated source pressure.....10^{-6} Torr
- Ion accelerating voltage.....8 kV
- Source slit width.....0.8 mm
- Collector slit width.....0.2 mm

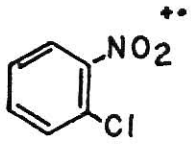
- No. of data points per scan.....100
- No. of steps per point.....3
- No. of scans.....5
- Maximum data spread accepted.....60

A narrow energy resolving β-slit (width = 4 mils = 0.1 mm) was used for maximum energy resolution and the accelerating voltage scan method was used to record all metastable peaks. In all cases, the metastable peak was recorded with V_1 = 9500 scan box units = 7600 volts and with $V = m_2/m_1 \times 9500$ scan box units = $m_2/m_1 \times 216$ volts. Introduction of all samples, both liquid and solid, was via the all glass heated inlet system.

Metastable peaks were deconvoluted assuming overlapping Gaussian-shaped peaks using the the Gaussian overlay in conjunction with the program MADCAP IV. (See Part III) The recorded peak is first stored in data block $\emptyset$. Overlapping Gaussian-shaped peaks are then generated and stored in data block 1. Variation by trial and error of three parameters (width at half-height, height, and position) for each assumed peak permits replication of the observed peak shapes.

T_s is calculated from the width at half-height of the inner Gaussian shaped peak. T_ℓ is calculated from the peak to peak distance of the wider dish-shaped peak. (See Figure IV-f) Both values are corrected for the main beam width at half-height as explained in PART III. Peak areas were determined using the Integrate (IN:) function of the program GASCAP.SV.

An idea of the precision obtained for a series of kinetic energy release determinations is given in Table IV-a. These data represent T values calculated from the width at half-height of the undeconvoluted metastable peak, obtained on three separate days.



$$\xrightarrow{-\,NO\cdot} \quad C_6H_4OCl^+$$

$Width_{m^*}$ (volts)	$Width_{MB}$ (volts)	T (meV)
168.0	2.8	62.9
166.8	2.8	62.0
165.3	2.8	60.9
		Mean =61.9
		s= 1.0

Table IV-a Precision of T value data.

It should be noted that precision in measuring metastable peak widths falls off rapidly as peak intensity decreases and as noise increases. In addition, accuracy is greater for wide peaks than for narrow peaks due to a greater effect from the main beam. A realistic estimated value for error in the T values for non-decomvoluted metastable peaks is about ± 5 % . Deconvolution decreases both precision and accuracy since the composite peaks cannot be assumed to posess strictly Gaussian shapes. Energy release values for deconvoluted peak shapes are estimated to posess an error of ± 10 % .

Before using our system in a new situation, we studied several known metastable processes to see how our results would compare with those of previous workers. Table IV-b shows the results of two such comparisons.

TOLUENE		$M^{+\cdot} - H\cdot$	$M^{+\cdot} - C_2H_2\cdot$
(Our study)	T (meV)	21.7	3.6
(Ref. 20)	T (meV)	17.2	3.0

Table IV-b A comparison of our results with those of previous workers.

Our values seem to be about 20 % larger than those found by COOKS et al. This can be explained by noting two things:

a) In our study, main beam corrections to the measured metastable peak width were made as follows:

$$m^*_{corr} = \left[(m^*)^2 - (m_2/m_1 \cdot MB)^2 \right]^{\frac{1}{2}}$$

whereas COOKS et al. used the correction:

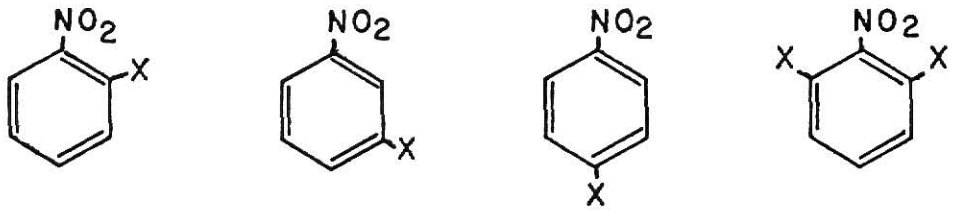
$$m^*_{corr} = m^* - (m_2/m_1 \cdot MB)$$

Our method leads to larger values for the corrected metastable peak width than does the older method. This, in turn, leads to larger kinetic energy release values.

b) Differences in instrumental paramaters from one mass spectrometer to another will also lead to differences in the recorded values for T.

C) Results and discussion.

To clairify the reaction pathways involved in the loss of NO• from nitrobenzenes, we first looked at the metastable peak shapes associated with a series of 2-(ortho), 3-(meta), 4-(para) and 2,6- substituted nitrobenzenes.



ortho meta para 2,6-

Figure IV-e Various halo-nitrobenzenes. X = F , Cl or Br

All peaks recorded were composite, indicating that two processes were taking place. (See Figure IV-f) Deconvoluted peaks which were obtained by assuming three overlapping Gaussian-shaped peaks are shown in Figure IV-g. Kinetic energy release values obtained from these data are given in Table IV-c. Relative peak areas for the two processes are given in Table IV-d.

If we look at abundances (peak areas) for the o-, m-, and p-chloro nitrobenzenes, we find that the T_l process decreases markedly in intensity, relative to the T_s process, as we go from the o- and p- isomers to the m- isomer. This can be interpreted as meaning that T_l is associated with the three-centered transition state (See Figure IV-a) postulated by COOKS et al. An electron withdrawing m-chloro substituent would indeed be expected to strongly destabilize such a transition state.

Identification of the nature of the process associated with T_s is less clearcut. As noted previously, COOKS has postulated a four-center transition state for the rearrangement reaction, placing the oxygen on the 2 or 6 ring carbon. For T_s, there seems to be no discernible trend in relative abundances as one goes from F to Cl to Br or even from p- to o- to m-. Presumably, the blocking of the 2 and 6 positions by halogen groups should dramatically reduce the importance of a process which would place an oxygen atom on either of these positions. Our data would appear to eliminate any reaction pathway which would involve placing an oxygen atom on C_2 or C_6, including the four-center decomposition pathway (Figure IV-b) postulated by COOKS et al.

How then can we account for the results obtained by COOKS and HOLMES for the loss of both ^{13}CO and ^{12}CO from the $(M-NO)^+$ ion from $^{13}C_1$ labelled nitrobenzene? Table IV-e gives the energy release values for the loss of CO from the $(M-NO)^+$ daughter ion for a series of nitrobenzenes.

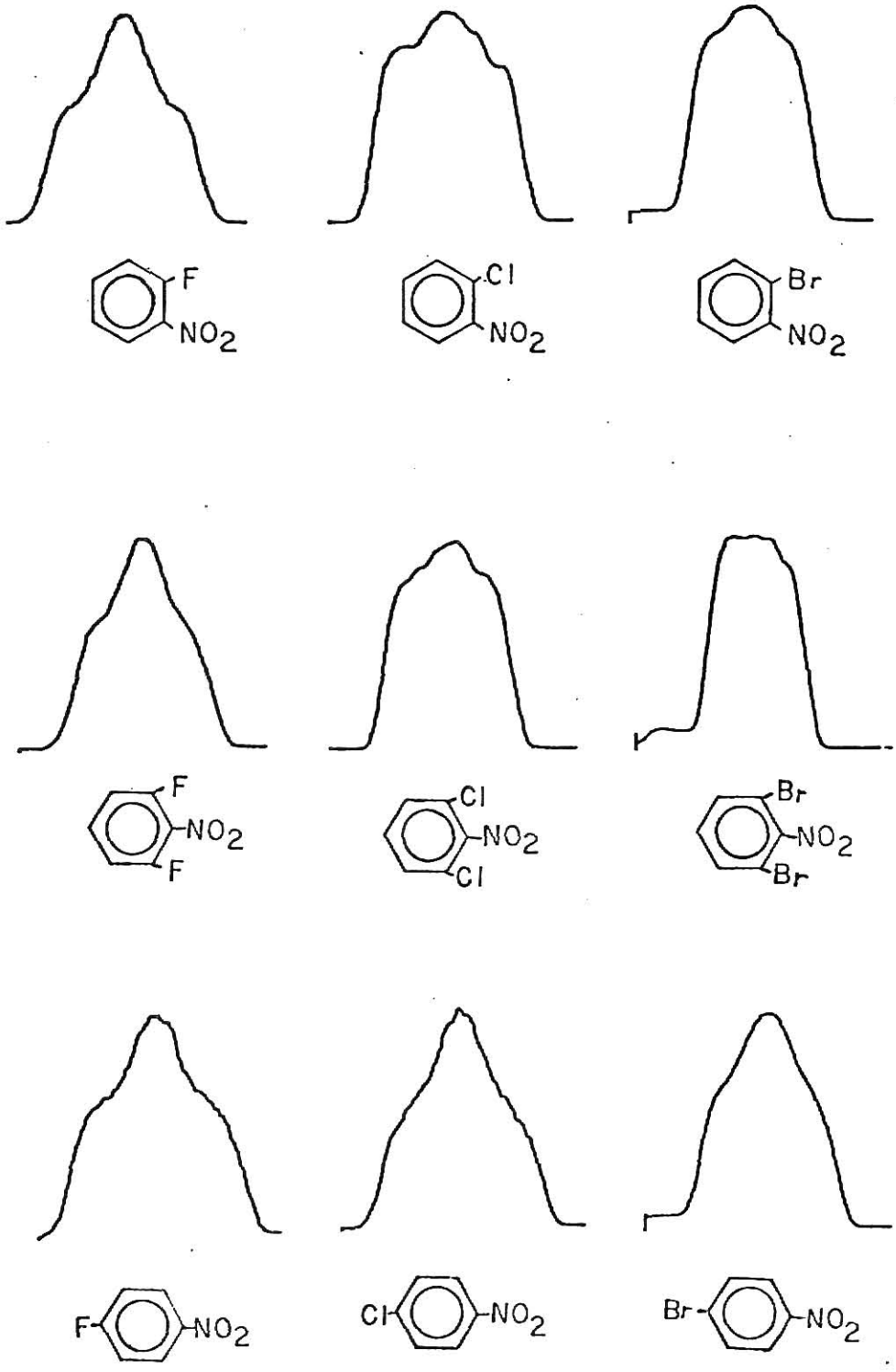


Figure IV-f Metastable peaks for loss of NO• from various halo-substituted nitrobenzenes.

