MASTER
IS-T-837

DETERMINATION OF BOND ENERGIES BY MASS SPECTROMETRY.
SOME TRANSITION METAL CARBONYLS

Gary Dean Michels

Based on a Ph.D. thesis submitted to Iowa State University

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Date Transmitted: January 1979

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-eng-82

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Determination of bond energies by mass spectrometry.

Some transition metal carbonyls

by

Gary Dean Michels

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry

Major: Physical Chemistry

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1978

TABLE OF CONTENTS

Abstract	Page vii
I. INTRODUCTION	1
II. BACKGROUND	3
A. Bond Energies	3
1. Defined quantities	3
2. Approximate quantities	21
3. Determination by mass spectrometry	29
B. Appearance Potential Measurements	38
1. Positive ions	38
2. Negative ions	43
III. INSTRUMENTAL	45
A. Mass Spectrometer	45
B. Computer	47
C. Interface	49
1. Hardware	49
2. Software	55
a. Description of the system	56
1). Acquire	61
2). Background subtract	64
3). Chain	65
4). Delta-least-squares	65
5). Eliminate	67
6). File save	67
7). IE print	67
8). Mass print	67
9). Normalization parameters	67
10). Optimize	68
11). Print table	68
12). Read data	70
13). Set electron energy	70
14). Time	70
15). Warren's plots	70

	Page
b. Operation of the system	74
c. Limitation of the system	76
3. Tests of the interface	77
IV. EXPERIMENTAL	85
A. Preparation and Synthesis	87
1. Pentacarbonyl bromides of Mn, Tc, and Re	87
a. $\text{Mn}(\text{CO})_5\text{Br}$	88
b. $\text{Tc}(\text{CO})_5\text{Br}$	88
c. $\text{Re}(\text{CO})_5\text{Br}$	88
2. Mixed-metal decacarbonyls	89
a. $\text{MnRe}(\text{CO})_{10}$	90
b. $\text{MnTc}(\text{CO})_{10}$	91
c. $\text{TcRe}(\text{CO})_{10}$	91
B. Purification and Identification	91
1. Group VIIB pentacarbonyl bromides	91
2. Group VIIB mixed-metal decacarbonyls	92
V. RESULTS AND DISCUSSION	100
A. Group VIB Carbonyls and Thiocarbonyls	108
1. Mass spectra	110
2. Ionization potentials	114
3. Ionic bond dissociation energies	117
4. Neutral dissociation energies and heats of formation	132
5. Conclusions	135
B. Group VIIB Metal and Mixed-Metal Decacarbonyls	137
1. Mass spectra	141
2. Ionization potentials	141
3. Ionic bond dissociation energies	144

	Page
4. Neutral dissociation energies and heats of formation	158
5. Conclusions	159
VI. SUGGESTIONS FOR FURTHER RESEARCH	160
VII. BIBLIOGRAPHY	164
VIII. ACKNOWLEDGMENTS	169
IX. APPENDIX A: DIAGNOSTIC PROGRAMS	171
A. D-A Test Number One (DATST1)	172
B. D-A Test Number Two (DATST2)	179
X. APPENDIX B: IONIZATION EFFICIENCY ACQUISITION SYSTEM	182

Determination of bond energies by mass spectrometry.

Some transition metal carbonyls

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A mass spectrometer has been interfaced to a PDP-12 computer. Various tasks associated with acquisition and processing of ionization efficiency data are implemented under computer control. Fragmentation data obtained in this manner are analyzed by a least-squares approach to obtain bond dissociation energies which are dependent upon chemical environments.

Two groups of transition metal carbonyls have been studied, $M(CO)_6$ and $M(CO)_5CS$ complexes of the Group VIB metals and $M_2(CO)_{10}$ complexes of the Group VIIB metals. Results for the hexacarbonyl complexes indicate that the measured fragmentation energies are in error by 0.25 ± 0.02 eV per CO produced. This is attributed to excitation of CO to the first vibrational state. Least-squares dissociation energies calculated from corrected data for $M(CO)_5CS$ complexes indicate that the M-CS bond is 3-4 times stronger than the M-CO bonds. Substitution of CS for CO in going from $M(CO)_6$ to $M(CO)_5CS$ weakens the remaining M-CO bonds by an average of 0.2 eV.

Previously unreported $\text{MnTc}(\text{CO})_{10}$ and $\text{TcRe}(\text{CO})_{10}$ are prepared by halide substitution of $\text{Tc}(\text{CO})_5\text{Br}$ and $\text{Re}(\text{CO})_5\text{Br}$ with $\text{Mn}(\text{CO})_5^-$ and $\text{Tc}(\text{CO})_5^-$, respectively. In the positive ion, metal and mixed-metal decacarbonyls are considered as $(\text{CO})_5\text{M}^+-\text{M}(\text{CO})_5$ complexes possessing five strong and five weak M-CO bonds. For $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$, M^+-M dissociation energies are 3.0 ± 0.1 and 4.0 ± 0.3 eV, respectively. These energies are 2.5 times greater than those reported for homolytic cleavage to $\text{M}(\text{CO})_5^+$ and $\text{M}(\text{CO})_5$.

I. INTRODUCTION

A molecule can be thought of as a storehouse of energy. This energy is proportioned among the bonds of the molecule. Since most chemical reactions involve the breaking of old bonds and the making of new ones, the chemistry of the molecule is reflected by the energy of its bonds. Individual bond energies can be used to predict chemical reactivity and to calculate heats of formation [1, pp. 158-170]. They are important in the consideration of molecular structure.

Several methods have been developed to measure bond energies [2, Chapters 3-5]. One of them is mass spectrometry. The purpose of this research was to utilize a mass spectrometer to determine bond energies.

The practicality of using a mass spectrometer to measure the energies of chemical bonds was demonstrated by Stevenson [3, 4], but the method was not developed to its fullest potential. The early mass spectroscopists were primarily instrumentalists whose major concern was to develop consistent methods for obtaining physical data from a mass spectrometer. There was considerable debate over whose method was superior [5, pp. 26-37]. The calculation of bond energies was of secondary importance. From the onset it was apparent that the physical measurements were inherently inaccurate. The errors were difficult if not impossible to correct. Calculated values of bond energies were often 20-30% higher than the corresponding calorimetric values [6]. The value of the mass spectroscopic method was uncertain. The question of how to obtain useful information from such an inaccurate

method was evaded. The challenge of this research was to answer that question.

If useful information is to be obtained by the mass spectroscopic method, the data must be obtained as precisely as possible and any conclusions must be formulated by comparative studies. For precision a computerized method for acquiring and interpreting the data was developed. For comparison, the mass spectrometry of the Group VIB carbonyls and thiocarbonyls and the Group VIB metal and mixed-metal decacarbonyls was studied. Through these studies a deeper insight into the concept of a bond energy and into the nature of the bonding in transition metal carbonyls was attained. A new molecular quantity was defined and utilized as the measure of a bond energy.

II. BACKGROUND

A. Bond Energies

The term "bond energy" is one of the most misused terms in science [7]. The reason for this is not obvious because the phrase is correct conceptually. Chemical bonds are the binding forces between the atoms in a molecule. The energies of these interactions are rightfully referred to as bond energies. But there is no unique, measurable quantity known as a bond energy. Rather, there are three quantities which are collectively known as bond energies. They are bond dissociation energy, bond energy term, and intrinsic bond energy [8-16, 17, pp. 153-167].

1. Defined quantities

The idea of a bond dissociation energy originated from the principle that the strength of a chemical bond could be given by the energy required to break it. The concepts of a bond energy term and an intrinsic bond energy developed from the approximation that the heat of formation of a compound consists of several independent terms. For an ideal gas these terms are the vibrational zero point energy; thermal energy of vibration, rotation, and translation; and the chemical binding energy. Thus, the heat of atomization of a molecule in the ideal gas state can be related to the strength of the bonds comprising the molecule. Although the concepts are founded upon different principles, each quantity can be represented by the energy of a reaction.

The energies are enthalpy changes measured at 25° C and referenced to the ideal gas state. The reactions are the defining processes for each of the three quantities. Because these processes can be either ionic or molecular, a distinction must be made between bond energies in the cation, molecule, or anion¹.

The dissociation energy of a bond $R-S^2$ in the positive ion, molecule, or negative ion, $D(R^{+,o,-} S)$, is defined as the enthalpy change for the dissociation:

A reactant molecule (ion) in its ground state dissociates into two fragments by the cleavage of a chemical bond. The fragments may be atoms, radicals, or other molecules, but all are formed in their ground states. For ionic dissociations one of the fragments will be charged, and it is necessary to specify which fragment carries the charge. This specification must be made such that the enthalpy change for the process is a minimum. This means that the positive charge must reside with the fragment with the lowest ionization potential or the negative charge must reside with the fragment which has the highest electron affinity.

¹The symbolism $+,o,-$ will be used to denote these cases.

²The capital letters A, B, and C will be used to represent atoms while R, S, and T represent polyatomic species.

From the definition of a bond dissociation energy it is apparent that the defined and measured quantities are the same. This is not true for bond energy terms and intrinsic bond energies. To determine bond energy terms or intrinsic bond energies a term must be assigned to each bond in the molecule such that the heat of atomization of the molecule to a specified atomic reference state is given by the sum of these terms over all of the bonds in the molecule. The measured energy is the heat of atomization of the molecule. The defined quantity is an energy sum.

The bond energy sum (i.e. the sum of the bond energy terms) in the cation, molecule, or anion, $\sum_i E_i^{+,0,-}$, is the enthalpy change for the reaction:

A molecule (molecular ion) in its ground state dissociates completely into its constituent atoms (ion and atoms) in their ground states.

The intrinsic bond energy sum, $\sum_i I_i^{+,0,-}$, for a molecule (ion) is defined in a similar manner. This sum is the enthalpy change for the atomization reaction:

The reactant molecule (molecular ion) dissociates from its ground state into its composite atoms (ion and atoms) in their valence states, the hypothetical electronic states of the atoms as they exist in the molecule.

Because valence state excitation energies cannot be measured experimentally and are difficult to calculate theoretically, the concept of an intrinsic bond energy has met with little use. From a pragmatic viewpoint it is easier to determine and report bond energy terms than to argue the merits of one quantity over the other. If valence state energies are known, it is possible to calculate intrinsic bond energies from bond energy terms. The difference between the two quantities lies in the choice of the final atomic states. More energy is required to dissociate a molecule into atoms in their valence states than into atoms in their ground states. The energy difference is the sum of the valence state excitation energies of the j atoms in the molecule, $\sum_j V_j$. The relationship between the enthalpy of atomization, ΔH_{atom} and the enthalpy of dissociation of atoms in their valence states, ΔH_{vs} follows directly:

$$\Delta H_{\text{vs}} = \Delta H_{\text{atom}} + \sum_j V_j. \quad (4)$$

By definition:

$$\Delta H_{\text{vs}} = \sum_i I_i^{+,0,-} \quad (5)$$

and:

$$\Delta H_{\text{atom}} = \sum_i E_i^{+,0,-} \quad (6)$$

so that:

$$\sum_i I_i^{+,0,-} = \sum_i E_i^{+,0,-} + \sum_j V_j \quad (7)$$

Although the use of bond energy terms has supplanted that of intrinsic bond energies, bond energy terms are on equal footing with bond dissociation energies. Dissociation energies are founded upon experimental practicality but not upon theory. Energy terms have a firm foundation in theory but are difficult to determine experimentally because individual energy terms cannot be defined. Both quantities serve a useful purpose and should be understood completely. The approach of Szwarc and Evans [18] is useful for comparing and contrasting the two quantities.

The relative positions of the atoms in a molecule composed of m atoms and n bonds can be described by a set of $3m-6$ independent coordinates. A set of n bond lengths $r_1, r_2, \dots, r_n$ and $3m-6-n$ bond angles $\alpha_1, \alpha_2, \dots, \alpha_{3m-6-n}$ can be chosen for this purpose. With this terminology it is possible to write the potential energy of the molecule, U , measured from an energy zero represented by the separated atoms as a function of the r 's and α 's:

$$U = U(r_1, r_2, \dots, r_n, \alpha_1, \dots, \alpha_{3m-n-6}) \quad (8)$$

and:

$$dU = \sum_{k=1}^n \frac{\partial U}{\partial r_k} dr_k + \sum_{i=1}^{3m-n-6} \frac{\partial U}{\partial \alpha_i} d\alpha_i \quad (9)$$

The first term of Eq. 9 is the variation in the potential energy of the molecule due merely to stretching the bonds. The integral of this term from the equilibrium bond distances, r_{ko} , to infinity is the heat of atomization of the molecule:

$$\Delta H_{\text{atom}} = \sum_{k=1}^n \int_{r_{ko}}^{\infty} \partial U / \partial r_k \, dr_k \quad (10)$$

If the integration path of Eq. 10 is chosen such that:

$$\begin{aligned} \alpha_i &= \alpha_{io} \\ r_k &= \gamma r_{ko} \end{aligned} \quad (11)$$

α_{io} and r_{ko} being the equilibrium values of the coordinates in the molecule and γ being a variable which changes from 1 to ∞ , each element of the sum can be defined as a bond energy term. Thus:

$$E_k = \int_{r_{ko,L}}^{\infty} \partial U / \partial r_k \, dr_k \quad (12)$$

where L denotes the integration path defined previously.

The dissociation energy of the bond can be expressed in a similar manner:

$$D_k = \int_{r_{ko,P}}^{\infty} dU / dr_k \, dr_k \quad (13)$$

where:

$$\frac{dU}{dr_k} = \frac{\partial U}{\partial r_k} + \sum_{i=1}^n \frac{\partial U}{\partial r_i} \frac{dr_i}{dr_k} + \sum_{j=1}^{3m-n-6} \frac{\partial U}{\partial \alpha_j} \frac{d\alpha_j}{dr_k} \quad (14)$$

(Σ' denotes the sum over all i 's except $i=k$). The integration is over the total change in the potential energy of the molecule caused by stretching the bond along r_k from r_{k0} to infinity. The integration path P is defined such that for every fixed value of r_k the remaining parameters r_i and α_j are determined from the set of $3m-7$ equations:

$$\begin{aligned}\frac{\partial U}{\partial r_i} &= 0 \quad \text{for } i \neq k \\ \frac{\partial U}{\partial \alpha_j} &= 0 \quad \text{for all } \alpha_j \text{'s.}\end{aligned}\tag{15}$$

The implication of this pathway is that when the bond is being broken the rest of the molecule adjusts its shape to minimize the energy of the process.

By substitution of dU/dr_k from Eq. 14 into Eq. 13 the dissociation energy and energy term of the k th bond can be compared directly.

Performing this operation yields the result:

$$D_k = \int_{r_{k0,P}}^{\infty} \frac{\partial U}{\partial r_k} dr_k + \int_{r_{k0,P}}^{\infty} A dr_k \tag{16}$$

where:

$$A = \sum_{i=1}^n \frac{\partial U}{\partial r_i} \frac{dr_i}{dr_k} + \sum_{j=1}^{3m-n-6} \frac{\partial U}{\partial \alpha_j} \frac{d\alpha_j}{dr_k} \tag{17}$$

Clearly the two quantities are different. The energy term for the k th bond is the work done in separating the atom from the molecule in such a way that the molecule swells infinitely while preserving its original shape. The dissociation energy of the same bond is the work done separating the atom from the molecule while the molecule adjusts its

shape to minimize its potential energy during the process. This structural rearrangement results in an energy of reorganization which isn't present in the energy term. This energy is given by the second term of Eq. 16.

The most significant difference between the two quantities has been stated previously. Bond energy terms cannot be obtained as directly measured quantities. They must be calculated from a bond energy sum. This calculation is not a trivial process [2, Chapter 6].

The energy sum for a molecule with n chemical bonds consists of n individual bond energy terms. This sum, when equated to the heat of atomization of the molecule, results in one equation with n unknowns:

$$\Delta H_{\text{atom}} = \sum_{i=1}^n E_i \quad (18)$$

This equation cannot be solved, but usually can be simplified. The simplification is made by grouping the energy terms of chemically equivalent bonds, since chemically equivalent bonds have the same energy term. If all of the bonds of the molecule were chemically equivalent (e.g. AB_n), the energy sum would reduce to one term. This term would be $1/n$ times the heat of atomization of the molecule. For example Eq. 18 reduces to:

$$\Delta H_{\text{atom}} (AB_n) = n E(A-B) \quad (19)$$

for molecules of the general formula AB_n . As is most likely the case, the reduced sum will involve more than one unknown (e.g. the energy

sum for the molecule $AB_{n-1}C$ simplifies to $(n-1) E(A-B) + E(A-C)$. In this case an arbitrary assumption must be introduced to solve for the individual energy terms. This assumption, known as the constancy assumption, asserts that the energy term for a given bond is constant from molecule to molecule. It is not an easy hypothesis to accept because it implies that bond energies are independent of chemical environment. However there is no alternative but to accept the constancy assumption if energy terms are to be calculated from heats of atomization.

Two approaches can be devised to calculate bond energy terms based upon this approximation. The first method is to combine the data from many different molecules to form a system of equations with at least as many unknowns as there are equations. This system can be solved by standard methods for the individual bond energy terms. When the calculation is done by this procedure there is no unique value for a given energy term. As more data are obtained for a greater variety of molecules, the existing values of energy terms may be readjusted in the process of calculating new terms. At any given time the reported value for an energy term will be the best value based upon existing information.

The second procedure for calculating energy terms is to use the terms calculated for molecules having n equivalent bonds (e.g. AB_n) as "primary" standards. These standard values are used to reduce other energy sums so that new energy terms can be determined. This collection

of information can be used to simplify additional energy sums producing values for different energy terms. As long as enough information is available the whole process can be repeated indefinitely.

As an example of this method consider the molecule $AB_{n-1}C$. For this molecule Eq. 18 reduces to:

$$\Delta H_{\text{atom}}(AB_{n-1}C) = (n-1) E(A-B) + E(A-C). \quad (20)$$

Substituting for $E(A-B)$ from Eq. 19 yields the result:

$$\Delta H_{\text{atom}}(AB_{n-1}C) = \frac{(n-1)}{n} \Delta H_{\text{atom}}(AB_n) + E(A-C) \quad (21)$$

which gives $E(A-C)$ in terms of the measured heats of atomization. These two values, $E(A-B)$ and $E(A-C)$, could then be used to determine $E(A-D)$ from the molecule $AB_{n-2}CD$ and so on. Hopefully this procedure will produce a consistent set of data (e.g. $E(A-C)$ calculated from Eq. 21 will agree with $E(A-C)$ determined from the heat of atomization of AC_n). Often this has been found not to be the case because bond energies are dependent upon chemical environments.

A method for determining energy terms independent of the constancy assumption has been developed as a result of this research. The insight for this development originated from the relationship between bond energy terms and bond dissociation energies.

The specific dissociation energies for the AB_n molecule are the enthalpy changes for each of the n processes:

$$\vdots$$

For the i th process ($i=1, 2, \dots, n$):

$$\Delta H_i = D_i(AB_{n-i} - B). \quad (23)$$

The sum of the enthalpies of all of the processes:

$$\sum_{i=1}^n \Delta H_i = \sum_{i=1}^n D_i(AB_{n-i} - B) \quad (24)$$

is the energy of the atomization reaction:

By definition this energy is the heat of atomization of the molecule which is the bond energy sum given by Eq. 19:

$$\sum_{i=1}^n \Delta H_i = \Delta H_{\text{atom}}(AB_n) = nE(A-B). \quad (26)$$

Substituting this relationship into Eq. 24 and dividing by n yields:

$$E(A-B) = 1/n \sum_{i=1}^n D_i(AB_{n-i} - B). \quad (27)$$

A molecular quantity, the A-B bond energy term, is given by the average of the specific bond dissociation energies of the molecule. If the molecule contains more than one kind of a bond, the energy terms cannot be calculated as averages of the bond dissociation energies. The bond energy sum will be given by a sum of dissociation energies, but the calculation will involve the solution of one equation in more than one unknown. This cannot be done without the constancy assumption. To avoid this assumption energy terms have to be calculated from the

energies of molecular fragmentations rather than the stepwise dissociation energies.

The mechanics of this method can be demonstrated by reconsidering the AB_n molecule. The n fragmentation reactions of this molecule are summarized by the general equation:

for $i = 1, 2, \dots, n$. The enthalpy changes for these fragmentations are sums of the dissociation energies of the molecule. For the i th process:

$$\Delta H_i = \sum_{j=1}^i D_j(AB_{n-j} - B). \quad (29)$$

These enthalpies can be related to the bond energy term, $E(A-B)$, through an application of Hess's Law. The n fragmentations of Eq. 28 can be reconstructed into n two step processes:

The enthalpy change for the complete process, ΔH_i , is the sum of the enthalpy changes of the two steps which by definition are bond energy sums. Therefore:

$$\Delta H_i = \sum_{k=1}^n E_k(A-B) - \sum_{\ell=1}^{n-i} E_{\ell}'(A-B) \quad (31)$$

where the prime differentiates the bond energy terms in the fragment from those in the molecule. Neglecting this differentiation and simplifying the bond energy sums yields a set of n equations relating the bond energy term to the i th fragmentation enthalpy:

$$\Delta H_i = i E(A-B) \quad (32)$$

for $i=1, \dots, n$. This over-determined system can be reduced to one equation in one unknown by requiring that the sum of the squares of the deviations of the calculated enthalpies from the measured enthalpies of fragmentation be a minimum [19, Chapters 5 and 6]. The equation obtained from the least-squares treatment is the desired result:

$$\sum_{i=1}^n i^2 E(A-B) = \sum_{i=1}^n i \Delta H_i. \quad (33)$$

The energy term calculated from Eq. 33 is an approximation to the exact quantity expressed by Eqs. 19 and 27. Substitution of ΔH_i from Eq. 29 into Eq. 33 shows that $E(A-B)$ is not the average of the specific bond dissociation energies:

$$\sum_{i=1}^n i^2 E(A-B) = \sum_{i=1}^n i \sum_{j=1}^i D_j(AB_{n-j} - B). \quad (34)$$

In the exact calculation each of the n dissociation energies is weighted equally by $1/n$. The approximate solution weights each energy unequally. By expanding and regrouping the dissociation energy sum of Eq. 34 and dividing by $\sum_{i=1}^n i^2$, it can be seen that the weighting factor of the i th dissociation energy is $\sum_{j=i}^n j / \sum_{i=1}^n i^2$:

$$E(A-B) = 1/\sum_{i=1}^n i^2 \left[\sum_{i=1}^n \sum_{j=i}^n j D_i(AB_{n-i} - B) \right]. \quad (35)$$

The assumption that there is no difference between the A-B energy term in the molecule and the fragment is the basis for the inequality of the weighting factors. In effect what has been assumed is that the molecule does not reorganize upon fragmentation.

The reorganizational energy of a fragment is the difference between its heat of atomization and the bond energy sum in the fragment as calculated from the energy terms in the parent molecule. The reorganization energy of the i th fragment of Eq. 28, O_i , is given by:

$$O_i = \Delta H_{i(\text{atom})}(AB_{n-i} - B) - \sum_{j=1}^{n-i} E(A-B) \quad (36)$$

where by definition:

$$\Delta H_{i(\text{atom})}(AB_{n-i} - B) = \sum_{\ell=1}^{n-i} E_{\ell}'(A-B). \quad (37)$$

Substituting Eq. 37 into Eq. 36 yields the relationship between the bond energy sum in the i th fragment and the molecule:

$$\sum_{\ell=1}^{n-i} E_{\ell}'(A-B) = \sum_{j=1}^{n-i} E(A-B) + O_i. \quad (38)$$

When this result is substituted into Eq. 31 and the bond energy sums are simplified, the exact system of equations is:

$$\Delta H_i = i E(A-B) + O_i \quad (39)$$

which is the same as Eq. 32 if the reorganization energies are neglected. The constancy assumption has been replaced by the assumption that

reorganization energies are negligible. This statement is not apparent from the preceding discussion because there are not environmental effects for the AB_n molecule. These effects however exist for the $AB_{n-1}C$ molecule.

The fragmentations of this molecule can be divided into two sets of reactions. The first group is the $n-1$ fragmentations:

where $i = 1, 2, \dots, n-1$. The product fragments in these equations contain the A-C bond. The second set of reactions consists of the n fragmentations which involve the cleavage of the A-C bond. The j th process is:

where the reaction set is generated by letting j vary from 0 to $n-1$. The enthalpy changes for the $2n-1$ fragmentations of Eqs. 40 and 41 are the measured quantities. These energies can be related to the bond energy terms of the molecule by the method described previously. Each fragmentation reaction is represented by a two step process. The molecule dissociates into its constituent atoms which recombine to form the products. By assuming that there is no difference between the energy term in the molecule and the fragment a series of observational equations are generated. In this case the equations are:

$$\Delta H_i = i E(A-B)_c \quad i = 1, 2, \dots, n-1 \quad (42)$$

for the first collection of fragmentations and:

$$\Delta H_j = (n-1)E(A-B)_C + E(A-C) - (n-1-j)E(A-B) \quad (43)$$

$$j=0, 1, \dots, n-1$$

for the second. These $2n-1$ equations can be reduced by the least-squares method to three equations in three unknowns, the normal equations. The normal equations can be solved directly for the bond energy terms. The calculated quantities would be the energy term for the AC bond, $E(A-C)$; the energy term for the AB bond in the presence of C, $E(A-B)_C$; and the energy term for the AB bond in the unsubstituted molecule, $E(A-B)$. These results will show whether the A_C bond differs in strength from the AB bonds and whether the A_C bond influences the strength of the AB bonds (i.e., either $E(A-C) = E(A-B)$ or $E(A-C) \neq E(A-B)$ and either $E(A-B)_C = E(A-B)$ or $E(A-B)_C \neq E(A-B)$). In other words the calculation allows for the determination of the energy terms without the constancy assumption.

To prove this contention it is necessary to show that a unique solution for $E(A-C)$, $E(A-B)_C$, and $E(A-B)$ exists. Unfortunately an explicit solution for each of the energy terms as a function of the measured fragmentation energies cannot be written without developing additional terminology. However there will be a unique solution if the determinant of the coefficient matrix of the normal equations is not zero. For this to be true at least three of the observational equations must be linearly independent. This follows from Eqs. 42 and 43.

The results of the preceding discussion have shown that the least-squares method is a powerful tool for elucidating bond energy terms. The method has been developed for two classes of molecules, AB_n and $AB_{n-1}C$, but is applicable to any molecule as long as the limitations of the procedure are understood and considered. There are three potential problems. Two involve the calculation of the energy terms and one involves their interpretation.

In the development of the procedure the assumption has been made that the fragmentation reactions for a molecule can be measured or calculated from other experimental data. These measurements are not easy to obtain for many molecules, because the fragments must be independent, stable moieties. Enough information must be available to generate as many equations as there are unknown energy terms. Even then a solution may not be possible, because there must be as many linearly independent observational equations as there are unknowns. Those situations where this isn't true can be remedied by finding an appropriate combination of the original energy terms so that the condition is met. Both the applicability and utility of the least-squares method will be restricted by these considerations.

The most significant limitation of the method is the assumption that energy terms can be calculated by neglecting fragment rearrangement energies. This assumption cannot be avoided because reorganization energies are generally not available from theoretical calculations, and they cannot be determined experimentally. Their experimental calculation requires precise knowledge of the bond energy terms of the parent

molecule, but the exact calculation of the energy terms by the least-squares method requires that the energies of reorganization be known. One quantity cannot be calculated without the other. The net effect is that the results of the least-squares calculation are ambiguous. There is no certainty whether an environmental effect is real or merely the result of neglecting reorganizations. For some molecules the data itself may suggest a solution to this problem. The calculated energy terms for the $AB_{n-1}C$ molecule provide such an example.

The A-B energy term may be affected by C. The value of $E(A-B)_C$ obtained from the least-squares solution will be ambiguous, because it may reflect the difference in rearrangement energies between those fragments containing C and those that do not. This question can be resolved by checking the internal consistency of the A-B energy term. If $E(A-B)$ calculated from the $AB_{n-1}C$ fragmentation enthalpies agrees with the value determined for the AB_n molecule, the effects due to fragment reorganization should be similar for both molecules. Any difference between $E(A-B)_C$ and $E(A-B)$ can be attributed to environmental effects. Their absolute values will involve reorganization energies. The extent to which these energies affect the accuracy of the terms can be determined by comparing the least-squares value of $E(A-B)$ with the exact value calculated from Eq. 19. If the energies of reorganization are small or by chance cancel, both results will agree. If the values do not coincide, the accuracy of the method and a qualitative understanding of the nature of fragment reorganization for these molecules can be obtained.

The least-squares method like the other methods for calculating energy terms is an approximation. None of the methods can be judged to be superior in an absolute sense. The data for each molecule must be judged separately. What is gained by avoiding the constancy assumption may be lost by neglecting energies of reorganization and vice versa.

The approximate methods for calculating bond energy terms have not detracted from their desirability or utility. An energy term is a molecular quantity. One term exists for the chemically equivalent bonds in a molecule. This term represents the amount of chemical energy that is stored in the bond. For this reason it is possible to compare bond strengths in different molecules through energy terms. The same considerations do not apply for bond dissociation energies because they are the sum of the energy required to break the bond and the energy absorbed or released when the resulting fragment or fragments reorganize to their minimum energy states. Therefore it is just as difficult to compare dissociation energies as it is to calculate energy terms.

2. Approximate quantities

The defining process for the bond energy sum (Eq. 2) stipulates that the molecular fragmentation must be to atoms. In many instances experimental data can be obtained where the fragmentation is not to atoms but to polyatomic ligands (e.g. $A(BC)_n \rightarrow A + nBC$). In these cases the definition can be extended and new molecular quantities can be defined. They are average bond dissociation energy and least-squares

bond dissociation energy. For clarity and ease of presentation the concepts will be developed for molecules consisting of polyatomic ligands bonded to a central atom.

The concept of an average bond dissociation energy has appeared in the literature [20], but no formal definition has been given. The idea probably originated from an application of Eq. 27 from which it can be seen that an A-B energy term is an average of the molecular dissociation energies. As a first approximation, the average bond dissociation energy of the A-R bond, $\bar{D}(A^{+,o,-}R)$, would be $1/n$ times the heat of the reaction:

where the reactant and products are ideal gases in their ground states at 25° C. The problem with specifying average dissociation energies in this manner is that the definition lacks generality. The average A-R and A-S bond dissociation energy in the $AR_{n-1}S$ molecule are indeterminant. A more general approach would be to define an average bond dissociation energy sum in a manner analogous to the bond energy sum (Eq. 2). The average bond energy sum in the cation, molecule, or anion $\sum_i \bar{D}_i^{+,o,-}$, would be the enthalpy change at 25° C for the reaction:

The reactant molecule (molecular ion) in its ground state fragments to its constituent atom (ion) and polyatomic ligands in their ground states. For ionic fragmentations the charge resides on the central

atom, although this may not be the lowest energy process.

According to this definition the individual quantities must be calculated from a dissociation energy sum. The same considerations will apply for these calculations as did for the calculation of energy terms from bond energy sums. For molecules containing n identical ligands the calculation will be exact. Otherwise, the assumption that the average dissociation energy of a bond is invariant from molecule to molecule will have to be made. This assumption can be circumvented by calculating average bond dissociation energies from the enthalpies of molecular fragmentation reactions rather than from an energy sum. The procedure is identical to the method developed for calculating bond energy terms but without the constancy assumption. Equations 28-43 apply directly with two changes in the notation. The atomic ligands B and C must be replaced by their polyatomic analogues R and S, and the symbol E must be replaced by $\bar{D}$ since average dissociation energies are the calculated quantities. The results of the least-squares calculation will be approximations to the "true" average dissociation energies of the bonds because the enthalpies of fragmentation include the reorganization energies of the fragments containing the central atom. Rather than to calculate an approximation of an approximate quantity, it is convenient to define a new quantity. This quantity is called a least-squares bond dissociation energy and is denoted by $\hat{D}$.

Least-squares bond energies cannot be related to the enthalpy change of a single defining process. Instead they are calculated from

the energies of all possible fragmentation reactions of a molecule. Hence a general definition of the quantity is not possible. Only a general description of the method of calculation can be given. The first step of this procedure is to write all possible fragmentation reactions for a given molecule and to identify the different kinds of bonds in the molecule and in those fragments which are not the ligands. The energy of each of these bonds is given by the appropriate least-squares bond energy. The next step is to rewrite each fragmentation reaction as a sum of two processes in which the molecule dissociates to its constituent atom(s) and ligand(s) which then recombine to form the desired fragments. When this is done, the energy of each fragmentation is written as a difference between the least-squares energy sum in the molecule and in the fragment. Every energy sum is simplified by noting that chemically equivalent bonds have the same least-squares bond energy. Like terms in the same equation are combined by assuming that least-squares energies are independent of the valence state of the central atom. The resulting set of equations constitutes the observational equations. These are transformed into the normal equations which are solved for the $\hat{D}$'s in the final two steps.

The limitations of this procedure are the same as those described previously for the calculation of energy terms by this method. There must be as many linearly independent observational equations as there are unknowns. The results must be interpreted cautiously since the rearrangement energies of the fragments are included in a calculated result.

Both average and least-squares bond dissociation energies have been defined experimentally. The definitions are intended to provide a practical means of calculating bond energies from experimental data. They reveal very little information about the nature of the quantities. By applying the definitions to a specific molecule, $A(BC)_n$, the molecular nature of the two quantities can be compared and contrasted. This will lead to a generalized understanding of the concepts so that they can be applied to any kind of molecule.