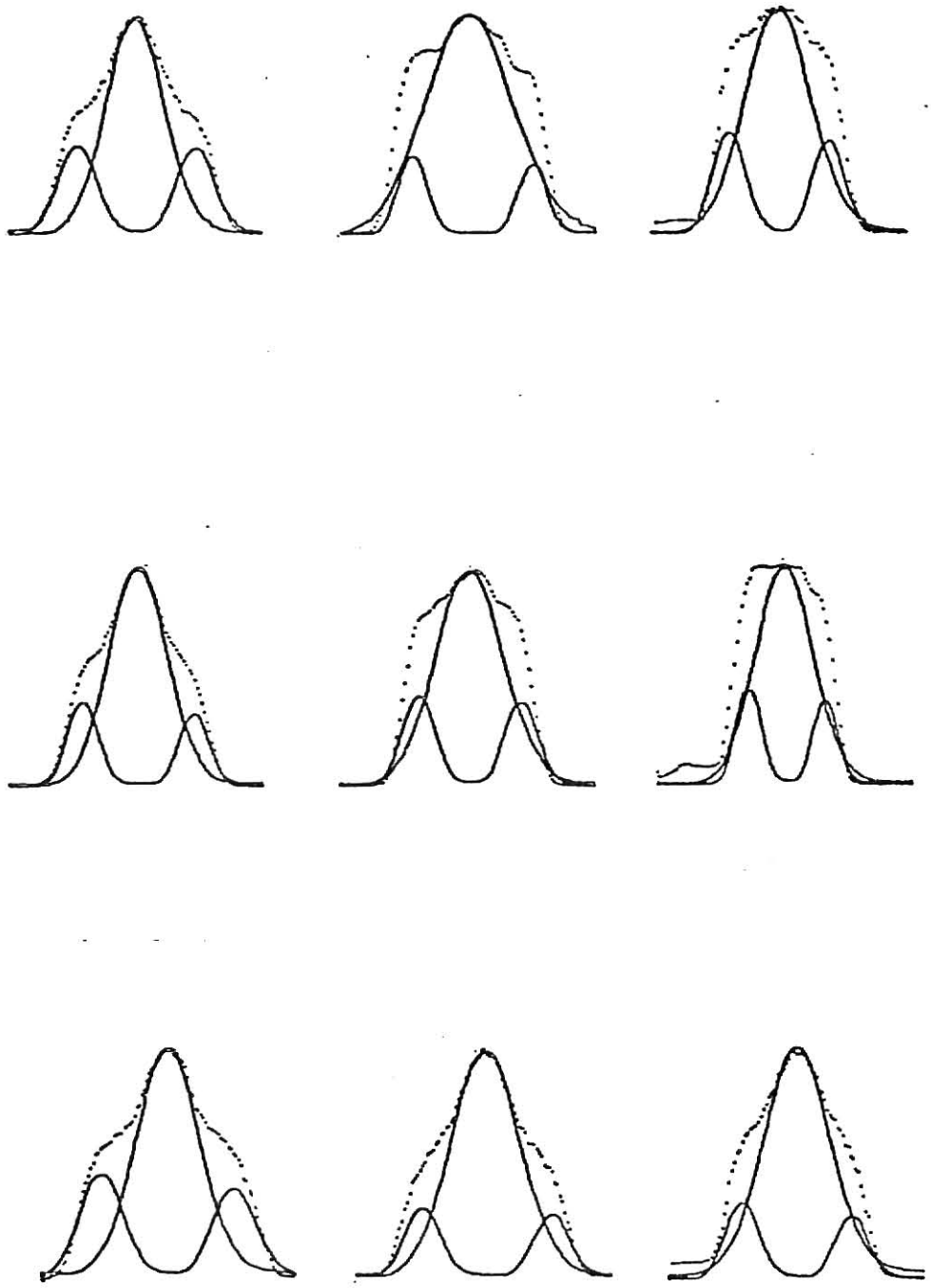


Figure IV-g Deconvoluted metastable peaks for loss of NO• from the halo-substituted nitrobenzenes shown in Figure IV-f.

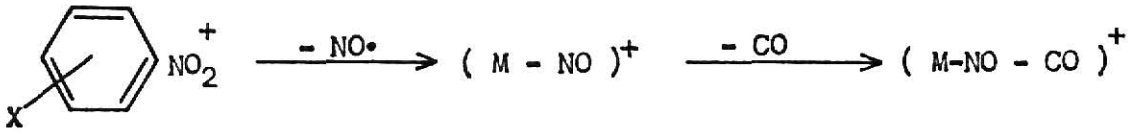
	T_S (meV)*			T_ℓ (meV)**		
	F	Cl	Br	F	Cl	Br
o-	15	25	25	38	41	41
2,6-	15	25	28	39	41	35
p-	15	20	25	49	51	50
m-	-	21	-	-	27	-

Table IV-c Kinetic energy release values for a series of halo-substituted nitrobenzenes.

	A_S (% of total)			A_ℓ (% of total)		
	F	Cl	Br	F	Cl	Br
o-	65	77	70	35	23	30
2,6-	73	72	73	27	28	27
p-	63	77	76	37	23	24
m-	-	90	-	-	10	-

Table IV-d Relative peak areas for a series of halo-substituted nitrobenzenes.

* Peak width is measured at half-height.
** Peak width is measured peak to peak.

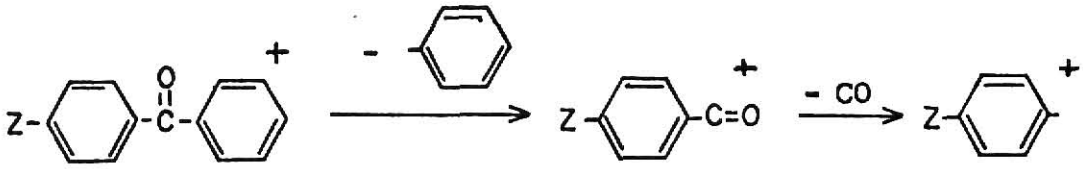


X	T (meV)
H-	53
o-Cl-	284
m-Cl-	243
p-Cl-	259
2,6-Cl_2-	224

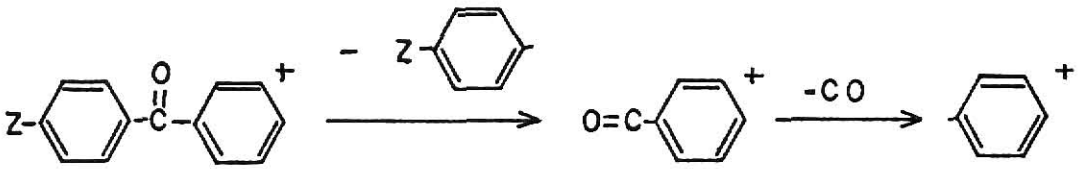
Table IV-e Kinetic energy release values for loss of CO in various substituted nitrobenzenes.

The five-fold increase in the energy release values upon substitution of Cl for H may be taken to indicate that the loss of CO from the $(M - NO)^+$ ion from nitrobenzene is quite different from the same loss in the halo-substituted cases. In support of this position, we have studied the effect of substituents on a similar reaction involving the loss of CO .

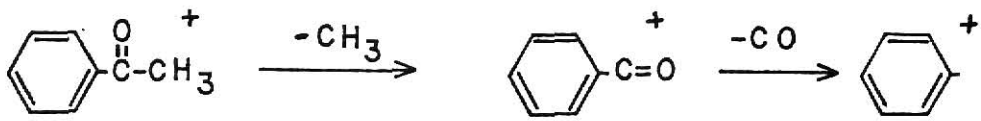
The decomposition of the molecular ion of benzophenone results in the formation of a positive ion in which the CO group is left attached to either phenyl group. Placement of a substituent on one of these phenyl groups provides a probe into the effect of substituents in a comparable reaction in which CO is lost. The data in Table IV-f show only small increases in the energy release values upon substitution of Cl for H. The absence of a large substituent effect on T would seem to indicate that the loss of CO from unsubstituted nitrobenzene is a special case and that $^{13}C_1$ labelling results may not be applicable to the substituted nitrobenzenes in general.



Z	T (meV)
H-	29.9
p-Cl-	35.0
$p\text{-}CH_3O$-	45.0
$p\text{-}NO_2$-	too weak to measure



Z	T (meV)
H-	29.9
p-Cl-	29.4
$p\text{-}CH_3O$-	30.3
$p\text{-}NO_2$-	29.8



Z	T (meV)
H-	28.4

Table IV-f Kinetic energy release values for loss of CO in various substituted benzophenones and in acetophenone.

A possible explanation is that the ring has opened before the ion begins to decompose:

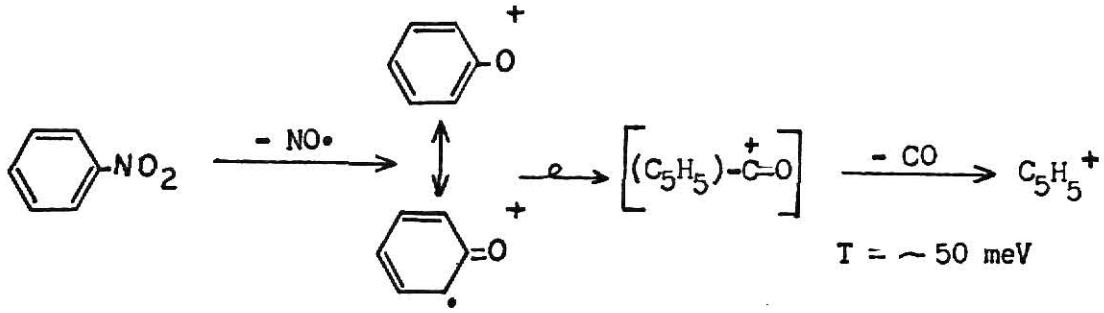


Figure IV-h Postulated metastable decomposition of nitrobenzene showing ring opening before loss of CO .

whereas for a substituted nitrobenzene:

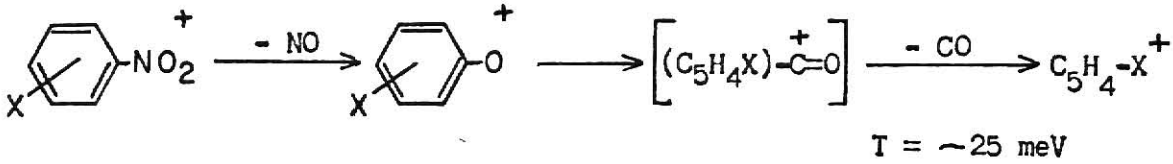
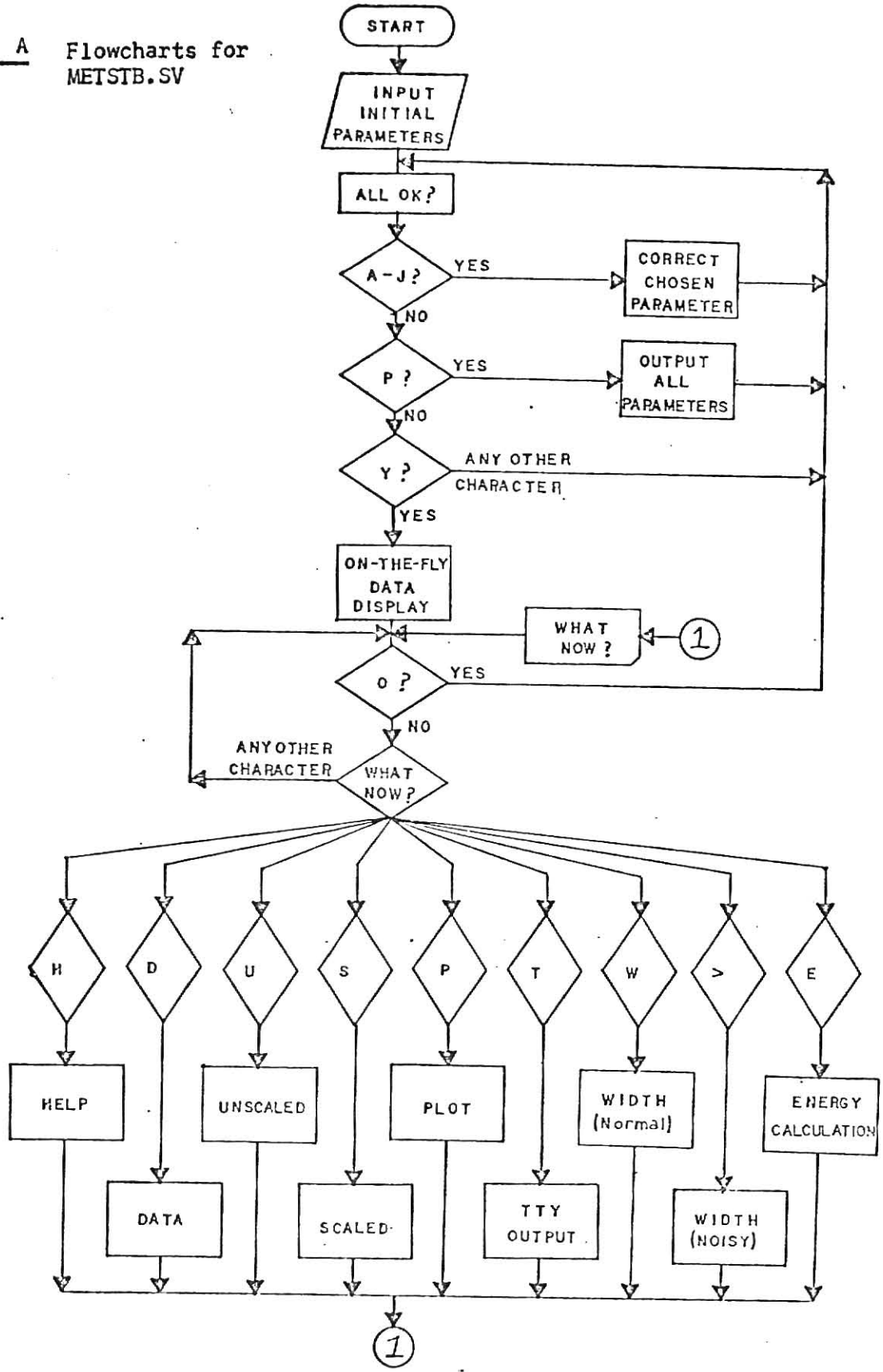


Figure IV-i Postulated metastable decomposition of substituted nitrobenzenes.

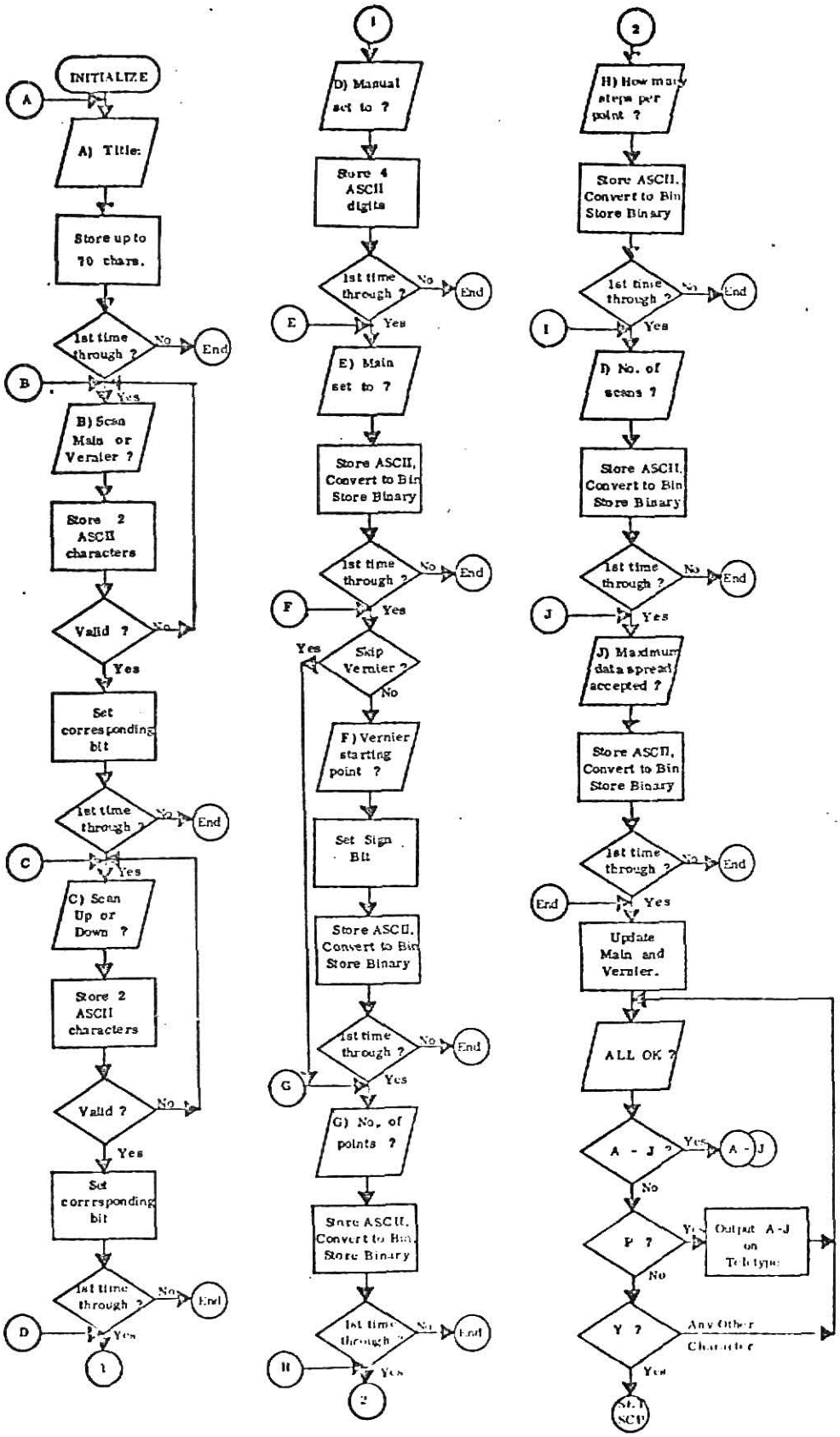
Our data indicate that the process associated with T_s is, in all probability, a simple cleavage decomposition involving loss on NO• following a preliminary nitro-nitrite rearrangement caused by the electron beam. (See Figure IV-c) This kind of situation is supported by studies which show simple cleavage type decompositions exhibit smaller energy release values than do those for which the rate determining step involves a rearrangement.[21]

A P P E N D I C E S

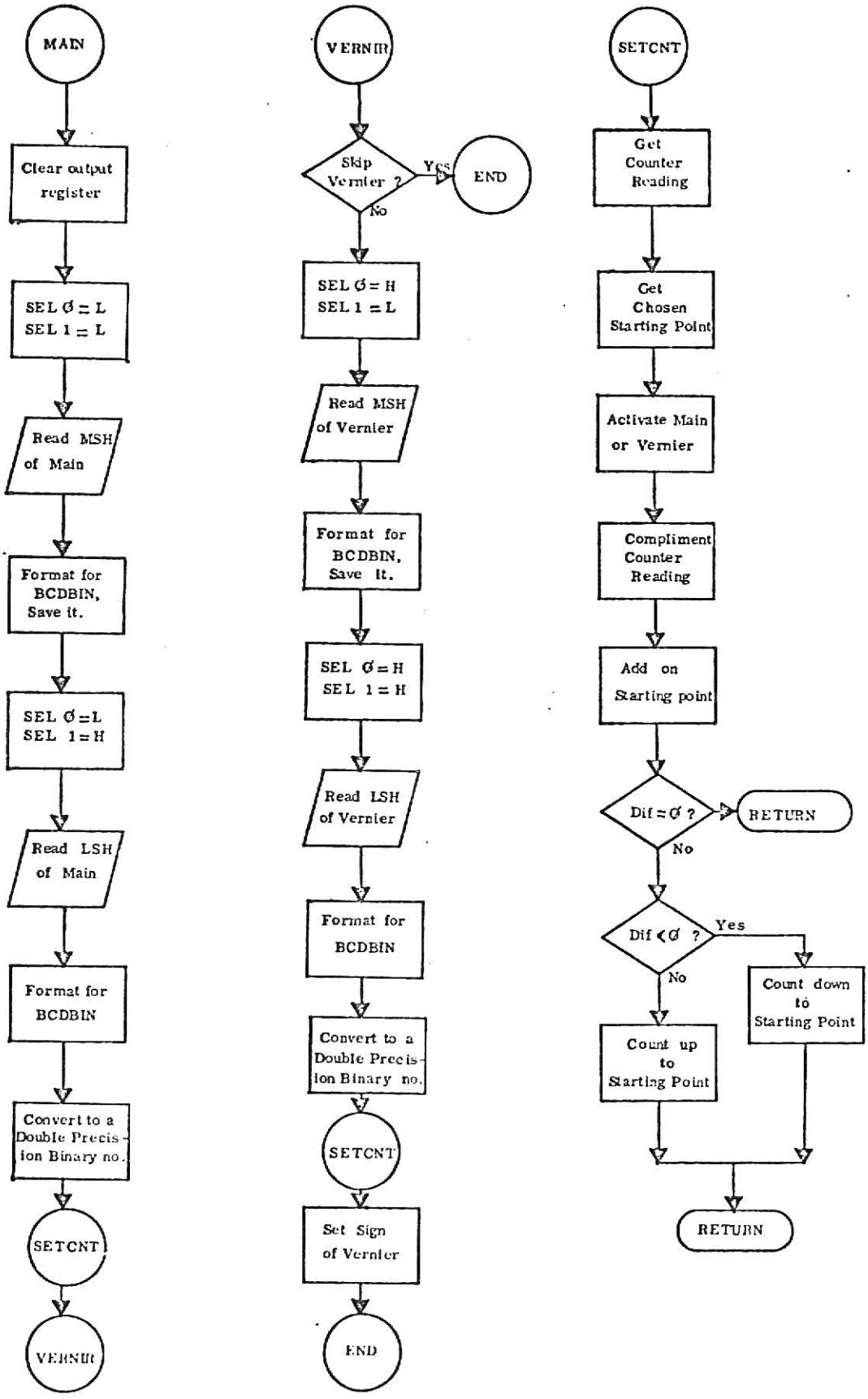
APPENDIX A Flowcharts for METSTB.SV



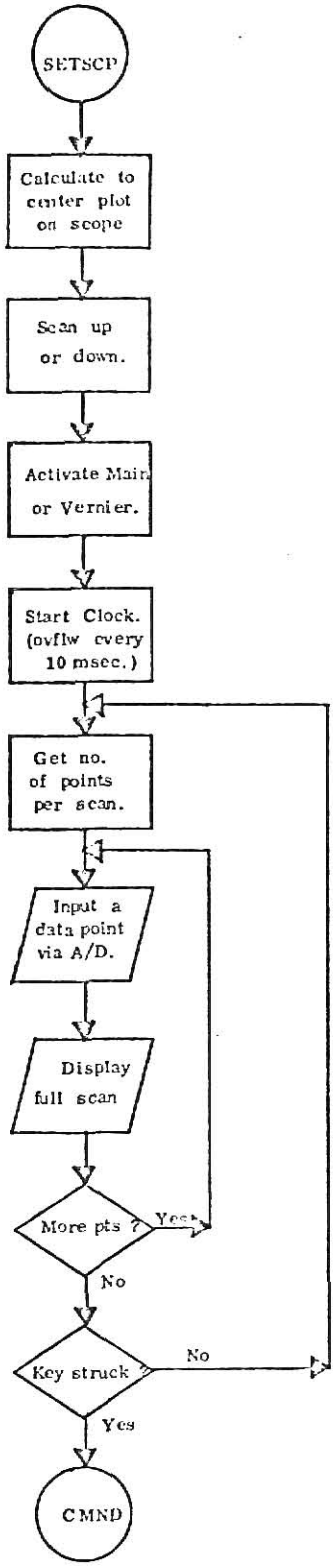
Flowchart #1 Overall Program - METSTB.SV