The two concepts are based upon the idea of calculating a molecular bond energy from the dissociation energies of a molecule. Average bond dissociation energies and least-squares bond energies are equal to a weighted sum of the specific bond dissociation energies of a molecule. For the $A(BC)_n$ molecule these relationships can be specified by transforming Eqs. 27 and 35:

$$\bar{D}(A-BC) = 1/n \sum_{i=1}^n D_i(A(BC)_{n-i} - BC) \quad (46)$$

and:

$$\hat{D}(A-BC) = \frac{1}{\sum_{i=1}^n i^2} \left[\sum_{i=1}^n \sum_{j=i}^n j D_i(A(BC)_{n-i} - BC) \right]. \quad (47)$$

The average bond dissociation energy is, as the name implies, an average of the specific dissociation energies while least-squares bond dissociation energies are weighted averages of the same dissociation energies. Qualitatively this conclusion will be true regardless of the nature of the molecule.

The molecular nature of the two quantities is founded upon their relation to the bond energy terms of the molecule. It is possible to derive this relationship for $\bar{D}(A-BC)$ by considering the fragmentation of $A(BC)_n$ as follows:

From the conservation of energy and the definitions of Eqs. 2 and 45, it follows that:

$$\sum_g \bar{D}_g = \sum_i E_i - \sum_k E_k \quad (49)$$

where:

$$\sum_g \bar{D}_g = \sum_{g=1}^n \bar{D}_g(A-BC) = n \bar{D}(A-BC), \quad (50)$$

$$\sum_i E_i = \sum_{i=1}^{2n} E_i = n E(A-BC) + n E(B-C)_{\text{bound}}, \quad (51)$$

and:

$$\sum_k E_k = \sum_{k=1}^n E_k' = n E(B-C)_{\text{free}}. \quad (52)$$

The subscripts bound and free differentiate between the energy term in the bound and free ligand. Substituting for $\sum_g \bar{D}_g$, $\sum_i E_i$, and $\sum_k E_k$ in Eq. 49 and eliminating n from the resulting equation yields:

$$\bar{D}(A-BC) = E(A-BC) + E(B-C)_{\text{bound}} - E(B-C)_{\text{free}}. \quad (53)$$

The average dissociation energy of the A-BC bond includes the difference between the energies of the bound and free B-C ligand. Qualitatively this conclusion will be true for the average dissociation energy of any bond in any molecule. The quantitative result is given by Eq. 49. The average energy sum is equal to the sum of the energy terms in the molecule minus the sum of the energy terms in the free ligand. If there is no difference between the bond energy terms in the free and bound ligands, the average energy sum is equal to its corresponding bond energy sum. With one additional assumption, the same conclusion is true for least-squares bond energies. The derivation is analogous.

The i th fragmentation of $A(BC)_n$ can be represented by the following mechanism:

The enthalpy change for this fragmentation, ΔH_i , is given by:

$$\Delta H_i = \sum_{j=1}^{2n} E_j - \left[\sum_{k=1}^{2(n-i)} E'_k + i E(B-C)_{\text{free}} \right] \quad (55)$$

where:

$$\sum_{j=1}^{2n} E_j = n E(A-BC) + n E(B-C)_{\text{bound}} \quad (56)$$

and:

$$\sum_{k=1}^{2(n-i)} E'_k = (n-i) E'(A-BC) + (n-i) E'(B-C)_{\text{bound}} \quad (57)$$

The prime superscript differentiates an energy term in the molecule from the corresponding term in the fragment. The relationship between ΔH_i and $\hat{D}(A-BC)$ follows from Eq. 32:

$$\Delta H_i = i \hat{D}(A-BC). \quad (58)$$

Substituting Eqs. 56, 57, and 58 into Eq. 55 gives:

$$i \hat{D}(A-BC) = n E(A-BC) - (n-i)E'(A-BC) + n E(B-C)_{\text{bound}} - (n-i)E'(B-C)_{\text{bound}} - i E(B-C)_{\text{free}}. \quad (59)$$

This equation can be simplified by postulating that corresponding energy terms in the fragment and molecule are equal. When this assumption is made the dependence upon i cancels and:

$$\hat{D}(A-BC) = E(A-BC) + E(B-C)_{\text{bound}} - E(B-C)_{\text{free}}. \quad (60)$$

As expected $\hat{D}(A-BC)$ approximates $\bar{D}(A-BC)$ within the limitation of the previous assumption. However this hypothesis does not obviate the molecular nature of the quantity. It will always be possible to write the least-squares energy of a bond as a linear combination of the energy terms of the molecule and fragments.

Least-squares bond dissociation energies are the ultimate approximate quantities. As long as the "right" fragmentation data are available, the method can be applied to any molecule. Depending upon the specific nature of the fragmentations (i.e. whether they are to atoms, polyatomic ligands, or some combination of the two), the results may approximate bond energy terms or average bond dissociation energies.

The important point to remember is that the least-squares energy of a bond will be a "good" molecular quantity as long as rearrangement energies are small in comparison to the inherent energy of the bond.

3. Determination by mass spectrometry

An experimental method for determining bond energies must provide a means of fragmenting a molecule, of identifying the fragments, and of measuring the energy of the process. A mass spectrometer is conveniently suited for this purpose. Electrons of known energies interact with a molecule to produce ionization and dissociation. The ionic fragments of the dissociation are mass analyzed and detected. In this capacity a mass spectrometer is a calorimeter used to measure the energies of ionic fragmentation reactions. These energies are used to calculate ionic bond energies.

Three physical measurements can be obtained by mass spectroscopy. They are ionization potentials, electron affinities, and appearance potentials. The ionization potential of a molecule $A_l B_m C_n \dots$, $IP(A_l B_m C_n \dots)$, is the energy required to remove an electron from the molecule. The quantity is formally defined as the change in internal energy for the process:

In a mass spectrometer the energy for this endothermic reaction is supplied by the kinetic energy of the electrons in the ionizing beam. Therefore Eq. 61 is more appropriately written as:

In this process the transition to the ionic state is vertical in contrast to the adiabatic transition of the definition. The molecular ion will be excited vibrationally and rotationally, and the measured ionization potential will include this excess energy.

The electron affinity of a molecule, $EA(A_l B_m C_n \cdots)$, is the energy released when the molecule acquires an electron. The concept is defined in the opposite sense as the energy of the reaction:

In a mass spectrometer the internal energy change of the reverse process is measured (i.e. $-EA(A_l B_m C_n \cdots)$). In many cases the energy released as the electron is absorbed is sufficient to dissociate the molecule so that the negative molecular ion is not formed and its electron affinity cannot be measured.

The appearance potential of either a positive or negative ionic fragment, $AP(A^{+,-})$, is the minimum electron energy necessary to produce that ion. Experimentally the quantity is defined as the internal energy change for the process:

for the positive ion or:

for the negative ion. Ideally the ionic and neutral products are formed at rest in their ground states. In reality the products are likely to possess kinetic energy and may be produced in excited states. It is apparent from the definitions that ionization potentials or electron affinities are appearance potentials of the molecular ion.

The possibility of using a mass spectrometer to determine bond energies rests upon the relationship between these physical measurements and the experimental definitions of bond energies. Appearance potentials are not directly related to bond energies. What can be correlated is the difference between the appearance potential of an ion and the ionization potential of the molecule in the case of positive ions. For negative ions the association is based upon the sum of an appearance potential and the electron affinity of the molecule. Subtracting Eq. 62 from Eq. 64 or adding Eqs. 63 and 65 yields the general result:

The change in internal energy for this fragmentation is given by:

$$\Delta E^+ = AP(A^+) - IP(A_l B_m C_n \cdots) \quad (67)$$

for the cationic process or:

$$\Delta E^- = AP(A^-) + EA(A_l B_m C_n \cdots) \quad (68)$$

for the anionic reaction. Eq. 66 can be compared directly with the defining processes of Eqs. 1 and 2. If a simple neutral product is formed by the cleavage of one bond, the fragmentation corresponds to

that defined for a bond dissociation energy. If the neutral products are atoms, the reaction agrees with that defined for a bond energy sum. However, herein lies the first limitation of the method, the identification of the neutral fragments.

A mass spectrometer only provides a means of identifying the mass of the charged fragment. The neutral fragment or fragments of a dissociation process cannot be identified. This restriction constrains the use of a mass spectrometer to studies of bond energies in diatomic molecules or molecules with central atoms in which the ligands are atoms or "simple" molecules. If the ligands are polyatomic, the energies of the bonds within the ligand must be greater than the central atom - ligand bond energy. For these kinds of molecules the assignment of neutral fragmentation products will be unambiguous.

Even in those cases where neutral fragments can be specified further considerations will limit the applicability of the method. The definitions of bond energies designate that the fragmentations must take place in the ideal gas state at 25° C. Furthermore the enthalpy change of the process referenced to the ground states of the reactant molecule and product fragments must be measured. In a mass spectrometer the fragmentation processes occur near room temperature at pressures less than 10^{-5} Torr. These conditions approximate those described in the definitions very well. The internal energy changes of the fragmentations are measured while changes in enthalpies are required. The difference between the two quantities is the $\Delta(PV)$ work

term. For the unimolecular decompositions which occur in a mass spectrometer this term has no meaning so that ΔE can be equated with ΔH . Thus the ΔE 's of Eqs. 67 and 68 can be replaced with ΔH 's, but the reference state is not the ground states of the reactant and products. The molecular ion is produced in an excited vibrational state and the fragments may contain excess energy. There is no alternative but to neglect these excitation energies if bond energies are to be determined by mass spectrometry. It is a good assumption that the molecular ion and all fragments are formed in their ground electronic states. The assumption that these species are formed without any excess vibrational, rotational, or kinetic energies severely restricts the accuracy of the method. If good quantitative results are to be obtained, a method must be devised to correct for excess energies.

The preceding discussion indicates that a mass spectrometer can be used to determine ionic fragmentation energies if the natural products can be identified and if excess energies can be neglected. The fragmentation enthalpies are given by Eqs. 67 and 68. These energies will be either an ionic bond dissociation energy or an ionic bond energy sum if Eq. 66 corresponds exactly to one of the definitions. Intrinsic bond energies cannot be determined by this method.

In general fragmentation energies are obtained for many different fragment ions of a molecule. The fragmentation data will resemble that described by Eqs. 28, 40, and 41 for the anion or cation. These data are amenable to treatment by the least-squares method whereby

ionic least-squares bond dissociation energies can be calculated. If the products are atoms, the least-squares energies will be ionic bond energy terms. If the products are polyatomic ligands or some combination of atoms and ligands, the least-squares energies themselves will be the calculated molecular quantities.

Only bond energies in the molecular ion can be related to the measured quantities. But the relative ease with which these bond energies can be determined by mass spectrometry is readily apparent. Unfortunately ionic bond energies are not as desirable as the same energies in the neutral molecule because the chemistry of the two species are different. For this reason the relationships between bond energies in the positive or negative molecular ion and those in the neutral molecule are of paramount importance for the complete realization of the potential of the method.

The correlation between ionic and neutral bond energies is based upon the principle that it is immaterial whether the molecule first dissociates and one of the fragments is ionized or whether the molecule is ionized first and then dissociates. For bond energy terms this means that the dissociation process should be written as:

Since the energy change for the overall process is independent of the path:

$$IP(A_{\ell} B_m C_n \dots) + \sum_i E_i^+ = \sum_i E_i + IP(A) \quad (70)$$

or:

$$IP(A_{\ell} B_m C_n \dots) - IP(A) = \sum_i E_i - \sum_i E_i^+ \quad (71)$$

for the cation-neutral fragment relationship and:

$$EA(A) - EA(A_{\ell} B_m C_n \dots) = \sum_i E_i - \sum_i E_i^- \quad (72)$$

for the anion-neutral fragment relationship. By following a similar procedure the analogous relationships can be obtained for intrinsic bond energies and bond dissociation energies. The results are given by the following equations:

$$IP(A_{\ell} B_m C_n \dots) - IP(A^*) = \sum_i I_i - \sum_i I_i^+, \quad (73)$$

$$EA(A^*) - EA(A_{\ell} B_m C_n \dots) = \sum_i I_i - \sum_i I_i^-, \quad (74)$$

$$IP(R_1 R_2) - IP(R_1) = D(R_1 - R_2) - D(R_1^+ - R_2), \quad (75)$$

$$EA(R_1) - EA(R_1 R_2) = D(R_1 - R_2) - D(R_1^- - R_2) \quad (76)$$

where A^* denotes the atom in its valence state.

The ionization potential and electron affinity of the ionic fragment are the keys to the interconnection of ionic and neutral bond energies. Once this information is obtained the appropriate bond

energy differences can be calculated. Only for bond dissociation energies or for molecules containing one kind of a chemical bond is a relationship between individual quantities possible. Equations 75 and 76 can be solved directly for the dissociation energy in the molecule. For the AB_n molecule the right-hand sides of Eqs. 71-74 reduce to $n[E(I)(A-B) - E(I)(A^{+,-}-B)]$ and the equations can be solved directly. If the molecule contains more than one kind of a bond the energy sums of Eqs. 71-74 will reduce to more than one term. A solution for the equations cannot be obtained without additional information or assumptions. Regardless, the following generalizations will always be true. Bond energies in the $+,-$ ion will parallel those in the molecule. Trends in ionic energies will usually reflect those in the molecules.

Ionic-neutral correlations can also be derived for the approximate quantities $\bar{D}$ and $\bar{D}$. Since average bond dissociation energies are defined for fragmentations into ligands rather than atoms, Eqs. 71 and 72 can be transformed directly to the corresponding equations for this quantity. Hence:

$$IP(A R_\ell S_m T_n \cdots) - IP(A) = \sum_i \bar{D}_i - \sum_i \bar{D}_i^+ \quad (77)$$

and:

$$EA(A) - EA(A R_\ell S_m T_n \cdots) = \sum_i \bar{D}_i - \sum_i \bar{D}_i^- \quad (78)$$

Least-squares bond dissociation energies are calculated from the fragmentation data of a molecule. Since the nature of these data are

dependent upon the molecule, no general ionic-neutral relationship can be derived. The results for the AR_n molecule will demonstrate the principles of this correlation. Applying the conservation of energy principle to each of the n processes:

yields:

$$IP(AR_n) + \Delta H_i^+ = \Delta H_i + IP(AR_{n-i}) \quad (80)$$

or:

$$-EA(AR_n) + \Delta H_i^- = \Delta H_i - EA(AR_{n-i}) \quad (81)$$

for $i = 1, n$. Since it can be shown (by a procedure analogous to the development of Eq. 32) that:

$$\Delta H_i^{+, o, -} = i \hat{D}(A^{+, o, -} - B), \quad (82)$$

Eqs. 80 and 81 can be rewritten as:

$$IP(AR_n) - IP(AR_{n-i}) = i [\hat{D}(A-R) - \hat{D}(A^+-R)] \quad (83)$$

and:

$$EA(AR_{n-i}) - EA(AR_n) = i [\hat{D}(A-R) - \hat{D}(A^--R)] \quad (84)$$

where $i = 1, 2, \dots, n$. The least-squares solutions of these systems of equations yield the desired results:

$$\sum_{i=1}^n i [IP(AR_n) - IP(AR_{n-i})] = \sum_{i=1}^n i^2 [\hat{D}(A-R) - \hat{D}(A^+-R)] \quad (85)$$

and:

$$\sum_{i=1}^n i [EA(AR_{n-i}) - EA(AR_n)] = \sum_{i=1}^n i^2 [\hat{D}(A-R) - \hat{D}(A^--R)]. \quad (86)$$

These equations relate a bond energy difference to the weighted average of the difference between the ionization potentials or electron affinities of the molecule and the fragment ions. The same qualitative conclusions will be true irrespective of the type of molecule. In general the ionization potentials and electron affinities for a majority of the fragments will be unknown so that least-squares energies in the molecule will have to be calculated by approximation. If the ionization potential or electron affinity of the central atom is known, $\hat{D}(A-R)$ can be approximated from the equations:

$$IP(AR_n) - IP(A) = n [\hat{D}(A-R) - \hat{D}(A^+-R)] \quad (87)$$

or:

$$EA(A) - EA(AR_n) = n [\hat{D}(A-R) - \hat{D}(A^--R)]. \quad (88)$$

These relationships follow from Eqs. 85 and 86 for the case where $i = n$. For other kinds of molecules a similar approach based upon the available information will have to be followed.

B. Appearance Potential Measurements

1. Positive ions

Appearance potentials cannot be obtained as directly measured quantities. They must be obtained from an analysis of the intensity of

an ion beam as a function of the electron bombarding energy for the ion of interest. Plots of these data result in ion current vs electron energy curves called ionization efficiency (IE) curves. A family of such curves for the positive ions from $W(CO)_6$ is shown in Figure 1. The appearance potentials must be determined by locating the threshold energy for each ion. It is difficult to specify these points accurately because the curves approach the energy axis asymptotically as a result of the thermal energy spread of the electron beam. In addition, the energy scale is not absolute. The contact and surface potentials of the electrodes, the Maxwellian nature of the electron energy distribution, and the potential gradients within the ion source are all factors which produce an additive correction to the energy scale which cannot be determined directly.

Several graphical [21-27], numerical [28-31], and experimental [32] methods have been developed to determine appearance potentials from ionization efficiency data. Each method is unique in its approach for locating the critical energy. All of the techniques require a calibration of the energy scale. The procedure is the same in every case. The unknown and calibrating gas (usually a rare gas) whose ionization potential is known from spectroscopic measurements are introduced simultaneously into the mass spectrometer. After the pressure has been adjusted such that their intensities are equal at some specific voltage, the two ionization efficiency curves are recorded. The difference, Δ , between the critical energies is determined and the appearance potential of the unknown is calculated

from the relationship:

$$AP(\text{unknown}) = \Delta + IP(\text{known}). \quad (89)$$

The procedure developed in this research to determine appearance potentials is an adaptation of the method of extrapolated voltage differences first proposed by Warren [25] in 1950. The method was designed to give appearance potential differences and was described by Warren as follows:

The ordinate scales are chosen so as to make the straight portions of the two curves parallel. The differences of voltages, δV , at various ordinates, I , are measured, and a graph of δV against I is drawn and extrapolated to zero beam intensity. We assume that the extrapolated value of δV is the difference between the appearance potentials. We appreciate that this procedure is quite arbitrary and that the extrapolation of any curve other than a perfectly straight line is liable to objection.

The basic assumption behind the method is that "near" onset all ionization efficiency curves have the same shape. To Warren the word "near" implied the lower 5 V of the curves.

In a modification of Warren's method Flesch, White and Svec [33] interpreted the word "near" to be the lower 2.4 V of the IE curves. Experimentally it was found that the curves due to the molecular and fragment ions of CrO_2Cl_2 and CrO_2F_2 had the same shape within this region. If the curves were normalized to give equal intensities at a point approximately 2.4 eV above onset, appearance potential differences could be obtained directly from Warren's plots (i.e. the δV vs I graphs) without making the linear portions of the curves parallel. Subsequent studies [34,35] indicated that the lower 1.5-2.0 V of many IE curves

could be superimposed.

These data suggest that Warren's initial assumption can be extended to mean that "near" onset all IE curves can be made parallel to one another. Warren's method can be developed into an iterative process for determining appearance potential differences. The IE curves are drawn so that the lower 1.5-2.0 V are approximately parallel. The Δ obtained from these data is a first approximation to the true value. After renormalizing the curves to this voltage difference, another Warren's plot is made, and a second approximation is obtained. The process is continued until a consistent result is obtained. If the modified assumption is correct, the Warren's plots will converge from a sloped to a horizontal line, but this need not be the case. As long as the points of the plots define straight lines which have consistent intercepts, good values for appearance potentials can be obtained.

There are many cases where it is impossible to make the curves parallel. For instance the IE curves of the lighter fragment ions of a molecule are more elongated than those of the heavier fragments. This effect is demonstrated in Figure 1. It is due to an increased number of processes contributing to the formation of the lower m/z fragments. The Warren's plots for the lighter ions will possess either a maximum or a minimum value. There will be no apparent straight line through the points, and the extrapolated voltages will be arbitrary. The solution of this dilemma was first implied by Flesch and Svec [36]: "The determination of an appearance

potential, AP, thus reduces to finding some unique point in this low-energy portion of the IE curve which can be compared with a similar point on the IE curve of an electron energy calibrant ion." Rather than to determine voltage differences by making the lower energy regions parallel, it is more advantageous to determine them by comparing similar portions of the curves. These portions are specified by the location of the unique point. This point is established by finding that point on an IE curve such that an increase in electron energy by ΔX eV produces an N-fold increase in ion intensity. The range, ΔX , and the normalization multiple, N, are usually in the interval of 1.0-2.0 volts and 10-20, respectively. The "times-one" point is the lower bound and the "times-N" point is the upper bound to similar regions of both IE curves. The voltage difference is obtained from a Warren's plot of the energy differences of the x-1, x-2, ..., x-N points. If the curves have the same shape in this interval, the plots will be horizontal lines. Otherwise the voltage difference should be determined from the intercept of the least-squares line through the points.

This method is merely a simplified extension of the iterative procedure described previously. A boundary condition eliminates the process of making the curves parallel. Two parallel curves have the same "slopes" (i.e. their first derivatives are equal). Once the "slope" condition is met the curves will be parallel. The boundary condition is not set by the first derivative of the IE curves but rather by the slope of a line connecting two points on each curve. These

two lines are actually what are made parallel not the curves themselves. But if both curves have the same shape in this region, they too will be parallel. The slope of the lines must be specified by two conditions (viz. ΔI and ΔE). Since the ordinate scale is relative, the relationship between the final and initial intensity, I_f and I_i must be multiplicative. Hence:

$$I_f = N I_i. \quad (90)$$

The final and initial energy, V_f and V_i are related in the usual manner:

$$V_f = V_i + \Delta X. \quad (91)$$

Both ΔX and N are the range and normalization multiple as defined previously. The energy at the upper bound of the region, V_f , is referred to as the normalization energy.

The obvious advantage of this method is that it is easily adapted for computerized interpretation of ionization efficiency data.

2. Negative ions

There is a difference between the ionization efficiency curves of positive and negative ions. In the formation of a positive ion the product electrons are available to carry away any excess energy. However for negative ions formed by electron capture ($AB + e^- \rightarrow AB^-$) or dissociative capture ($AB + e^- \rightarrow A^- + B$) there are no electrons to carry away the excess energy. The anions are formed by a resonance process which occurs over a relatively narrow energy range. These

types of processes usually occur from 0-15 V and are evidenced by a sharp peak in the ionization efficiency curve. It is possible to form a negative and positive ion simultaneously in a mass spectrometer by an ion pair process ($AB + e^- \rightarrow A^+ + B^- + e^-$). In this case a product electron is available to carry away the excess energy. The IE curve for the negative ion in this region (> 15 V) will resemble that of a positive ion.

Appearance potentials for negative ions are commonly obtained by linear extrapolation [23] on the low energy side of a resonance peak. In some cases the energy of the resonance maximum is reported. If two peaks overlap, a deconvolution procedure [37] can be used to obtain satisfactory results. As is the case with positive ions, the energy scale must be calibrated. The O^- ion produced by resonance dissociation of CO is often used for this purpose.

III. INSTRUMENTAL

To facilitate the rapid and precise determination of appearance potentials a mass spectrometer was interfaced to a mini-computer. The nature of the experiment requires that the intensity of an ion must be obtained as a function of the electron accelerating energy. Numerical rather than graphical (see Figure 1) information is desired. Hence, the computer and mass spectrometer must work simultaneously to produce digitized ionization efficiency data. This information must be processed by the computer so that extrapolated voltage differences can be obtained. To accomplish these tasks the digital nature of the computer and the analog nature of the mass spectrometer have to be reconciled.

A. Mass Spectrometer

The mass spectrometer used for this research was the positive-negative (+/-) mass spectrometer which was designed and built in these laboratories [38]. The instrument consists of two 15-cm radius, 60° magnetic sectors in a horizontal plane. Positive and negative ions are obtained simultaneously from a single electron beam. The gaseous cations are extracted, accelerated, mass analyzed, and detected in one direction and the anions in the opposite direction. The ion source is at ground potential and the analyzer tubes and collectors are at ± 2000 V. The normal mass range is from 1-400. Unit resolution with a 10% valley is achieved at mass 350.

Figure 1. Ionization efficiency curves for the positive ions of $W(CO)_6$.

The electron accelerating energy is set by specifying the potential between the filament and the ion box. This voltage is supplied by an 85 V voltage regulator tube and can be varied from 0 to -85 V with respect to the ion box by a 15 turn helical potentiometer. For automatic scanning of the electron energy the potentiometer is connected to a variable-speed, motor-driven control.

The ions are detected by a magnetic electron multiplier (Bendix Corporation Model M-310). Currents from this device are measured by a battery-operated electrometer amplifier (Keithley Model 601). The 0-1 V dc output of the electrometer floats at analyzer tube potential. A DC-DC converter [39] is used to reference this signal to ground potential. The converter is essentially a unity gain dc isolation amplifier. It has a time constant of 0.25 s. The output voltage deviates from linearity by less than 0.5 mV over the 0-1 V range.

B. Computer

A PDP-12 computer (Digital Equipment Corporation) was used to acquire and process numerical ionization efficiency data. The PDP-12 consists of a single central processor with two distinct operating modes, each with its own instruction set. It operates in one mode as a LINC computer and in the other as a PDP-8/I. Instruction execution times range from 1.6-4.8 μ s. There is one active register, the accumulator. Core memory consists of 8192 (8K) 12-bit words.

The peripheral devices attached to the computer include an ASR-33 Teletype, a line printer-plotter (Matrix Model 1110A), a cathode ray tube display, two magnetic tape drives controlled by a buffered subprocessor (TU56), a real time clock (KW12A), an analog-to-digital (A-D) converter (AD12), and six relays. The CRT display, LINC tapes, A-D converter, and relays are controlled by LINC mode programming. The other devices are programmed in 8-mode. In addition the PDP-12 contains two programmable parallel processors with their own instruction sets. The floating point processor, FPP, is used to perform arithmetic operations on floating point numbers. The analytical instrument package, AIP, is an A-D converter used for fast sampling at rates up to 50 kHz.

Typically analog information is processed by the AD12 analog converter and multiplexer. The device consists of 16 input channels, a sample and hold, a multiplexer, and a 10-bit A-D converter. Eight of the channels (0-7) are controlled by continuously variable 10-turn potentiometers. The other eight channels (10-17) are for external inputs. These inputs are taken from phone jacks and are connected through preamplifiers to the converter. The acceptable voltage range of these inputs is ± 1 V with a sensitivity of about 2 mV per count. Since one bit of the converter is a sign bit, the converter range is from -777_8 (-511_{10}) to $+777_8$ (511_{10}). Normal sampling of a selected channel, conversion to a 10-bit signed number, and transfer of the converted binary number to the accumulator takes 18.2 μ s.

Programs can be written for the PDP-12 in FORTRAN, FOCAL, or assembler language. Two operating systems are available to facilitate the writing of programs. The DIAL and OS/8 systems contain the required software for editing, assembling, loading and storing programs. A third operating system, AIPOS, is used for data acquisition and manipulation and for its input-output and file handling capabilities.

C. Interface

The interface consists of the elements required for the link between the +/- mass spectrometer and the PDP-12 computer. These components are the hardware and the software. The computer must provide the mass spectrometer with analog information in the form of the electron accelerating energy. The mass spectrometer must provide the computer with digital information in the form of the intensity of an ion. The electronic components, the hardware, needed to produce these results are a digital-to-analog (D-A) converter and an analog-to-digital converter respectively. The programs required to acquire, process, and interpret the IE data comprise the software of the interface.

Although the possibility exists for interfacing both halves of the +/- instrument to the computer, only the positive ion capacity of the instrument was developed. Both the hardware and software reflect this limitation.

1. Hardware

For the purpose of sampling positive ion intensities, the output of the DC-DC converter was connected directly to channel 11 of the

AD12 A-D converter of the PDP-12. This converter was chosen for the interface instead of the AIP for ease of programming and because the slow response time of the DC-DC converter eliminated the need for fast sampling. The 0-1 V output of the DC-DC converter and the $(-1)-1$ V input of the A-D are compatible. Only half of the range of the A-D converter is used, but the sensitivity of 2 mV/count is well-within the noise limitations of the positive ion signals. One modification was made on the DC-DC converter. For convenience a divider network was placed in parallel with the 0-1 V output. As a result of this modification, a 40 k Ω load is always across the DC-DC converter output.

A 12-bit digital-to-analog converter, which was designed and built in the Ames Laboratory at Iowa State University, was used to supply the electron accelerating energy. A circuit diagram for the converter and its interface to the input/output bus of the PDP-12 are given in Figure 2. The converter is addressed in 8-mode by the digital-to-analog converter (DAC) instruction whose octal value is 6374. According to Figure 2, the operation of the converter can be summarized as follows. When the D-A is addressed (device select 37), the binary information in the accumulator is transferred to an outboard holding register (during IOP 4) which is presented to the D-A inputs. The D-A operates continuously on the contents of the holding register to provide an analog output voltage. This voltage is amplified, inverted, and supplied directly to the ion source filament. Because

the ion box serves as a common ground for the mass spectrometer and the computer, the connection can be made in this manner. The only change that was made in the existing emission regulator circuit was to add a switch to allow the filament potential to be set either manually or by the computer.

As far as the ionization efficiency experiment is concerned, the replacement of the electron energy potentiometer by the D-A converter produced one change. The electron accelerating voltage is no longer continuously variable. It must be incremented under program control. The voltage of the smallest increment is fixed by calibrating the D-A circuit. In this case the 0-10 V signal from the D-A converter is amplified and inverted to yield a 0-(-40.95) V output. The judicious choice of -40.95 V as the maximum output voltage specifies 0.01 V as the smallest voltage step. In other words, the addition of 1 to the binary value in the accumulator produces a change of 10 mV in the electron energy. This conclusion follows from the fact that the largest octal number which can be converted by the 12 bit D-A is 7777. Its decimal equivalent is 4095. In general the electron energy will be equal to 1/100 of the decimal equivalent of the octal number to be converted. The restriction of the energy interval to 40.95 V and the specification of the energy to 0.01 V do not limit the ionization efficiency experiment in any way.

Both the A-D and D-A converters were tested to verify their performance. The tests were implemented by diagnostic programs written

in assembler language for the PDP-12. The monotonicity of the A-D converter and the operation of the 16 A-D channels were checked with an existing program (MAINDEC 12-D6CC-D, A TO D TEST). Since the program samples each of the channels and displays their octal values simultaneously on the CRT display, the nature of the test is visual. Qualitatively the operation of the converter was checked by turning the potentiometers (channels 0-7) and by noting a corresponding increase or decrease in the converted value. The quantitative operation of the converter was demonstrated by connecting a calibrated and variable voltage source to the inputs (channels 10-17). In every case the observed and calculated values of the converted input voltage were equal to within ± 1 count.

To facilitate the testing of the D-A converter, a low voltage (0-1 V) output was provided (Figure 2). This output was connected to channel 10 of the A-D converter so that it could be used to verify the operation of the D-A converter. Two diagnostic programs, DATST1 and DATST2, were written to certify the operation of the D-A converter by utilizing this option. In the first program, DATST1, the accumulator is slowly incremented from 0_8 to 7777_8 then decremented back to 0_8 , endlessly. The value of the increment is fixed but may be set to any binary number in the 12 bit range before the program is started. At each step the value of the accumulator is converted to an analog voltage. This voltage is reconverted to a binary number. The octal values of the D-A input and the A-D output are displayed simultaneously

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Figure 2. Circuit diagram for the PDP-12/mass spectrometer interface. Digital-to-analog converter (top center), holding register (right), and I/O bus connections (bottom center and left).

on the CRT display. Since the D-A converter operates on 12 bits and the A-D converter operates on 9 bits, the three least significant bits of the D-A input will be lost in the process. However if the hardware functions correctly, the A-D value should equal the D-A value divided by 8. The numbers should count up and then down at the same rate when the least significant three bits of the D-A input are incremented from 7_8 to 0_8 . When this diagnostic test was made, the two numbers were equivalent throughout the entire range independent of the size of the increment. Both numbers changed simultaneously to within ± 2 counts of the D-A input when the increment was 1.

The second test, DATST2, functions in a similar manner with three exceptions. The increment is fixed at 10_8 and is always upwards at the fastest rate possible. That is, the accumulator is counted from 0_8 to 7777_8 in steps of 10_8 repeatedly. Neither the input nor the output of the D-A are displayed, but the digital output is plotted vertically on the oscilloscope screen with two points per step. If the D-A converter functions correctly, two parallel lines are produced continuously on the oscilloscope screen. This result was produced successfully after an initial grounding problem was corrected.

For further reference, a complete listing of the two diagnostic programs is given in Appendix A.

2. Software

Although FORTRAN and FOCAL were available, the software for the interface was written in assembler language. If one of the high level

languages was used, the size and efficiency of the software would be limited. Neither of the languages could be adapted for programming the line printer or the D-A converter. The program was composed and edited with the DIAL operating system. The source program was assembled by the FPP assembler. The resulting binary program was built into a function program for the Analytical Instrument Package Operating System, AIPOS. All 8K of core memory is used by the program.

The software consists of several subprograms which were combined to form a single program, the Ionization Efficiency Acquisition System (IEAS). Since each subprogram performs a specific task associated with the ionization efficiency experiment, the IEAS is a command structured system. Each routine is assigned a command code, the first alphabetic character of its mnemonic descriptor, such that when the command is typed the routine is executed. This function is performed by a command overlord dispatcher in the IEAS. Most of the routines require the input of data. This information is checked and if any errors are found, an error handler types an appropriate error code and returns control to the overlord processor. A summary of the commands and error codes is given in Tables 1 and 2, respectively. The alphabetic characters not listed in Table 1 are undefined commands and are reserved for future expansion. Additional error codes can be added when needed.

a. Description of the system When the IEAS is ready to accept a command, the command overlord processor types an asterisk. All

Table 1. IEAS command summary.