Flowchart #2 Input of parameters - METSTB.DL

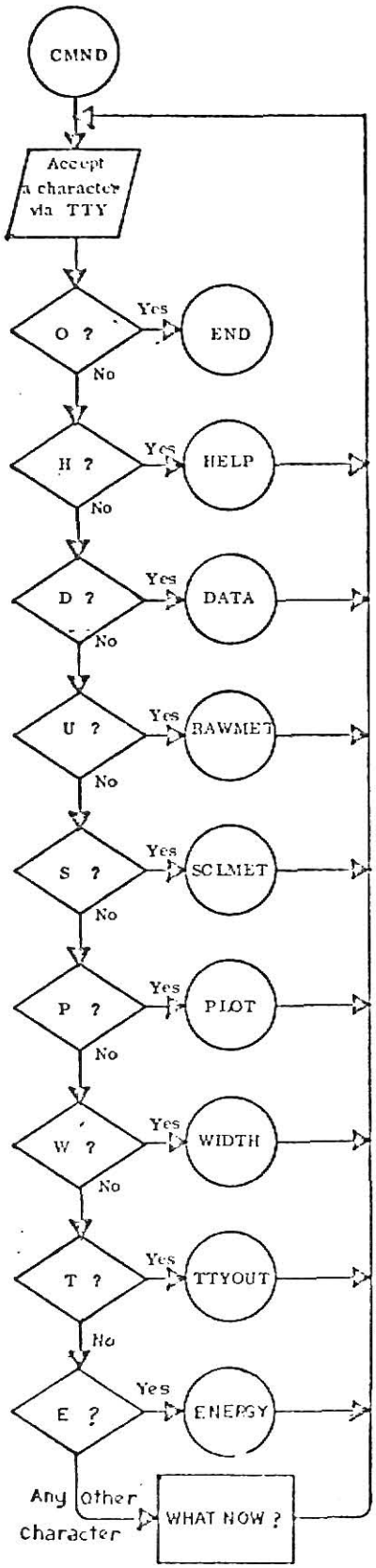


Flowchart #3 Reset MAIN and VERNIER counters - METSTB.DT



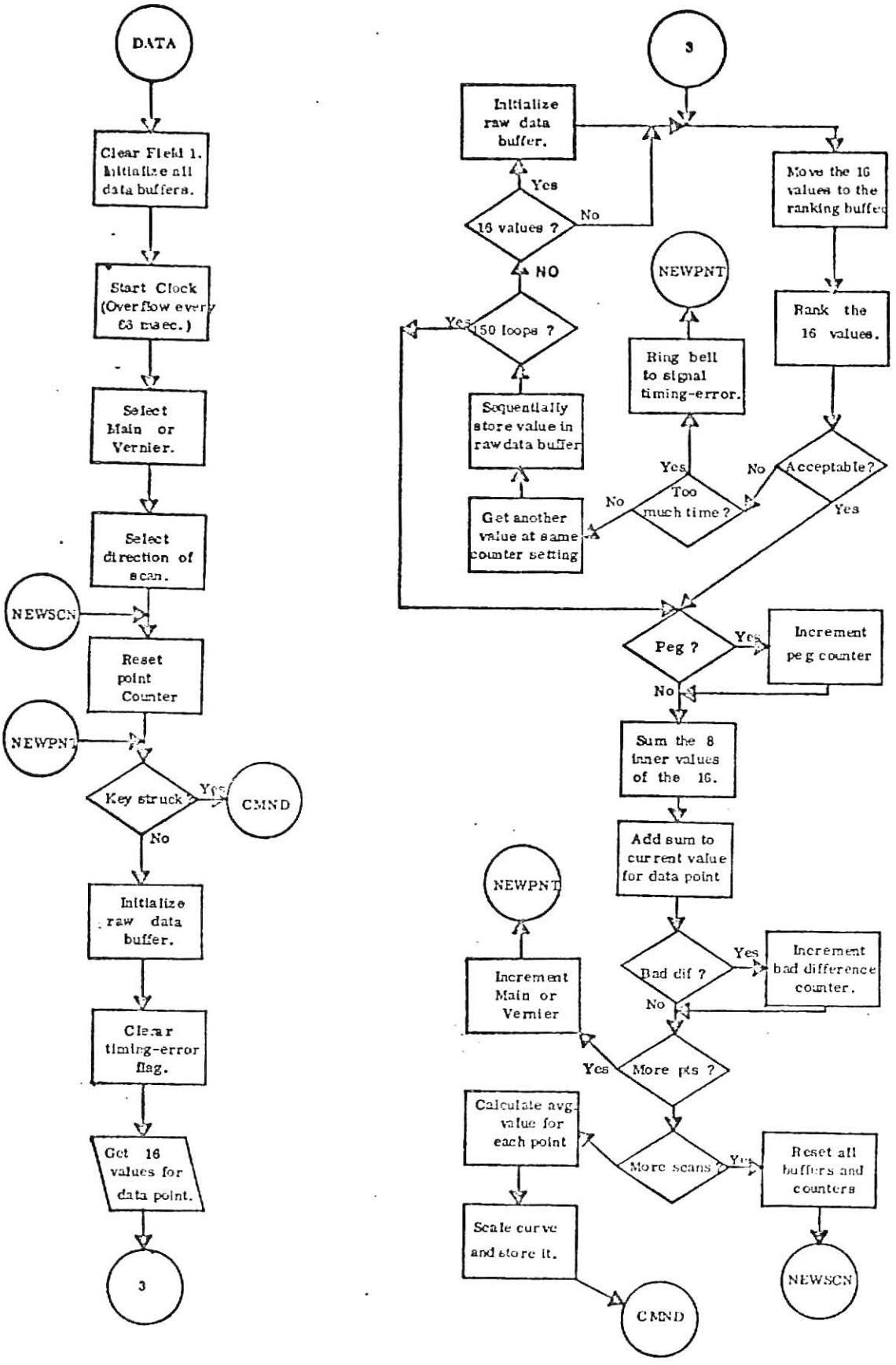
Flowchart #4a

On-the-fly scope data display
METSTB.DT

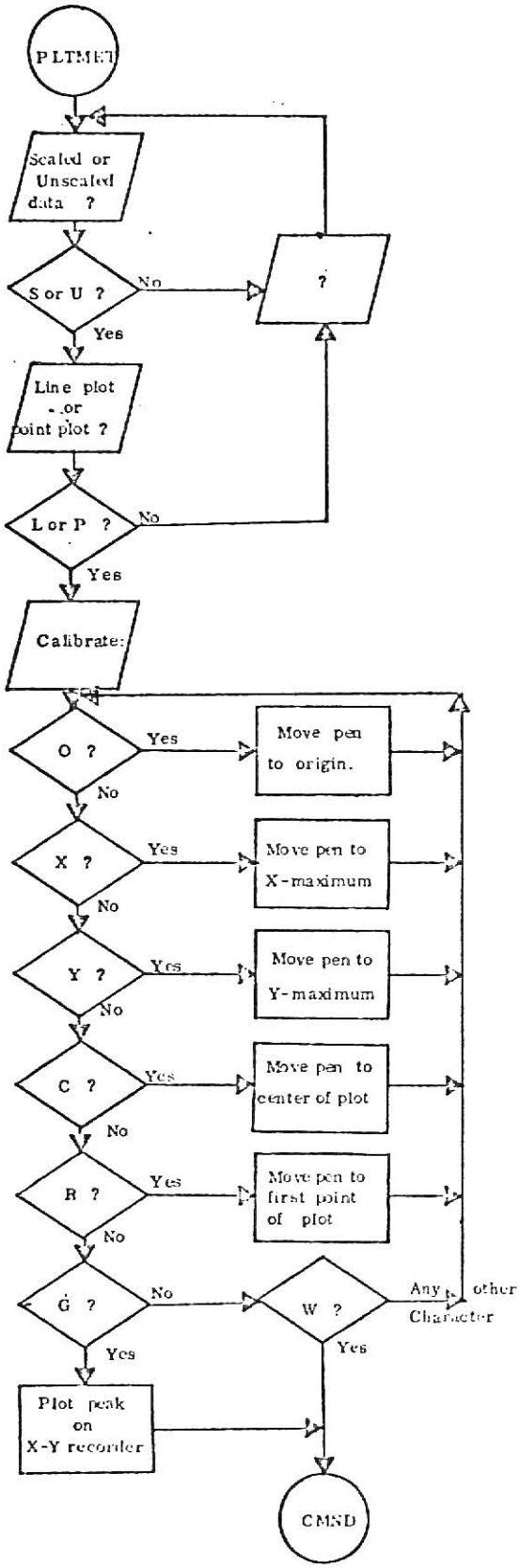


Flowchart #4b

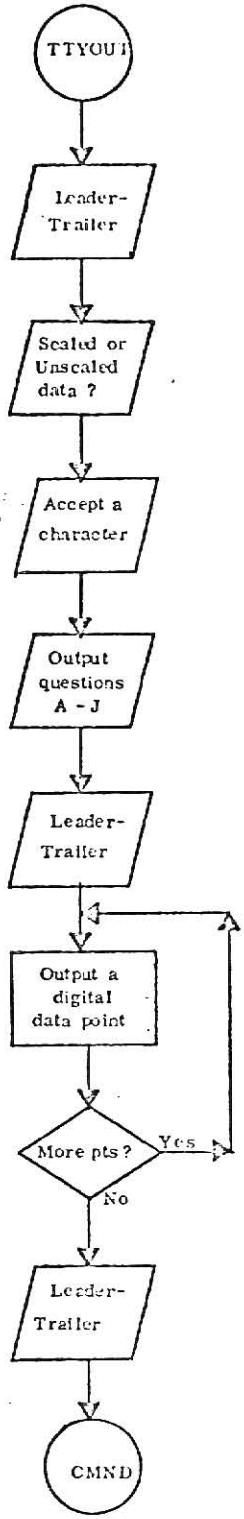
Summary of the INSTRUCTION MODE



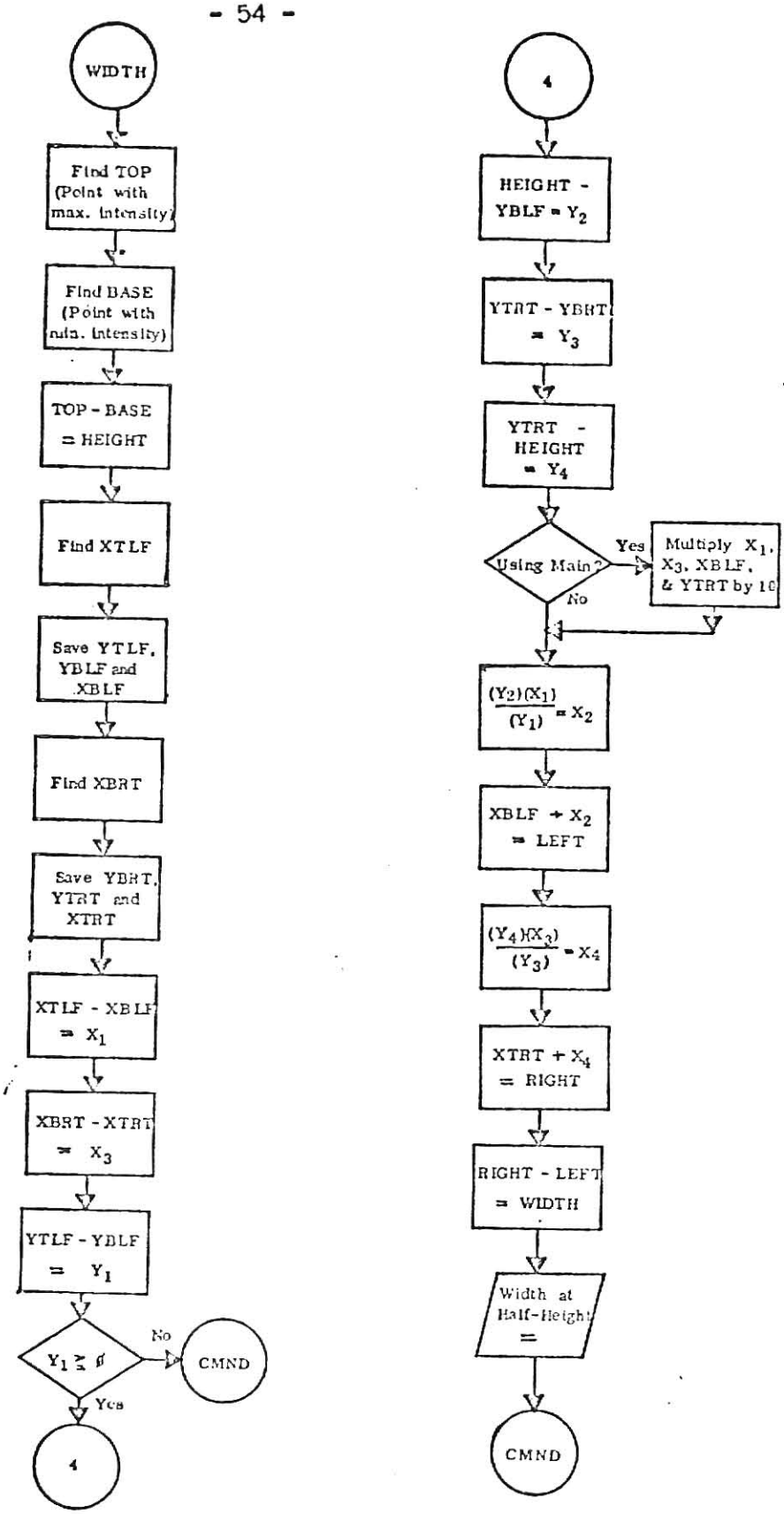
Flowchart #5 Main data acquisition routine - METSTB.DT



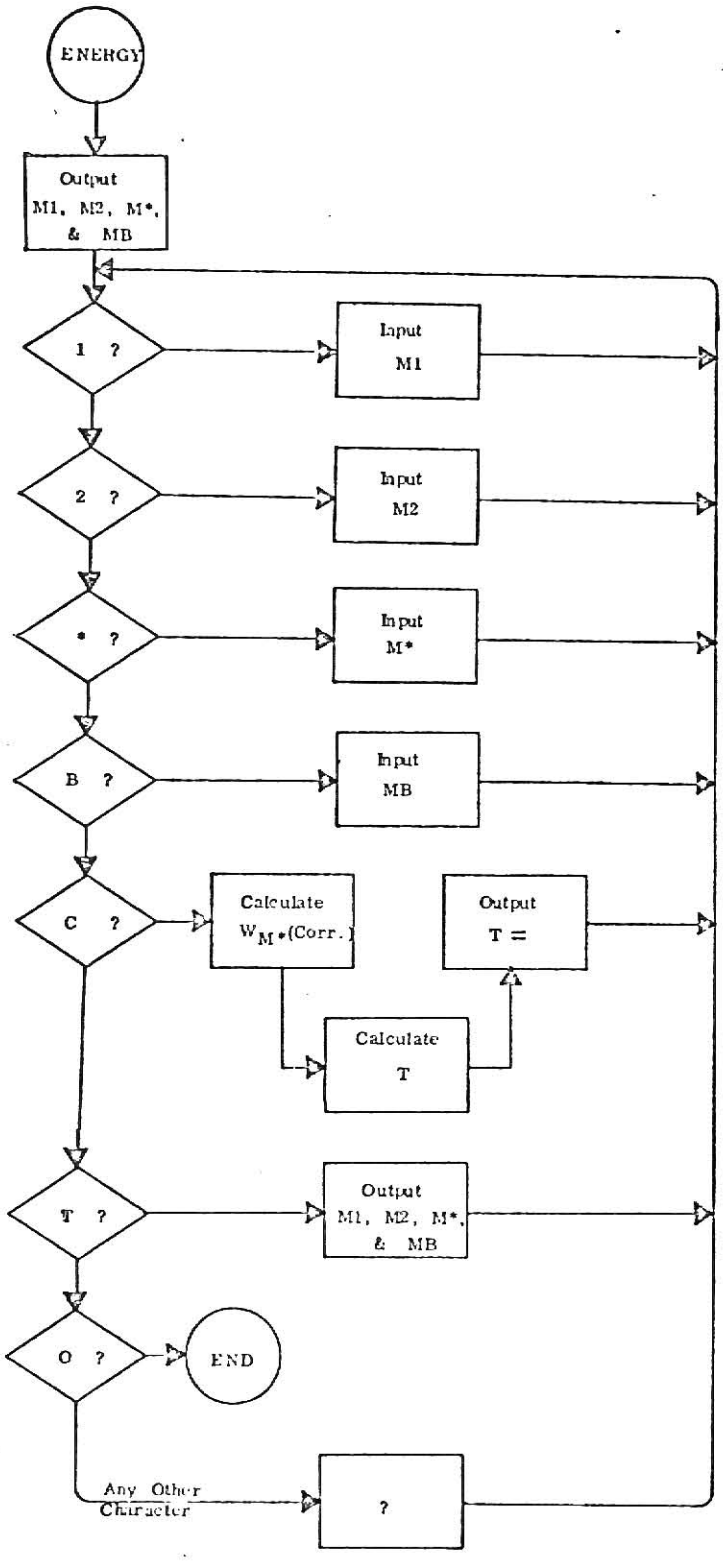
Flowchart #6a X-Y Plotter output METSTB.OT



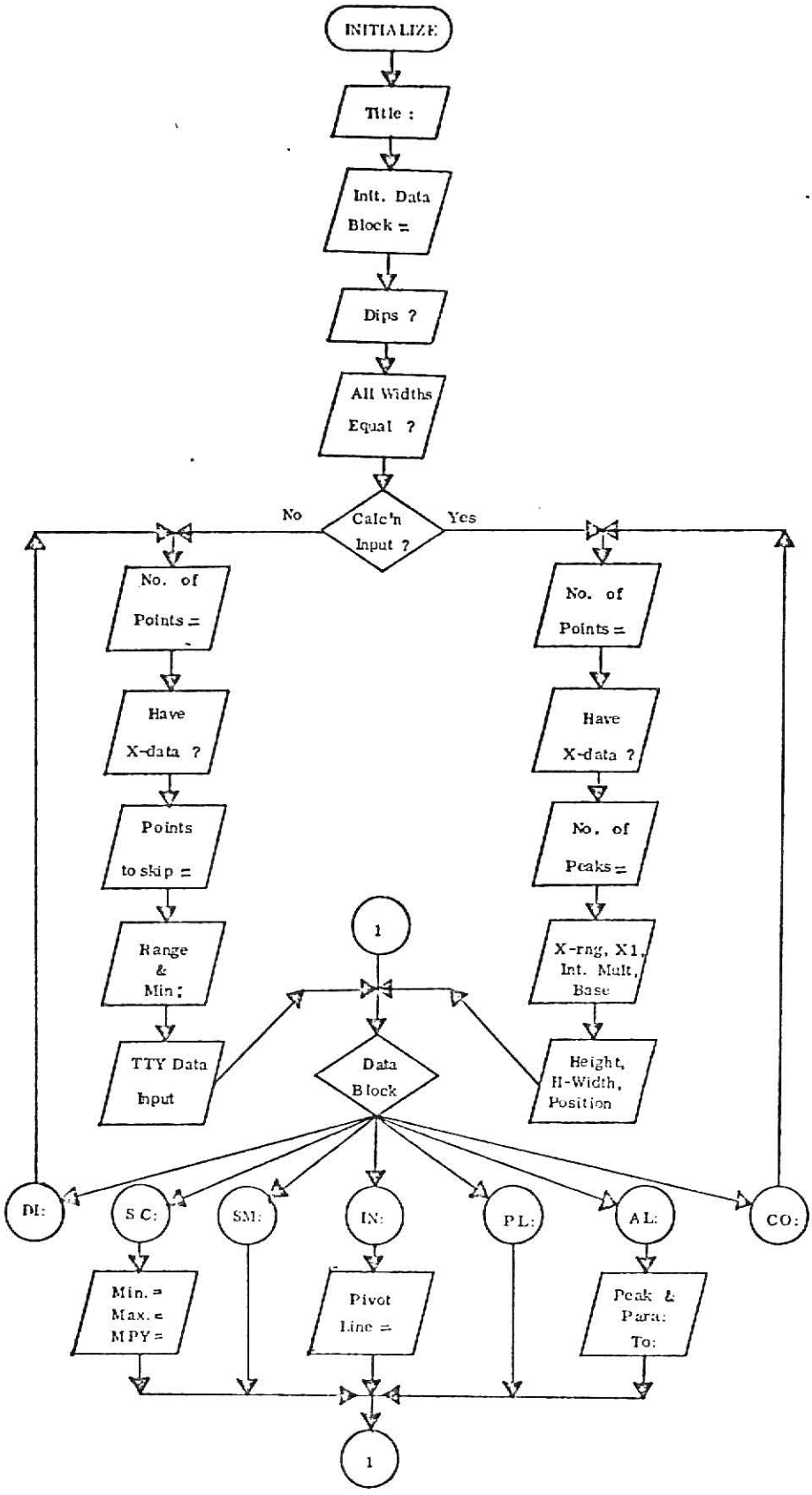
Flowchart #6b TTY-PTP Output - METSTB.OT



Flowchart #7 Calculation of the width of the peak at half-height METSTB.OT



Flowchart #8 Calculation of the energy release value (T)
METEGY.SV



Flowchart #9 Overall program - GASCAP.SV

ILLEGIBLE DOCUMENT

THE FOLLOWING DOCUMENT(S) IS OF POOR LEGIBILITY IN THE ORIGINAL

THIS IS THE BEST COPY AVAILABLE

APPENDIX B METSTB.DS Description Program

NAME OF PROGRAM : METSTB.SV

GENERAL PURPOSE : TO COLLECT, PROCESS, AND OUTPUT METASTABLE PEAK DATA USING THE MS-9 MASS SPECTROMETER.