Command letter	Mnemonic code	Explanation
A	ACQIR	Ionization efficiency data are acquired, normalized, and stored.
B	BCKSUB	A background interference is acquired and subtracted from the IE data. The resultant data are normalized and stored.
C	CAIN	Up to seven commands may be chained and executed sequentially.
D	DELSQ	Warren's deltas and their least-squares intercepts are printed on the line printer.
E	ELIM	The IE data for the last ion are eliminated from the IE table.
F	FILSAV	The information in the IE table is saved on magnetic tape.
I	IEPRNT	The unnormalized IE data are printed on the teletype.
M	MASPRT	The normalized data for the ion whose mass is specified are printed on the teletype.
N	NORPRM	The normalization multiple and range may be changed to new values.
O	OPTMIZ	The gain and scan limits for an IE curve are optimized.
P	PRNTAB	The IE table is printed on the line printer.
R	READTA	A specified IE file is read from magnetic tape.

Table 1. Continued

Command letter	Mnemonic code	Explanation
S	SETEE	The electron energy is set manually by entering the desired value.
T	TIME	The delay time is set to the specified value.
W	WARPLT	Warren's plots are printed on the line printer.

Table 2. IEAS error codes

Code	Explanation
?0	The command is not alphabetic.
?1	An undefined command was typed.
?2	Ionization efficiency data are being saved in a preexisting file.
?3	$1000 \leq \text{ion mass} < 1$.
?4	$40.95 < \text{starting energy} < 0$.
?5	$40.95 < \text{energy increment} \leq 0$.
?6	The starting energy minus the scan range must be greater than or equal to zero.
?7	Acquisition buffer will overflow. The scan range divided by the energy increment must be greater than zero but less than 512.
?10	$8,000 \leq \text{number of scans} < 1$.
?11	An ion intensity is less than or equal to zero.
?12	The largest normalization multiple that could be found was less than the preset value.
?13	The smallest normalization multiple is greater than the desired value. The starting energy is too low.
?14	The number of IE curves for which there is normalized data stored in the IE buffer exceeds 15.
?15	Another acquisition will cause the IE buffer's capacity to be exceeded.
?16	There are no data in the IE table for an ion of the specified mass.

Table 2. Continued

Code	Explanation
?17	The normalization multiple is less than or equal to zero.
?20	The normalization range is less than or equal to zero.
?21	$87.5 \text{ sec} \leq \text{delay time} \leq 0.01 \text{ sec.}$
?22	The IE table is cleared.

commands are single alphabetic characters and are executed as soon as they are typed and followed by a carriage return. If an illegal command is entered the error handler will type either a ?0 or a ?1. The RUBOUT key may be used to eliminate a typed command before it is executed. A new command can then be typed in its place and executed. While a command is being executed the typing of a CONTROL/C or a CONTROL/R halts its execution and returns program control to either the AIPOS job controller or to the command overlord, respectively.

1). Acquire The mass of the ion (IM), starting energy (SE), energy increment (EI), range of the energy scan (R), and the number of scans (NS) are the parameters requested by the acquisition program. Each parameter is typed in response to its abbreviation followed by a colon. The RUBOUT key can be used to correct any errors before a response is terminated with a carriage return. All of the parameters are entered as positive decimal numbers. The ion mass and number of scans are integers while the starting energy, energy increment, and scan range are specified to the nearest 0.01 V. The data are checked and any errors are signaled by codes 3-10. After the last parameter is entered, the electron energy is set to the starting energy and the program awaits the typing of a G (for GO). During this time the user manually adjusts the magnetic focus to the desired mass and adjusts the intensity to produce a full-scale deflection on the electrometer. When a G is typed the IE curve is acquired. The typing of any other letter will cause control to be transferred to the command overlord. The

acquisition process is summarized in Figure 3. The electron energy is varied in discrete steps given by the energy increment. After each step there is a programmed delay of 0.25 s to allow the electrodes in the ion source to respond to the change in potential and the electrometer and DC-DC converter to respond to the corresponding change in ion intensity. Following this delay the ion intensity is sampled for 25 ms. During this period $1000_8(512_{10})$ consecutive samples are taken and averaged. The averaged intensity is added to the contents of the i th position in a data storage area which had been cleared before the scan was initiated. The electron energy is not recorded because there is a one-to-one correspondence between the digital input and analog output of the calibrated D-A converter. The electron energy of the i th step, V_i , is related to the i th position of the acquisition vector:

$$V_i = SE - i(EI) \quad (92)$$

where SE and EI are the starting energy and energy increment, respectively. Hence, the energy-intensity dependence is transformed into a position-intensity relationship. A single scan of an IE curve is the sum of the intensity data acquired by scanning down from and back to the starting energy. The data for each scan are summed to produce the resulting IE curve. By acquiring the data in this manner any linear variation in sample pressure during the scan time will be averaged in the data. Upon completion of the last scan the IE data in the

Figure 3. Timing cycle for the variation of electron energy during the acquisition of an ionization efficiency curve.

acquisition vector are normalized (pp. 41-43). In the normalization process energies are found for the 15 equally spaced intensities in the region of the IE data bounded by two points separated by 1.5 V that have an intensity ratio of 15 (i.e. the 15 energies at the x_1 , x_2 , ..., x_N points are found). If the data cannot be normalized, either error code 12 or 13 is typed. Linear interpolation is used to determine the energies to the nearest 0.01 V. The normalized energies are stored consecutively in a column of an IE table. This column is labeled by the mass of the ion. After the data are stored, the number of columns and amount of space remaining in the IE table are checked. Error conditions are signaled by codes 14 and 15. Command is then passed to the overlord processor.

2). Background subtract After the ion mass, starting energy, energy interval, range, and number of scans have been entered and a G typed, the IE data are acquired in the usual manner. The normalization process is inhibited and a carriage return-line feed is typed on the teletype. The program pauses and waits for another G subcommand. During this time the mass can be adjusted to the valley between peaks or to another ion which has similar intensity and energy dependence as the background. After the G is typed, the background IE curve is acquired and subtracted from the initial data. The corrected data are normalized. If an intensity less than or equal to zero is found during the normalization process a ?11 is typed. Otherwise, if the normalization condition is met, the normalized data are stored in the IE table and command is returned to the overlord processor.

3). Chain In response to the message, TYPE COMMAND SEQUENCE FOLLOWED BY A), up to seven command codes are entered followed by the) and a carriage return. The commands are executed sequentially. The asterisk typed by the overlord indicates when the process is completed. Since the number of commands typed or the terminator,), are not checked, caution must be exercised when utilizing this command.

4). Delta-least-squares The D command is executed without any input. Each column of normalized energies in the IE table is subtracted from the first column. The original table is overwritten with the energy differences. Least-squares slopes and intercepts are calculated for energy differences (Δ 's) at equal relative intensity differences (1, 2, ..., 15) for each column of the delta table. In the calculation the first two points are not used. These results are saved, and the delta table and intercepts are printed by the line printer. An example of the output for the positive ions from $\text{Mo}(\text{CO})_6$ is given in Figure 4. Each row corresponds to an energy difference at a relative intensity from 1 to 15. The energy differences are obtained by subtracting the normalized energies of an ion from those of the reference ion, the first column of the IE table (loc. cit. p 26). All data are rounded to the nearest 0.01 V. The columns are not labeled, but are listed in the order in which the data were obtained. From left to right the differences are for $\text{Mo}(\text{CO})_5^+$, $\text{Mo}(\text{CO})_4^+$, $\text{Mo}(\text{CO})_3^+$, $\text{Mo}(\text{CO})_2^+$, $\text{Mo}(\text{CO})^+$, and Mo^+ . After the output is completed, program control is restored to the command processor.

DELTA TABLE					
1.44	3.00	4.67	6.25	7.83	9.54
1.48	3.06	4.72	6.31	7.92	9.64
1.50	3.08	4.75	6.33	7.96	9.69
1.52	3.09	4.76	6.35	7.99	9.71
1.54	3.10	4.78	6.36	8.00	9.73
1.53	3.10	4.77	6.36	8.00	9.73
1.53	3.10	4.78	6.36	8.00	9.73
1.53	3.09	4.77	6.35	7.99	9.73
1.53	3.08	4.76	6.34	7.98	9.71
1.52	3.08	4.75	6.34	7.96	9.69
1.51	3.06	4.74	6.32	7.94	9.66
1.49	3.05	4.73	6.31	7.92	9.64
1.48	3.04	4.71	6.29	7.89	9.61
1.46	3.02	4.69	6.27	7.86	9.57
1.44	3.00	4.67	6.25	7.83	9.54
LEAST-SQUARES INTERCEPTS					
1.56	3.14	4.81	6.39	8.06	9.80

Figure 4. Tabular printout of the energy differences, deltas, at relative intensities 1,2,...,15 (rows) and their least-squares intercepts. Each column is the data for an individual ion printed in the order of acquisition. From left to right these data are for $\text{Mo}(\text{CO})_5^+$, $\text{Mo}(\text{CO})_4^+$, $\text{Mo}(\text{CO})_3^+$, $\text{Mo}(\text{CO})_2^+$, $\text{Mo}(\text{CO})^+$, Mo^+ .

5). Eliminate The elimination command causes the last column of data in the IE table to be erased. Successive execution of this command will erase the whole IE table which is signaled by a ?22.

6). File save The F command causes the current contents (either the IE or delta table) of the normalization buffer to be saved on magnetic tape. The data are saved in the output file previously specified by the user to be created by the AIPOS job control processor. The file is automatically indexed when program control returns to the AIPOS processor after the operation is completed.

7). IE print The contents of the acquisition buffer (i.e. the unnormalized IE data) is dumped on the teletype when the I command is executed. The data are listed in tabular form. The energy and intensity of each step is listed in descending order. The intensities are positive decimal integers. Command returns to the overlord processor when the operation is completed or if a CONTROL/R is typed.

8). Mass print When the mass of an ion is entered in response to the MASS: request, the program searches for its data in the IE table. If none is found error code 16 is typed. Otherwise the relative intensities and their corresponding energies are listed in tabular form on the teletype. Control is returned to the overlord when the table is finished.

9). Normalization parameters The normalization range and multiple are preset to 1.5 V and 15 respectively, but this command is used to reset the parameters to any positive value greater than zero.

The normalization multiple is entered first in response to the INTENSITY MULTIPLE: request. It is followed by the NORM RANGE: request for the desired energy range. The parameters are checked (error codes 17 and 20), and stored before control returns to the command processor. Subsequent IE data will be normalized with these conditions.

10). Optimize The starting energy, energy increment, and energy range are requested and entered in the same manner as they were for the acquisition program. One scan of the IE curve is acquired after the G subcommand is typed. If the data can be normalized the energy and intensity of the x1 and xN(15) points are typed. No data is stored in the IE table. If the curve cannot be normalized, either error codes 12 or 13 are typed. In both cases the program is recycled. When the most favorable conditions for the starting energy, energy range, and multiplier gain have been determined, control is returned to the command processor by typing a CONTROL/R.

11). Print table This command is executed before the D command to print the IE table on the line printer. Figure 5 shows a representative output. The normalized energies of the positive ions from Mo(CO)₆ are given in the table. Each column corresponds to the data for a particular ion and each row to an energy at a relative intensity from 1 to 15, but the columns and rows are not labeled. Since the data are entered into the table in the order in which the IE curves were acquired, the column labels are implied. From left to right the ions are Mo(CO)₆⁺, Mo(CO)₅⁺, Mo(CO)₄⁺, Mo(CO)₃⁺, Mo(CO)₂⁺, Mo(CO)⁺ and Mo⁺. After the table is printed, the program exits to the command overlord.

IE TABLE

8.32	9.76	11.32	12.99	14.57	16.15	17.86
8.55	10.04	11.62	13.28	14.86	16.47	18.19
8.71	10.21	11.79	13.45	15.04	16.67	18.41
8.84	10.36	11.93	13.60	15.19	16.83	18.55
8.94	10.48	12.04	13.72	15.30	16.95	18.67
9.05	10.58	12.15	13.82	15.41	17.05	18.78
9.14	10.68	12.24	13.92	15.50	17.14	18.87
9.23	10.77	12.32	14.00	15.58	17.22	18.96
9.32	10.85	12.40	14.08	15.66	17.30	19.03
9.40	10.92	12.48	14.16	15.74	17.37	19.09
9.49	11.00	12.55	14.23	15.81	17.43	19.15
9.57	11.07	12.62	14.30	15.88	17.49	19.21
9.66	11.14	12.69	14.37	15.95	17.55	19.26
9.74	11.20	12.75	14.43	16.01	17.60	19.31
9.82	11.26	12.82	14.49	16.07	17.65	19.36

Figure 5. Tabular printout of electron energies at 15 equally spaced intensity intervals (rows) in a 1.5 V range. The data, tabulated from left to right for the ions in order of acquisition (columns), are for Mo(CO)_6^+ , Mo(CO)_5^+ , Mo(CO)_4^+ , Mo(CO)_3^+ , Mo(CO)_2^+ , Mo(CO)^+ , and Mo^+ .

12). Read data The input file specified in the AIPOS function command is read from magnetic tape into the normalization buffer. Control is returned to the overlord after the operation is completed.

13). Set electron energy The filament to ion box potential is set automatically to the energy typed in response to the ENERGY: request. Any energy greater than zero but less than 40.96 is accepted. The program exits to the command processor.

14). Time After the T command is executed the phrase, DELAY TIME(SEC):, is typed on the teletype. The delay time is entered and followed by a carriage return. If the time is not between 0.01 and 87.5 s, ?21 is typed. Otherwise the new value replaces the preset time of 0.25 s. Control is returned to the overlord.

15). Warren's plots All data required for the execution of the W command are provided internally from the results of the delta-least-squares program. For each ion (column) in the delta table the energy differences are plotted as a function of the relative intensity (row) on the line printer. An example of the output is given in Figure 6. The Warren's plots, which are for the fragment ions from Mo(CO)_6 , are plotted two to the page. The ordinates cover a 0.4 V range in 0.05 V divisions. Alternate divisions are labeled. The abscissas are not labeled and are divided into 15 equidistant intervals. This division is variable and is adjusted to the value of the normalization multiple. In this case the implied labels are 0, 1, ..., 15.

Figure 6. Printout of Warren's plots for the positive ions of Mo(CO)_6 . Mo(CO)_5^+ (top), Mo(CO)_4^+ (bottom).

Figure 6. Continued. Mo(CO)_3^+ (top), Mo(CO)_2^+ (bottom).

Figure 6. Continued. Mo(CO)^+ (top), Mo^+ (bottom).

The deltas are plotted as + signs. The least-squares lines are drawn through all but the first (leftmost) two points. The plots are not labeled but are drawn in the order in which the data were acquired from the top to the bottom of each consecutive page. The plots in Figure 6 are for $\text{Mo}(\text{CO})_5^+$, $\text{Mo}(\text{CO})_4^+$, $\dots$, Mo^+ respectively. The program exits in the normal manner when all plots are completed.

A complete and documented listing of the IEAS program is provided in Appendix B for further reference.

b. Operation of the system The IEAS program is stored on magnetic tape. Before any data can be processed the program must be loaded into memory and started. The tape containing the IEAS program is placed on tape drive 0 and an AIPOS data tape is placed on tape drive 1. After the AIPOS system has been started [40, Appendix A], the program is loaded and started by a function call to the AIPOS job control language processor [40, Chapter 1]. The general format of this call is:

function output file = input files. (93)

Since the IEAS can accommodate only one output and one input file, the specific command is:

IEAS LT1: X.ext = Y.ext. (94)

LT1 assigns the output and input files to tape unit 1. Mnemonic descriptions of the files are X and Y. They are defined by the user and may be from 1-6 alphanumeric characters long. The abbreviation ext denotes an extension code of 1-3 characters which is an optional

description of the file. Usually three digits are used to distinguish different files of the same type (i.e. 001, 002 etc.). The input file must be and the output file must not be listed on the tape's index before the command is accepted. Both, none, or just one of the files may be specified. However an output file must be given if there is an input file. The function call is terminated by a carriage return and the IEAS program types an asterisk if the procedure was completed successfully. The program is ready to accept commands.

The fragmentation energy data for a compound are acquired in a certain manner. The IE data for the molecular ion are acquired first and the data for the remaining ions are obtained in the order of descending mass. When this procedure is followed the molecular ion serves as a secondary calibrant for the energy scale, all energy differences are positive, the extrapolated voltage differences are the desired fragmentation energies for the calculation of ionic least-squares bond energies (Eq. 67), and the data for the ions (Figures 4-6) are labeled implicitly. It will be necessary to determine the IP of the molecule in another acquisition session. The general rule to be followed is that the first curve to be acquired is the reference curve and it must be for the ion with the lowest AP. All data must be acquired with the same normalization conditions.

There is also a logical procedure for acquiring the IE data of an ion. First, the optimization routine is used to locate the normalization energy (i.e. the electron energy of the x15 point). This is

accomplished by scanning a 10 V segment above onset in 0.25 V steps. If an error code ?12 is typed the starting energy is decreased and the intensity is increased to produce a full-scale deflection on the electrometer. If a ?13 is typed the starting energy is increased and the intensity is decreased. When the normalization energy is found, a 2 V scan in 0.05 or 0.1 V increments starting at 0.2 V above its value is acquired to insure that acquisition conditions are correct. Once the optimum conditions have been certified, this region is acquired by the acquisition command. For most ions five scans in 0.05 V increments produce satisfactory results. For noisy signals 50 or 100 scans in 0.1 V steps will enhance the signal to noise ratio so that reproducible results are obtained. In these cases it is also possible to change the number of samples per step internally from 1000₈ to any number divisible by two up to 10000₈.

After all of the fragmentation data are acquired, the information in the IE table is saved on tape or is processed and printed with a PDW command sequence. Control is returned to the AIPOS program so that another acquisition session can be initiated.

c. Limitation of the system When an ion has a background interference, no normalization energy can be found. These interferences, which may be due to a monoisotopic ion at the same mass, a metastable peak, or scattered ions, cannot be removed by the background subtraction routine. However, the IE data can be acquired and printed on the teletype with the I command. The background can be subtracted

manually by a linear least-squares fit of the base of the curve. The resulting data also will have to be normalized and processed by hand.

3. Tests of the interface

The accuracy and reproducibility of the complete system for obtaining ionization energies, fragmentation energies, and bond energies were tested by two experiments. The first experiment was designed to verify the accuracy of the method by measuring the ionization potentials of the rare gases using Xe as a reference. The results of this study are given in Table 3. The observed voltage differences listed in the third column represent an average of six individual determinations made during the course of one week. Their standard deviations are well within the limitations of the method itself and verify the day to day operation of the system. The average percent error for the determinations is 1.06% which is cause for some concern. These data indicate that the magnitude of the error is proportional to the size of the voltage difference which implies that there may be a calibration error in the D-A converter. The error may also be instrumental in nature. Since the path of the ions as they are drawn from the ion source is bent by the magnetic field of the collimating magnet of the electron beam, ions of different masses will be formed at different places and hence different potentials in the ion source. If this is the case, the error should show a dependence upon the square root of the mass of the ion. The data of Table 3 substantiate this conclusion. The errors are inversely

Table 3. Ionization energy differences (eV) from Xe for the rare gases

Atom	Mass	Observed Δ	Accepted Δ	Error	% Error
He	4	12.582 $\pm$ 0.008	12.456	0.126	1.01
Ne	20	9.482 $\pm$ 0.004	9.434	0.048	0.51
Ar	40	3.673 $\pm$ 0.005	3.629	0.044	1.21
Kr	84	1.897 $\pm$ 0.005	1.869	0.028	1.50

proportional to the square root of the mass of the ion. Thus the error in the energy differences can be related to the sum of two contributions, k_1 times the observed Δ and k_2 times the reciprocal of the square root of the mass of the atom. A least-squares solution using this model and the data of Table 3 gives $k_1 = -0.002$ and $k_2 = 0.31$ with a standard error of estimate of 0.002 eV. Three conclusions can be drawn from this information. First, the model correlates very well with the data, second, the calibration of the D-A is not a significant cause of the errors and third, the absolute accuracy of the method is limited by conditions within the ion source.

The second experiment was designed to verify the operation of the system by comparing data acquired, normalized, and processed using the computer method, to previous data which were acquired graphically and processed manually. In this case the data were the experimentally determined fragmentation energies (i.e. the Warren's deltas) for the positive ions of the Group VIB hexacarbonyls. The results of this experiment are summarized in Table 4. Each energy represents the average of at least six individual determinations. For $\text{Cr}(\text{CO})_6$ two sets of data were obtained by the computerized system. The first set was taken before the D-A converter was calibrated and when compared to the other set, demonstrates that calibration errors are possible. Once the calibration was performed there is little difference between the computer-determined and graphical data. A comparison of the results for $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ also demonstrates

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Table 4. Fragmentation energies (eV) for the positive ions of the Group VIB hexacarbonyls

Ion	Cr(CO) ₆			Mo(CO) ₆
	IEAS uncalibrated	IEAS calibrated	Graphical	IEAS calibrated
M(CO) ₅ ⁺	1.40±0.02	1.43±0.01	1.43±0.02	1.56±0.01
M(CO) ₄ ⁺	2.03±0.02	2.03±0.01	2.00±0.01	3.15±0.01
M(CO) ₃ ⁺	2.93±0.03	2.93±0.01	2.90±0.01	4.83±0.02
M(CO) ₂ ⁺	4.13±0.03	4.09±0.03	4.07±0.02	6.40±0.02
M(CO) ⁺	5.67±0.03	5.61±0.02	5.58±0.03	8.06±0.03
M ⁺	7.10±0.05	6.94±0.01	7.03±0.02	9.78±0.06

Mo(CO)_6		W(CO)_6	
Graphical		IEAS Calibrated	Graphical
1.64 $\pm$ 0.02		1.70 $\pm$ 0.02	1.76 $\pm$ 0.03
3.18 $\pm$ 0.02		3.62 $\pm$ 0.02	3.68 $\pm$ 0.03
4.85 $\pm$ 0.02		5.46 $\pm$ 0.01	5.50 $\pm$ 0.03
6.44 $\pm$ 0.04		7.69 $\pm$ 0.03	7.92 $\pm$ 0.02
8.16 $\pm$ 0.04		9.76 $\pm$ 0.05	10.02 $\pm$ 0.05
9.94 $\pm$ 0.05		12.41 $\pm$ 0.04	12.41 $\pm$ 0.14

that both methods are in close agreement. Although the agreement of specific fragmentation energies is not exact in all cases, the ionic least-squares bond energies calculated from the graphical and computerized data are indistinguishable. These results, which were calculated by the procedure described by Eqs. 30-33, are furnished in Table 5. In general the calculated values for least-squares bond dissociation energies are insensitive to small variations in fragmentation energies.

A final experiment was designed to test the response time of the instrument. In this experiment IE data for Cr(CO)_6^+ were acquired at different delay times. The results are summarized in Table 6. Over the four-fold range of delay times tested the energy data show only a very slight dependence upon the acquisition rate. As a result, IE data for most ions were obtained with a typical delay time of 0.1 s instead of the preset value of 0.25 s.

Table 5. $\hat{D}(M^+-CO)$ (eV) for the group VIB hexacarbonyls

Compound	IEAS Calibrated	Graphical	IEAS Uncalibrated
$Cr(CO)_6$	1.10 ± 0.03	1.10 ± 0.04	1.12 ± 0.04
$Mo(CO)_6$	1.61 ± 0.01	1.63 ± 0.01	-
$W(CO)_6$	1.97 ± 0.04	2.00 ± 0.04	-

Table 6. Normalized energies (eV) for $\text{Cr}(\text{CO})_6^+$ at different delay times

Relative Intensity	Delay time (seconds)					
	0.30	0.25	0.20	0.15	0.10	0.075
1	8.88	8.88	8.87	8.86	8.85	8.84
2	9.15	9.15	9.15	9.13	9.14	9.13
3	9.32	9.30	9.30	9.30	9.30	9.30
4	9.44	9.44	9.43	9.42	9.43	9.41
5	9.54	9.55	9.54	9.53	9.53	9.52
6	9.64	9.64	9.64	9.63	9.63	9.62
7	9.73	9.74	9.73	9.72	9.71	9.71
8	9.81	9.81	9.81	9.80	9.80	9.79
9	9.90	9.89	9.89	9.89	9.88	9.87
10	9.98	9.97	9.97	9.97	9.96	9.94
11	10.06	10.05	10.05	10.05	10.03	10.02
12	10.14	10.13	10.13	10.13	10.12	10.10
13	10.22	10.22	10.21	10.21	10.19	10.19
14	10.30	10.29	10.30	10.28	10.27	10.27
15	10.38	10.38	10.37	10.36	10.35	10.34

IV. EXPERIMENTAL

The purpose of the experimental work was to synthesize the Group VIIB mixed-metal decacarbonyls $\text{MnRe}(\text{CO})_{10}$, $\text{MnTc}(\text{CO})_{10}$, and $\text{TcRe}(\text{CO})_{10}$. The preparation and characterization of $\text{ReMn}(\text{CO})_{10}$ have been described previously [41]. De Jong and Wiles [42] speculated that $\text{MnTc}(\text{CO})_{10}$ was formed in low yields (< 10%) when $^{99\text{m}}\text{Tc}(\text{CO})_5$ produced from the β decay of $^{99}\text{Mo}(\text{CO})_6$ reacted with photochemically produced $\cdot\text{Mn}(\text{CO})_5$. The compound was characterized only by its radioactivity. Technetium-rhenium decacarbonyl has not been reported. The general approach to the synthesis of these compounds is to react the pentacarbonyl anion, $\text{M}(\text{CO})_5^-$, of one metal atom with the pentacarbonyl halide, $\text{M}'(\text{CO})_5\text{X}$, of the other:

Both reactants are produced from the corresponding homonuclear metal decacarbonyls. Reduction with sodium amalgam in tetrahydrofuran (THF) under an inert atmosphere yields the desired anion:

while the halide is formed by a direct reaction with the halogen:

There are two ambiguities in this sequence which had to be resolved. First, bromine was arbitrarily chosen as the halogen because the

pentacarbonyl bromides are easily prepared [43] and because the bromide ion is a good leaving group for the nucleophilic substitution reaction (Eq. 95). The second question concerning which metal pentacarbonyl anion and bromide should be reacted together was resolved experimentally in the synthesis of MnRe(CO)_{10} .

All of the preparations were done at room temperature under an atmosphere of dry nitrogen. The glassware was dried in an oven at 120°C and was assembled immediately before use. Tetrahydrofuran was distilled from lithium aluminum hydride and the decacarbonyls, which were obtained from Pressure Chemical Company (3419-25 Smallman St., Pittsburgh, Pa. 15201), were purified by vacuum sublimation. Technetium decacarbonyl had been prepared from the radioactive ^{99}Tc isotope. This isotope, whose half-life is 2.12×10^5 years, is a weak β emitter ($\beta_{\text{max}} = 0.3 \text{ MeV}$). When used on a small scale ($< 50 \text{ mg}$), it does not present a serious health hazard because the β rays are stopped by the glassware and there is no associated γ radiation. When using larger quantities ($> 250 \text{ mg}$) a distance of 30 cm must be maintained from the working area to avoid the small amount of very soft x-rays produced by the action of the β particles on glass [44, Appendix I]. When working with $\text{Tc}_2(\text{CO})_{10}$ the sample size was limited to 100 mg. The material was handled with protective gloves, and all reactions were done in a well-ventilated hood.

The mixed-metal decacarbonyls were purified by preparative gas chromatography. The preparative collections were performed with

an Aerograph Model A-700 gas chromatograph using a 0.25 in. x 15 ft. 3% SE-30 glass column. The compounds were collected in a 3 mm o.d. glass capillary tube (5 cm in length) loosely plugged at one end with glass wool and fitted directly to the exit port of the thermal conductivity detector. Once the retention times were established, the compounds were collected with the filaments of the detector turned off to prevent sample decomposition. Two consecutive 45 μ l injections of a saturated pentane solution were used for each preparative collection.

All products were identified by their infrared spectra in the carbonyl absorption region ($2150 - 1900 \text{ cm}^{-1}$). The infrared spectra were obtained in cyclohexane and were recorded with a Perkin-Elmer Model 337 spectrometer. Positions of the peaks were determined with an expanded scale recorder calibrated in the carbonyl region with gaseous CO. The mixed-metal decacarbonyls were also identified by their mass spectra. The masses of the molecular ions were obtained from the +/- mass spectrometer described previously.

A. Preparation and Synthesis

1. Pentacarbonyl bromides of Mn, Tc, and Re

The pentacarbonyl bromides were prepared by a modification of the method of Abel and Wilkinson [43]. The reactions were done at 25°C (instead of 40°) in carbon disulfide (instead of carbon tetrachloride) using a 10% molar excess of bromine (instead of a 30% excess).

a. Mn(CO)₅Br A suspension of Mn₂(CO)₁₀ (2.0 g, 5.13 mmol) in 40 ml of carbon disulfide was stirred while Br₂ (0.3 ml, 5.64 mmol) in 15 ml of carbon disulfide was added dropwise over a period of 30 min. After removal of the solvent, a yellow-orange product was collected by vacuum sublimation in 90% yield.

IR(cyclohexane) 2051s, 2019w, 2001m.

b. Tc(CO)₅Br A 5 ml aliquot of a solution of Br₂ (0.1 ml, 1.95 mmol) in carbon disulfide (40 ml) was added slowly (10 min) to a suspension of Tc₂(CO)₁₀ (0.10 g, 0.21 mmol) in 10 ml of carbon disulfide. The solvent was removed under reduced pressure and 74 mg of product was obtained from the residue by vacuum sublimation at 50 - 70° C.

The infrared spectrum of the sublimate revealed the presence of [Tc(CO)₄Br]₂ as an impurity. IR (cyclohexane) 2055s, 2024w, 1994m, ([Tc(CO)₄Br]₂) 2045s, 2012m, 1974m.

c. Re(CO)₅Br Bromine (0.1 ml, 1.95 mmol) in 10 ml of carbon disulfide was added dropwise over a period of 10 min to Re₂(CO)₁₀ (1.0 g, 1.54 mmol) in 25 ml of carbon disulfide. After the solution was evaporated to dryness under reduced pressure, the white crystalline product, Re(CO)₅Br, was separated from the residue by vacuum sublimation. The desired compound was obtained in 90% yield.

IR(methylcyclohexane) 2044s, 2012w, 1982m.

2. Mixed-metal decacarbonyls

The general procedure for synthesizing and purifying the mixed-metal decacarbonyls of Mn, Tc, and Re was developed through the preparation of MnRe(CO)_{10} . This approach was dictated by the radioactive nature, availability (1.111 g), and expense (> \$1,000/g) of $\text{Tc}_2(\text{CO})_{10}$. The experimental techniques for the preparation and reaction of the pentacarbonyl anions in an inert atmosphere and water-free environment were developed. The reaction was scaled for the use of small quantities (100-150 mg) of reactants. The conditions for optimizing the yield of MnRe(CO)_{10} were developed as was the methodology for its separation and purification from the $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ side products.

The major obstacle to the synthesis of MnRe(CO)_{10} proved to be the choice of reactants. Either Re(CO)_5^- or Mn(CO)_5^- can be chosen as the nucleophile. The logical option was to react Re(CO)_5^- with $\text{Mn(CO)}_5\text{Br}$ since Re(CO)_5^- is the stronger nucleophile [45]. When this reaction was done, a gas chromatographic analysis of the product gave $\text{Mn}_2(\text{CO})_{10}$ (22%), ReMn(CO)_{10} (8%), and $\text{Re}_2(\text{CO})_{10}$ (70%). The yield of ReMn(CO)_{10} was too low to make this synthetic route feasible. The alternate procedure was to react stoichiometric amounts of Mn(CO)_5^- and $\text{Re(CO)}_5\text{Br}$. The sublimate of this reaction contained $\text{Mn}_2(\text{CO})_{10}$ (11%), MnRe(CO)_{10} (77%), and $\text{Re}_2(\text{CO})_{10}$ (12%). A dramatic increase in the yield of MnRe(CO)_{10} was realized by changing to the less reactive nucleophile Mn(CO)_5^- . A general explanation for this phenomenon was given by

Dessy and Weissman [46]. When the Mn-Re bond is formed, $\text{Re}(\text{CO})_5^-$ will cleave it forming the more stable $\text{Re}_2(\text{CO})_{10}$ molecule and $\text{Mn}(\text{CO})_5^-$ which is oxidized to $\text{Mn}_2(\text{CO})_{10}$ upon exposure to air. The nucleophilic strength of $\text{Mn}(\text{CO})_5^-$ is insufficient to break the Mn-Re bond. The large percentage of $\text{Re}_2(\text{CO})_{10}$ formed from the reaction with $\text{Re}(\text{CO})_5^-$ provides additional evidence for this explanation. As a result, the optimum method for synthesizing the mixed-metal carbonyls is to react the weakest nucleophile with the corresponding bromide. Since the nucleophilic strength increases down the family, $\text{MnTc}(\text{CO})_{10}$ and $\text{TcRe}(\text{CO})_{10}$ were prepared by the following reactions:

and:

a. $\text{MnRe}(\text{CO})_{10}$ Manganese decacarbonyl (102 mg, 0.26 mmol) was reduced to $\text{Mn}(\text{CO})_5^-$ by stirring for 45 min in 25 ml of THF with excess sodium amalgam (0.7g Na, 30.4 mmol and 10 ml Hg). The amalgam was removed through a stopcock at the bottom of the flask. Rhenium pentacarbonyl bromide (205 mg, 0.51 mmol) in 15 ml of THF was added dropwise over a period of 30 min. The solvent was removed under reduced pressure leaving a reddish brown residue. Sublimation at 60°C under a high vacuum onto a water-cooled probe yielded a mixture of $\text{Mn}_2(\text{CO})_{10}$ (11%), $\text{MnRe}(\text{CO})_{10}$ (77%), and $\text{Re}_2(\text{CO})_{10}$ (12%).

b. MnTc(CO)₁₀ A solution of Mn₂(CO)₁₀ (41 mg, 0.11 mmol) in 25 ml of THF was stirred 45 min with excess sodium amalgam (0.7g Na, 30.4 mmol and 10 ml Hg). After the amalgam was removed, Tc(CO)₅Br (approximately 60 mg, 0.19 mmol) in 20 ml of THF was added slowly. When the addition was completed (30 min), the solution was evaporated to dryness under reduced pressure. The volatile components of the residue were collected by vacuum sublimation. Gas chromatographic analysis of the sublimate showed that a mixture of Mn₂(CO)₁₀ (42%), MnTc(CO)₁₀ (55%), and Tc₂(CO)₁₀ (3%) had been produced.

c. TcRe(CO)₁₀ Technetium decacarbonyl (103 mg, 0.22 mmol) in 25 ml of THF was stirred with 5% sodium amalgam (0.7g Na, 30.4 mmol and 10 ml Hg) for 15 min. The amalgam was removed and Re(CO)₅Br (165 mg, 0.41 mmol) in 20 ml of THF was added dropwise over a period of 15 min. The reaction mixture was evaporated and sublimed. The sublimate was found to contain Tc₂(CO)₁₀ (37%), TcRe(CO)₁₀ (52%), and Re₂(CO)₁₀ (11%).