SOURCE : PROGRAMMED BY MARLIN FRIESEN (SPRING 1974)
FLOWCHART #1 GIVES AN OVERALL SUMMARY

A) METSTB.SY (SYMBOL)
00000-00177 (BASE PAGE + NECESSARY OPCODES)

B) METSTB.DL (DIALOG) ***SEE FLOWCHART #2***
(INPUT OF PARAMETERS, STORAGE OF
00200-01577 THOSE PARAMETERS ON PAGE ZERO.)

C) METSTB.DT (DATA) ***SEE FLOWCHARTS #3,4,&5***
(RECORDING OF DATA AS PER INSTRUC-
01600-05577 TIONS IN DIALOG SECTION.)

D) METSTB.OT (OUTPUT) ***SEE FLOWCHARTS #6 & 7***
(OUTPUT OF METASTABLE PEAK DATA.
05600-06777 A)DIGITAL, B)SCOPE, C) X-Y
PLOTTER, OR D) PAPER TAPE.
ALSO WIDTH AT HALF HEIGHT.)

E) METSTB.SR (SUBROUTINES)
07000-07177 (BCDBIN & BINBCD)

F) METEGY.SV (ENERGY CALCULATION)
20000-20577 (CALCULATION OF ENERGY RELEASE VALUE)
SEE FLOWCHART # 8

G) TLTPE4.SV (VAN SWAAY'S TELETYPE DRIVER)
07200-07577

H) TLTP44.BN (SAME TELETYPE DRIVER)
24200-24577 (NEW LOCATION)

I) EAEFPP.BN (EAE-FLOATING POINT PACKAGE)
25000-27577

J) END (PROGRAM CONTAINS ONLY A "$")

****UNDERLINED STATEMENTS ARE TYPED BY COMPUTER****

TO ASSEMBLE PROGRAM: ***PLACE TAPE ON DTAØ***

(IN RESPONSE TO .)

```
.R PAL8                    (HIT CARRIAGE RETURN)
METDLR.BN,TTY:<METSTB.SY,METSTB.DL,METSTB.SR,END/N     (CARR. RET)
```

(SYMBOL TABLE WILL BE PRINTED OUT ON TTY.)

```
.R PAL8                    (HIT CARRIAGE RETURN)
METDOT.BN,TTY:<METSTB.SY,METSTB.DT,METSTB.OT,END/N     (CARR. RET)
```

(SYMBOL TABLE WILL BE PRINTED OUT ON TTY)

```
.R PAL8                    (HIT CARRIAGE RETURN)
METEGY.BN,TTY:<METSTB.EN,END/N          (HIT CARRIAGE RETURN)
```

(SYMBOL TABLE WILL BE PRINTED OUT ON TTY)

TO LOAD PROGRAM:

(IN RESPONSE TO .)

```
.R ABSLDR                  (HIT CARRIAGE RETURN)
*TLTP44.BN                 (HIT CARRIAGE RETURN)
*EAEFPP.BN                 (HIT CARRIAGE RETURN)
*METEGY.BN                 (HIT ALT MODE)

.SAVE DTAØ METEGY.SV

.R ABSLDR                  (HIT CARRIAGE RETURN)
*METEGY.SV/2/I             (HIT CARRIAGE RETURN)
*TLTPE4.SV/I               (HIT CARRAIGE RETURN)
*METDLR.BN                 (HIT CARRIAGE RETURN)
*METDOT.BN                 (HIT ALTMODE)

.SAVE DTAØ METSTB.SV       (HIT CARRIAGE RETURN)
```

TO RUN PROGRAM:

(BRING UP OS-8, IF NOT ALREADY OPERATING.DETAILED INSTRUCTIONS FOUND IN INTRODUCTION TO PROGRAMING-1972)

(IN RESPONSE TO .)

```
.RUN DTAØ METSTB.SV              (HIT CARRIAGE RETURN)
```

METSTB 1 !!!

A)TITLE: (TYPE ANYTHING YOU LIKE, UP TO 1 FULL LINE. HIT CAR.-RET)

PLEASE SET ACC TO SWEEP AND ESA TO MANUAL !!!

(A REMINDER TO THE OPERATOR - DO IT !)

B) SCAN MAIN(MA) OR VERNIER(VE)?

(-A RESPONSE OF "MA" ACTIVATES ONLY THE MAIN SCAN.
NOTE THAT IN THIS CASE, QUEST. F WILL BE OMITTED AND THE VERNIER SET TO ZERO.
-A RESPONSE OF "VE" WILL ACTIVATE ONLY THE VERNIER SCAN.

-ANY OTHER RESPONSE WILL CAUSE QUEST. B TO BE REPEATED.)

C) SCAN UP(UP) OR DOWN(DO)?

(-A RESPONSE OF "UP" CAUSES VERNIER OR MAIN TO SCAN UP FROM DESIGNATED STARTING POINT.
-A RESPONSE OF "DO" CAUSES VERNIER OR MAIN TO SCAN DOWN.

-ANY OTHER RESPONSE WILL CAUSE QUEST. C TO BE REPEATED.)

D) MANUAL SET TO?

(TYPE UP TO FOUR DIGITS FROM Ø TO 9999.
THIS VALUE REPRESENTS ESA (MANUAL) SETTING.)
ONLY 4 DIGITS ACCEPTED

PLEASE SET MANUAL TO THIS VALUE !!!

(A REMINDER THAT THE MANUAL THUMB-SWITCH MUST BE SET BY HAND.)

E) MAIN SET TO?

(TYPE UP TO FOUR DIGITS FROM Ø TO 9999.
THIS VALUE REPRESENTS THE INITIAL ACC (MAIN) SETTING.)
ONLY 4 DIGITS ACCEPTED

F) VERNIER STARTING POINT?

(TYPE IN A SIGNED THREE DIGIT NUMBER AND INCLUDE DECIMAL POINT BETWEEN LAST TWO DIGITS.
EXAMPLES: -05.0 +15.5 +25.0 -00.5 ETC.

VALUE MUST BE ENTERED USING THE ABOVE FORMAT

<<<NOTE THAT QUEST. F IS NOT ASKED UNLESS THE VERNIER WAS ACTIVATED IN QUEST. B. ACTIVATING THE MAIN IN QUEST. B AUTOMATICALLY SETS VERNIER TO -00.0.

<<<NEVER USE THE VERNIER IN SUCH A WAY AS TO BEGIN OR END A SCAN AT + OR - 00.0. THE COUNTER WILL GIVE ERRONEOUS RESULTS.)

G) NO. OF POINTS?

(TYPE UP TO FOUR DIGITS FROM 10 TO 1000.
NUMBERS LARGER THAN 1000 WILL BE ACCEPTED BUT WILL GIVE ERRONEOUS RESULTS DUE TO LIMITED CORE SPACE.)

H) HOW MANY STEPS PER POINT?

(TYPE UP TO TWO DIGITS FROM 1 TO 99.
THIS VALUE REPRESENTS THE NUMBER OF TIMES THE COUNTER INCREMENTS BEFORE THE NEXT DATA POINT IS RECORDED.)
ONLY TWO DIGITS ACCEPTED

I) NO. OF SCANS?

(TYPE UP TO FOUR DIGITS FROM 1 TO 9999.)
ONLY 4 DIGITS ACCEPTED

J) MAXIMUM DATA SPREAD ACCEPTABLE?

(TYPE UP TO FOUR DIGITS FROM 1 TO 1000.)
ONLY FOUR DIGITS ACCEPTED

ALL OK?

(AT THIS POINT, BOTH THE MAIN AND THE VERNIER SHOULD BE IN ACCORD WITH YOUR ENTRIES FOR QUESTIONS E AND F.
THE COMPUTER IS NOW IN THE "CORRECTION MODE".
THE FOLLOWING ARE VALID 1-CHARACTER RESPONSES IN THIS MODE:
ALL OTHER CHARACTERS ARE NOT ACCEPTED

[A - J] TYPING ONE OF THE LETTERS A-J CAUSES THE CORRESPONDING QUESTION TO BE TYPED OUT. ANSWER AS BEFORE.
COMPUTER REMAINS IN CORRECTION MODE.

[P] TYPING A P CAUSES THE ENTIRE INPUT PARAMETER SECTION (QUESTIONS A THROUGH J) TO BE TYPED OUT.
COMPUTER REMAINS IN CORRECTION MODE.

[Y] TYPING A Y INDICATES TO THE COMPUTER THAT NO CORRECTIONS ARE NECESSARY. ON-THE-FLY DATA ACQUISITION IS IMMEDIATELY DISPLAYED ON THE SCOPE, CORRESPONDING TO INSTRUCTIONS GIVEN IN QUESTIONS A THROUGH J. (SEE FLOWCHART #4A)

*** COMPUTER IS NOW IN "INSTRUCTION MODE" ***

THE FOLLOWING ARE VALID 1-CHARACTER RESPONSES IN THIS MODE.
ALL OTHER CHARACTERS ARE NOT ACCEPTED
***AND THE QUESTION "WHAT NOW?" WILL BE ***
***PRINTED. (SEE FLOWCHART #4B)

(O) - ALL OK? (CHANGE INPUT PARAMETERS)

(COMPUTER RETURNS TO CORRECTION MODE)

(H) - HELP (PRINT OUT POSSIBLE RESPONSES)

(D) - DATA (GO TO MAIN DATA ACQUISITION) (FLOWCHART #5)

(TAKE DATA ACCORDING TO INSTRUCTIONS A - J.)

(U) - UNSCALED DATA (PUT UNSCALED PEAK ON SCOPE)

(S) - SCALED DATA (PUT SCALED PEAK ON SCOPE)

(P) - PLOT (GO TO THE X-Y PLOTTER ROUTINE) (FLOWCHART #6A)

(W) - WIDTH (CALCULATE WIDTH OF PEAK AT HALF-HEIGHT) (FLOWCHART #7)

(>) - ALT WIDTH (WIDTH FOR NOISY OR DISH-SHAPED PEAKS)

(T) - TTY OUTPUT (OUTPUT DATA VIA TTY OR PTP) (FLOWCHART #6B)

(E) - ENERGY (CALCULATE ENERGY RELEASE VALUE) (FLOWCHART #3)

THE FOLLOWING EXPLAINS USE OF THE PLOT P FUNCTION

SCALED (S) OR UNSCALED (U) DATA?

(-A RESPONSE OF "S" CAUSES THE SCALED DATA TO BE PLOTTED.

-A RESPONSE OF "U" CAUSES THE UNSCALED DATA TO BE PLOTTED.

LINE PLOT (L) OR POINT PLOT (P) ?

(-A RESPONSE OF "L" RESULTS IN A SOLID LINE PLOT.

-A RESPONSE OF "P" RESULTS IN A POINT PLOT.

-ANY OTHER RESPONSE TO THESE QUESTIONS CAUSES THEIR REPETITION)

CALIBRATE: (SET UP PLOTTER USING THE FOLLOWING COMMANDS.)