B. Purification and Identification

1. Group VIIB pentacarbonyl bromides

The infrared spectra in the CO stretching region agreed with the literature spectra [47] within 2 cm⁻¹. Except for Tc(CO)₅Br there was no indication of any impurities. No attempt was made to isolate pure Tc(CO)₅Br. The halide was extracted from the tetracarbonyl dimer with THF immediately before use.

2. Group VIIB mixed-metal decacarbonyls

The homonuclear and heteronuclear decacarbonyls are separated easily on nonpolar columns by gas chromatography. The separation is by molecular weight. Dimanganese decacarbonyl is eluted first followed by $\text{MnTc}(\text{CO})_{10}$, $\text{Tc}_2(\text{CO})_{10}$, $\text{MnRe}(\text{CO})_{10}$, $\text{TcRe}(\text{CO})_{10}$, and $\text{Re}_2(\text{CO})_{10}$. The difference in retention times between the mixed-metal carbonyls and the corresponding monometal complexes is sufficient for preparative work. However it is necessary to operate the injector, column, and detector at relatively low temperatures to avoid decomposition of the compounds.

As shown in Figures 7-9, the sublimates of each preparation separate into three peaks. For these chromatograms the 3% SE-30 column was held at 130° C and the injector and detector at 135° C. A flow rate of 150 ml/min of the helium carrier gas was used. These conditions provided a workable compromise between collection efficiency, peak shape, and resolution. With the filaments of the thermoconductivity detector on, $\text{Mn}_2(\text{CO})_{10}$ is collected with 60% recovery at these temperatures. A 10% improvement is obtained with the filaments off. The 150 ml/min flow rate is necessary to obtain good peak shapes and to allow a reasonable time for one collection (15 min). The resolution between $\text{MM}'(\text{CO})_{10}$ and the $\text{M}_2(\text{CO})_{10}$ and $\text{M}'_2(\text{CO})_{10}$ impurities is sufficient in every case to allow two injections within 30 s to be separated and collected simultaneously (Figure 8). The size of an injection (45 μl) was limited by the low solubility of the decacarbonyls

Figure 7. Gas chromatogram of a saturated pentane solution of the sublimate from a preparation of $\text{MnRe}(\text{CO})_{10}$.

Figure 8. Gas chromatogram for two injections of a saturated pentane solution of the sublimate from a preparation of $\text{MnTc}(\text{CO})_{10}$.

Figure 9. Gas chromatogram of a saturated pentane solution of the sublimate from a preparation of $\text{TcRe}(\text{CO})_{10}$.

in pentane. After 20 preparative collections (5 hr, 2 injections/collection), enough material (5-10 mg) was collected for mass spectrometric studies and further characterization. Very pure $\text{MnRe}(\text{CO})_{10}$ and $\text{TcRe}(\text{CO})_{10}$ (> 99%) were obtained in this manner. The Mn-Tc compound could not be separated from a small impurity of $\text{Mn}_2(\text{CO})_{10}$ (1-3%).

The gas chromatographic peaks labeled in Figures 7-9 were identified by the infrared spectra of collected samples in the region from 2100-1950 cm^{-1} . The spectra of the homonuclear decacarbonyls and $\text{MnRe}(\text{CO})_{10}$ have been reported [43] and identification was made by direct comparison. The identification of $\text{MnTc}(\text{CO})_{10}$ and $\text{TcRe}(\text{CO})_{10}$ was based upon retention times and qualitative comparison of their infrared spectra with the other decacarbonyls. Both compounds are eluted between the respective homonuclear decacarbonyls (Figures 8 and 9) as expected. The infrared spectra of the compounds are compared in Figures 10a and 10b. The $\text{M}_2(\text{CO})_{10}$ species belong to the D_{4d} point group and have three infrared-active C-O stretching modes, $2B_2 + E_1$. The energy of these vibrations decrease in the order $B_2 > E_1 > B_2'$ with respective intensities of medium, very strong, and medium as shown in Figure 10a. The mixed-metal derivatives most likely belong to the C_{4v} point group for which there are six infrared-active C-O vibrations ($4A_1 + 2E$). The spectrum of $\text{MnRe}(\text{CO})_{10}$ (Figure 10b) does not contain six bands but rather three bands in qualitative agreement with the homonuclear complexes (Figure 10a). The explanation as proposed by Flitcroft,

Figure 10. Carbonyl region of the infrared spectra of the Group VIIB dimetal (A) and mixed-metal (B) decacarbonyls.

Huggins, and Kaesz [43] is that the six bands are grouped into three sets $2A_1$, $2E$, and $2A_1'$. One mode of each set is either weak and cannot be observed or superimposed upon the other intense band. The spectra of $MnTc(CO)_{10}$ and $TcRe(CO)_{10}$ are in qualitative agreement with the spectrum of $MnRe(CO)_{10}$ as shown in Figure 10b. The shoulder on the low energy A_1' band of $MnTc(CO)_{10}$ cannot be accounted for on the basis of any impurity and lends some support to the argument of superimposition. The small band at 2013 cm^{-1} in this spectrum is due to the presence of $Mn_2(CO)_{10}$. The numerical results for the spectra of Figures 10a and 10b are tabulated in Table 7.

The mixed-metal decacarbonyls were also identified by their mass spectra. For $MnRe(CO)_{10}$, $MnTc(CO)_{10}$, and $TcRe(CO)_{10}$ the mass-to-charge ratios of the molecular ions were found to be 522, 434, and 566 respectively. The fragmentation patterns of the compounds are characterized by the stepwise loss of CO. The spectrum of $MnTc(CO)_{10}$ is monoisotopic. Each dimetal fragment of $MnRe(CO)_{10}$ and $TcRe(CO)_{10}$ has two isotopes in the approximate ratio of 5:3 due to the presence of Re.

Table 7. Carbonyl stretching frequencies (cm^{-1}) for the metal and mixed-metal decacarbonyls of Mn, Tc, and Re^a

Compound	Stretching Frequency					
	Found			Reported ^b		
$\text{Mn}_2(\text{CO})_{10}$	2044	2013	1983	2044	2013	1983
$\text{Tc}_2(\text{CO})_{10}$	2065	2017	1984	2064	2017	1984
$\text{Re}_2(\text{CO})_{10}$	2070	2014	1976	2070	2014	1976
$\text{MnRe}(\text{CO})_{10}$	2054	2017	1978	2054	2017	1978
$\text{MnTc}(\text{CO})_{10}$	2051	2024	1979, 1975			
$\text{TcRe}(\text{CO})_{10}$	2067	2017	1979			

^a Measured in cyclohexane solution.

^b Ref. [43].

V. RESULTS AND DISCUSSION

Fragmentation energies (Eq. 67) for the positive ions from two families of substituted metal carbonyls were determined and used to calculate ionic least-squares bond dissociation energies. In both cases the compounds were of the type $M(CO)_5L$ containing an octahedral distribution of the carbonyl groups and ligand, L, about a central metal atom, M. The fragmentation reactions of these molecules are of the form:

and:

From the energies of these reactions the M-CO and M-L bond energies were determined by the least-squares method.

The first class of compounds to be studied were the Group VIB hexacarbonyls and pentacarbonyl thiocarbonyls ($M = Cr, Mo, W$; $L = CO, CS$). For these compounds the C-O and C-S bond energies are two to five times stronger than the M-CO and M-CS bond energies, hence the molecules dissociate by cleavage of the M-C bonds rather than the C-O or C-S bonds. The calculation of ionic least-squares bond dissociation energies from the fragmentation energies is a direct application of the concepts presented previously (pp. 23-25) for molecules of the

form AR_n and $AR_{n-1}S$. Since the fragmentations are to ligands rather than to atoms, the calculated bond energies are approximate. They do not allow for the difference between the C-O or C-S bond energies in the bound and free carbonyl and thiocarbonyl ligands (Eq. 60). The calculated quantities are $\hat{D}(M^+-CO)_H$, the metal-carbonyl bond energy in the hexacarbonyls; $\hat{D}(M^+-CO)_T$, the metal-carbonyl bond energy in the thiocarbonyls; and $\hat{D}(M^+-CS)$, the metal-thiocarbonyl bond energy. The fragmentation energies and average bond dissociation energies, $\bar{D}(M^+-CO)_H$, for the hexacarbonyls have been determined previously [6, 48-50]. However, they were redetermined in this study so that the instrumental conditions and methods of calculation would be the same for both the hexacarbonyls and thiocarbonyls, thus enabling a precise comparison of their bond energies. The hexacarbonyl data also provided a convenient reference for determining the accuracy of the mass spectrometric method, since $\bar{D}(M^+-CO)_H$ can be calculated (Eq. 77) from the thermochemical results for $\bar{D}(M-CO)_H$ [20, 51-55] and compared with the values obtained from this work.

Samples of the thiocarbonyls were provided by Dr. B. D. Dombek (Iowa State University). Since both the thiocarbonyls and hexacarbonyls can fragment to give $M(CO)_n^+$ ions ($n=0,1,\dots,5$), the measured fragmentation energies of these ions will be incorrect unless the samples are pure. For the hexacarbonyls purity was not a problem, but it was for the thiocarbonyls which are prepared from the hexacarbonyls [56]. The thiocarbonyl complexes of Cr and W were obtained with less than 0.1%

hexacarbonyl impurity by preparative gas chromatography [57]. The molybdenum compound was not sufficiently stable to be purified by this method. From an analysis of the intensities of the molecular ions, it was determined that the sample of $\text{Mo}(\text{CO})_5\text{CS}$ contained 30-40% $\text{Mo}(\text{CO})_6$. The magnitude of this impurity precluded obtaining any meaningful data for the $\text{Mo}(\text{CO})_n^+$ ($n=0,1,\dots,5$) ions. Fragmentation energies were obtained only for those ions containing the CS ligand.

The hexacarbonyls and thiocarbonyls are sufficiently volatile at room temperature so that the vapors over the solid compounds can be introduced into the ion source of the $\pm$ mass spectrometer by means of a variable viscous leak. The gas pressure in the ion source was adjusted to approximately 2×10^{-6} torr. The ion source temperature was less than 100°C which is below the temperature at which thermal decomposition of the hexacarbonyls was observed by Junk and Svec [58]. It was assumed that no significant decomposition of the carbonyls or thiocarbonyls occurred. The mass range of the molecular and fragment ions of interest is within the normal operating limits of the $\pm$ mass spectrometer. The instrument was operated at 2000 V ion accelerating energy. A constant ionizing current of $2\ \mu\text{a}$ was used for the Cr and Mo complexes. To compensate for their lower volatility, the data for the tungsten compounds were obtained with $8\ \mu\text{a}$ of ionizing current.

Fragmentation energies were determined for the major isotope of each metal-containing ion by the modification of Warren's method described previously (pp. 41-43). A range of 1.5 V and a normalization multiple of 15 were used. The data for $\text{Cr}(\text{CO})_5\text{CS}$ and $\text{W}(\text{CO})_5\text{CS}$ were obtained graphically while those for $\text{Mo}(\text{CO})_5\text{CS}$ and the metal hexacarbonyls

were acquired by the computer method, IEAS. The reported values for the fragmentation energies and ionization potentials are averages of 4-6 individual determinations obtained during a period of 1-2 weeks. The energy scale was calibrated using the ground state ionization of Xenon.

The homonuclear and heteronuclear dimetal decacarbonyls of the Group VIIB elements ($M = \text{Mn, Tc, Re}$; $L = \text{M}(\text{CO})_5$) were the second class of compounds to be studied. The primary interest in these compounds was to obtain the metal-metal bond energies. Since the C-O bonds are much stronger than the M-CO or M-M bonds, Eqs. 100 and 101 are characteristic of the fragmentation reactions. The reactions are slightly more complex because the M-C bonds in the ligand are weaker than the M-L bond. Fragmentation by cleavage of the M-M bond (Eq. 101) is a minor process. The major process is:

where the symbolism $\text{M}(\text{M}')$ indicates that the two metal atoms may be the same or different. For bonding purposes these complexes can be considered as molecules of the form RS_{10} or $\text{S}_5\text{A}((\text{A}')\text{S}_5)$. The former description implies that ten equivalent carbonyls are bonded to the central $\text{M}(\text{M}')$ moiety. According to this interpretation one ionic bond energy, $\hat{D}_0(\text{M}(\text{M}')^+-\text{CO})$, would be calculated from a least-squares treatment of the fragmentation data. The latter model distinguishes the M-C energies of the two $\text{M}(\text{CO})_5$ groups. Two quantities would be calculated by the least-squares method, $\hat{D}(\text{M}(\text{M}')^+-\text{CO})$ and $\hat{D}'(\text{M}(\text{M}')^+-\text{CO})$. The energy of the M-(M') bond is calculated from the fragmentation energies of the processes:

It must be emphasized that the energy of the first fragmentation process ($n=0$) is not the energy of the M-(M') bond. The energy of this process, as well as the energies of the remaining processes ($n = 1, 2, \dots, 5$), reflects the difference between the M-C energies in the free and bound $\text{M}(\text{CO})_5$ ((M')(CO) $_5$) ligand. In other words, the M^+-CO ((M') ^+-CO) energy in the $\text{M}(\text{CO})_5^+$ ((M')(CO) $_5^+$) ion is different from the M-CO ((M')-CO) energy in the $\text{M}(\text{CO})_5$ ((M')(CO) $_5$) radical both of which differ from the M(M')-CO energies in the dimetal ion. The least-squares method allows for the separation of these effects. Three quantities can be calculated, $\hat{D}(\text{M}^+-\text{M}')$, $\hat{D}(\text{M}^+-\text{CO})$ ($\hat{D}((\text{M}')^+-\text{CO})$), and $\hat{D}(\text{M}-\text{CO})$ ($\hat{D}((\text{M}')-\text{CO})$). All M-C energies include the difference between the C-O energy in the bound and free carbonyl.

Samples of $\text{Mn}_2(\text{CO})_{10}$, $\text{Tc}_2(\text{CO})_{10}$, and $\text{Re}_2(\text{CO})_{10}$ were obtained from commercial sources and were purified by vacuum sublimation before use. The mass spectrum of $\text{Tc}_2(\text{CO})_{10}$ indicated a small impurity ($< 10\%$) of a compound which was identified as $\text{TcRe}(\text{CO})_{10}$. Pure $\text{Tc}_2(\text{CO})_{10}$ was obtained by preparative gas chromatography. No impurities were noted in $\text{Mn}_2(\text{CO})_{10}$ or $\text{Re}_2(\text{CO})_{10}$. The mixed-metal decacarbonyls were synthesized and purified as described in Chapter 3. The small amount of $\text{Mn}_2(\text{CO})_{10}$ in the Mn-Tc complex did not preclude a determination of

the Mn-Tc⁺ dissociation energy since Tc(CO)_n⁺ (n=0,1,...,5) and Mn(CO)₅ are produced by cleavage of the Mn-Tc bond.

Because the +/- mass spectrometer is not equipped with a direct insertion probe, the vapors over the solid decacarbonyls had to be introduced directly into the mass spectrometer. This method of introducing the samples was practical only for Mn₂(CO)₁₀ which was estimated to be comparable in volatility at room temperature to the hexacarbonyl and thiocarbonyl complexes of tungsten. Ion source pressures of 2×10^{-6} torr could be obtained for this compound. For the other samples it was necessary to heat the inlet system. Even then, source pressures varied from 1.5×10^{-6} torr for MnTc(CO)₁₀ to 1×10^{-7} torr for Re₂(CO)₁₀. The lower pressures for the rhenium-containing complexes resulted in lower ion currents with poorer signal-to-noise ratios making their fragmentation data difficult to obtain. These difficulties were further compounded by the fact that the masses of the molecular ions of the decacarbonyls, ranging from 390 for Mn₂(CO)₁₀⁺ to 654 for Re₂(CO)₁₀⁺, are outside the normal operating limits of the +/- mass spectrometer. In order to obtain ionization efficiency data for these compounds it was necessary to operate at lower ion accelerating voltages. At maximum magnetic field strength Mn₂(CO)₁₀⁺ and Re₂(CO)₁₀⁺ were focused on the collector at 1600 V and 975 V, respectively. Accelerating voltages for the other compounds were intermediate between these values. Operation at these accelerating voltages resulted in a reduction of sensitivity and resolution. It was

estimated that ion currents were reduced by a factor of three from those obtained at normal operating voltages, 2000-2200 V. In the worst case, the instrument was only capable of separating two mass units at 30-50% valley. This meant that adjacent isotopes of the same ion would be superimposed or overlap. However, separations of 28 mass units (loss of CO) were obtained easily, and resolution was not a limitation in determining fragmentation energies for the dimetal ions, $M(M')(CO)_{10-n}^+$ ($n = 0, 1, \dots, 10$). Only the rhenium-containing ions were not monoisotopic. Isotopic interferences are not a problem because the method is not sensitive enough to differentiate fragmentation energies for different isotopes of the same ion. In several cases dimetal and monometal ions from the same compound were adjacent in mass (e.g. $Mn_2(CO)_3^+$ (194) and $Mn(CO)_5^+$ (195) from $Mn_2(CO)_{10}$ and $MnRe(CO)_3^+$ (326, 324) and $Re(CO)_5^+$ (327, 325) from $MnRe(CO)_{10}$). In these instances adjacent masses could not be resolved completely, but accurate fragmentation energies could be obtained for both ions. The energies of the two fragmentation processes are different by approximately 4 eV so that the higher energy process, the formation of the dimetal ion, does not interfere with the ionization efficiency data for the monometal ion. The small interference in the ionization efficiency curve of the dimetal ion, due to the monometal ion, was corrected with a linear least-squares fit of the baseline.

Although the +/- mass spectrometer was being used beyond its intended specifications, fragmentation data were obtained for $Mn_2(CO)_{10}$,

MnTc(CO)_{10} , $\text{Tc}_2(\text{CO})_{10}$, MnRe(CO)_{10} , and $\text{Re}_2(\text{CO})_{10}$. The combination of small sample size, low volatility, and low signal-to-noise ratios made it impossible to obtain any fragmentation data for TcRe(CO)_{10} . The mass spectrum of this compound was obtained with a Dupont Model 21-490 mass spectrometer. The sample was introduced into the ion source via a direct insertion probe.

All fragmentation energies were determined for the major isotope of each metal-containing ion by the IEAS. Much of the data could not have been obtained without this system because signal-to-noise ratios were enhanced considerably by the repetitive acquisition of noisy ionization efficiency data. A range of 1.5 V and a normalization multiple of 15 were used. For many of the ions, particularly $\text{M(M') (CO)}_{10-n}^+$ ($n = 0, 1, 2, 3$), it was necessary to subtract an interference, assumed to be due to a metastable process, by using a linear least-squares fit of the baseline of the IE curves. The reported value of a fragmentation energy or an ionization potential is an average of 4-6 individual determinations obtained over the period of at least one week. All data were obtained with $8 \mu\text{a}$ of ionizing current. It was assumed that the decacarbonyls did not decompose in the ion source or in the heated inlet system. The latter assumption was tested with $\text{Tc}_2(\text{CO})_{10}$. No difference was found between the fragmentation energies obtained with and without the inlet heated. The electron energy scale was calibrated with xenon.

A. Group VIB Carbonyls and Thiocarbonyls

During the past decade there has been considerable experimental and theoretical interest in transition metal thiocarbonyl complexes [59]. Particular emphasis has been placed upon the comparative nature of the M-CO and M-CS bond. As a result the Group VIB metal thiocarbonyls, $M(CO)_5CS$, have received much attention recently. The preparation and chemistry of these compounds has been described by Dombek and Angelici [57, 60, 61]. Their studies revealed that CS forms a much more stable M-C bond than does CO, activates the metal atom toward CO substitution particularly in the trans position, and undergoes electrophilic addition and nucleophilic attack more readily than CO. The increased stability of the M-CS bond relative to the M-CO bond was also confirmed by Poliakoff from low temperature matrix isolation studies [62, 63]. There was no evidence from his experiments of the "trans" labilizing effect of the thiocarbonyl ligand. Both cis and trans carbonyl groups were found to be lost with equal probability to form a pentacoordinated photoproduct. In accordance with these results Butler et al. [64] found the M-CS force constants to be much larger than either the axial or equatorial M-CO force constants. However the latter two quantities differed significantly. The axial constants are less than the equatorial constants which do not differ from the M-CO force constants in the corresponding metal hexacarbonyls. All of the experimental evidence concerning the comparative strength of the M-CO and M-CS bonds in the $M(CO)_5CS$ complexes is consistent with the theoretical

calculations of Richards [65] and Lichtenberger and Fenske [66] which show that CS is both a better σ donor and π acceptor than CO. The stronger π acidity of the thiocarbonyl ligand lessens the extent to which the metal $\delta\pi$ electrons can be shared with the carbonyl ligands. This effect, along with the increased donor ability of CS, results in a stronger M-CS than M-CO bond and causes the M-CO bonds in the thio-carbonyls to be weaker than those in the respective $M(CO)_6$ complexes. The experimental evidence strongly suggests that this weakening effect is localized in the trans M-CO bond.

The purpose of the present work was to account for the bonding in these complexes by obtaining quantitative results for the energies of the M-CO and M-CS bonds via mass spectrometry. As a calorimeter a mass spectrometer is of limited utility. In the absence of ionization potentials for pertinent moieties only ionic bond dissociation energies can be obtained by this method. In order to relate the measured fragmentation energies to the desired dissociation energies, it is necessary to neglect any excess energy that may be imparted to the fragments during the electron impact process. Hence the results, although precise to a few tenths of kilocalories, are generally accurate to only two to ten kilocalories. Despite these limitations it was anticipated that reliable results could be obtained from a comparative study of the Group VIB thiocarbonyls and carbonyls.

1. Mass spectra

The 50 eV mass spectra of the $M(CO)_5CS$ and corresponding $M(CO)_6$ complexes of Cr, Mo, and W are presented as histograms in Figs. 11-13. Fragmentation patterns of the hexacarbonyls are in agreement with those obtained previously [6]. In the case of $Mo(CO)_5CS$ a rather large $Mo(CO)_6$ impurity prevented the accurate measurement of the carbonyl-containing ions $Mo(CO)_n^+$ ($n = 0, 1, \dots, 5$). The reported spectrum was corrected on the basis of the fragmentation pattern of $Mo(CO)_6$.

In each figure there is a definite similarity between the two spectra. Substitution of CS for CO in going from $M(CO)_6$ to $M(CO)_5CS$ results in only a slight modification of the fragmentation pattern. In fact the same, as yet unexplained, trend in the intensities of $W(CO)_5^+$, $Mo(CO)_5^+$, $Mo(CO)_4^+$, $Cr(CO)_5^+$, $Cr(CO)_4^+$, and $Cr(CO)_3^+$ appears to be followed to a lesser extent in the analogous thiocarbonyl ions $W(CO)_4CS^+$, $Mo(CO)_4CS^+$, $Mo(CO)_3CS^+$, $Cr(CO)_4CS^+$, $Cr(CO)_3CS^+$, and $Cr(CO)_2CS^+$. The most significant feature of the $M(CO)_5CS$ spectra is the predominance of the ions containing the CS ligand. In this respect these spectra are similar to those reported for various cyclopentadienyl-manganese thiocarbonyl complexes [67, 68]. These data strongly suggest that the M-CS bond is stronger than the M-CO bond. However, conclusions about the strengths of the bonds based solely on fragmentation data should be regarded cautiously since fragmentation patterns are dependent upon the relative stabilities of the ions formed. Conclusive evidence can only be obtained from the energetics of the fragmentation processes.

Figure 11. Monoisotopic mass spectra (50 eV) of $\text{Cr(CO)}_5\text{CS}$ and Cr(CO)_6 .

Figure 12. Monoisotopic mass spectra (50 eV) of $\text{Mo(CO)}_5\text{CS}$ and Mo(CO)_6 .

Figure 13. Monoisotopic mass spectra (50 eV) of $W(CO)_5CS$ and $W(CO)_6$.

2. Ionization potentials

Listed in Table 8 are the measured ionization potentials of the hexacarbonyl and pentacarbonyl thiocarbonyl complexes of the Group VIB metals. For comparison the ionization potentials determined by photoelectron spectroscopy are given in the final column. In general there is good agreement between the results from both methods. The discrepancy between the values for $\text{Cr}(\text{CO})_5\text{CS}$ and $\text{W}(\text{CO})_5\text{CS}$ illustrates that results can be obtained quite precisely (i.e. to a few hundredths of eV) but are probably accurate to a few tenths of eV. As reported previously [66,69], the ionization potentials of the thiocarbonyl complexes average about 0.3 eV lower than those for their respective hexacarbonyl complexes indicating that the metal b_2 and e orbitals are destabilized with respect to the t_{2g} orbitals of the hexacarbonyls. Although simple arguments based upon the greater π -acidity of the thiocarbonyl ligand would predict the opposite, this result correlates directly with empirical evidence [70] that substitution of a ligand in a metal carbonyl complex with one having a lower ionization potential will decrease the ionization potential of the resulting complex by 10-20% of the difference (i.e. $\text{IP}(\text{CO}) = 14.01$ eV, $\text{IP}(\text{CS}) = 11.34$ eV, and $\Delta\text{IP}(\text{CO-CS}) = 2.67$ eV, hence $\Delta\text{IP}(\text{M}(\text{CO})_6 - \text{M}(\text{CO})_5\text{CS})$ should be in the range of 0.3-0.5 eV). From previous studies which relate this change to the relative σ -donor and π -acceptor abilities of the ligands [71, 72], these data suggest that CS is a stronger σ -donor than CO. Although the theoretical calculations of Lichtenberger and Fenske [66] confirm this

Table 8. Ionization potentials (eV) of the Group VIB hexacarbonyls and pentacarbonyl thiocarbonyls

Compound	Electron Impact Results	Photoelectron Results ^a
$\text{Cr}(\text{CO})_6$	8.42 ± 0.03	8.40 ± 0.02
$\text{Cr}(\text{CO})_5\text{CS}$	8.31 ± 0.03	8.16 ± 0.02
$\text{Mo}(\text{CO})_6$	8.46 ± 0.01	8.50 ± 0.02
$\text{Mo}(\text{CO})_5\text{CS}$	8.18 ± 0.02	---
$\text{W}(\text{CO})_6$	8.60 ± 0.02	8.56 ± 0.02
$\text{W}(\text{CO})_5\text{CS}$	8.22 ± 0.01	8.30 ± 0.02^b

^aHexacarbonyl results are taken from Ref. [69] and those for the thiocarbonyls from Ref. [66].

^bAverage of the range reported in Ref. [66] for the U' component.

result, the destabilization of the metal orbitals in the thiocarbonyl complexes (i.e. lower ionization potentials) was shown to be a consequence of donation from the CS π -bonding orbitals and not from the σ orbitals.

In addition to yielding qualitative insights into the nature of the bonding within metal carbonyl complexes, ionization potentials provide valuable quantitative information which is seldom utilized in bonding studies by mass spectrometry. Consider that the ionization and fragmentation of a metal carbonyl, $M(CO)_n$, occurs by the following pathways:

It follows that:

$$IP(M(CO)_n) - IP(M) = n \bar{D}(M-CO) - n \bar{D}(M^+-CO), \tag{105}$$

where $\bar{D}(M^+-CO)$ and $\bar{D}(M-CO)$ are the average bond dissociation energies in the parent ion and molecule, respectively. The difference between the ionization potential of the molecule and that of the central metal atom is equal to the difference between the total energy of the M-C bonds in the molecule and ion. In the case under consideration it is possible to calculate the M-C bond energy in the molecule directly from measured values for $IP(M(CO)_n)$ and $\bar{D}(M^+-CO)$ and from the spectroscopic ionization potential of the central metal atom. This is not

possible in general (e.g. $M(\text{CO})_{n-1}^+L$) because the bond energy sums do not simplify to one unknown. In these cases the ionization potential difference is valuable for relating bonding trends in the ion to those in the molecule and is useful in approximating neutral dissociation energies from measured ionic values.

3. Ionic bond dissociation energies

A mass spectrometer provides a facile means of determining ionic bond dissociation energies from the energetics of molecular fragmentations. However, its value for this purpose is seriously limited as a result of indeterminate errors due to excess kinetic and excitation energies in the fragmentation processes. These errors cast doubt upon the accuracy of the data and interpretation of the results. By determining the M-C energies in the hexacarbonyls, which are known accurately from combustion calorimetry, it was hoped that the method could be calibrated.

The important fragmentation processes and their energies for the hexacarbonyl complexes of Cr, Mo, and W are tabulated in Table 9. The fragmentations in the first column have to be assigned tentatively because only the mass-to-charge ratios of the product ions are known. On the basis of the energies of the processes and simple thermodynamic considerations (e.g. $D(\text{C-O}) = 11.14 \text{ eV}$), these assignments are very probably correct. Evidence supporting this conclusion was obtained from a mass spectrometer designed to record the spectrum of the neutral fragments produced from electron impact processes [73]. As expected a

Table 9. Fragmentation processes and their energies (eV) for the Group VIB hexacarbonyls

Assumed Process	ΔH		
	$\text{Cr}(\text{CO})_6$	$\text{Mo}(\text{CO})_6$	$\text{W}(\text{CO})_6$
$\text{M}(\text{CO})_6^+ \rightarrow \text{M}(\text{CO})_5^+ + \text{CO}$	1.43 ± 0.01	1.56 ± 0.01	1.70 ± 0.02
$\rightarrow \text{M}(\text{CO})_4^+ + 2\text{CO}$	2.03 ± 0.01	3.15 ± 0.01	3.62 ± 0.02
$\rightarrow \text{M}(\text{CO})_3^+ + 3\text{CO}$	2.93 ± 0.01	4.83 ± 0.02	5.46 ± 0.01
$\rightarrow \text{M}(\text{CO})_2^+ + 4\text{CO}$	4.09 ± 0.03	6.40 ± 0.02	7.69 ± 0.03
$\rightarrow \text{M}(\text{CO})^+ + 5\text{CO}$	5.61 ± 0.02	8.06 ± 0.03	9.76 ± 0.05
$\rightarrow \text{M}^+ + 6\text{CO}$	6.94 ± 0.01	9.78 ± 0.06	12.41 ± 0.04

signal at m/z 28 was observed in the mass spectrum of the neutral fragments produced from $\text{Cr}(\text{CO})_6$ [74]. The fragment was identified as CO on the basis of its ionization potential. Chromium hexacarbonyl was the only compound with sufficient volatility to be introduced into the neutral fragment mass spectrometer at the pressures required for these experiments.

The fragmentation enthalpies listed in Table 9 are in fair agreement with the values determined by previous investigators [6, 48-50]. Neglecting any effects due to kinetic energies or excitation energies, the data represent the energy required to remove successive carbonyl groups from the molecular ion. This is evidenced by the monotonic increase in enthalpies with increased fragmentation. The energy of the first process is a dissociation energy for the M^+-CO bond. Energies of the remaining processes are sums of the dissociation energies given in Table 10. Excluding the first, each entry in the table is obtained by taking successive differences of the processes and energies of Table 9. When considered collectively for a given compound, the cited values for the energies represent six values of the M^+-CO bond energy. Differences between the dissociation energies for a particular complex are the result of variations in reorganizational energies of the ions. It can be concluded from these data that the dissociation energies are in the order $D(\text{W}^+-\text{CO}) > D(\text{Mo}^+-\text{CO}) > D(\text{Cr}^+-\text{CO})$. This order holds for every row in Table 10 but need not be the case if reorganizational energies vary widely for a series of compounds

Table 10. Specific bond dissociation energies (eV) of the ions from hexacarbonyl compounds of the Group VIB elements

Dissociation Process	Bond Dissociation Energy		
	Cr	Mo	W
$M(CO)_6^+ \rightarrow M(CO)_5^+ + CO$	1.43	1.56	1.70
$M(CO)_5^+ \rightarrow M(CO)_4^+ + CO$	0.60	1.59	1.92
$M(CO)_4^+ \rightarrow M(CO)_3^+ + CO$	0.90	1.68	1.84
$M(CO)_3^+ \rightarrow M(CO)_2^+ + CO$	1.16	1.57	2.23
$M(CO)_2^+ \rightarrow M(CO)^+ + CO$	1.52	1.66	2.07
$M(CO)^+ \rightarrow M^+ + CO$	1.33	1.72	2.65

being compared. For making comparisons between different compounds, a single quantity is desired which is related to the specific bond dissociation energies of the chemically equivalent bonds of a molecule and which is free from reorganizational effects. In this case such a quantity is given by the average of the six dissociation energies and is called appropriately the average bond dissociation energy, $\bar{D}(M^+-CO)$. This bond energy is one-sixth the enthalpy of the final process listed in Table 9. There are no reorganizational effects for this reaction since fragmentation is complete. Values for $\bar{D}(M^+-CO)$ are shown in the second column of Table 11. The ordering of bond strengths is readily apparent from these data. Unfortunately average bond dissociation energies cannot be calculated for molecules having more than one set of chemically equivalent bonds (e.g. $M(CO)_{n-1}L$). The energy to fragment completely such a molecule would be equal to a sum of terms, one for each set of equivalent bonds. As a result a new method was developed for interpreting fragmentation energies.

Considering the fragmentation reactions given in Table 9 and the nature of the bonding in the hexacarbonyl complexes, a single quantity is desired for the M^+-CO bond energy. This quantity will be denoted as $\hat{D}(M^+-CO)$. If the i th fragmentation is envisioned as occurring in the following manner:

Table 11. Ionic bond dissociation energies (eV) for $M(\text{CO})_6$ compounds

Compound	$\bar{D}(\text{M}^+-\text{CO})$		$\hat{D}(\text{M}^+-\text{CO})$	Δ
	Electron Impact	Calorimetric		
$\text{Cr}(\text{CO})_6$	1.16 ± 0.01	0.83 ± 0.01	1.10 ± 0.03	0.27
$\text{Mo}(\text{CO})_6$	1.63 ± 0.01	1.35 ± 0.01	1.61 ± 0.01	0.26
$\text{W}(\text{CO})_6$	2.07 ± 0.01	1.74 ± 0.01	1.97 ± 0.04	0.23

the i th fragmentation enthalpy is equal to the energy required to break six M-CO bonds, $6\hat{D}(M^+-CO)$, minus the energy gained in forming the product ion, $(6-i)\hat{D}(M^+-CO)$. Hence it follows that:

$$\begin{array}{c} \begin{bmatrix} 6-5 \\ 6-4 \\ 6-3 \\ 6-2 \\ 6-1 \\ 6-0 \end{bmatrix} \end{array} \hat{D}(M^+-CO) = \begin{array}{c} \begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{bmatrix} \end{array} \hat{D}(M^+-CO) = \begin{array}{c} \begin{bmatrix} 1.43 \\ 2.03 \\ 2.93 \\ 4.09 \\ 5.61 \\ 6.94 \end{bmatrix} \end{array} \text{ or } \begin{array}{c} \begin{bmatrix} 1.56 \\ 3.15 \\ 4.83 \\ 6.40 \\ 8.06 \\ 9.78 \end{bmatrix} \end{array} \text{ or } \begin{array}{c} \begin{bmatrix} 1.70 \\ 3.62 \\ 5.46 \\ 7.69 \\ 9.76 \\ 12.41 \end{bmatrix} \end{array} , \quad (107)$$

depending upon the compound being considered. These six equations, the observational equations, in one unknown, when solved by the least-squares method [19], give the results listed in the fourth column of Table 11. Of particular interest is a comparison of the least-squares dissociation energies with the average dissociation energies calculated previously (column two of Table 11). Agreement between the two quantities is very good. This is particularly encouraging in view of the fact that it was necessary to assume that the M^+-CO energies were the same in all fragments and the molecular ion in order to generate the observational equations.

Given in the third column of Table 11 are the calorimetric values for $\bar{D}(M^+-CO)$. These energies were obtained via Eq. 105 with n equal to six using the ionization potentials of the hexacarbonyls determined in this study, spectroscopic values for the ionization potentials of the metal atoms (6.76, 7.10 and 7.98 eV for Cr, Mo, and W, respectively [75]) and $\bar{D}(M-CO)$'s from a recent calorimetric study [55] (1.11, 1.57,

and 1.85 eV for $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$, respectively). As anticipated the electron impact and calorimetric dissociation energies do not agree. The differences between $\hat{D}(\text{M}^+-\text{CO})$ and the calorimetric values for $\bar{D}(\text{M}^+-\text{CO})$ are given under the Δ heading in the final column of Table 11. The errors in the mass spectrometric results are surprisingly constant for all three compounds. The lack of a mass dependence seemingly eliminates fragment kinetic energies as a probable cause. Their magnitudes are too low to be a result of electronic excitations, but are highly suggestive of vibrational excitation. In fact the average, 0.25 ± 0.02 eV, agrees with the vibrational fundamental of CO, 0.27 eV. This lends itself to the interpretation that CO carries one quantum of vibrational energy during the cleavage of the M-CO bond. Direct evidence supporting this hypothesis was obtained by determining the ionization potential of CO produced by the fragmentation of $\text{Cr}(\text{CO})_6$ by electron impact. If CO is produced in its first ($v=1$) vibrational state, its ionization potential should be lowered by this amount. Using the recently developed "neutrals" mass spectrometer [73], with Ar as a calibrating gas the ionization potential of CO from gaseous CO was determined to be 14.0 ± 0.1 eV which is in excellent agreement with the spectroscopic value of 14.01 eV. The ionization potential of CO from $\text{Cr}(\text{CO})_6$ was measured as 13.7 ± 0.1 eV. As anticipated the ionization potential of CO was lowered by approximately 0.3 eV. Similar results have been obtained for CO produced from ketones [76].

Listed in Table 12 are the fragmentation processes and energies obtained for the $M(CO)_5CS$ complexes of Cr, Mo, and W. On the basis of the results for the hexacarbonyls, each energy has been corrected by 0.25 eV for every CO produced. By analogy with CO it was assumed that loss of CS would also occur with one quantum of excess vibrational energy. Therefore 0.16 eV, the fundamental vibrational energy of CS, was also subtracted from those processes involving the rupture of the M^+-CS bond. A cursory examination of Table 12 reveals that the fragmentation processes can be grouped into two sets. The first five reactions involve the formation of fragment ions containing the thiocarbonyl ligand while the remaining six do not. The energies of each set increase regularly with increased fragmentation of the molecular ion. Neglecting any effects caused by reorganization of the fragments, the energy of each process can be attributed to the breaking and making of M^+-CS or M^+-CO bonds. A series of observational equations can be generated in the same manner as was done for the hexacarbonyl compounds. Two sets of equations were developed from different models for the bonding in the thiocarbonyls. First, it was assumed that the five M^+-CO bonds in the thiocarbonyl compounds were energetically equivalent but different in energy from the M^+-CS bond and from the M^+-CO bonds in the hexacarbonyl compounds. Three quantities can be calculated on the basis of this model $\hat{D}(M^+-CO)_T$, $\hat{D}(M^+-CO)_H$, and $\hat{D}(M^+-CS)$. The subscripts T and H differentiate the M^+-CO energy in those ions containing the thiocarbonyl ligand from

Table 12. Fragmentation processes and their energies (eV) for the Group VIB thiocarbonyls

Assumed Process	ΔH		
	Cr(CO) ₅ CS	Mo(CO) ₅ CS	W(CO) ₅ CS
$M(CO)_5CS^+ \rightarrow M(CO)_4CS^+ + CO$	0.83±0.03	0.93±0.04	1.27±0.04
$\rightarrow M(CO)_3CS^+ + 2CO$	1.41±0.03	2.34±0.04	2.89±0.04
$\rightarrow M(CO)_2CS^+ + 3CO$	2.06±0.03	3.46±0.09	4.49±0.04
$\rightarrow M(CO)CS^+ + 4CO$	2.81±0.03	5.28±0.04	6.61±0.04
$\rightarrow M(CS)^+ + 5CO$	4.12±0.03	6.64±0.09	8.60±0.04
$\rightarrow M(CO)_5^+ + CS$	2.11±0.06		3.08±0.14
$\rightarrow M(CO)_4^+ + CO + CS$	2.40±0.04		4.49±0.11
$\rightarrow M(CO)_3^+ + 2CO + CS$	3.09±0.04		5.98±0.11
$\rightarrow M(CO)_2^+ + 3CO + CS$	4.30±0.07		8.08±0.27
$\rightarrow M(CO)^+ + 4CO + CS$	5.47±0.07		10.10±0.21
$\rightarrow M^+ + 5CO + CS$	6.44±0.06		12.34±0.13

those which do not. The M^+-CO energy in the hexacarbonyls can be calculated from the fragmentation energies of $Cr(CO)_5CS$ and $W(CO)_5CS$ because the thiocarbonyls fragment to give ions of the form $M(CO)_n^+$ and because the least-squares treatment allows for the dependence of bond dissociation energies upon molecular environments. Application of the previous considerations to the fragmentation processes of Table 12 yields the following systems of equations:

$$\begin{bmatrix} 1 & 0 & 0 \\ 2 & 0 & 0 \\ 3 & 0 & 0 \\ 4 & 0 & 0 \\ 5 & 0 & 0 \\ 5 & 1 & -5 \\ 5 & 1 & -4 \\ 5 & 1 & -3 \\ 5 & 1 & -2 \\ 5 & 1 & -1 \\ 5 & 1 & 0 \end{bmatrix} \begin{bmatrix} \hat{D}(M^+-CO)_T \\ \hat{D}(M^+-CS) \\ \hat{D}(M^+-CO)_H \end{bmatrix} = \begin{bmatrix} 0.83 \\ 1.41 \\ 2.06 \\ 2.81 \\ 4.12 \\ 2.11 \\ 2.40 \\ 3.09 \\ 4.30 \\ 5.47 \\ 6.44 \end{bmatrix} \quad \text{or} \quad \begin{bmatrix} 1.27 \\ 2.89 \\ 4.49 \\ 6.61 \\ 8.60 \\ 3.08 \\ 4.49 \\ 5.98 \\ 8.08 \\ 10.10 \\ 12.34 \end{bmatrix} \quad (108)$$

for $Cr(CO)_5CS$ and $W(CO)_5CS$, respectively and:

$$\begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{bmatrix} \begin{bmatrix} \hat{D}(M^+-CO)_T \end{bmatrix} = \begin{bmatrix} 0.93 \\ 2.34 \\ 3.46 \\ 5.28 \\ 6.64 \end{bmatrix} \quad (109)$$

for $Mo(CO)_5CS$. The results of the least-squares solution of these equations are given in Table 13. The data clearly show that in the positive ion the M^+-CS bonds are considerably stronger than the M^+-CO bonds which are weakened with respect to the M^+-CO bonds in the hexacarbonyls. These conclusions are in agreement with the previously published results for the Group VIB thiocarbonyl complexes [57,64].

Table 13. Least-squares bond dissociation energies (eV) calculated for the thiocarbonyls assuming equivalence of the five M^+-CO bonds

Compound	$\hat{D}(M^+-CO)_H$	$\hat{D}(M^+-CO)_T$	$\hat{D}(M^+-CS)$
$Cr(CO)_5CS$	0.92 ± 0.07	0.76 ± 0.04	2.47 ± 0.29
$Mo(CO)_5CS$	---	1.28 ± 0.04	---
$W(CO)_5CS$	1.86 ± 0.09	1.64 ± 0.05	3.82 ± 0.37

A recent electron impact study of cyclopentadienylmanganese thiocarbonyl and carbonyl complexes [68] and a recent X-ray structural investigation of trans-W(CO)₄(CNC₆H₁₁)CS [77] have also shown the M-CS bond to be stronger than the M-CO bond. In contradiction to the present findings the electron impact results show the M⁺-CO bonds in the thiocarbonyl complexes to be stronger than those of the carbonyl analogs. This discrepancy can presumably be attributed to a crossover in the electronic properties of CS and CO [78]. Analogous with the hexacarbonyl compounds, the M⁺-CO dissociation energies decrease in the order W > Mo > Cr. For Cr and W the M⁺-CS bond strengths show a similar dependence. Presumably the Mo⁺-CS bond energy lies between the two. Values for $\hat{D}(M^+-CO)_H$ are in excellent agreement with the calorimetric energies in Table 11 for the hexacarbonyl compounds.

On the basis of experimental evidence [51] and force constant calculations [64], the data of Table 12 were fit to a second model. The five carbonyl ligands of the M(CO)₅CS complexes were not considered equivalent. One of them, presumably the trans CO, was assumed to be more weakly bound than the rest. The two calculated dissociation energies are $\hat{D}'(M^+-CO)_T$ and $\hat{D}(M^+-CO)_T$ denoting the weak bond and strong bonds, respectively. For the purpose of generating the observational equations, the assumption was made that the weaker M⁺-CO bond was broken first. For Cr(CO)₅CS and W(CO)₅CS, the equations are:

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 1 & 2 & 0 & 0 \\ 1 & 3 & 0 & 0 \\ 1 & 4 & 0 & 0 \\ 1 & 4 & 1 & -5 \\ 1 & 4 & 1 & -4 \\ 1 & 4 & 1 & -3 \\ 1 & 4 & 1 & -2 \\ 1 & 4 & 1 & -1 \\ 1 & 4 & 1 & 0 \end{bmatrix} \begin{bmatrix} \hat{D}'(M^+-CO)_T \\ \hat{D}(M^+-CO)_T \\ \hat{D}(M^+-CS) \\ \hat{D}(M^+-CO)_H \end{bmatrix} = \begin{bmatrix} 0.83 \\ 1.41 \\ 2.06 \\ 2.81 \\ 4.12 \\ 2.11 \\ 2.40 \\ 3.09 \\ 4.30 \\ 5.47 \\ 6.44 \end{bmatrix} \quad \text{or} \quad \begin{bmatrix} 1.27 \\ 2.89 \\ 4.49 \\ 6.61 \\ 8.60 \\ 3.08 \\ 4.49 \\ 5.98 \\ 8.08 \\ 10.10 \\ 12.34 \end{bmatrix} \quad (110)$$

and:

$$\begin{bmatrix} 1 & 0 \\ 1 & 1 \\ 1 & 2 \\ 1 & 3 \\ 1 & 4 \end{bmatrix} \begin{bmatrix} \hat{D}'(M^+-CO)_T \\ \hat{D}(M^+-CO)_T \end{bmatrix} = \begin{bmatrix} 0.93 \\ 2.34 \\ 3.46 \\ 5.28 \\ 6.64 \end{bmatrix} \quad (111)$$

for $\text{Mo}(\text{CO})_5\text{CS}$. The calculated dissociation energies are tabulated in Table 14. There have been slight reductions in the $M^+-\text{CS}$ dissociation energies, but more significantly the destabilizing effect of the CS ligand is limited to the weaker $M^+-\text{CO}$ bond. Dissociation energies of the remaining four carbonyls do not differ from those in the $\text{M}(\text{CO})_6$ complexes. The relative energy ordering $\text{W} > \text{Mo} > \text{Cr}$ has been preserved in all cases. The exact agreement between these results and the M-C force constants strongly suggests that trans CO has been labilized.

Since both models fit the data equally well, an experiment was designed to differentiate the two cases. The fragmentation of trans- $(^{13}\text{CO})\text{W}(\text{CO})_4\text{CS}$ was studied in an attempt to ascertain whether there is a specific or a random loss of the labeled CO. The specificity of the fragmentation:

Table 14. Least-squares bond dissociation energies (eV) for the thiocarbonyls calculated with the assumption that one M^+-CO bond is weaker than the rest

Compound	$\hat{D}(M^+-CO)_H$	$\hat{D}(M^+-CO)_T$	$\hat{D}'(M^+-CO)_T$	$\hat{D}(M^+-CS)$
$Cr(CO)_5CS$	0.92 ± 0.07	0.80 ± 0.10	0.65 ± 0.24	2.42 ± 0.33
$Mo(CO)_5CS$	---	1.44 ± 0.06	0.86 ± 0.14	---
$W(CO)_5CS$	1.86 ± 0.07	1.84 ± 0.09	1.10 ± 0.23	3.55 ± 0.32

was found to be dependent upon the electron accelerating energy. At electron energies of 50 eV the labeled carbonyl is lost to form more than twice as much unlabeled $\text{W}(\text{CO})_4\text{CS}^+$ as predicted on a statistical basis. However near onset (i.e. at that electron energy equal to the fragmentation energy) the loss of ^{13}CO is random. The results are inconclusive in distinguishing the two models.

4. Neutral dissociation energies and heats of formation

Bond energies in the molecule and molecular ion for complexes of the type $\text{M}(\text{CO})_n$ were shown to be related according to Eq. 105.

The analogous relationship for $\text{M}(\text{CO})_5\text{CS}$ complexes is:

$$\text{IP}(\text{M}(\text{CO})_5\text{CS}) - \text{IP}(\text{M}) = 5\hat{\text{D}}(\text{M}-\text{CO})_{\text{T}} + \hat{\text{D}}(\text{M}-\text{CS}) - 5\hat{\text{D}}(\text{M}^+-\text{CO})_{\text{T}} - \hat{\text{D}}(\text{M}^+-\text{CS}) \quad (113)$$

where it has been assumed that the five carbonyls are equivalent and the substitution of $\hat{\text{D}}$ for $\bar{\text{D}}$ has been made. Using values determined in this study for the ionization potentials of the thiocarbonyl complexes (Table 8, column 2) and spectroscopic values for the metals, the differences of the left-hand side of Eq. 113 are 1.55 ± 0.03 , 1.08 ± 0.02 , and 0.24 ± 0.01 eV for $\text{Cr}(\text{CO})_5\text{CS}$, $\text{Mo}(\text{CO})_5\text{CS}$, and $\text{W}(\text{CO})_5\text{CS}$, respectively. Dissociation energy sums are larger in the molecule than in the molecular ion as a result of the loss of an electron from a bonding orbital. If it is assumed that:

$$\hat{D}(M^+-CO)_H - \hat{D}(M^+-CO)_T = \hat{D}(M-CO)_H - \hat{D}(M-CO)_T \quad (114)$$

(i.e. the difference between the M-CO dissociation energy in the hexacarbonyls and thiocarbonyls is the same in both the ion and molecule), $\hat{D}(M-CO)_T$ and $\hat{D}(M-CS)$ can be calculated. Approximate values for these quantities are listed in Table 15. The results for $\hat{D}(M-CO)_T$ were obtained from Eq. 114 using the values of $\hat{D}(M^+-CO)_H$ and $\hat{D}(M^+-CO)_T$ from Table 13. For $Mo(CO)_5CS$ the calorimetric value of 1.35 ± 0.01 eV was used for $\hat{D}(M^+-CO)_H$. Values for $\hat{D}(M-CO)_H$ were given previously and were taken from Pilcher, Ware, and Pittam [55]. Substitution of $\hat{D}(M^+-CO)_T$ and $\hat{D}(M^+-CS)$ from Table 13 (and the results for $\hat{D}(M-CO)_T$) into Eq. 113 yields the values for $\hat{D}(M-CS)$ in the final column of Table 15. Although slightly larger than their respective ionic counterparts, dissociation energies in the molecules follow the same trends as those in the ion and the same conclusions are applicable.

The corrected fragmentation data and ionization potentials also yield information about the heats of formation of $Cr(CO)_5CS$ and $W(CO)_5CS$ in the gas phase. Subtraction of the appearance potentials (fragmentation energies plus the ionization potential of the molecule) of the ions from the hexacarbonyls and the respective appearance potentials of the $M(CO)_n^+$ ($n = 0, 1, \dots, 5$) ions from thiocarbonyls gives six values for the energy of the substitution reaction:

Table 15. Least-squares dissociation energies (eV) in the Group
VIB thiocarbonyls

Compound	$\hat{D}(\text{M-CO})_T$	$\hat{D}(\text{M-CS})$
$\text{Cr}(\text{CO})_5\text{CS}$	0.94 ± 0.08	3.10 ± 0.50
$\text{Mo}(\text{CO})_5\text{CS}$	1.50 ± 0.04	---
$\text{W}(\text{CO})_5\text{CS}$	1.60 ± 0.10	4.10 ± 0.70

These energies are tabulated in Table 16. Known values for the heats of formation of gaseous $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$, -9.42 ± 0.02 and -9.17 ± 0.04 eV, respectively [53,54], and for CO and CS, -1.146 ± 0.002 and 2.91 ± 0.26 eV respectively [79], along with the average energies of the substitution reaction gives $\Delta H_f^\circ(\text{Cr}(\text{CO})_5\text{CS}, \text{g}) = -6.3 \pm 0.3$ eV and $\Delta H_f^\circ(\text{W}(\text{CO})_5\text{CS}, \text{g}) = -6.2 \pm 0.3$ eV. These results are in agreement with gaseous heats of formation of $\text{Cr}(\text{CO})_5\text{CS}$, -6.7 ± 0.3 eV, and $\text{W}(\text{CO})_5\text{CS}$, -6.7 ± 0.3 eV, calculated directly from the appearance potentials of the metal ions:

Spectroscopic values of the ionization potentials of the metal atoms [75], $\Delta H_f(\text{Cr}) = 4.12$ eV, and $\Delta H_f(\text{W}) = 8.75$ eV [80] were used for this calculation in addition to the heats of formation of CO and CS. The precision of the results is such that it is impossible to differentiate the heats of formation of the compounds. An average, -6.5 ± 0.3 eV, of the results from the two methods of calculation is the preferred value for both complexes.

5. Conclusions

A comparison of the dissociative energetics of the Group VIB carbonyl and thiocarbonyl complexes has led to a more complete understanding of molecular fragmentation of carbonyls by electron impact and of bonding in metal thiocarbonyls. It is probable that dissociation

Table 16. Substitution energies (eV) for the process $M(CO)_5CS + CO \rightarrow M(CO)_6 + CS$

Related Ion	Metal Atom	
	Cr	W
$M(CO)_5^+$	0.82	1.24
$M(CO)_4^+$	0.76	0.99
$M(CO)_3^+$	0.80	0.89
$M(CO)_2^+$	1.09	1.01
$M(CO)^+$	1.00	1.21
M^+	<u>0.88</u>	<u>1.05</u>
Average	0.89 ± 0.13	1.06 ± 0.15

of CO or CS from metal carbonyls or thiocarbonyls is accompanied by excitation of the free ligands to their first vibrational state. When fragmentation energies are corrected for this effect, reliable values for the M-CO and M-CS dissociation energies are obtained from a least-squares fit of the data. The strength of the M-CS bond is found to be of the order of a normal single bond, 70-90 kcal/mole and is three to four times stronger than its carbonyl analogue. Substitution of CS for CO in going from $M(CO)_6$ to $M(CO)_5CS$ weakens the remaining M-CO bonds by an average of 5 kcal/mole. It was impossible in this study to distinguish if all of the carbonyls were weakened or if the effect was localized in the trans-carbonyl ligand. Results obtained in this study are in agreement with previously published data for the $M(CO)_5CS$ complexes [60-66].

B. Group VIIB Metal and Mixed-Metal Decacarbonyls

The Group VIIB metal decacarbonyls, $M_2(CO)_{10}$ ($M_2 = Mn_2, Tc_2, Re_2$, and $MnRe$), have been examined by a variety of techniques with the goal of determining bonding properties of the M-M and M-CO bonds. A major interest has been obtaining reliable comparative data for the variation of M-M bond strengths in descending order within the Group. The results from several such studies are summarized in Table 17. It is apparent from these data that the M-M bond energies of the homonuclear compounds increase in the order $Mn < Tc < Re$. However there is some discrepancy as to where the heteronuclear compound $MnRe(CO)_{10}$ fits into the sequence.

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Table 17. Parameters relating M-M bond strengths from various experiments

Complex	M-M Distance (Å) ^a	Reduction Potentials E _{1/2} (volts) ^b	Electronic Transitions σ→σ* (cm ⁻¹) ^c	Force Constants k _{MM} (Md/Å) ^d
Mn ₂ (CO) ₁₀	2.923	-1.03	29,240	0.59
Tc ₂ (CO) ₁₀	3.036	--	31,700	0.72
Re ₂ (CO) ₁₀	3.02	-1.66	32,260	0.82
MnRe(CO) ₁₀	2.96	-1.39	31,000	0.81

^aMn₂(CO)₁₀, Tc₂(CO)₁₀, and Re₂(CO)₁₀ Refs. [81-83]; MnRe(CO)₁₀ Ref. [84].

^bRef. [85].

^cRef. [86].

^dRef. [87].

^eRef. [88].

^fRef. [89].

^gRef. [90].

Dissociation Energies D(M-M) (eV) ^e	Overlap Populations ^f	Activation Energies $\Delta H^\ddagger$ (kcal/mole) ^g
1.08	0.0572	36.2
1.84	0.1844	--
1.94	0.2103	38.6
2.18	0.2259	--

The present mass spectrometric study was initiated with the intent of extending previous experiments [88,91] to obtain accurate thermochemical information for the final members of the series MnTc(CO)_{10} and TcRe(CO)_{10} . Results for the M(CO)_6 and $\text{M(CO)}_5\text{CS}$ complexes of Cr, Mo, and W indicated that accurate bond dissociation energies could be obtained from a least-squares analysis of fragmentation data which were corrected by 0.25 eV per M-CO bond broken. A plausible explanation for this correction was that the product CO's were excited vibrationally by one quantum. It was assumed that similar considerations would apply to the decacarbonyls.

During the course of this investigation it was realized that the energy of the process:

was incorrectly being associated with the energy of the $\text{M}^+\text{-M}$ bond. For this to be true it has to be assumed that the dissociation energies $D(\text{M}_2^+-\text{CO})$, $D(\text{M}^+-\text{CO})$, and $D(\text{M-CO})$ must be equal. Since small differences in these quantities cause relatively large variations in the resulting dissociation energies (Eq. 117) and hence lead to faulty interpretation of the M-M bond strengths, it is necessary to calculate a value of $D(\text{M}^+\text{-M})$ independent of these effects. The least-squares method of interpreting fragmentation energies provides such a method. More precise and complete data were obtained for the Mn_2 , Tc_2 , Re_2 , and MnRe complexes to facilitate application of this method.

1. Mass spectra

The 50 eV mass spectra of the dimetal ions from $\text{MnTc}(\text{CO})_{10}$ and $\text{TcRe}(\text{CO})_{10}$ are shown in Fig. 14. The spectra of the remaining decacarbonyls were similar to those reported previously [88]. On a qualitative basis the fragmentation patterns of $\text{MnTc}(\text{CO})_{10}$ and $\text{TcRe}(\text{CO})_{10}$ are very similar to those of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Tc}_2(\text{CO})_{10}$, respectively. The low abundance of the $\text{M}_2(\text{CO})_9^+$ to $\text{M}_2(\text{CO})_6^+$ ions from $\text{MnTc}(\text{CO})_{10}$ is in agreement with the equally low intensities of these ions for $\text{Mn}_2(\text{CO})_{10}$ and $\text{MnRe}(\text{CO})_{10}$. This trend is undoubtedly related to the presence of manganese in the complexes, but is yet unexplained. The spectra of $\text{Tc}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$ and $\text{TcRe}(\text{CO})_{10}$ show a similar trend in low abundances for the $\text{M}_2(\text{CO})_9^+$ and $\text{M}_2(\text{CO})_8^+$ ions.

2. Ionization potentials

Ionization potentials are recorded in Table 18 for all members of the Group VIIB decacarbonyls except $\text{TcRe}(\text{CO})_{10}$. Due to instrumental limitations and sample size no information about the energetics of this compound was obtained. The results of this study are in good agreement with those obtained previously [88]. However, the electron impact values are significantly greater than the photoelectron results for $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$. This discrepancy can be attributed to the inability of the former method to distinguish between ionization from the $6a_1$ (listed in Table 18) and the $6e_3$ (8.35 and 8.57 eV for $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$, respectively) levels. The data appear to indicate that

Figure 14. The 50 eV mass spectra of MnTc(CO)_{10} and TcRe(CO)_{10} .

Table 18. Ionization potentials (eV) of the Group VIIB metal and mixed-metal decacarbonyls

Compound	Electron Impact	Photoelectron ^a
$\text{Mn}_2(\text{CO})_{10}$	8.32 ± 0.01	8.02
$\text{Tc}_2(\text{CO})_{10}$	8.22 ± 0.01	--
$\text{Re}_2(\text{CO})_{10}$	8.49 ± 0.02	8.07
$\text{MnTc}(\text{CO})_{10}$	8.16 ± 0.02	--
$\text{MnRe}(\text{CO})_{10}$	8.22 ± 0.01	--

^aRef. [92].

the metal orbitals in the mixed complexes are destabilized with respect to those in the corresponding dimetal complexes.

3. Ionic bond dissociation energies

Fragmentation energies for the dimetal ions are summarized in Table 19. Energies of each process have been corrected by n times 0.25 ± 0.02 eV, where n is the number of CO's produced in the decomposition. Although assignment of the neutral products for each decomposition must be regarded as tentative, it is highly probable that they are correct on the basis of thermodynamic considerations and previous experience with Group VIB hexacarbonyl complexes. The monotonic increase in fragmentation energies for a given complex correlates directly with the number of M_2^+-CO bonds broken, suggesting that reorganizational energies are of minor importance. Notable exceptions are the fragmentation energies for the $M_2(CO)_8^+$ and $M_2(CO)_7^+$ ions from those complexes containing manganese. For $MnRe(CO)_{10}$ less energy is required to remove three carbonyls than two.

The data of Table 19 can be fitted to two models (I and II) for the calculation of least-squares bond dissociation energies. The complexes can be considered as $M_2(CO)_{10}$ moieties possessing ten chemically equivalent M_2^+-CO bonds or as $(CO)_5MM(CO)_5$ moieties having two sets of five equivalent bonds. Chemical intuition suggests the former while the data for $Mn_2(CO)_{10}$ and the mixed-metal complexes suggest the latter. One quantity, $\hat{D}(M_2^+-CO)$, is calculated from the first model. For this case the observational equations are:

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Table 19. Fragmentation energies (eV) for the $M_2(CO)_n^+$ ions from the dimetal decacarbonyls

Assumed Process	ΔH	
	$Mn_2(CO)_{10}$	$Tc_2(CO)_{10}$
$M_2(CO)_{10}^+ \rightarrow M_2(CO)_9^+ + CO$	0.74 ± 0.07	0.96 ± 0.03
$\rightarrow M_2(CO)_8^+ + 2CO$	0.90 ± 0.04	2.33 ± 0.03
$\rightarrow M_2(CO)_7^+ + 3CO$	0.91 ± 0.03	3.83 ± 0.03
$\rightarrow M_2(CO)_6^+ + 4CO$	1.27 ± 0.03	4.99 ± 0.03
$\rightarrow M_2(CO)_5^+ + 5CO$	2.16 ± 0.04	5.97 ± 0.02
$\rightarrow M_2(CO)_4^+ + 6CO$	4.15 ± 0.03	7.53 ± 0.03
$\rightarrow M_2(CO)_3^+ + 7CO$	5.12 ± 0.04	9.17 ± 0.03
$\rightarrow M_2(CO)_2^+ + 8CO$	5.91 ± 0.03	10.59 ± 0.04
$\rightarrow M_2(CO)^+ + 9CO$	6.69 ± 0.04	12.52 ± 0.03
$\rightarrow M_2^+ + 10CO$	7.05 ± 0.04	13.61 ± 0.05

$\text{Re}_2(\text{CO})_{10}$	ΔH	
	$\text{MnTc}(\text{CO})_{10}$	$\text{MnRe}(\text{CO})_{10}$
1.01 ± 0.05	0.99 ± 0.04	0.96 ± 0.02
2.74 ± 0.06	---	1.09 ± 0.04
4.23 ± 0.06	1.13 ± 0.05	0.96 ± 0.03
5.89 ± 0.07	1.38 ± 0.04	1.33 ± 0.05
7.55 ± 0.09	2.25 ± 0.04	2.18 ± 0.05
9.44 ± 0.05	4.31 ± 0.04	4.87 ± 0.05
11.19 ± 0.06	5.80 ± 0.03	6.44 ± 0.09
12.71 ± 0.04	7.46 ± 0.10	8.84 ± 0.05
14.36 ± 0.11	10.07 ± 0.05	11.84 ± 0.09
16.05 ± 0.12	12.14 ± 0.14	14.45 ± 0.07

$$\begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \end{bmatrix} [\hat{D}(M_2^+-CO)] = \begin{bmatrix} \Delta H_9 \\ \Delta H_8 \\ \Delta H_7 \\ \Delta H_6 \\ \Delta H_5 \\ \Delta H_4 \\ \Delta H_3 \\ \Delta H_2 \\ \Delta H_1 \\ \Delta H_0 \end{bmatrix} \quad (118)$$

where ΔH_n is the fragmentation enthalpy for the $M_2(CO)_n^+$ ion ($n = 9, 8, \dots, 0$). For the second model two quantities, $\hat{D}'(M_2^+-CO)$ and $\hat{D}(M_2^+-CO)$, are calculated from the following equations:

$$\begin{bmatrix} 1 & 0 \\ 2 & 0 \\ 3 & 0 \\ 4 & 0 \\ 5 & 0 \\ 5 & 1 \\ 5 & 2 \\ 5 & 3 \\ 5 & 4 \\ 5 & 5 \end{bmatrix} \begin{bmatrix} \hat{D}'(M_2^+-CO) \\ \hat{D}(M_2^+-CO) \end{bmatrix} = \begin{bmatrix} \Delta H_9 \\ \Delta H_8 \\ \Delta H_7 \\ \Delta H_6 \\ \Delta H_5 \\ \Delta H_4 \\ \Delta H_3 \\ \Delta H_2 \\ \Delta H_1 \\ \Delta H_0 \end{bmatrix} \quad (119)$$

where ΔH_n ($n = 9, 8, \dots, 0$) is as defined previously. In generating this system of equations the assumption was made that there were two sets of five M_2^+-CO bonds, one weak and one strong. No attempt was made to correlate the quantities with the two $M(CO)_5$ halves of the molecules. The results of the calculations suggest strongly that this is the case (vide infra). In addition it should be emphasized that any effects due to reorganizational energies have been neglected in both calculations.