(O)- A RESPONSE OF "O" MOVES THE PEN TO THE X-Y ORIGIN OF THE PLOT.

(X)- A RESPONSE OF "X" MOVES THE PEN TO THE PLOT'S MAXIMUM X VALUE.

(Y)- A RESPONSE OF "Y" MOVES THE PEN TO THE PLOT'S MAXIMUM Y VALUE.

THESE THREE COMMANDS CAN BE USED TO DRAW
A BOX AROUND THE PLOT

(C)- A RESPONSE OF "C" MOVES THE PEN TO THE CENTER OF THE PLOT.

(R)- A RESPONSE OF "R" MOVES THE PEN TO THE PLOT'S FIRST DATA POINT.
THIS COMMAND IS INCLUDED TO AVOID PEN
MOVEMENT ON PLOT INITIATION

(G)- A RESPONSE OF "G" COMMENCES ACTUAL PLOTTING. UPON COMPLETION, PROGRAM CONTROL RETURNS TO THE INSTRUCTION MODE.

**** ANY OTHER RESPONSE ECHOES A "?" ****

STRIKING ANY KEY DURING THE ACTUAL PLOTTING*
ABORTS THE PLOT AND RETURNS PROGRAM CONTROL
TO THE INSTRUCTION MODE

THE FOLLOWING EXPLAINS USE OF THE ENERGY E FUNCTION

M1= +0.00000-->M2 +0.00000 M* WIDTH= +0.00000 MB WIDTH= +0.00000

(- TYPING A "1" ALLOWS INPUT OF THE MOLECULAR WEIGHT FOR THE PARENT ION M1+.

- TYPING A "2" ALLOWS INPUT OF THE MOLECULAR WEIGHT FOR THE DAUGHTER ION M2+.

- TYPING A "*" ALLOWS INPUT OF THE METASTABLE PEAK WIDTH AT HALF HEIGHT.

- TYPING A "B" ALLOWS INPUT OF THE MAIN BEAM PEAK WIDTH AT HALF HEIGHT.

INPUT CAN BE ANY DECIMAL FLOATING POINT
NUMBER WITHIN THE LIMITS: +-999.99999

OVERFLOW IS INDICATED BY A LINE OF ********

- TYPING A "T" CAUSES OUTPUT FOR CURRENT VALUES OF THE VARIABLES M1, M2, M*, AND MB.

- TYPING A "C" CAUSES CALCULATION AND OUTPUT OF THE ENERGY RELEASE VALUE.

$$T = \frac{\left(\frac{M2}{M1}\right)^2 (0.05)(1)}{\left(\frac{M1}{M1-M2}\right)(1)} \cdot \frac{(M^* \text{ CORR})^2}{V}$$

- TYPING A "W" CAUSES OUTPUT OF METASTABLE PEAK WIDTH CORRECTED FOR THE MAIN BEAM WIDTH.

$$M^* \text{ CORR} = \left((M^*)^2 - (MB \times M2/M1)^2 \right)^{1/2}$$

- TYPING AN "0" RETURNS PROGRAM CONTROL TO THE CORRECTION MODE.

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

TO GET BACK TO THE KEYBOARD MONITOR, TYPE CTRL/C IN EITHER THE CORRECTION MODE OR THE INSTRUCTION MODE.

TO GET A LISTING OF THIS DESCRIPTION, GET A LISTING OF THE PROGRAM: METSTB.DS.

```
.R PIP          (HIT CARRIAGE RETURN)
*TTY:<METSTB.DS/A/T      (HIT CARRIAGE RETURN)
```

APPENDIX C GASCAP.SV Description program.

NAME OF PROGRAM: GASCAP.SV

GENERAL PURPOSE: TO DECONVOLUTE OVERLAPING METASTABLE PEAKS THROUGH PEAK GENERATION AND COMPARISON.

SOURCE: PROGRAMMED BY GERALD W. DELANEY (12/19/69)

MADCAP IV, A MULTIPLEX ADC AND ANALOG PLOTTING PROGRAM. (DECUS # 8-237)

FLOWCHART #9 GIVES AN OVERALL SUMMARY

TO RUN PROGRAM:

(BRING UP ØS-8, IF NOT ALREADY OPERATING. DETAILED INSTRUCTIONS FOUND IN INTRO TO PROGRAMING -1972)

(IN RESPONSE TO .)

. RUN DTAØ GASCAP.SV (HIT CARRIAGE RETURN)

#

```
GASCAP IV!

TITLE:          (TYPE ANYTHING YOU LIKE. TERMINATE WITH ALT MODE.)

INITIAL DATA BLOCK NO.=0          (PUT RAW DATA INTO BLOCK Ø)
WANT ABSORPTION DIPS?N            (ALWAYS ANSWER NO.)
ALL WIDTHS EQUAL?N                (ALWAYS ANSWER NO.)

CALC'N  INPUT?N                   (N- ACCEPTS RAW DATA FROM PTR.
                                   Y- ACCEPTS PARAMETERS TO COMPUTE
                                      NEW SPECTRUM.)


NO. OF POINTS=100                 (ALWAYS 100 IN THIS STUDY.)
HAVE X DATA?N                     (ALWAYS ANSWER NO.)
PTS. TO SKIP? Ø                   (REFERS TO POINTS ON PAPER TAPE.)

RANGE AND MIN                     (REFERS TO Y AXIS)
Y: 500 Ø                          (ALWAYS PUT  500 AND Ø)

DATA:

TTY I/O ? Y                       (ALWAYS ANSWER YES; DON'T HAVE HIGH
                                   SPEED READER.)

Ø012  ØØØ2  ØØØ3  ØØØ3  ØØØ5  ØØØ3  ØØØ4  ØØØ6  ØØØ5  ØØ11
ØØØ5  ØØ11  ØØ13  ØØ17  ØØ25  ØØ31  ØØ41  ØØ57  ØØ8Ø  Ø114
Ø159  Ø177  Ø229  Ø277  Ø349  Ø394  Ø444  Ø511  Ø556  Ø6Ø3
Ø643  Ø7Ø7  Ø723  Ø743  Ø754  Ø734  Ø752  Ø777  Ø755  Ø765
Ø76Ø  Ø76Ø  Ø733  Ø7Ø7  Ø716  Ø713  Ø731  Ø7Ø5  Ø749  Ø733
Ø698  Ø711  Ø697  Ø715  Ø727  Ø724  Ø722  Ø723  Ø772  Ø773
Ø735  Ø762  Ø779  Ø728  Ø717  Ø7Ø9  Ø645  Ø533  Ø571  Ø526
Ø464  Ø428  Ø392  Ø3Ø2  Ø254  Ø215  Ø173  Ø119  ØØ97  ØØ71
ØØ52  ØØ41  ØØ27  ØØ15  ØØØ9  ØØØ6  ØØØ4  ØØØ2  ØØØ3  ØØØ3
ØØØ3  ØØØ2  ØØØ1  ØØØ2  ØØØ1  ØØØ2  ØØØ1  ØØØ1  ØØØ1  ØØØ1

ØSM:                              (SMOOTH BLOCK ZERO DATA, IF YOU WISH.)

ØSC:                              (SCALE BLOCK Ø DATA;  Ø-5ØØ)

MIN=       1
MAX=     785
MPY=   Ø.637

        ***RAW DATA IN BLOCK Ø IS NOW READY FOR COMPARISON***
```

```
1CO:                              (COMPUTE A NEW SPECTRUM IN BLOCK 1)


NEW CALCULATION:

NO. OF POINTS= 100                (SAME AS FOR BLOCK Ø)
HAVE X DATA?N                     (ALWAYS ANSWER NO)
NO. OF PEAKS=3                    (ALWAYS ASSUMED 3 PEAKS FOR THIS STUDY)

X RNG, X1, INT. MPLR, BASE:       (XRNG=X-AXIS RANGE; DEPENDS ON M*)
300 Ø 1 Ø                         (X1=INITIAL POINT ON X-AXIS)
                                  (INT. MPLR=1)
                                  (BASE= BASELINE; SET TO ZERO)

HGT, H-WIDTH, POS:                (ENTER VALUES FOR EACH PEAK)
300 20 100
470 31 150
295 20 200


COOL IT !                         (COMPUTER IS CALCULATING SPECTRUM.)

              ***GENERATED PEAK IS DISPLAYED ON SCOPE***

SW:                               (DISPLAY BLOCK Ø ON SCOPE.)

SW:                               (RE-DISPLAY BLOCK 1.)

SU:                               (SUBTRACT BLOCK 1 FROM BLOCK Ø)

SU:                               (SUBTRACT AGAIN TO RESTORE DISPLAY)

1AL:                              (ALTER PARAMETERS FOR THE 3 PEAKS.)

PEAK AND PARA #'S:1 1             (GIVE PEAK #, THEN PARAMETER #)
TO:280                            (CHANGE THE HEIGHT OF PEAK 1 TO 280)

              ***   N 1:     HEIGHT OF PEAK N.
              ***   N 2:     WIDTH OF PEAK N.
              :::   N 3:     POSITION OF PEAK N.

              ***   Ø 1      INTENSITY MULTIPLIER.
              ***   Ø 2:     BASELINE

              ***   N Ø:     PRINTS PARAMETERS FOR PEAK N.
              ***   Ø Ø:     PRINTS OUT ALL PARAMETERS.
                             (EXIT IS MADE WITHOUT COMPUTING
                              SPECTRUM IN EITHER CASE.)

              ***   Ø -1:    EXIT ALTERATION MODE AND COMPUTE A
                             SPECTRUM FROM THE CURRENT PARAMETERS.
```

```
ØPL:                                (PLOT DATA IN BLOCK Ø ON X-Y PLOTTER)

CALIBRATE:
LINE PLOT?N                         ( Y - LINE PLOT.)
                                    ( N - POINT PLOT.)

OXOXOYOYOYOXOG                      (CALIBRATE PLOTTER; THEN COMMENCE
                                     PLOTTING.)

TURN PLTR OFF!                      (PLOTTER MUST BE TURNED OFF AS
                                     PROGRAM RETUNS TO SCOPE ROUTINES.)

1IN:                                (INTEGRATE DATA IN BLOCK 1.)

PIVOT LINE (Ø-5ØØ)= Ø               (USED Ø FOR ALL WORK IN THIS STUDY.)
MPY= Ø.49Ø629E-Ø1                   (I DIVIDED THIS NUMBER INTO 5Ø,ØØØ
                                     TO GET REASONABLE NUMBER FOR THE
                                     AREA UNDER THE CURVE.)
```

TO GET BACK TO THE KEYBOARD MONITOR, HIT THE HALT SWITCH.
SET THE SWITCH REGISTER TO 76Ø5.
THEN HIT ADDR LOAD, EXTD ADDR LOAD, CLEAR, AND CONT.