Results of the least-squares calculations are given in Table 20. Also listed for each calculation is the standard error of estimate

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Table 20. Least-squares M_2^+ -CO dissociation energies (eV)

Complex	I	
	$\hat{D}(M_2^+-CO)$	Std Error of Estimate
$Mn_2(CO)_{10}$	0.67 ± 0.04	0.77
$Tc_2(CO)_{10}$	1.32 ± 0.02	0.38
$Re_2(CO)_{10}$	1.58 ± 0.02	0.34
$MnTc(CO)_{10}$	0.94 ± 0.09	1.73
$MnRe(CO)_{10}$	1.09 ± 0.12	2.18

II		
$\hat{D}'(M_2^+-CO)$	$\hat{D}(M_2^+-CO)$	Std Error of Estimate
0.48 ± 0.06	1.06 ± 0.11	0.47
1.21 ± 0.02	1.54 ± 0.04	0.16
1.49 ± 0.03	1.74 ± 0.05	0.22
0.41 ± 0.04	1.97 ± 0.07	0.31
0.40 ± 0.04	2.44 ± 0.08	0.35

(i.e. the standard deviation of the differences between the calculated and measured fragmentation energies) which is taken as a measure of how well the model fits the experimental data. If all the M_2^+-CO bonds are considered equivalent, the ionic bond strengths are in the order $Mn_2 < MnTc < MnRe < Tc_2 < Re_2$. However this description does not explain satisfactorily the bonding, especially for the mixed-metal complexes. In every case a significant improvement in the standard error of estimate is obtained assuming there are five weak and five strong M_2^+-CO bonds. This description leads to some interesting conclusions. The splitting of dissociation energies (i.e. $\hat{D}'(M_2^+-CO) - \hat{D}(M_2^+-CO)$) is pronounced for the heteronuclear complexes and is surprisingly evident in the homogeneous complexes. For the latter, the effect decreases from $Mn_2(CO)_{10}$ to $Re_2(CO)_{10}$. Values of $\hat{D}'(M_2^+-CO)$ for $MnTc(CO)_{10}$ and $MnRe(CO)_{10}$ are the same as or perhaps slightly lower than that for $Mn_2(CO)_{10}$, suggesting that the weak bonds originate from the $Mn(CO)_5$ portion of the molecule. Furthermore, the M^+-CO bonds in the $Tc(CO)_5$ and $Re(CO)_5$ halves of these molecules are stronger than the strong bonds in $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$, respectively. These data fit nicely into the following description of the bonding. Electron density is shifted to Tc and Re resulting in increased π donation and hence stronger M^+-CO bonds in the $Tc(CO)_5$ and $Re(CO)_5$ portions of the molecule. A concomitant weakening of the bonds in the $M(CO)_5$ halves of the molecules takes place. Hence the $M(CO)_5$ ligands can be ranked on a crude electronegativity scale; $Mn(CO)_5 <$

$\text{Tc}(\text{CO})_5 \approx \text{Re}(\text{CO})_5$. Data from $\text{TcRe}(\text{CO})_{10}$ would presumably establish the order for $\text{Tc}(\text{CO})_5$ and $\text{Re}(\text{CO})_5$.

Metal-metal dissociation energies are calculated from fragmentation energies for $\text{M}(\text{CO})_n^+$ ions. Assignment of the decomposition processes producing these ions (Eq. 103), although reasonable, is highly speculative. For the n th process ($n = 5, 4, \dots, 0$):

$$\Delta H'_n = 5\hat{D}'(\text{M}_2^+-\text{CO}) + 5\hat{D}(\text{M}_2^+-\text{CO}) + \hat{D}(\text{M}^+-\text{M}) - 5\hat{D}(\text{M}-\text{CO}) - n\hat{D}(\text{M}^+-\text{CO}) \quad (120)$$

where $\Delta H'_n$ is the fragmentation energy for $\text{M}(\text{CO})_n^+$; $\hat{D}'(\text{M}_2^+-\text{CO})$ and $\hat{D}(\text{M}_2^+-\text{CO})$ are as defined previously for the five weak-five strong model; $\hat{D}(\text{M}^+-\text{M})$ is the least-squares dissociation energy for the ionic M-M bond; and $\hat{D}(\text{M}-\text{CO})$ and $\hat{D}(\text{M}^+-\text{CO})$ are the dissociation energies for the M-CO bonds in $\text{M}(\text{CO})_5$ and $\text{M}(\text{CO})_5^+$, respectively. When combined with the fragmentation data for the $\text{M}_2(\text{CO})_n^+$ ions ($n = 9, 8, \dots, 0$), the system cannot be solved because the coefficients of $\hat{D}(\text{M}^+-\text{M})$ and $\hat{D}(\text{M}-\text{CO})$ are linearly dependent. However results can be obtained for the combination $\hat{D}(\text{M}^+-\text{M}) - 5\hat{D}(\text{M}-\text{CO})$. In matrix form the observational equations are:

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 \\ 5 & 0 & 0 & 0 \\ 5 & 1 & 0 & 0 \\ 5 & 2 & 0 & 0 \\ 5 & 3 & 0 & 0 \\ 5 & 4 & 0 & 0 \\ 5 & 5 & 0 & 0 \\ 5 & 5 & 1 & -5 \\ 5 & 5 & 1 & -4 \end{bmatrix} \begin{bmatrix} \hat{D}'(\text{M}_2^+-\text{CO}) \\ \hat{D}(\text{M}_2^+-\text{CO}) \\ \hat{D}(\text{M}^+-\text{M}) - 5\hat{D}(\text{M}-\text{CO}) \\ \hat{D}(\text{M}^+-\text{CO}) \end{bmatrix} = \begin{bmatrix} H_9 \\ H_8 \\ H_7 \\ H_6 \\ H_5 \\ H_4 \\ H_3 \\ H_2 \\ H_1 \\ H_0 \\ H_{-5} \\ H_{-4} \end{bmatrix}$$

$$\begin{bmatrix} 5 & 5 & 1 & -3 \\ 5 & 5 & 1 & -2 \\ 5 & 5 & 1 & -1 \\ 5 & 5 & 1 & 0 \end{bmatrix} \begin{bmatrix} \Delta H'_3 \\ \Delta H'_2 \\ \Delta H'_1 \\ \Delta H'_0 \end{bmatrix}. \quad (121)$$

Unfortunately $M(\text{CO})_n^+$ ions are produced in very low abundance and it was not possible to obtain complete energetic data. Energies that were obtained are listed in Table 21. Each energy has been corrected by 0.25 eV per M-CO bond broken. Although the data are fragmentary, dissociation energies were obtained and are given in Table 22. Values for $\hat{D}'(\text{M}_2^+-\text{CO})$ and $\hat{D}(\text{M}_2^+-\text{CO})$ are unchanged from their values in Table 20 and are not listed.

Numerical results for $\hat{D}(\text{Tc}^+-\text{CO})$ calculated from the data for $\text{Tc}_2(\text{CO})_{10}$ and $\text{MnTc}(\text{CO})_{10}$ are in agreement, as are those for $\hat{D}(\text{Re}^+-\text{CO})$ calculated from the data for $\text{Re}_2(\text{CO})_{10}$ and $\text{MnRe}(\text{CO})_{10}$. Dissociation energies are in the expected order $\hat{D}(\text{Mn}^+-\text{CO}) < \hat{D}(\text{Tc}^+-\text{CO}) < \hat{D}(\text{Re}^+-\text{CO})$. Results for $\hat{D}(\text{M}^+-\text{M}) - 5\hat{D}(\text{M}-\text{CO})$ are not altogether satisfying because of large uncertainties. Values for $\hat{D}(\text{M}^+-\text{M})$ listed in the final column of the table were calculated from these data using the results for $\hat{D}(\text{M}-\text{CO})$ given in the fourth column. These quantities were calculated using Eq. 105 ($n=5$) and the results for $\hat{D}(\text{M}^+-\text{CO})$ from the second column, spectroscopic ionization potentials of the metal atoms (7.43, 7.28, and 7.87 eV for Mn, Tc, and Re, respectively), the measured ionization potential of $\cdot\text{Mn}(\text{CO})_5$ [93] (8.44 eV) and approximate values for the ionization potentials of $\cdot\text{Tc}(\text{CO})_5$ and $\cdot\text{Re}(\text{CO})_5$ (8.27 and 8.94 eV, respectively). These were calculated assuming:

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Table 21. Fragmentation energies (eV) for the $M(CO)_n^+$ ions from the dimetal decacarbonyls

Assumed Process	ΔH	
	$Mn_2(CO)_{10}$	$Tc_2(CO)_{10}$
$M_2(CO)_{10}^+ \rightarrow M(CO)_5 + M(CO)_5^+$	1.20 ± 0.03	1.39 ± 0.04
$\rightarrow M(CO)_5 + M(CO)_4^+ + CO$	2.98 ± 0.04	3.75 ± 0.03
$\rightarrow M(CO)_5 + M(CO)_3^+ + 2CO$	3.83 ± 0.05	5.46 ± 0.02
$\rightarrow M(CO)_5 + M(CO)_2^+ + 3CO$	4.73 ± 0.08	---
$\rightarrow M(CO)_5 + M(CO)^+ + 4CO$	5.32 ± 0.16	---

^aCharge remains on fragment containing Tc.

^bCharge remains on fragment containing Re.

ΔH		
$\text{Re}_2(\text{CO})_{10}$	$\text{MnTc}(\text{CO})_{10}^a$	$\text{MnRe}(\text{CO})_{10}^b$
1.59 ± 0.05	1.24 ± 0.04	1.79 ± 0.06
4.55 ± 0.06	3.40 ± 0.09	4.16 ± 0.05
---	5.47 ± 0.06	---
---	---	---
---	---	---

Table 22. Least-squares dissociation energies (eV); $\hat{D}(M^+-CO)$, $\hat{D}(M-CO)$, and $\hat{D}(M^+-M)$

Compound	$\hat{D}(M^+-CO)$	$\hat{D}(M^+-M) - 5\hat{D}(M-CO)$	$\hat{D}(M-CO)$	$\hat{D}(M^+-M)$
$Mn_2(CO)_{10}$	1.0 ± 0.2	-1.1 ± 0.6	1.2 ± 0.2	4.9 ± 1.0
$Tc_2(CO)_{10}$	2.0 ± 0.1	-2.1 ± 0.6	2.2 ± 0.1	9.1 ± 0.9
$Re_2(CO)_{10}$	3.0 ± 0.4	0.2 ± 1.6	3.2 ± 0.4	16.1 ± 2.4
$MnTc(CO)_{10}$	2.1 ± 0.2^a	-0.1 ± 1.0^b	2.3 ± 0.2^b	11.5 ± 1.6
$MnRe(CO)_{10}$	2.4 ± 0.6^c	-0.5 ± 2.5^b	2.6 ± 0.6^b	12.4 ± 3.8

$^a M^+ = Tc^+$.

$^b \hat{D}(M-CO) = \hat{D}(Mn-CO)$.

$^c M^+ = Re^+$.

$$\frac{\text{IP}(\text{Mn}(\text{CO})_5)}{\text{IP}(\text{Mn})} = \frac{\text{IP}(\text{M}(\text{CO})_5)}{\text{IP}(\text{M})} \quad (122)$$

Uncertainties in the values for $\hat{D}(\text{M}^+-\text{M})$ are large however, and attaching real quantitative significance to the data is questionable. In fact, except for $\hat{D}(\text{Mn}^+-\text{Mn})$ the dissociation energies are unreasonably high for single bonds. Because of this, the following thermochemical cycle was developed to check the results:

Data required for the calculations are summarized in Table 23. In addition, the spectroscopic values for the ionization potentials of the metals and $\Delta H_f^\circ(\text{CO}) = -1.146 \pm 0.002$ eV were used. Since thermochemical information is available only for $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$, results are limited to $\text{D}(\text{Mn}^+-\text{Mn})$ and $\text{D}(\text{Re}^+-\text{Re})$. Calculated values for these quantities are 3.0 ± 0.1 and 4.0 ± 0.3 eV, respectively. These results are considerably more reasonable than the analogous

Table 23. Ancillary thermochemical data

Quantity	Energy (eV)	
	Mn	Re
$AP(M_2^+)$	15.37 ± 0.04	24.54 ± 0.12
$\Delta H_{\text{sub}}(M_2(CO)_{10})$	0.83 ± 0.02^a	0.97 ± 0.01^a
$\Delta H_f^\circ(M_2(CO)_{10})$	-17.39 ± 0.04^b	-17.13 ± 0.22^c
$\Delta H_{\text{sub}}(M)$	2.91 ± 0.04^d	7.98 ± 0.07^d

^aRef. [94].^bRef. [95].^cRef. [96].^dRef. [97].

results in Table 22. The energies are representative of those for normal single bonds, and there is a moderate increase from Mn^+-Mn to Re^+-Re . In view of this evidence it is doubtful whether even qualitative conclusions can be based on the least-squares results. At this point analysis of the failure of the least-squares method is only speculative. The inaccurate results can be attributed to any one or a combination of three possibilities: (1) assignments for the decomposition processes are incorrect, (2) further corrections are needed for excess energies, and (3) there are insufficient data to justify the least squares calculation.

4. Neutral dissociation energies and heats of formation

Dissociation energies in the molecules cannot be approximated from the data for ions because ionization potentials are not known for M_2 moieties. Since a bonding electron is lost in forming the positive ions, it is anticipated that the neutral bond energies would be slightly larger (0.2-0.3 eV) than those in the ion.

Due to the limited amount of thermochemical data available for $\text{M}_2(\text{CO})_{10}$ and $\text{M}(\text{CO})_5$ complexes, heats of formation cannot be calculated for these compounds. Energies of the substitution reactions:

can be calculated from the difference of appearance potentials for fragments common to both decacarbonyls. Average results are 0.2 ± 0.2 and 0.4 ± 0.4 eV, respectively.

5. Conclusions

A least-squares analysis of the fragmentation data for the Group VIIB decacarbonyls was successful in determining M_2^+-CO bond energies but not M^+-M energies. In the ions the metal-carbon bonding is best described by considering the molecules as $(CO)_5M^+-M(CO)_5$ moieties with five weak and five strong M_2^+-CO bonds. Average M_2^+-CO energies range from 0.77 to 1.62 eV for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, respectively and are comparable to the M^+-CO energies for the Group VIB hexacarbonyls. Metal-metal dissociation energies are approximately 2.5 times those reported on the basis of the fragmentation:

$D(Mn^+-Mn)$ and $D(Re^+-Re)$ are 3.0 ± 0.1 and 4.0 ± 0.3 eV, respectively.

VI. SUGGESTIONS FOR FURTHER RESEARCH

With most thesis research there are ideas that were not pursued, questions that were not answered, or modifications and improvements that were not made. The present research is no exception. In this section areas for improvement are summarized and suggestions for instrumental modifications and further studies are made.

If the +/- mass spectrometer is to be used for further thermochemical research with transition metal carbonyl complexes, two major modifications should be made. Pole pieces should be reshaped and slits narrowed to increase mass range and resolution. In addition the ion source should be equipped with a direct insertion probe for samples of low volatility.

As far as computerized acquisition of ionization efficiency data is concerned, the acquisition rate could be increased substantially if the electrometer and DC-DC converter were replaced by a high gain DC amplifier which interfaces the anode of the electron multiplier directly to the A to D converter. Several suggestions are also in order for improving the software of the system. The background subtraction routine should be rewritten so that the baseline over a specified energy range could be fitted by linear regression and subtracted. Since the "times-1" point is located near the baseline in a region of high uncertainty, the normalization algorithm should be written to locate a point at higher energy (e.g. the "times-5" point)

and back-interpolate to the "times-1" point. This modification would improve the precision of the data. As a further modification, the IEAS should make use of the CRT. Ionization efficiency curves should be displayed as the data are acquired. Warren's plots should also be displayed, enabling more rapid interpretation of the data. As a final improvement, the "deltas" (energy differences) for each ion, which are saved on tape, should be averaged and reported with the uncertainty upon command at any time during a study.

A major question left unresolved in this research is the failure to obtain reasonable and accurate M^+-M dissociation energies using the least-squares method. It is possible that the source of this error is in values for $\hat{D}(M^+-CO)$. If this is the case, results from the fragmentation data for the $M(CO)_n^+$ ions from the pentacarbonyl halides should help clarify the problem. These ions are present in reasonable abundances in the mass spectra of the Mn and Re complexes [98].

Possibilities for further research in the field of metal carbonyls are seemingly unlimited. However, studies should be limited to "simple" complexes, i.e., molecules containing two or possibly three different ligands where the bond energies in the ligands are much stronger than the metal-ligand bond energies to be measured. One such family of compounds are the Group VIB isocyanides. Listed in Table 24 are uncorrected fragmentation data for $W(CO)_5CNCH_3$. Least-squares values for $\hat{D}(M^+-CO)$ and $\hat{D}(W^+-CNCH_3)$ from these data are 1.82 ± 0.02 and 3.95 ± 0.16 eV, respectively. Comparison of the corrected result for $\hat{D}(M^+-CO)$,

Table 24. Fragmentation data (eV) for $\text{W}(\text{CO})_5\text{CNCH}_3$

Process	Energy
$\text{W}(\text{CO})_5\text{CNCH}_3 \rightarrow \text{W}(\text{CO})_5\text{CNCH}_3^+$	7.98 ± 0.05^a
$\text{W}(\text{CO})_5\text{CNCH}_3^+ \rightarrow \text{W}(\text{CO})_4\text{CNCH}_3 + \text{CO}$	9.60 ± 0.06
$\rightarrow \text{W}(\text{CO})_3\text{CNCH}_3^+ + 2\text{CO}$	11.58 ± 0.06
$\rightarrow \text{W}(\text{CO})_2\text{CNCH}_3^+ + 3\text{CO}$	13.31 ± 0.06
$\rightarrow \text{W}(\text{CO})\text{CNCH}_3^+ + 4\text{CO}$	15.33 ± 0.06
$\rightarrow \text{WCNCH}_3^+ + 5\text{CO}$	17.14 ± 0.07
$\rightarrow \text{W}^+ + 5\text{CO} + \text{CNCH}_3$	21.02 ± 0.10

^aRelative to Xe.

1.57 ± 0.02 , with that for W^+-CO from $W(CO)_6$ and $W(CO)_5CS$ reveals that the W^+-CO energy is lower in the isocyanide than in either the hexacarbonyl or thiocarbonyl. Values for $\hat{D}(W^+-CNCH_3)$ and $\hat{D}(W^+-CS)$ cannot be differentiated, but on the basis of the carbonyl energies, it is concluded that $CNCH_3$ is bound stronger than CS . Since the Cr and Mo complexes are known, data could also be obtained for them. It would be interesting to compare these results with those for the $M(CO)_5NCCH_3$ complexes.

In conclusion it is noted that results of this study have been limited to positive ions. Only half the potential of the $+/-$ instrument was utilized. In theory it is possible that similar results could be obtained for the negative ions.

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VIII. ACKNOWLEDGMENTS

The purpose of graduate study is to develop the student into a "professional person." It is the responsibility of the student to strive to attain the maturity of mind that is befitting of a scientist. It is the responsibility of the major advisor to judge continually the students progress toward this goal and provide direction where and when needed. To me this development was personal. In this respect I would like to express my utmost gratitude and appreciation to Dr. H. J. Svec for allowing me the opportunity to develop as an individual with a minimum of interference. There are, however, those times when ideas and data have to be discussed with someone very close to the work. This position was filled by Jerry Flesch. Ours was a complementary relationship both professionally and personally. So synergetic was our interaction that it is impossible to separate the origin of many ideas presented in this thesis. Both of us benefited immensely as a result. And now reflecting upon the past I know it is impossible to express my gratitude in writing. Finally there are those who played various roles in my development to whom I extend my appreciation:

To Duane Dombek for providing samples of the thiocarbonyls.

To Bill Thomas and John Homer for designing and constructing the $\pm$ interface and for their efforts to keep the computer running.

To Bill Deissler for obtaining the neutrals data.

To my wife, Therese, for her love, affection, and understanding through our tenure as graduate students at Iowa State University.

And finally to those who were also a part of my experience as a graduate student I can only offer memories of the way we were.

IX. APPENDIX A: DIAGNOSTIC PROGRAMS

The complete and documented listings of the two assembler language programs which were written to test the D-A converter are given here. Statement numbers are in the first column of the printout, memory locations are in the second, and the binary program is in the third. The rest of the listing is the source program.

A. D-A Test Number One (DATST1)

```

0000      *20
0001      /*****
0002      /
0003      /
0004      /          DATST1
0005      /
0006      /
0007      /DIGITAL TO ANALOG TEST ONE
0008      /
0009      /
0010      /WRITTEN BY GARY MICHELS
0011      /
0012      /
0013      /
0014      /
0015      /FEBRUARY 1977
0016      /
0017      /
0018      /*****
0019      PMODE
0020      DNL=6374          /DA INST CODE
0021      *100
0022      /
0023      /VARIABLES
0024      /
0025      0100  0000  TMP1,  0
0026      0101  0000  TMP2,  0
0027      0102  0000  TMP3,  0
0028      0103  0001  CONST,  1
0029      0104  0007  K7,      7
0030      0105  7776  M2,      -2
0031      0106  7774  M4,      -4
0032      0107  0600  PTRNAD, PATTRN
0033      /
0034      /SUBROUTINE LINKS
0035      /
0036      KEEP=4000 400 .
0037      0110  0330  KEEPA
0038      DISPLAY=4000 400 .
0039      0111  0400  DSPLAY
0040      UNPACK=4000 400 .
0041      0112  0262  UNPAKA
0042      *200
0043      /
0044      /MAIN PROGRAM
0045      /
0046      0200  7300  START,  CLA CLL          /CLEAR AC AND LINK
0047      0201  1105          TAD M2          /SET THE UP
0048      0202  3254          DCA TSTCNT       /AND DOWN COUNT
0049      0203  1103          TAD CONST       /SET THE D TO A
0050      0204  3255          DCA INCR        /INPUT
0051      0205  1103          TAD CONST       /SET THE STEP
0052      0206  3256          DCA STEP        /COUNTER
0053      0207  3261          DCA DIGVAL     /CLEAR THE D TO A INPUT
0054      0210  1261  TEST,  TAD DIGVAL     /GET THE INPUT
0055      0211  6374          DAC            /CONVERT IT
0056      0212  4512          UNPACK         /DIGITIZE AND STORE
0057      0213  0515          DIGAD         /PATTERN FOR DISPLAY
0058      0214  6141          LINC
0059      0215  .            LMODE          /SAMPLE D TO A
0060      0216  0110          SAM 10        /OUTPUT
0061      0217  0002          PDP
0062      0218  .            PMODE
0063      0219  4512          UNPACK         /DIGITIZE AND STORE

```

0076	0220	0543	ANLAD	/PATTERN FOR DISPLAY
0077	0221	4510	KEEP	/REFRESH THE SCREEN
0100	0222	7404	OSR	/CHECK THE RIGHT SWITCHES
0101	0223	7710	SPA CLA	/FOR A HOLD
0102	0224	5214	JMP .-10	/STOP THE D TO ACOUNT AND HOLD
0103	0225	1257	TAD DCONST	/DELAY SO WE
0104	0226	3260	DCA DELAY	/CAN SEE
0105	0227	4510	KEEP	/THE
0106	0230	2260	ISZ DELAY	/DISPLAY
0107	0231	5227	JMP .-2	
0110	0232	1261	TAD DIGVAL	/STEP
0111	0233	1255	TAD INCR	/THE D TO A
0112	0234	3261	DCA DIGVAL	/INPUT
0113	0235	7100	CLL	
0114	0236	1256	TAD STEP	/BOP OUR
0115	0237	1103	TAD CONST	/STEP
0116	0240	3256	DCA STEP	/CHECKER
0117	0241	7010	RAR	/ARE WE AT THE
0120	0242	7700	SMA CLA	/TOP?
0121	0243	5210	JMP TEST	/NO,CONTINUE
0122	0244	1103	TAD CONST	/YES,RESET THE
0123	0245	3256	DCA STEP	/STEP CHECKER
0124	0246	1103	TAD CONST	/NEGATE THE
0125	0247	7041	CIA	/D TO A
0126	0250	3255	DCA INCR	/INCREMENT
0127	0251	2254	ISZ TSTCNT	/COMPLETED ONE PASS?
0130	0252	5210	JMP TEST	/NO,CONTINUE
0131	0253	5200	JMP START	/YES,START AGAIN
0132	0254	0000	TSTCNT, 0	
0133	0255	0000	INCR, 0	
0134	0256	0000	STEP, 0	
0135	0257	7760	DCONST, -20	
0136	0260	0000	DELAY, 0	
0137	0261	0000	DIGVAL, 0	
0140			/	
0141			/UNPACK SUBROUTINE	
0142			/	
0143	0262	0000	UNPAKA, 0	/ENTER WITH NUMBER IN AC
0144	0263	7004	RAL	/ROTATE FIRST BIT TO LINK
0145	0264	3100	DCA TMP1	/STORE THE REST
0146	0265	7010	RAR	/NOW STORE THE
0147	0266	3101	DCA TMP2	/FIRST BIT
0150	0267	1106	TAD M4	/SET THE COUNTER
0151	0270	3324	DCA DIGCTR	/FOR FOUR DIGITS
0152	0271	1662	TAD I UNPAKA	/GET AND SAVE
0153	0272	3325	DCA DSPBUF	/STORAGE ADDRESS
0154	0273	2262	ISZ UNPAKA	/BOP FOR THE RETURN
0155	0274	1101	UNPAK, TAD TMP2	/RESTORE THE
0156	0275	7004	RAL	/LINK AND
0157	0276	1100	TAD TMP1	/NUMBER
0160	0277	7004	RAL	/ROTATE THREE
0161	0300	7006	RTL	/PLACES LEFT
0162	0301	3100	DCA TMP1	/SAVE THE NUMBER
0163	0302	7010	RAR	/AND THE
0164	0303	3101	DCA TMP2	/LINK
0165	0304	1100	TAD TMP1	/GET THE NUMBER
0166	0305	0104	AND K?	/AND MASK OUT FIRST 9 BITS
0167	0306	7004	RAL	/SET UP CORRECT
0170	0307	1107	TAD PTRNAD	/PATTERN ADDRESS
0171	0310	3326	DCA POINTR	
0172	0311	1100	TAD M2	/SET COUNT FOR
0173	0312	3327	DCA COUNT	/BOTH HALVES OF PATTERN
0174	0313	1726	AGAIN, TAD I POINTR	/STORE THE

0175	0314	3725	DCA I DSPBUF	/FIRST HALF
0176	0315	2326	ISZ POINTR	/IN THE DISPLAY
0177	0316	2325	ISZ DSPBUF	/BUFFER
0200	0317	2327	ISZ COUNT	/DONE YET?
0201	0320	5313	JMP AGAIN	/NO, DO SECOND HALF
0202	0321	2324	ISZ DIGCTR	/DONE WITH 4 DIGITS?
0203	0322	5274	JMP UNPAK	/NO, CONTINUE
0204	0323	5662	JMP I UNPAK	/YES, RETURN TO MAINLINE
0205	0324	0000	DIGCTR, 0	
0206	0325	0000	DSPBUF, 0	
0207	0326	0000	POINTR, 0	
0210	0327	0000	COUNT, 0	
0211			/	
0212			/REFRESHER SUBROUTINE	
0213			/	
0214	0330	0000	KEEPA, 0	
0215	0331	4511	DISPLY	/DISPLAY THE
0216	0332	0433	HEAD-1	/HEADING
0217	0333	0100	100	
0220	0334	4511	DISPLY	/DISPLAY THE D TO A
0221	0335	0504	INFO-1	/INPUT AND OUTPUT
0222	0336	0000	0	
0223	0337	5730	JMP I KEEPA	/RETURN
0224			PAGE	
0225			/	
0226			/DISPLAY SUBROUTINE	
0227			/	
0230	0400	0000	DSPLAY, 0	
0231	0401	1600	TAD I DSPLAY	/GET AND SAVE THE
0232	0402	3214	DCA BUFA	/ADDRESS
0233	0403	2200	ISZ DSPLAY	/GET THE VERTICAL
0234	0404	1600	TAD I DSPLAY	/LOCATION
0235	0405	3232	DCA YVALUE	
0236	0406	2200	ISZ DSPLAY	/BOP FOR THE RETURN
0237	0407	6141	LINC	/GET INTO LINC
0240			LMODE	/MODE
0241	0410	0011	CLR	/CLEAR AC, MQ, AND LINK
0242	0411	0061	SET I 1	/SET THE HORIZONTAL
0243	0412	0000	0	/COORDINATE
0244	0413	0063	SET I 3	/GET THE
0245	0414	0000	BUFA, 0	/BUFFER
0246	0415	1003	LDA 3	/COUNT
0247	0416	0017	COM	/NEGATE IT
0250	0417	4421	STC .+2	/STORE IT
0251	0420	0062	SET I 2	/SET THE LOOP
0252	0421	0000	0	/COUNTER
0253	0422	2432	ADD YVALUE	/GET THE Y LOCATION
0254	0423	1763	REPEAT, DSC I 3	/DISPLAY THE
0255	0424	1763	DSC I 3	/PATTERN
0256	0425	0222	XSK I 2	/DONE WITH THE BUFFER?
0257	0426	6423	JMP REPEAT	/NO, CONTINUE
0260	0427	0002	PDP	/YES, RETURN
0261			Pmode	
0262	0430	7300	CLA CLL	/TO CALLING
0263	0431	5600	JMP I DSPLAY	/ROUTINE
0264	0432	0000	YVALUE, 0	
0265			/HEADING BUFFER	
0266	0433	0024	24	/HEADING COUNT
0267	0434	0000	HEAD-1	
0270	0435	0000	0	
0271	0436	0000	0	
0272	0437	0000	0	
0273	0440	0000	0	

0274	0441	0000	0	
0275	0442	4177	4177	
0276	0443	3641	3641	/D
0277	0444	0000	0	
0300	0445	0000	0	
0301	0446	4040	4040	
0302	0447	4077	4077	/T
0303	0450	4177	4177	
0304	0451	7741	7741	/D
0305	0452	0000	0	
0306	0453	0000	0	
0307	0454	4477	4477	
0310	0455	7744	7744	/A
0311	0456	0000	0	
0312	0457	0000	0	
0313	0460	0000	0	
0314	0461	0000	0	
0315	0462	0000	0	
0316	0463	0000	0	
0317	0464	0000	0	
0320	0465	0000	0	
0321	0466	0000	0	
0322	0467	0000	0	
0323	0470	4477	4477	
0324	0471	7744	7744	/A
0325	0472	0000	0	
0326	0473	0000	0	
0327	0474	4040	4040	
0330	0475	4077	4077	/T
0331	0476	4177	4177	
0332	0477	7741	7741	/D
0333	0500	0000	0	
0334	0501	0000	0	
0335	0502	4177	4177	
0336	0503	3641	3641	/D
0337			/CONVERSION BUFFER	
0340	0504	0024	24	/BUFFER COUNT
0341	0505	0000	INFO. 0	
0342	0506	0000	0	
0343	0507	0000	0	
0344	0510	0000	0	
0345	0511	0000	0	
0346	0512	0000	0	
0347	0513	0000	0	
0350	0514	0000	0	
0351	0515	0000	DIGAD. 0	
0352	0516	0000	0	
0353	0517	0000	0	
0354	0520	0000	0	
0355	0521	0000	0	
0356	0522	0000	0	
0357	0523	0000	0	
0360	0524	0000	0	
0361	0525	0000	0	
0362	0526	0000	0	
0363	0527	0000	0	
0364	0530	0000	0	
0365	0531	0000	0	
0366	0532	0000	0	
0367	0533	0000	0	
0370	0534	0000	0	
0371	0535	0000	0	
0372	0536	0000	0	

0373	0537	0000	0	
0374	0540	0000	0	
0375	0541	0000	0	
0376	0542	0000	0	
0377	0543	0000	ANLAD.	0
0400	0544	0000	0	
0401	0545	0000	0	
0402	0546	0000	0	
0403	0547	0000	0	
0404	0550	0000	0	
0405	0551	0000	0	
0406	0552	0000	0	
0407	0553	0000	0	
0410	0554	0000	0	
0411			PAGE	
0412	0600	4136	PATTRN.	4136
0413	0601	3641		3641 /0
0414	0602	2101		2101
0415	0603	0177		0177 /1
0416	0604	4523		4523
0417	0605	2151		2151 /2
0420	0606	4122		4122
0421	0607	2651		2651 /3
0422	0610	2414		2414
0423	0611	0477		0477 /4
0424	0612	5172		5172
0425	0613	0651		0651 /5
0426	0614	1506		1506
0427	0615	4225		4225 /6
0430	0616	4443		4443
0431	0617	6050		6050 /7

NO ERRORS

AGAIN 0313
ANLND 0543
BUFA 0414
CONST 0103
COUNT 0327
DAC 6374
DCONST 0257
DELAY 0260
DIGAD 0515
DIGCTR 0324
DIGVAL 0261
DISPLY 4511
DSPBUF 0325
DSPLAY 0400
HEADR 0434
INCR 0255
INFO 0505
KEEP 4510
KEEPR 0330
K7 0104
M2 0105
M4 0106
PATRN 0600
POINTR 0326
PIKNAD 0107
REPEAT 0423
START 0200
STEP 0256
TEST 0210
TMP1 0100
TMP2 0101
TMP3 0102
TSTCNT 0254
UNPACK 4512
UNPAK 0274
UNPAKA 0262
YVALUE 0432

B. D-A Test Number Two (DATST2)

```

0000      *20
0001      /*****
0002      /
0003      /
0004      /          DATST2
0005      /
0006      /
0007      /DIGITAL TO ANALOG TEST TWO
0010      /
0011      /
0012      /WRITTEN BY GARY MICHELS
0013      /
0014      /
0015      /FEBRUARY 1977
0016      /
0017      /
0020      /*****
0021      /
0022      /MAIN PROGRAM
0023      /
0024      PMODE
0025      DAC=6374      /DA INST CODE
0026      *200
0027      0200 7300 START, CLA CLL      /CLEAR AC AND LINK
0030      0201 1221      TAD BUFA      /STORE BUFFER ADDRESS
0031      0202 3017      DCA I 17      /IN AUTO REGISTER
0032      0203 3222      DCA DIGVAL    /CLEAR THE DA INPUT
0033      0204 6374 AGAIN, DAC        /CONVERT THE AC
0034      0205 3222      DCA DIGVAL    /SAVE THE INPUT
0035      0206 4225      JMS DISPLY    /DISPLAY THE BUFFER
0036      0207 6141      LINC
0037      LMODE      /GET INTO LINC MODE
0040      0210 0110      SAM 10      /CONVERT THE OUTPUT
0041      0211 0002      PDP
0042      PMODE      /BACK TO 8 MODE
0043      0212 1224      TAD K400      /ADJUST CONVERTED NUM FOR SCREEN
0044      0213 3417      DCA I 17      /STORE IN BUFFER
0045      0214 1222      TAD DIGVAL    /GET THE INPUT
0046      0215 1223      TAD K10      /INCREMENT BY 8
0047      0216 7440      SZA          /IS IT ZERO?
0050      0217 5204      JMP AGAIN     /NO, REPEAT
0051      0220 5200      JMP START     /YES, START AGAIN
0052      0221 5777 BUFA,  BUFR-1
0053      0222 0000 DIGVAL, 0
0054      0223 0010 K10, 10
0055      0224 0400 K400, 400
0056      /
0057      /DISPLAY SUBROUTINE
0060      /
0061      0225 0000 DISPLY, 0
0062      0226 6141      LINC
0063      LMODE      /INTO L MODE
0064      0227 0011      CLR          /CLEAR AC, MQ, AND LINK
0065      0230 0062      SET I 2      /SET HORIZONTAL
0066      0231 1777      1777      /AXIS
0067      0232 0063      SET I 3      /SET BUFFER
0070      0233 3777      3777      /ADDRESS
0071      0234 0064      SET I 4      /SET THE
0072      0235 6777      -1000      /COUNT
0073      0236 1023      LDA I 3      /GET CONVERTED DA OUTPUT
0074      0237 0162      DIS I 2      /DISPLAY
0075      0240 0162      DIS I 2      /TWICE

```

0076	0241	0224	XSK I 4	/BUFFER DISPLAYED?
0077	0242	6236	JMP .-4	/NO, CONTINUE
0100	0243	0002	PDP	/YES, RETURN
0101			PMODE	/TO 8 MODE
0102	0244	5625	JMP I DISPLY	/AND MAINLINE
0103			*6000	
0104	6000	0000	BUFFR, 0	/DISPLAY BUFFER

NO ERRORS

NCAIN 0204
 BUFA 0221
 BUFR 6000
 DAC 6374
 DIGVAL 0222
 DISPLY 0225
 K10 0223
 K400 0224
 START 0200

X. APPENDIX B: IONIZATION EFFICIENCY
ACQUISITION SYSTEM

A documented listing of the binary and source programs for the IEAS follows. The AIPOS monitor and FPP library routines AMOD, FCON, FTYPE, and GETNUM are not included in the printout. The first, second and third columns are statement numbers, core locations, and binary output, respectively. The remaining information is the source listing.

```

0001                                LISTON
0002                                /*****
0003                                /
0004                                /
0005                                /           I E A S
0006                                /
0007                                /
0010                                /IONIZATION EFFICIENCY ACQUISITION
0011                                /SYSTEM
0012                                /
0013                                /
0014                                /WRITTEN BY GARY MICHELS
0015                                /
0016                                /
0017                                /MARCH 1976
0020                                /
0021                                /
0022                                /*****
0023                                /
0024                                /           FIELD 0
0025                                /
0026                                /HEADER AND IE TABLE
0027                                /      ORG 03000
0030 03000 0001 HEADR.    1                /NUMBER OF HEADER BLOCKS
0031 03001 0003          3                /NUMBER OF DATA BLOCKS
0032 03002 0000          0                /DATA FORMAT
0033 03003 0000          0
0034 03004 0000          0
0035 03005 0000 NIE.    0.                /NUMBER OF IE CURVES
0036 03006 0000
0037 03007 0000
0038 03010 0004 NORMUL. 15.                /NUMBER OF POINTS/CURVE
0039 03011 3600
0040 03012 0000
0041 03013 0001 NORANG. 1.5                /NORMALIZATION RANGE
0042 03014 3000
0043 03015 0000
0044                                /MASS VECTOR
0045                                /      ORG 03030
0046 03030 0000 MASLOC. 0
0047                                /LSTSQ INTERCEPTS
0048                                /      ORG 03110
0049 03110 0000 INCEPT. 0
0050                                /LSTSQ SLOPES
0051                                /      ORG 03170
0052 03170 0000 SLOPE. 0
0053                                /LSTSQ WEIGHTING FACTORS
0054                                /      ORG 03250
0055 03250 0000 WTLOC. 0
0056                                /MINIMUM DELTA FOR EACH ION
0057                                /      ORG 03330
0058 03330 0000 MINLOC. 0
0059                                /
0060                                /IE TABLE
0061                                /
0062                                /      ORG 03400
0063 03400 0000 IELOC. 0
0064                                /
0065                                /INTENSITY VECTOR
0066                                /
0067                                /      ORG 05000