TO GET A LISTING OF THIS DESCRIPTION, GET A LISTING OF THE PRGM:
GASCAP.DS

```
.R PIP
*TTY:<DTAØ:GASCAP.DS/A/T            (HIT CARRAIGE RETURN)
```

APPENDIX D TLTPE4.DS Description program.

```
PAGE 1 OF TLTPE4.DS (VAN SWAAY) 2/12/74

TLTPE4.DS DESCRIBES THE FUNCTIONS OF TLTPE4.SV, WHICH IS A SAVE
IMAGE OF A TELETYPE DRIVER OCCUPYING PAGES 35 AND 36 OF
FIELD 0 (07200-07577). THE DRIVER HAS THE FOLLOWING ENTRY POINTS:

CHRIN   =7432           CHROUT  =7352
CRLF    =7437           MSGIN   =7200
MSGOUT  =7400           OCTIN   =7472
OCTOUT  =7541           WDSCAN  =7446

ALL BUFFERS USED IN THE DRIVER MUST BE LOCATED IN THE SAME FIELD
AS THE CALLING PROGRAM; BEFORE THE CALL, THE DATA FIELD MUST BE
SET TO THAT OF THE CALLING PROGRAM.


CHRIN IGNORES THE AC CONTENTS; IT ACCEPTS AN 8-BIT ASCII CHARACTER
FROM THE KEYBOARD AND RETURNS IT IN THE AC.


CHROUT PRINTS AN 8-BIT CHARACTER HELD IN THE AC, AND RETURNS
WITH A CLEAR AC. THE LINK IS NOT TOUCHED. BEFORE CHROUT IS USED
THE FIRST TIME, THE PRINTER FLAG MUST BE SET, NORMALL BY THE
INSTRUCTIONS  CLA; TLS, WHICH COULD BEST BE INSERTED AT THE
START OF THE PROGRAM.


CRLF GIVES A CARRIAGE RETURN AND LINE FEED, AND RETURNS WITH A
CLEAR AC. CRLF IGNORES THE CONTENTS OF THE AC ON ENTRY. CRLF CALLS
CHRIN AS PART OF ITS ROUTINE.


MSGIN ACCEPTS A STRING OF CHARACTERS ENTERED FROM THE KEYBOARD
AND PACKS THEM IN 6-BIT STRIPPED ASCII. THE ROUTINE
REQUIRES TWO PARAMETERS:
        JMS MGIN
        ADDRESS         /STARTING ADDRESS OF TEXT BUFFER
        LENGTH          /NUMBER OF WORDS IN THE BUFFER
RETURN,                 /RETURN TO MAIN PROGRAM WITH CLEAR AC

MSGIN ACCEPTS ALL CHARACTERS FROM THE KEYBOARD EXCEPT THE FOLLOWING:
        CTRL/C FORCES NON-DESTRUCTIVE RETURN TO THE MONITOR;
        CTRL/U DELETES THE CURRENT LINE AND ACCEPTS A NEW ONE;
        RUBOUT DELETES THE LAST CHARACTER ENTERED; A RUBOUT BEYOND
                THE FRONT OF THE LINE ECHOES AS ↑U AND CRLF TO ACCEPT
                A NEW LINE OF TEXT;
        LINE FEED IS IGNORED ON ENTRY.
MSGIN REJECTS CHARACTERS ENTERED AFTER THE BUFFER IS FULL; FURTHER
ENTRIES ARE ECHOED AS 'BELL'.
THE ROUTINE MAINTAINS A FULL WORD OF 0 AT THE END OF THE TEXT,
SO THAT THE CAPACITY OF A BUFFER IS 2(BUFFER LENGTH-1).
```

PAGE 2 OF TLTPE4.DS (VAN SWAAY) 2/12/74

MSGOUT PRINTS A CHARACTER STRING STORED IN 6-BIT STRIPPED ASCII,
WHICH MAY BE GENERATED WITH THE PAL8 'TEXT' PSEUDO-OP, OR WITH
MSGIN. IF THE ROUTINE IS ENTERED WITH -1 IN THE AC, THE TERMINATING
'CRLF' IS SUPPRESSED; WITH ALL OTHER VALUES OF THE AC ON ENTRY,
THE TEXT STRING IS TERMINATED WITH CARRIAGE RETURN AND LINE FEED.
MSGIN REQUIRES ONE PARAMETER:

```
        JMS MSGIN
        ADDRESS         /STARTING ADDRESS OF TEXT BUFFER
RETURN,                 /RETURN TO MAIN PROGRAM WITH CLEAR AC.
```

OCTIN ACCEPTS Ø-4 UNSIGNED OCTAL DIGITS FROM THE KEYBOARD, AND RETURNS
WITH THE OCTAL WORD IN THE AC. INVALID ENTRIES PRODUCE AN ERROR
RETURN WITH UNDEFINED CONTENTS OF THE AC. IF NO DIGITS ARE ENTERED
BEFORE THE 'RETURN' KEY IS STRUCK, THE ROUTINE ACCEPTS THE COMMAND
AS A VALID ENTRY OF Ø.
ON EXIT FROM OCTIN, THE ASCII CODES OF THE CHARACTERS
ENTERED REMAINS ACCESSIBLE (E.G. TO MGSOUT) IN A BUFFER STARTING
AT LOCATION OCTIN-3. OCTIN RECOGNIZES ALL EDITING COMMANDS OF
MSGIN. THE CALLING SEQUENCE TO OCTIN IS:

```
        JMS OCTIN
ERROUT,                 /ERROR RETURN, UNDEFINED AC
RETURN,                 /NORMAL RETURN WITH OCTAL WORD IN AC
```

OCTOUT PRINTS A 4-DIGIT OCTAL NUMBER HELD IN THE AC ON ENTRY.
THE CONTENTS OF THE LINK ON ENTRY ARE IGNORED; THE CONTENTS OF
THE LINK ON EXIT ARE UNDEFINED; THE AC=Ø ON EXIT.

WDSCAN IS A ROUTINE WHICH COMPARES THE CONTENTS OF THE AC HELD
ON ENTRY WITH ENTRIES IN A TABLE. THE TABLE CONSISTS OF 2-WORD
ENTRIES FOR EACH COMPARISON:

```
        TABLE,  FIRST TEST WORD
                REPLY TO FIRST TEST WORD
                SECOND TEST WORD
                REPLY TO SECOND TEST WORD
                .....
                .....
                Ø       /TABLE ENDS WITH A TRAILING TEST WORD OF ZERO
```

LITERATURE CITED

1 J.A. HIPPLE and E.U. CONDON, Phys. Rev., 68, 54 (1945).

2 A. YEO and D. WILLIAMS, Chem. Comm., 957 (1969).

3 R.G. COOKS, J.H. BEYNON, R.M. CAPRIOLI AND R.G. LESTER, Metastable Ions, Elsevier Scientific Pub. Co., Amsterdam: (1973) p.41 .

4-a M. BARBER, W.A. WOLSTENHOLME and K.R. JENNINGS, Nature, 214 , 664 (1967).

4-b G. EADON, C. DJERASSI, J.H. BEYNON and R.M. CAPRIOLI, Org. Mass Spectrom., 5 , 917 (1971).

5 J.H. BEYNON, Anal. Chem., 42 , 97A (Jan. 1970).

6 See Ref. 3, p. 41.

7 See Ref. 3, p. 49.

8 J.H. BEYNON and R.G. COOKS, Research/Development, 22 , 26 (1971).

9 See Ref. 3, p. 39.

10 K.C. SMYTH and T.W. SHANNON, J. Chem. Phys., 51 , 4633 (1969).

11 J.H. BEYNON, R.M. CAPRIOLI, W.E BAITINGER and J.W. AMY, Org. Mass Spectrom., 3 , 661 (1970).

12 E.G. JONES, L.E. BAUMAN, J.H. BEYNON and R.G. COOKS, Org. Mass Spectrom., 7 , 185 (1973).

13 J.H. BEYNON and A.E. FONTAINE, Z. Naturforsch., 22a , 334 (1967).

14 R.G. COOKS, M. BERTRAND, J.H. BEYNON, M.E. RENNEKAMP and D.W. SETSER, J. Amer. Chem. Soc., 95 , 1732 (1973).

15 J.H. BEYNON, M. BERTRAND and R.G. COOKS, Org. Mass Spectrom., 7 , 785 (1973).

16 Introduction to Programming, Digital Equipment Corporation, Maynard, Massachusetts, (1972).

17-a J.H. BEYNON, R.A. SAUNDERS and A.E. WILLIAMS, Ind. Chim. Belge, 29 , 311 (1964).

17-b M.M. BURSEY and F.W. McLAFFERTY, J. Amer. Chem. Soc., 88 , 5023 (1966).

17-c S. MEYERSON, I. PUSKAS and E.K. FIELDS, J. Amer. Chem. Soc., 88 , 4974 (1966).

17-d H. BUDZIKIEWICZ, C. DJERASSI and D.H. WILLIAMS, Mass Spectrometry of Organic Compounds, Holden-Day : San Francisco, Calif. (1967) p. 575.

18 J.H BEYNON, M. BERTRAND and R.G. COOKS, J. Amer. Chem. Soc., 95 , 1739 (1973).

19 R.G. COOKS and HOLMES, private communication.

20 R.G. COOKS, J.H. BEYNON, M. BERTRAND, M.K. HOFFMAN, Org. Mass Spectrom., 7 , 1303 (1973).

21 E.G. JONES, J.H. BEYNON and R.G. COOKS, J. Chem. Phys., 57 , 2652 (1972).

22 M.C. FLOWERS, Chem. Commun., 235 (1965).

V I T A

Marlin Dean FRIESEN was born in York, Nebraska on February 25, 1946. He grew up on a farm near Bradshaw, Nebraska where he lived with his parents, Mr. and Mrs. Henry C. FRIESEN and family, until his graduation from Bradshaw High School in 1964.

He entered Bethel College, North Newton, Kansas in August 1964 where he majored in Chemistry. After receiving a Bachelor of Arts degree from this school in 1968, he served with the Mennonite Central Committee as a conscientious objector to military service. From September 1968 through August 1969, he followed French language studies at l'Ecole d'Administration in Brussels, Belgium. From September 1969 through May 1971, he taught French language courses in Chemistry, Physics, Math and English in a Kimbanguiste Secondary School in N'Kamba-Jerusalem, Bas-Zaire, ZAIRE (Africa).

The author entered graduate school at Kansas State University, Manhattan, Kansas in August 1971. He became a Master of Science candidate in Analytical Chemistry under the direction of Dr. M.K. HOFFMAN.

In August 1972, he married the former Christine PEUGEOT of Versailles, FRANCE. They have two children: Timothée, born on May 2, 1973 and Ken, born on November 4, 1974.

SOFTWARE FOR ION KINETIC ENERGY SPECTROMETRY
and
THE METASTABLE LOSS OF NO· FROM HALO-NITROBENZENES

by

MARLIN DEAN FRIESEN

B.A., Bethel College, 1968

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1974

ABSTRACT

Our MS-9 mass spectrometer has been modified to permit observation and collection of refocussed metastable ion data using either the accelerating voltage or electrostatic sector scan modes. Software has been developed to provide rapid acquisition of precise and reproducable data along with data reduction capabilities for both graphical and digital output.

The loss of NO· from molecular ions of various halo-nitrobenzenes has been studied using this system. Metastable peak widths are used to determine the manner in which internal energy is partitioned to the kinetic and internal energies of the products of these reactions. Such measurements provide structural information on parent ions, daughter ions and mechanisms of the metastable decompositions. Existence of two competitive unimolecular processes for this decomposition is confirmed. Data are given which support a previous hypothesis associating the large kinetic energy release process with a 3-centered transition state. However, the smaller kinetic energy release may be due to a nitro-nitrite isomerization followed by simple cleavage rather than a previously postulated 4-centered mechanism.