```

```

0070 05000 0000 DTALOC, 0
0071 /
0072 /CONTROL CHARACTER HANDLER
0073 /
0074 ORG 07000
0075 07000 0000 CNTRL, 0 /INTERUPT ENTRY
0076 07001 1236 TAD CNTABA /SET TABLE POINTER
0077 07002 3240 DCA TEMP1
0100 07003 1235 TAD CCOUNT /SET COUNT
0101 07004 3241 DCA TEMP2
0102 07005 1600 CNTRL1, TAD I CNTRL /GET CONTROL CHARACTER
0103 07006 1640 TAD I TEMP1 /COMPARE WITH
0104 07007 7650 SNA CLA /TABLE ENTRY
0105 07010 5227 JMP CNTRL3 /MATCH?
0106 07011 2240 ISZ TEMP1 /BOP POINTER
0107 07012 2241 ISZ TEMP2 /AND COUNT
0110 07013 5205 JMP CNTRL1 /TRY AGAIN
0111 07014 1600 TAD I CNTRL /CONTROL R?
0112 07015 1640 TAD I TEMP1
0113 07016 7640 SZA CLA
0114 07017 5225 JMP CNTRL2 /NO, IGNORE
0115 07020 1231 TAD CNTABL /YES, RETURN
0116 07021 7041 CIA /A CARRIAGE RETURN
0117 07022 3600 DCA I CNTRL
0120 07023 2237 ISZ CTLFLG /SET FLAG
0121 07024 5227 JMP CNTRL3
0122 07025 2200 CNTRL2, ISZ CNTRL
0123 07026 2200 ISZ CNTRL /IGNORE CHARACTER
0124 07027 2200 CNTRL3, ISZ CNTRL /NORMAL
0125 07030 5600 JMP I CNTRL /RETURN
0126 /CONTROL CHAR TABLE
0127 07031 7563 CNTABL, -215 /CR
0130 07032 7566 -212 /LF
0131 07033 7575 -203 /CNTRL C
0132 07034 7556 -222 /CNTRL R
0133 07035 7775 CCOUNT, -3 /TABLE COUNT
0134 07036 7031 CNTABA, CNTABL /TABLE ADDRESS
0135 07037 0000 CTLFLG, 0
0136 07040 0000 TEMP1, 0
0137 07041 0000 TEMP2, 0
0140 LITORG 07400
0141 /
0142 / FIELD 1
0143 /
0144 ORG 10010
0145 /
0146 /AUTO INDEX REGISTERS
0147 /
0150 10010 0000 AUX0, 0
0151 10011 0000 AUX1, 0
0152 10012 0000 AUX2, 0
0153 10013 0000 AUX3, 0
0154 10014 0000 AUX4, 0
0155 10015 0000 AUX5, 0
0156 10016 0000 AUX6, 0
0157 10017 0000 AUX7, 0
0160 /
0161 /FPP INDEX REGISTERS
0162 /
0163 10020 0000 FXR0, 0
0164 10021 0000 FXR1, 0
0165 10022 0000 FXR2, 0

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0166 10023 0000 FXR3, 0
0167 10024 0000 FXR4, 0
0170 10025 0000 FXR5, 0
0171 10026 0000 FXR6, 0
0172 10027 0000 FXR7, 0
0173 /
0174 /FPP APT
0175 /
0176 10030 1111 APT, 1111
0177 10031 0000 FPC, 0
0200 10032 0020 FXR0
0201 10033 2600 B0
0202 10034 0000 OPR, 0
0203 10035 0000 0
0204 10036 0000 0
0205 10037 0000 0
0206 /
0207 /MONITOR LINKS
0210 /
0211 10040 0021 READ, 21
0212 10041 0022 WRITE, 22
0213 10042 0025 RETURN, 25
0214 10043 7624 UNIT, 7624
0215 10044 7634 STBLK, 7634
0216 10045 7635 NBLK, 7635
0217 10046 7636 IUNIT, 7636
0220 10047 7646 ISTBLK, 7646
0221 /
0222 /VARIABLES
0223 /
0224 10050 0000 BKGFLG, 0
0225 10051 0000 CHNFLG, 0
0226 10052 0027 TSTFLG, 27
0227 10053 0000 0
0230 10054 0000 0
0231 10055 7037 CNTRFA, CTLFLG
0232 10056 1460 PUCNTA, PCNT
0233 10057 2377 PBUFA, LPBUF-1
0234 10060 0706 ERRA, ERR
0235 10061 2343 DIGA, DIG
0236 10062 2344 DIG1A, DIG+1
0237 10063 7000 CNTRLA, CNTRL
0240 10064 0177 CNTRLH, 177
0241 10065 0727 XIT, EXIT
0242 10066 0214 CMND1A, COMND1
0243 10067 0000 ERRNUM, 0
0244 10070 0000 COUNTL, 0
0245 10071 0000 SENRGY, 0
0246 10072 0000 ENIVL, 0
0247 10073 0000 NSTEPS, 0
0250 10074 0000 NSCANS, 0
0251 10075 0000 ENERGY, 0
0252 10076 0000 HWPTR, 0
0253 10077 0000 LWPTR, 0
0254 10100 0000 CHAR, 0
0255 10101 0000 0
0256 10102 0000 0
0257 10103 0000 0
0260 10104 0000 0
0261 10105 0000 0
0262 10106 0000 0
0263 10107 0000 0

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0264 10110 0000 TPARM. 0 /TAPE PARAMETER
0265 10111 6201 CDF 0 /LIST
0266 10112 3000 HEADR
0267 10113 2000 2000
0270 10114 0000 TBLK. 0
0271 10115 0000 0
0272 10116 0000 0
0273 /
0274 /SUBROUTINE LINKS
0275 /
0276 ACQUI=4000 400 .
0277 10117 1062 ACQ
0300 CHKFLG=4000 400 .
0301 10120 0771 CKFLG
0302 FPPGO=4000 400 .
0303 10121 1006 FPPG
0304 GETPRM=4000 400 .
0305 10122 0736 GPARM
0306 GETTY=4000 400 .
0307 10123 1400 GTTY
0310 GNUMB=4000 400 .
0311 10124 1600 GNUM
0312 LPCTL=4000 400 .
0313 10125 1000 LPTRC
0314 PUCRLF=4000 400 .
0315 10126 1537 PCRLF
0316 PWSTR=4000 400 .
0317 10127 1464 PSTR
0320 PUTLP=4000 400 .
0321 10130 1440 PLPTR
0322 PUTTY=4000 400 .
0323 10131 1313 PTTY
0324 SAMPLE=4000 400 .
0325 10132 1200 SAMPL
0326 TABSP=4000 400 .
0327 10133 1552 TBSP
0330 TRAP=4000 400 .
0331 10134 1031 TRP
0332 /
0333 /CONSTANTS
0334 /
0335 10135 0002 K2. 2
0336 10136 0003 K3. 3
0337 10137 0004 K4. 4
0340 10140 0007 K7. 7
0341 10141 0011 K11. 11
0342 10142 0077 K77. 77
0343 10143 0260 K260. 260
0344 10144 0304 K304. 304
0345 10145 0777 K777. 777
0346 10146 4704 K4704. 4704
0347 10147 7776 M2. -2
0350 10150 7746 M32. -32
0351 10151 7527 M251. -251
0352 10152 7477 M301. -301
0353 10153 7471 M307. -307
0354 10154 6000 M2000. -2000
0355 /
0356 /REQUIRED INSTRUCTIONS
0357 /
0360 DAC=6374
0361 LINC=6141

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0362
0363
0364

SAM111=0111
PDP=0002
PAGE

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0365          EJECT
0366          /
0367          /COMMAND OVERLORD DISPATCHER
0370          /
0371 10200 6201 COMAND, CDF 0
0372 10201 1063      TAD CNTRLA      /INITIALIZE CONTROL
0373 10202 3464      DCA I CNTRLH    /CHARACTER HANDLER
0374 10203 1440      TAD I READ      /INITIALIZE AIPOS
0375 10204 3040      DCA READ        /MONITOR
0376 10205 1441      TAD I WRITE     /I/O LINKS
0377 10206 3041      DCA WRITE
0400 10207 1442      TAD I RETURN
0401 10210 3042      DCA RETURN
0402 10211 6211      CDF 10
0403 10212 1146      TAD K4704        /INITIALIZE ELECTRON
0404 10213 6374      DAC              /ENERGY
0405 10214 7300 COMND1, CLA CLL
0406 10215 3050      DCA BKGFLG      /CLEAR
0407 10216 3051      DCA CHNPLG      /ALL
0410 10217 3054      DCA TSTFLG+2    /FLAGS
0411 10220 6201      CDF 0
0412 10221 3455      DCA I CNTRFA
0413 10222 6211      CDF 10
0414 10223 1057      TAD PBUFA        /INITIALIZE
0415 10224 3010      DCA AUX0        /PUT STRING
0416 10225 3456      DCA I PUCNTA    /ROUTINES
0417 10226 4525      LPCTL           /SET LP TO
0420 10227 0006      PRNT            /PRINT MODE
0421 10230 4531      PUTTY
0422 10231 2347      ASTER           /PRINT ASTERISK
0423 10232 4523      GETTY           /GET
0424 10233 0100      CHAR           /COMMAND
0425 10234 0002      2              /CHARACTER
0426 10235 1100 COMND2, TAD CHAR      /IT MUST
0427 10236 1152      TAD M301
0430 10237 7510      SPA
0431 10240 5304      JMP CNTRR        /BE
0432 10241 1150      TAD M32
0433 10242 7700      SMO CLA ;
0434 10243 5304      JMP CNTRR        /ALPHABETIC
0435 10244 1100      TAD CHAR        /FORM
0436 10245 0142      AND K77         /CORRECT
0437 10246 1251      TAD TTYJMP      /JUMP
0440 10247 3250      DCA .+1
0441 10250 0000      0
0442 10251 5651 TTYJMP, JMP I .+0    /DISPATCH
0443 10252 0310      ACQUIR          /A
0444 10253 0315      BCKSUB          /B
0445 10254 0330      CAIN           /C
0446 10255 0400      DELSQ          /D
0447 10256 0423      ELIM           /E
0450 10257 0426      FILSAV         /F
0451 10260 0306      CMNDER         /G
0452 10261 0306      CMNDER         /H
0453 10262 0465      IEPRNT         /I
0454 10263 0306      CMNDER         /J
0455 10264 0306      CMNDER         /K
0456 10265 0306      CMNDER         /L
0457 10266 0475      MASPRT         /M
0460 10267 0505      NORPRM         /N
0461 10270 0600      OPTMIZ         /O

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0462	10271	0627	PRNTAB	/P
0463	10272	0306	CMNDER	/Q
0464	10273	0641	READTA	/R
0465	10274	0660	SETEE	/S
0466	10275	0671	TIME	/T
0467	10276	0306	CMNDER	/U
0470	10277	0306	CMNDER	/V
0471	10300	0677	WRPLT	/W
0472	10301	0306	CMNDER	/X
0473	10302	0306	CMNDER	/Y
0474	10303	0306	CMNDER	/Z
0475			/ILLEGAL COMMAND CHARACTER	
0476	10304	7300	CNTERR, CLA CLL	
0477	10305	5460	JMP I ERRA	
0500			/UNDEFINED COMMAND	
0501	10306	7001	CMNDER, IAC	
0502	10307	5460	JMP I ERRA	
0503			/	
0504			/	
0505			/*****COMMAND ROUTINES*****/	
0506			/	
0507			/	
0510			/ACQUIRE IE DATA	
0511	10310	4522	ACQUIR, GETPRM	/GET INITIAL PARAMETERS
0512	10311	4517	ACQUI	/ACQUIRE DATA
0513	10312	4521	FPPGO	
0514	10313	3340	NORM	/NORMALIZE DATA
0515	10314	5465	JMP I XIT	/RETURN
0516			/ ACQUIE DATA AND SUBTRACT BACKGROUND	
0517			/BEFORE NORMALIZING	
0520	10315	4522	BCKSUB, GETPRM	/GET INITIAL PARAMETERS
0521	10316	4517	ACQUI	/ACQUIRE DATA
0522	10317	2050	ISZ BKGFLG	/SET SUBTRCT FLAG
0523	10320	4531	PUTTY	/SEND OUT A CRLF
0524	10321	1547	MYCRLF	/TO LET US KNOW
0525	10322	4517	ACQUI	/ACQUIRE BACKGROUND
0526	10323	4521	FPPGO	
0527	10324	3340	NORM	/NORMALIZE
0530	10325	7300	CLA CLL	
0531	10326	3050	DCA BKGFLG	/CLEAR FLAG
0532	10327	5465	JMP I XIT	/RETURN
0533			/CHAIN PROGRAMS	
0534			/ENTER UP TO 7 COMMANDS	
0535			/FOLLOWED BY)	
0536	10330	7001	CAIN, IAC	/SET CHAIN
0537	10331	3051	DCA CHNFLG	/FLAG
0540	10332	3366	DCA CARCNT	/CLEAR COUNT
0541	10333	4531	PUTTY	/PRINT
0542	10334	1723	CMS	/CHAIN MESSAGE
0543	10335	4523	GETTY	/WAIT FOR
0544	10336	0100	CHAR	/COMMAND CHARACTER
0545	10337	0010	10	/STRING
0546	10340	1364	TAD CHARA	/COUNT CHARACTERS
0547	10341	3017	DCA AUX7	
0550	10342	1417	TAD I AUX7	/GET A CHARACTER
0551	10343	1151	TAD M251	/CHECK FOR)
0552	10344	7650	SNA CLA	
0553	10345	5352	JMP .+5	/DONE
0554	10346	7040	CMA	/BOP COUNT
0555	10347	1366	TAD CARCNT	/BY
0556	10350	3366	DCA CARCNT	/-1
0557	10351	5342	JMP .-7	/REPEAT

0560	10352	1364	TAD CHARA	/RESET CHARACTER
0561	10353	3017	DCA AUX7	/POINTER
0562	10354	1417	TAD I AUX7	/GET COMMAND CHARACTER
0563	10355	3100	DCA CHAR	/STORE
0564	10356	5765	JMP I CMND2A	/DISPATCH
0565	10357	2366	CHN1, ISZ CARCNT	/CHAIN DONE?
0566	10360	5354	JMP .-4	/NOPE
0567	10361	7300	CLA CLL	/YEP, CLEAR
0570	10362	3051	DCA CHNFLG	/CHAIN FLAG
0571	10363	5465	JMP I XIT	/RETURN
0572	10364	0077	CHARA, CHAR-1	
0573	10365	0235	CMND2A, COMND2	
0574	10366	0000	CARCNT, 0	
0575			PAGE	
0576			/CALCULATE THE DELTAS AND LEAST-SQUARE	
0577			/INTERCEPTS	
0600			/PRINT ON LINE PRINTER	
0601	10400	4533	DELSQ, TABSP	/CENTER
0602	10401	0074	74	/HEADING
0603	10402	4527	PUSTR	/PRINT
0604	10403	1777	DELHED-1	/HEADING
0605	10404	4530	PUTLP	
0606	10405	4521	FPPGO	/CALCULATE AND
0607	10406	4151	*DELTA	/PRINT DELTAS
0610	10407	4533	TABSP	
0611	10410	0066	66	/CENTER AND
0612	10411	4527	PUSTR	/PRINT
0613	10412	2132	LSQHED-1	/HEADING
0614	10413	4530	PUTLP	
0615	10414	4521	FPPGO	
0616	10415	4354	LSTSQ	/CALCULATE INTERCEPTS
0617	10416	4526	PUCRLF	/END THE LINE
0620	10417	4530	PUTLP	/PRINT ON LP
0621	10420	4525	LPCTL	/END
0622	10421	0004	REOT	/TRANSMISSION
0623	10422	5465	JMP I XIT	/RETURN
0624			/ELIMINATE CURRENT IE DATA FROM TABLE	
0625	10423	4521	ELIM, FPPGO	/DO IT THIS
0626	10424	4256	ELIMIE	/WAY
0627	10425	5465	JMP I XIT	/RETURN
0630			/SAVE HEADER AND DELTA TARI F	
0631	10426	6201	FILSAV, CDF 0	
0632	10427	1144	TAD K304	/DATA FORMAT
0633	10430	3660	DCA I HEADA	
0634	10431	1443	TAD I UNIT	/CHECK BIT 0
0635	10432	7104	CLL RAL	/OF UNIT NUMBER
0636	10433	7430	SZL	
0637	10434	5261	JMP FILERR	/EXISTING FILE
0640	10435	7030	CML RAR	/NEW FILE, SET
0641	10436	3443	DCA I UNIT	/BIT 0
0642	10437	1137	TAD K4	/FILE LENGTH
0643	10440	3445	DCA I NBLK	/SET
0644	10441	1443	TAD I UNIT	/SET UNIT FROM
0645	10442	0142	AND K77	/JOB CONTROL
0646	10443	3110	DCA TPARM	/TO PARMETER LIST
0647	10444	1444	TAD I STBLK	/STARTING BLOCK
0650	10445	3114	DCA TBLK	/TO PARMETER LIST
0651	10446	6211	CDF 10	
0652	10447	6224	RIF	/STANDARD
0653	10450	6202	CIF 0	/MONITOR
0654	10451	4441	JMS I WRITE	/I/O CALL
0655	10452	0110	TPARM	

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0656 10453 1110      TAD TPARM      /AND
0657 10454 7710      SPA CLA
0660 10455 5253      JMP .-2      /WAIT TILL DONE
0661 10456 6202      CIF 0
0662 10457 5442      JMP I RETURN  /EXIT TO AIPOS
0663 10460 3002 HEADR, HEADR+2
0664 10461 7300 FILERR, CLA CLL      /ATTEMPT TO SAVE
0665 10462 6211      CDF 10
0666 10463 1135      TAD K2      /DATA IN A PRE-
0667 10464 5460      JMP I ERRA   /EXISTING FILE
0670      /PRINT RAW IE DATA ON TTY
0671 10465 4531 IEPRNT, PUTTY      /PRINT
0672 10466 2026      IEHED      /HEADING
0673 10467 1073      TAD NSTEPS   /SET INDEX
0674 10470 7041      CIA      /COUNTER
0675 10471 3024      DCA FXR4     /FOR FPP
0676 10472 4521      FPPGO      /PRINT ENERGIES
0677 10473 4271      IEPRIN     /AND INTENSITIES
0700 10474 5465      JMP I XIT    /RETURN
0701      /PRINT NORM ENERGIES FOR A GIVEN MASS
0702      /ON THE TTY
0703 10475 4531 MASPRT, PUTTY      /GET
0704 10476 2230      MMS1      /THE
0705 10477 4524      GNUMB     /MASS
0706 10500 4531      PUTTY      /PRINT
0707 10501 2200      MASHED     /HEADING
0710 10502 4521      FPPGO      /AND
0711 10503 4612      MPRINT     /ENERGIES
0712 10504 5465      JMP I XIT    /RETURN
0713      /RESET NORMALIZATION PARAMETERS
0714 10505 4531 NORPRM, PUTTY      /GET THE
0715 10506 2237      NMS1      /INTENSITY
0716 10507 4524      GNUMB     /MULTIPLE
0717 10510 4521      FPPGO
0720 10511 4722      NMUL      /CHANGE IT
0721 10512 4531      PUTTY      /GET THE
0722 10513 2264      NMS2      /ENERGY
0723 10514 4524      GNUMB     /RANGE
0724 10515 4521      FPPGO
0725 10516 4735      NRRANG     /CHANGE IT
0726 10517 5465      JMP I XIT    /RETURN
0727      PAGE
0730      /OPTIMIZE GAIN AND ENERGY LIMITS
0731      /ACQUISITION 1 PASS
0732      /RECYCLE TILL CONTROL R
0733 10600 7001 OPTMIZ, IAC
0734 10601 3054      DCA TSTFLG+2 /SET TEST FLAG
0735 10602 4531 OPTM1, PUTTY      /GET
0736 10603 1700      AMS2      /STARTING
0737 10604 4524      GNUMB     /ENERGY
0740 10605 4521      FPPGO
0741 10606 3162      STRTEN
0742 10607 4531      PUTTY      /GET
0743 10610 1705      AMS3      /ENERGY
0744 10611 4524      GNUMB     /INTERVAL
0745 10612 4521      FPPGO
0746 10613 3213      ENTRVL
0747 10614 4531      PUTTY      /GET
0750 10615 1712      AMS4      /ENERGY
0751 10616 4524      GNUMB     /RANGE
0752 10617 4521      FPPGO
0753 10620 3244      RANGE

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0754	10621	7201	CLA IAC	/SET ACQUISITION
0755	10622	3074	DCA NSCANS	/1 PASS
0756	10623	4517	ACQUI	/ACQUIRE AND
0757	10624	4521	FPPGO	/NORMALIZE
0760	10625	3340	NORM	/DATA
0761	10626	5202	JMP OPTM1	/LOOP
0762			/PRINT NORMALIZED ENERGIES AS A TABLE	
0763			/ON THE LINE PRINTER	
0764	10627	4533	PRNTAB, TABSP	/CENTER AND
0765	10630	0076	76	
0766	10631	4527	PUSTR	/PRINT HEADING
0767	10632	2300	TABHED-1	
0770	10633	4530	PUTLP	/ON LP
0771	10634	4521	FPPGO	/PRINT TABLE
0772	10635	4746	PTABL	
0773	10636	4525	LPCTL	/END OF
0774	10637	0004	REOT	/TRANSMISSION
0775	10640	5465	JMP I XIT	/RETURN
0776			/INPUT IE DATA FILE	
0777	10641	6201	RENDTA, CDF 0	
1000	10642	1446	TAD I IUNIT	/SET TAPE UNIT
1001	10643	0142	AND K77	/TO PARAMETER
1002	10644	3110	DCA TPARM	/LIST
1003	10645	1447	TAD I ISTBLK	/SET STARTING
1004	10646	3114	DCA TBLK	/BLOCK
1005	10647	6211	CDF 10	
1006	10650	6224	RIF	/CALL MONITOR
1007	10651	6202	CIF 0	
1010	10652	4440	JMS I READ	
1011	10653	0110	TPARM	
1012	10654	1110	TAD TPARM	/WAIT TILL DONE
1013	10655	7710	SPA CLA	
1014	10656	5254	JMP .-2	
1015	10657	5465	JMP I XIT	/RETURN
1016			/SET ELECTRON ENERGY	
1017	10660	4531	SETEE, PUTTY	/GET
1020	10661	2016	EMS	/ELECTRON
1021	10662	4524	GNUMB	/ENERGY
1022	10663	4521	FPPGO	/AND CHANGE
1023	10664	3162	STRTEN	/IT
1024	10665	1071	TAD SENRGY	/SENT IT
1025	10666	6374	DAC	/OUT
1026	10667	7300	CLA CLL	
1027	10670	5465	JMP I XIT	/RETURN
1030			/RESET DELAY TIME	
1031	10671	4531	TIME, PUTTY	/GET
1032	10672	2314	TMS	/DELAY
1033	10673	4524	GNUMB	/TIME
1034	10674	4521	FPPGO	/CONVERT
1035	10675	5037	DELTIM	/AND STORE
1036	10676	5465	JMP I XIT	/RETURN
1037			/PRINT WARRENS PLOTS ON LINE PRINTER	
1040	10677	4521	WRPLT, FPPGO	
1041	10700	5072	WARPLT	
1042	10701	4525	LPCTL	/RESET TO PRINT
1043	10702	0006	PRNT	/MODE
1044	10703	4525	LPCTL	/END
1045	10704	0004	REOT	/TRANSMISSION
1046	10705	5465	JMP I XIT	/RETURN
1047			***ERROR HANDLER***	
1050	10706	3067	ERR, DCA ERRNUM	/SAVE CODE NUMBER
1051	10707	1067	TAD ERRNUM	/GET


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1052 10710 7012      RTR
1053 10711 7010      RAR          /FIRST
1054 10712 0140      AND K7       /DIGIT
1055 10713 1143      TAD K260     /MAKE ASCII
1056 10714 3461      DCA I DIGA   /AND SAVE
1057 10715 1067      TAD ERRNUM   /GET
1060 10716 0140      AND K7       /SECOND DIGIT
1061 10717 1143      TAD K260     /MAKE ASCII
1062 10720 3462      DCA I DIG1A   /SAVE
1063 10721 4531      PUTTY        /PRINT
1064 10722 2337      ERRMS        /ERROR MESSAGE
1065 10723 1054      TAD TSTFLG+2  /OPTIMIZATION?
1066 10724 7640      SZA CLA
1067 10725 5734      JMP I OPTMA   /YES, RECYCLE
1070 10726 5466      JMP I CMND1A  /NO, RETURN
1071                /ROUTINES EXIT HERE
1072 10727 7300      EXIT, CLA CLL
1073 10730 1051      TAD CHNFLG    /CHAINING?
1074 10731 7640      SZA CLA
1075 10732 5735      JMP I CHNA    /YES, CONTINUE
1076 10733 5466      JMP I CMND1A  /NO, TO OVERLORD
1077 10734 0602      OPTMA, OPTM1
1100 10735 0357      CHNA, CHN1
1101                /
1102                /
1103                /*****SUBROUTINES*****/
1104                /
1105                /
1106                /GET AQUISITION PARAMETERS
1107 10736 0000      GPARM, 0
1110 10737 4531      PUTTY        /GET
1111 10740 1673      AMS1         /ION
1112 10741 4524      GNUMB        /MASS
1113 10742 4521      FPPGO
1114 10743 3130      MASS
1115 10744 4531      PUTTY        /GET
1116 10745 1700      AMS2         /STARTING
1117 10746 4524      GNUMB        /ENERGY
1120 10747 4521      FPPGO
1121 10750 3162      STRTEN
1122 10751 4531      PUTTY        /GET
1123 10752 1705      AMS3         /ENERGY
1124 10753 4524      GNUMB        /INTERVAL
1125 10754 4521      FPPGO
1126 10755 3213      ENTRVL
1127 10756 4531      PUTTY        /GET
1130 10757 1712      AMS4         /ENERGY
1131 10760 4524      GNUMB        /RANGE
1132 10761 4521      FPPGO
1133 10762 3244      RANGE
1134 10763 4531      PUTTY        /GET
1135 10764 1716      AMS5         /NUMBER OF
1136 10765 4524      GNUMB        /SCANS
1137 10766 4521      FPPGO
1140 10767 3313      SCANS
1141 10770 5736      JMP I GPARM
1142                /CHECK FOR CONTROL R
1143 10771 0000      CKFLG, 0
1144 10772 6201      CDF 0
1145 10773 1455      TAD I CNTRFA  /GET FLAG
1146 10774 6211      CDF 10
1147 10775 7640      SZA CLA       /CONTROL R?

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1150 10776 5466      JMP I CMND1A      /YES.OVRELOD EXIT
1151 10777 5771      JMP I CKFLG      /NO.RETURN
1152                PAGE
1153                /LINE PRINTER REMOTE CONTROL
1154                /NECESSARY INSTRUCTIONS
1155                MPCD=6644
1156                CLAR=1
1157                RLTER=2
1160                RFFED=3
1161                REOT=4
1162                RESET=5
1163                PRNT=6
1164                PLT=7
1165                SPP=10
1166                RESPP=11
1167 11000 0000 LPTRC, 0
1170 11001 1600      TAD I LPTRC      /GET ARGUEMENT
1171 11002 2200      ISZ LPTRC      /BOP THE POINTER
1172 11003 6644      MPCD      /SEND OUT TO LP
1173 11004 7300      CLA CLL      /CLEAR AC
1174 11005 5600      JMP I LPTRC      /RETURN
1175                /START FPP AND WAIT TILL DONE
1176                /RESTART AFTER ALL TRAPS
1177                /PROGRAM COUNTER AT CALL+1
1200 11006 0000 FPPG, 0
1201 11007 6552      FPICL      /RESET FPP
1202 11010 1141      TAD K11      /LOCKOUT CPU.F1
1203 11011 6553      FPCOM      /LOAD COMMAND REGISTER
1204 11012 7200      CLA
1205 11013 1606      TAD I FPPG      /GET PC
1206 11014 3031      DCA FPC      /STORE IN APT
1207 11015 2206      ISZ FPPG
1210 11016 1230 FPPG1, TAD APTA      /GET APT POINTER
1211 11017 6555      FPST      /START FPP
1212 11020 7402      HLT      /SKIP IF STARTED
1213 11021 6557      FPIST      /INTERRUPT FLAG SET?
1214 11022 5221      JMP .-1      /READ STATUS.SKIP
1215 11023 7004      RAL      /INSTRUCTION
1216 11024 7700      SMA CLA      /TRAP CAUSE EXIT?
1217 11025 5606      JMP I FPPG      /NO.RETURN
1220 11026 4534      TRAP      /YES.HANDLE TRAP
1221 11027 5216      JMP FPPG1      /RESTART FPP
1222 11030 0030 APTA, APT
1223                /TRAP HANDLER
1224                /TRAP4-JMS TO OPERAND
1225                /TRAP5-ERROR EXIT
1226 11031 0000 TRP, 0
1227 11032 7344      CLA CLL CMA RAL /MINUS TWO
1230 11033 1031      TAD FPC      /BACK UP
1231 11034 3252      DCA TRPIN      /PC TO GET
1232 11035 1652      TAD I TRPIN      /TRAP INSTRUCTION
1233 11036 7006      RTL      /ROTATE TO 0
1234 11037 7006      RTL      /GOOD PLACE
1235 11040 0140      AND K7      /USE BITS 9-11
1236 11041 1244      TAD TRPJ      /CREATE JUMP
1237 11042 3243      DCA .+1      /SAVE AWAY
1240 11043 0000      0      /DISPATCH
1241 11044 5642 TRPJ, JMP I .-2      /PROTOTYPE INSTRUCTION
1242 11045 1053      TRP3
1243 11046 1054      TRP4
1244 11047 1056      TRP5
1245 11050 1060      TRP6

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1246	11051	1061	TRP7	
1247	11052	0000	TRPIN, 0	
1250	11053	5631	TRP3, JMP I TRP	/UNDEFINED
1251	11054	4434	TRP4, JMS I OPR	/SUBROUTINE EXIT
1252	11055	5631	JMP I TRP	/RETURN
1253	11056	1034	TRP5, TAD OPR	/GET ERROR CODE
1254	11057	5460	JMP I ERRA	/ERROR EXIT
1255	11060	5631	TRP6, JMP I TRP	/UNDEFINED
1256	11061	5631	TRP7, JMP I TRP	/UNDEFINED
1257			/IE AQUISITION	
1260	11062	0000	ACQ, 0	
1261	11063	1050	TAD BKGFLG	
1262	11064	7640	SZA CLA	/ZERO BUFFER?
1263	11065	5277	JMP .+12	/NO SKIP
1264	11066	1154	TAD M2000	/ZERO
1265	11067	3070	DCA COUNTL	
1266	11070	1367	TAD DATLOA	
1267	11071	3011	DCA AUX1	/DATA
1270	11072	6201	CDF 0	
1271	11073	3411	DCA I AUX1	
1272	11074	2070	ISZ COUNTL	/BUFFER
1273	11075	5273	JMP .-2	
1274	11076	6211	CDF 10	
1275	11077	1370	TAD DATAD	/SET HIGH
1276	11100	3076	DCA HWPTR	/WORD POINTER
1277	11101	1076	TAD HWPTR	/SET LOW
1300	11102	7001	IAC	/WORD
1301	11103	3077	DCA LWPTR	/POINTER
1302	11104	1071	TAD SENRGY	/SAVE
1303	11105	3075	DCA ENERGY	/STARTING ENERGY
1304	11106	1075	TAD ENERGY	/AND
1305	11107	6374	DAC	/SEND IT OUT
1306	11110	7300	CLA CLL	
1307	11111	4523	GETTY	/WAIT FOR
1310	11112	0100	CHAR	/GO
1311	11113	0001	1	/COMMAND
1312	11114	1100	TAD CHAR	/IS IT A G?
1313	11115	1153	TAD M307	
1314	11116	7640	SZA CLA	
1315	11117	5466	JMP I CMNDIA	/NO RETURN
1316	11120	1074	TAD NSCANS	/YES SET SCAN
1317	11121	7041	CIA	
1320	11122	3365	DCA SCANL	/LOOP
1321	11123	1073	ACQ1, TAD NSTEPS	/SET STEP
1322	11124	7041	CIA	
1323	11125	3366	DCA STEPL	/LOOP
1324	11126	4532	ACQ2, SAMPLE	/SAMPLE ION INTENSITY
1325	11127	4520	CHKFLG	/CONTROL R?
1326	11130	2076	ISZ HWPTR	/INCREMENT HIGH
1327	11131	2076	ISZ HWPTR	/POINTER BY 2
1330	11132	2077	ISZ LWPTR	/INCREMENT LOW
1331	11133	2077	ISZ LWPTR	/POINTER BY 2
1332	11134	1072	TAD ENIVL	/GET INTERVAL
1333	11135	7041	CIA	/NEGATE
1334	11136	1075	TAD ENERGY	/DECREMENT
1335	11137	3075	DCA ENERGY	/ELECTRON ENERGY
1336	11140	2366	ISZ STEPL	/STEP DOWN DONE?
1337	11141	5326	JMP ACQ2	/NO REPEAT
1340	11142	1073	TAD NSTEPS	/YES
1341	11143	7041	CIA	/RESET STEP
1342	11144	3366	DCA STEPL	/LOOP
1343	11145	1147	ACQ3, TAD M2	/DECREMENT

1344	11146	1076	TAD HWPTR	/HIGH POINTER
1345	11147	3076	DCA HWPTR	
1346	11150	1147	TAD M2	/DECREMENT
1347	11151	1077	TAD LWPTR	/LOW POINTER
1350	11152	3077	DCA LWPTR	
1351	11153	1072	TAD ENIVL	/INCREMENT
1352	11154	1075	TAD ENERGY	/ELECTRON
1353	11155	3075	DCA ENERGY	/ENERGY
1354	11156	4532	SAMPLE	/SAMPLE ION INTENSITY
1355	11157	4520	CHKFLG	/CONTROL R?
1356	11160	2366	ISZ STEPL	/STEP UP DONE?
1357	11161	5345	JMP ACQ3	/NO, REPEAT
1360	11162	2365	ISZ SCANL	/SCAN DONE?
1361	11163	5323	JMP ACQ1	/NO, DO NEXT SCAN
1362	11164	5662	JMP I ACQ	/YES, RETURN
1363	11165	0000	SCANL, 0	
1364	11166	0000	STEPL, 0	
1365	11167	4777	DATLOA, DTALOC-1	
1366	11170	5000	DATAD, DTALQC	
1367			PAGE	
1370			/SET ELECTRON ENERGY, DELAY, SAMPLE	
1371			/ION INTENSITY	
1372	11200	0000	SAMPL, 0	
1373	11201	1301	TAD NSAM	/SET SAMPLE
1374	11202	7041	CIA	/COUNTER
1375	11203	3302	DCA SAML	
1376	11204	3303	DCA ACHI	/CLEAR DOUBLE
1377	11205	3304	DCA ACLO	/PRECISION AC
1400	11206	1075	TAD ENERGY	/SEND OUT
1401	11207	6374	DAC	/ELECTRON ENERGY
1402	11210	7300	CLA CLL	
1403	11211	1305	TAD DCONST	/DELAY
1404	11212	3306	DCA OTRL	/BY DOING
1405	11213	2307	ISZ INRL	/NOTHING
1406	11214	5213	JMP .-1	
1407	11215	2306	ISZ OTRL	
1410	11216	5213	JMP .-3	
1411	11217	6141	SAMPL1, LINC	/LINC MODE SET
1412	11220	0111	SAM11	/SAMPLE SIGNAL
1413	11221	0002	PDP	/0 MODE SET
1414	11222	7510	SPA	/POSITIVE?
1415	11223	7200	CLA	/NO, SET TO ZERO
1416	11224	7100	CLL	
1417	11225	1304	TAD ACLO	/ADD INTENSITY TO
1420	11226	3304	DCA ACLO	/DPAC
1421	11227	7004	RAL	
1422	11230	1303	TAD ACHI	
1423	11231	3303	DCA ACHI	
1424	11232	2302	ISZ SAML	/DONE SAMPLING?
1425	11233	5217	JMP SAMPL1	/NO, REPEAT
1426	11234	1310	TAD NSHIFT	/YES, AVERAGE INTENSITY
1427	11235	7041	CIA	
1430	11236	3311	DCA NTIMES	/DIVIDE
1431	11237	1303	TAD ACHI	/BY
1432	11240	7110	CLL RAR	/ROTATING
1433	11241	3303	DCA ACHI	
1434	11242	1304	TAD ACLO	
1435	11243	7010	RAR	/DPAC
1436	11244	3304	DCA ACLO	
1437	11245	2311	ISZ NTIMES	/DIVISION DONE?
1440	11246	5237	JMP .-7	/NO, ROTATE AGAIN
1441	11247	6201	CDF 0	

1442	11250	1050	TAD BKGFLG	/YES,CHECK FOR
1443	11251	7640	SZA CLA	/BACKGROUND SUBTRACTION
1444	11252	5264	JMP SAMPL2	/SUBTRACT
1445	11253	7100	CLL	/ADD SAMPLED
1446	11254	1304	TAD ACLO	/INTENSITY
1447	11255	1477	TAD I LWPTR	/TO
1450	11256	3477	DCA I LWPTR	/BUFFER
1451	11257	7004	RAL	
1452	11260	1476	TAD I HWPTR	
1453	11261	3476	DCA I HWPTR	
1454	11262	6211	CDF 10	
1455	11263	5600	JMP I SAMPL	/RETURN
1456	11264	7100	SAMPL2, CLL	/SUBTRACT
1457	11265	1304	TAD ACLO	/SAMPLED INTENSITY
1460	11266	7041	CIA	
1461	11267	1477	TAD I LWPTR	/FROM BUFFER
1462	11270	3477	DCA I LWPTR	
1463	11271	7004	RAL	
1464	11272	3312	DCA LSAVE	
1465	11273	7040	CIMH	
1466	11274	1476	TAD I HWPTR	
1467	11275	1312	TAD LSAVE	
1470	11276	3475	DCA I HWPTR	
1471	11277	6211	CDF 10	
1472	11300	5600	JMP I SAMPL	/RETURN
1473	11301	1000	NSAM, 1000	
1474	11302	0000	SAML, 0	
1475	11303	0000	ACHI, 0	
1476	11304	0000	ACLO, 0	
1477	11305	7764	DCONST, -14	/ .25 SEC
1500	11306	0000	OTRL, 0	
1501	11307	0000	INRL, 0	
1502	11310	0011	NSHIFT, 11	
1503	11311	0000	NTIMES, 0	
1504	11312	0000	LSAVE, 0	
1505			/	
1506			/*I/O SUBROUTINES**	
1507			/	
1510			/OUTPUT A LIST TO THE TTY	
1511			/LIST ADDRESS IN CALL+1	
1512			/LIST IN FIELD 1	
1513	11313	0000	PTTY, 0	
1514	11314	1713	TAD I PTTY	/GET ARGUEMENT
1515	11315	3335	DCA LISTP	/SAVE
1516	11316	2313	ISZ PTTY	/BOP THE POINTER
1517	11317	1735	TAD I LISTP	/GET THE COUNT
1520	11320	3341	DCA PBUFL	/PARAMETER COUNT
1521	11321	1335	TAD LISTP	/BOP LIST
1522	11322	7001	IAC	/POINTER AND
1523	11323	3340	DCA PBUFRA	/SAVE AS ADDRESS
1524	11324	6224	RIF	/STANDARD
1525	11325	6202	CIF 0	/MONITOR
1526	11326	4441	JMS I WRITE	/I/O CALL
1527	11327	1336	PUPARM	
1530	11330	1336	TAD PUPARM	/STANDARD WAIT
1531	11331	7710	SPA CLA	/TILL DONE
1532	11332	5330	JMP .-2	
1533	11333	4520	CHKFLG	/CONTROL R?
1534	11334	5713	JMP I PTTY	/DONE,RETURN
1535	11335	0000	LISTP, 0	
1536	11336	0040	PUPARM, 40	/PARAMETER
1537	11337	6211	CDF 10	/LIST

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1540 11340 0000 PBUFRA, 0
1541 11341 0000 PBUFL, 0
1542 11342 0000 0
1543 11343 0000 0
1544 11344 0000 0
1545 PAGE
1546 /GET A LIST FROM THE TTY
1547 /CALL+1=STORAGE LOCATION IN FIELD 1
1550 /CALL+2=LIST LENGTH
1551 11400 0000 GTTY, 0
1552 11401 1600 TAD I GTTY /GET BUFFER ADDRESS
1553 11402 3222 DCA GBUFA /SAVE IN PARAMETER LIST
1554 11403 2200 ISZ GTTY /BOP POINTER
1555 11404 1600 TAD I GTTY /GET LIST LENGTH
1556 11405 3223 DCA GBUFL /SAVE IN PARAMETER LIST
1557 11406 2200 ISZ GTTY /BOP FOR RETURN
1560 11407 6224 RIF /STANDARD
1561 11410 6202 CIF 0 /MONITOR
1562 11411 4440 JMS I READ /CALL
1563 11412 1420 GTPARM
1564 11413 1220 TAD GTPARM /STANDARD
1565 11414 7710 SPA CLA /WAIT
1566 11415 5213 JMP .-2
1567 11416 4520 CHKFLG /CONTROL R?
1570 11417 5600 JMP I GTTY /DONE, RETURN
1571 11420 0040 GTPARM, 40 /PARAMETER
1572 11421 6211 CDF 10 /LIST
1573 11422 0000 GBUFA, 0
1574 11423 0000 GBUFL, 0
1575 11424 0000 0
1576 11425 0000 0
1577 11426 0000 0
1600 /PUT A LIST CREATED THROUGH PUT STRING
1601 /ON THE TTY
1602 11427 0000 BUTTY, 0
1603 11430 1260 TAD PCNT /GET LIST LENGTH
1604 11431 3457 DCA I PBUFA /AND STORE HERE
1605 11432 4531 PUTTY /SO WE CAN USE
1606 11433 2377 LPBUF-1 /OUR TTY PUTTER
1607 11434 1057 TAD PBUFA /RESET BUFFER
1610 11435 3010 DCA AUX0 /POINTER
1611 11436 3260 DCA PCNT /CLEAR COUNT
1612 11437 5627 JMP I BUTTY /RETURN
1613 /OUTPUT TO LINE PRINTER
1614 11440 0000 PLPTR, 0
1615 11441 6224 RIF
1616 11442 6202 CIF 0 /STANDARD
1617 11443 4441 JMS I WRITE /I/O
1620 11444 1455 LPARM /CALL
1621 11445 1255 TAD LPARM
1622 11446 7710 SPA CLA /DONE?
1623 11447 5245 JMP .-2 /NO, CHECK AGAIN
1624 11450 4520 CHKFLG /CONTROL R?
1625 11451 1057 TAD PBUFA /YES, RESET
1626 11452 3010 DCA AUX0 /BUFFER POINTER
1627 11453 3260 DCA PCNT /CLEAR COUNT
1630 11454 5640 JMP I PLPTR /RETURN
1631 11455 0050 LPARM, 50 /PARAMETER LIST
1632 11456 6211 CDF 10
1633 11457 2400 LPBUF
1634 11460 0000 PCNT, 0
1635 11461 0000 0

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1636	11462	0000	0	
1637	11463	0000	0	
1640		/PUT STRING ROUTINES		
1641	11464	0000	PSTR, 0	/CALLED IN 8 MODE
1642	11465	1664	TAD I PSTR	/GET STRING ADDRESS
1643	11466	2264	ISZ PSTR	/BOP POINTER
1644	11467	4320	JMS SETPTR	/INITIALIZE
1645	11470	4326	JMS PSTRGO	/SEND IT OUT
1646	11471	5664	JMP I PSTR	/RETURN
1647	11472	0000	PSTRA, 0	/FPP ENTRY
1650	11473	1335	TAD CONLOA	/GET ADDRESS
1651	11474	4320	JMS SETPTR	/INITIALIZE
1652	11475	4326	JMS PSTRGO	/SEND TO BUFFER
1653	11476	5672	JMP I PSTRA	/RETURN TO FPP
1654	11477	0000	PSTRA1, 0	/SAME AS PSTRA
1655	11500	1335	TAD CONLOA	/BUT PURGES
1656	11501	4320	JMS SETPTR	/DECIMAL POINT
1657	11502	1411	PSTR1, TAD I AUX1	
1660	11503	0010	DCA PUSAV	
1661	11504	1316	TAD PUSAV	
1662	11505	1317	TAD M256	
1663	11506	7650	SNA CLA	/DECIMAL POINT?
1664	11507	5677	JMP I PSTRA1	/YES, RETURN
1665	11510	1316	TAD PUSAV	/NO, STORE AWAY
1666	11511	3410	DCA I AUX0	
1667	11512	2260	ISZ PCNT	
1670	11513	2336	ISZ PUTCTR	
1671	11514	5302	JMP PSTR1	
1672	11515	5677	JMP I PSTRA1	/RETURN
1673	11516	0000	PUSAV, 0	
1674	11517	7522	M256, -256	
1675	11520	0000	SETPTR, 0	
1676	11521	3011	DCA AUX1	/SAVE ADDRESS
1677	11522	1411	TAD I AUX1	/GET LENGTH
1700	11523	7041	CIA	/AND
1701	11524	3336	DCA PUTCTR	/SET THE COUNT
1702	11525	5720	JMP I SETPTR	/RETURN
1703	11526	0000	PSTRGO, 0	
1704	11527	1411	TAD I AUX1	/GET A CHARACTER
1705	11530	3410	DCA I AUX0	/STORE IN PBUF
1706	11531	2260	ISZ PCNT	/BOP PARAMETER COUNT
1707	11532	2336	ISZ PUTCTR	/STRING DONE?
1710	11533	5327	JMP .-4	/NO, REPEAT
1711	11534	5726	JMP I PSTRGO	/YES, RETURN
1712	11535	2352	CONLOA, CONLOC-1	
1713	11536	0000	PUTCTR, 0	
1714		/PUT OUT CRLF AT AUX0		
1715	11537	0000	PCRLF, 0	
1716	11540	1350	TAD CR	/GET RETURN
1717	11541	3410	DCA I AUX0	/SAVE AWAY
1720	11542	1351	TAD LF	/GET LINE FEED
1721	11543	3410	DCA I AUX0	/SAVE AWAY
1722	11544	2260	ISZ PCNT	/BOP PARAMETER
1723	11545	2260	ISZ PCNT	/COUNT BY 2
1724	11546	5737	JMP I PCRLF	/RETURN
1725	11547	0002	MYCRLF, 2	
1726	11550	0215	CR, 215	
1727	11551	0212	LF, 212	
1730		/TAB SPACE ROUTINES		
1731	11552	0000	TBSP, 0	/CALLED IN 8 MODE
1732	11553	1752	TAD I TBSP	/GET SPACE COUNT
1733	11554	7041	CIA	/AND SET UP LOOP

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1734 11555 3336      DCA PUTCTR      /COUNTER
1735 11556 2352      ISZ TBSP        /BOP FOR RETURN
1736 11557 4367      JMS TBSPGO      /PUT THEM OUT
1737 11560 5752      JMP I TBSP      /RETURN
1740 11561 0000 TBSPA, 0      /FPP TRAP ENTRY
1741 11562 1023      TAD FXR3        /GET NUMBER OF SPACES
1742 11563 7041      CIA            /SET LOOP
1743 11564 3336      DCA PUTCTR      /COUNTER
1744 11565 4367      JMS TBSPGO      /PUT THEM OUT
1745 11566 5761      JMP I TBSPA     /RETURN
1746 11567 0000 TBSPGO, 0
1747 11570 1376      TAD SP          /GET ASCII SP
1750 11571 3410      DCA I AUX0      /SAVE THRU INDEX 0
1751 11572 2260      ISZ PCNT        /BOP PARAMETER COUNT
1752 11573 2336      ISZ PUTCTR      /DONE?
1753 11574 5370      JMP .-4         /NO,CONTINUE
1754 11575 5767      JMP I TBSPGO    /YES,RETURN
1755 11576 0240 SP, 240
1756                PAGE
1757                /GET H. NUMBER FROM THE TTY
1760 11600 0000 GNUM, 0
1761 11601 1207      TAD NUMA        /SET UP STRING
1762 11602 3013      DCA AUX3        /POINTER
1763 11603 4523      GETTY          /GET THE
1764 11604 1610      NUML           /NUMBER
1765 11605 0012      12             /10 DIGITS MAXIMUM
1766 11606 5600      JMP I GNUM      /RETURN
1767 11607 1607 NUMA, NUML-1
1770 11610 0000 NUML, 0
1771 11611 0000      0
1772 11612 0000      0
1773 11613 0000      0
1774 11614 0000      0
1775 11615 0000      0
1776 11616 0000      0
1777 11617 0000      0
2000 11620 0000      0
2001 11621 0000      0
2002                /**SPECIAL FPP CALLED ROUTINES**
2003                /PASS A CHARACTER TO FPP
2004 11622 0000 GCHAR, 0
2005 11623 1413      TAD I AUX3      /GET A CHARACTER
2006 11624 3024      DCA FXR4        /PASS THRU INDEX 4
2007 11625 5622      JMP I GCHAR     /RETURN
2010                /INCLUSIVE OR
2011                /ADDRESS OF A IN BASE REGISTER ONE
2012                /B IN LSW OF FAC
2013                /RETURN WITH RESULT IN LSW OF FAC
2014 11626 0000 OR, 0
2015 11627 7300      CLA CLL
2016 11630 1640      TAD I BAS1A     /GET ADDRESS
2017 11631 3241      DCA ORPTR       /SAVE
2018 11632 1641      TAD I ORPTR     /GET A
2019 11633 7040      CMA             /COMPLIMENT A
2020 11634 0037      AND APT+7       /INTERSECT B
2021 11635 1641      TAD I ORPTR     /ADD A
2022 11636 3037      DCA APT+7       /STORE RESULT
2023 11637 5626      JMP I OR        /RETURN
2026 11640 2605 BAS1A, B1+2
2027 11641 0000 ORPTR, 0
2030                /SET LINE PRINTER TO PLOT MODE
2031 11642 0000 STPLOT, 0

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2032	11643	4525	LPCTL	
2033	11644	0007	PLT	
2034	11645	5642	JMP I STPLOT	
2035			/LABEL WARRENS PLOTS	
2036	11646	0000	LABEL, 0	
2037	11647	4525	LPCTL	/SET PRINT
2040	11650	0006	PRNT	/MODE ON LP
2041	11651	4525	LPCTL	/AND ISSUE A
2042	11652	0003	RFFED	/FORM FEED
2043	11653	4533	TABSP	/CENTER
2044	11654	0072	72	
2045	11655	4527	PUSTR	/PRINT FIRST
2046	11656	2052	LABL1-1	/LINE
2047	11657	4530	PUTLP	
2050	11660	4533	TABSP	/CENTER SECOND
2051	11661	0101	101	/LINE
2052	11662	4527	PUSTR	
2053	11663	2076	LABL2-1	/AND
2054	11664	4530	PUTLP	/PRINT
2055	11665	4533	TABSP	/CENTER THIRD
2056	11666	0071	71	/LINE
2057	11667	4527	PUSTR	/AND
2060	11670	2103	LABL3-1	/PRINT
2061	11671	4530	PUTLP	
2062	11672	5646	JMP I LABEL	/RETURN

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2063                                EJECT
2064                                /
2065                                /
2066                                /*****HEADINGS AND MESSAGES*****/
2067                                /
2070                                /
2071 11673 0004 AMS1,      4
2072 11674 0311          311          /I
2073 11675 0315          315          /M
2074 11676 0272          272          /:
2075 11677 0240          240
2076 11700 0004 AMS2,      4
2077 11701 0323          323          /S
2100 11702 0305          305          /E
2101 11703 0272          272          /:
2102 11704 0240          240
2103 11705 0004 AMS3,      4
2104 11706 0305          305          /E
2105 11707 0311          311          /I
2106 11710 0272          272          /:
2107 11711 0240          240
2110 11712 0003 AMS4,      3
2111 11713 0322          322          /R
2112 11714 0272          272          /:
2113 11715 0240          240
2114 11716 0004 AMS5,      4
2115 11717 0316          316          /N
2116 11720 0323          323          /S
2117 11721 0272          272          /:
2120 11722 0240          240
2121 11723 0047 CMS,      47
2122 11724 0324          324          /T
2123 11725 0331          331          /Y
2124 11726 0320          320          /P
2125 11727 0305          305          /E
2126 11730 0240          240
2127 11731 0303          303          /C
2130 11732 0317          317          /O
2131 11733 0315          315          /M
2132 11734 0315          315          /M
2133 11735 0301          301          /A
2134 11736 0316          316          /N
2135 11737 0304          304          /D
2136 11740 0240          240
2137 11741 0323          323          /S
2140 11742 0305          305          /E
2141 11743 0321          321          /O
2142 11744 0325          325          /U
2143 11745 0305          305          /E
2144 11746 0316          316          /N
2145 11747 0303          303          /C
2146 11750 0305          305          /E
2147 11751 0240          240
2150 11752 0306          306          /F
2151 11753 0317          317          /O
2152 11754 0314          314          /L
2153 11755 0314          314          /L
2154 11756 0317          317          /O
2155 11757 0327          327          /W
2156 11760 0305          305          /E
2157 11761 0304          304          /D

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2160	11762	0240	240	
2161	11763	0302	302	/B
2162	11764	0331	331	/Y
2163	11765	0240	240	
2164	11766	0251	251	/)
2165	11767	0240	240	
2166	11770	0215	215	
2167	11771	0212	212	
2170	11772	0250	250	/C
2171			PAGE	
2172	12000	0015 DELHED.	15	
2173	12001	0304	304	/D
2174	12002	0305	305	/E
2175	12003	0314	314	/L
2176	12004	0324	324	/T
2177	12005	0301	301	/A
2200	12006	0240	240	
2201	12007	0324	324	/T
2202	12010	0301	301	/A
2203	12011	0302	302	/B
2204	12012	0314	314	/L
2205	12013	0305	305	/E
2206	12014	0215	215	
2207	12015	0212	212	
2210	12016	0007 EMS.	7	
2211	12017	0305	305	/E
2212	12020	0316	316	/N
2213	12021	0305	305	/E
2214	12022	0322	322	/R
2215	12023	0307	307	/G
2216	12024	0331	331	/Y
2217	12025	0272	272	/:
2220	12026	0024 IEHED.	24	
2221	12027	0240	240	
2222	12030	0305	305	/E
2223	12031	0316	316	/N
2224	12032	0305	305	/E
2225	12033	0322	322	/R
2226	12034	0307	307	/G
2227	12035	0331	331	/Y
2230	12036	0240	240	
2231	12037	0240	240	
2232	12040	0311	311	/I
2233	12041	0316	316	/N
2234	12042	0324	324	/T
2235	12043	0305	305	/E
2236	12044	0316	316	/N
2237	12045	0323	323	/S
2240	12046	0311	311	/I
2241	12047	0324	324	/T
2242	12050	0331	331	/Y
2243	12051	0215	215	
2244	12052	0212	212	
2245	12053	0023 LABL1.	23	
2246	12054	0305	305	/E
2247	12055	0316	316	/N
2250	12056	0305	305	/E
2251	12057	0322	322	/R
2252	12060	0307	307	/G
2253	12061	0331	331	/Y
2254	12062	0240	240	
2255	12063	0304	304	/D

2256	12064	0311	311	/I
2257	12065	0306	306	/F
2260	12066	0306	306	/F
2261	12067	0305	305	/E
2262	12070	0322	322	/R
2263	12071	0305	305	/E
2264	12072	0316	316	/N
2265	12073	0303	303	/C
2266	12074	0305	305	/E
2267	12075	0215	215	
2270	12076	0212	212	
2271	12077	0004 LABL2,	4	
2272	12100	0326	326	/V
2273	12101	0323	323	/S
2274	12102	0215	215	
2275	12103	0212	212	
2276	12104	0026 LABL3,	26	
2277	12105	0322	322	/R
2300	12106	0305	305	/E
2301	12107	0314	314	/L
2302	12110	0301	301	/A
2303	12111	0324	324	/T
2304	12112	0311	311	/I
2305	12113	0326	326	/V
2306	12114	0305	305	/E
2307	12115	0240	240	
2310	12116	0311	311	/I
2311	12117	0316	316	/N
2312	12120	0324	324	/T
2313	12121	0305	305	/E
2314	12122	0316	316	/N
2315	12123	0323	323	/S
2316	12124	0311	311	/I
2317	12125	0324	324	/T
2320	12126	0331	331	/Y
2321	12127	0215	215	
2322	12130	0212	212	
2323	12131	0212	212	
2324	12132	0212	212	
2325	12133	0032 LSQHED,	32	
2326	12134	0314	314	/L
2327	12135	0305	305	/E
2330	12136	0301	301	/A
2331	12137	0323	323	/S
2332	12140	0324	324	/T
2333	12141	0255	255	/-
2334	12142	0323	323	/S
2335	12143	0321	321	/Q
2336	12144	0325	325	/U
2337	12145	0301	301	/A
2340	12146	0322	322	/R
2341	12147	0305	305	/E
2342	12150	0323	323	/S
2343	12151	0240	240	
2344	12152	0311	311	/I
2345	12153	0316	316	/N
2346	12154	0324	324	/T
2347	12155	0305	305	/E
2350	12156	0322	322	/R
2351	12157	0303	303	/C
2352	12160	0305	305	/E
2353	12161	0320	320	/P

2354	12162	0324	324	/T
2355	12163	0323	323	/S
2356	12164	0215	215	
2357	12165	0212	212	
2360			PAGE	
2361	12200	0027 MASHED.	27	
2362	12201	0212	212	
2363	12202	0212	212	
2364	12203	0240	240	
2365	12204	0240	240	
2366	12205	0322	322	/R
2367	12206	0305	305	/E
2370	12207	0314	314	/L
2371	12210	0256	256	/.
2372	12211	0240	240	
2373	12212	0311	311	/I
2374	12213	0316	316	/N
2375	12214	0324	324	/T
2376	12215	0256	256	/.
2377	12216	0240	240	
2400	12217	0240	240	
2401	12220	0305	305	/E
2402	12221	0316	316	/N
2403	12222	0305	305	/E
2404	12223	0322	322	/R
2405	12224	0307	307	/G
2406	12225	0331	331	/Y
2407	12226	0215	215	
2410	12227	0212	212	
2411	12230	0006 MMS1.	6	
2412	12231	0315	315	/M
2413	12232	0301	301	/A
2414	12233	0323	323	/S
2415	12234	0323	323	/S
2416	12235	0272	272	/:
2417	12236	0240	240	
2420	12237	0024 NMS1.	24	
2421	12240	0311	311	/I
2422	12241	0316	316	/N
2423	12242	0324	324	/T
2424	12243	0305	305	/E
2425	12244	0316	316	/N
2426	12245	0323	323	/S
2427	12246	0311	311	/I
2430	12247	0324	324	/T
2431	12250	0331	331	/Y
2432	12251	0240	240	
2433	12252	0315	315	/M
2434	12253	0325	325	/U
2435	12254	0314	314	/L
2436	12255	0324	324	/T
2437	12256	0311	311	/I
2440	12257	0320	320	/P
2441	12260	0314	314	/L
2442	12261	0305	305	/E
2443	12262	0272	272	/:
2444	12263	0240	240	
2445	12264	0014 NMS2.	14	
2446	12265	0316	316	/N
2447	12266	0317	317	/O
2450	12267	0322	322	/R
2451	12270	0315	315	/M

2452	12271	0240	240	
2453	12272	0322	322	/R
2454	12273	0301	301	/A
2455	12274	0316	316	/N
2456	12275	0307	307	/G
2457	12276	0305	305	/E
2460	12277	0272	272	/:
2461	12300	0240	240	
2462	12301	0012	TABHED, 12	
2463	12302	0311	311	/I
2464	12303	0305	305	/E
2465	12304	0240	240	
2466	12305	0324	324	/T
2467	12306	0301	301	/A
2470	12307	0302	302	/B
2471	12310	0314	314	/L
2472	12311	0305	305	/E
2473	12312	0215	215	
2474	12313	0212	212	
2475	12314	0022	TMS, 22	
2476	12315	0304	304	/D
2477	12316	0305	305	/E
2500	12317	0314	314	/L
2501	12320	0301	301	/A
2502	12321	0331	331	/Y
2503	12322	0240	240	
2504	12323	0324	324	/T
2505	12324	0311	311	/I
2506	12325	0315	315	/M
2507	12326	0305	305	/E
2510	12327	0240	240	
2511	12330	0250	250	/C
2512	12331	0323	323	/S
2513	12332	0305	305	/E
2514	12333	0303	303	/C
2515	12334	0251	251	/)
2516	12335	0272	272	/:
2517	12336	0240	240	
2520	12337	0007	ERRMS, 7	
2521	12340	0215	215	
2522	12341	0212	212	
2523	12342	0277	277	/?
2524	12343	0000	DIG, 0	
2525	12344	0000	0	/ERROR CODE
2526	12345	0215	215	
2527	12346	0212	212	
2530	12347	0003	ASTER, 3	
2531	12350	0215	215	
2532	12351	0212	212	
2533	12352	0252	252	/*
2534	12353	0000	CONLOC, 0	
2535			PAGE	
2536	12400	0000	LPBUF, 0	
2537			PAGE	

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2540                                EJECT
2541                                /
2542                                /
2543                                /***** FPP CODE *****/
2544                                /
2545                                /
2546                                /FPP BASE PAGE
2547                                /
2550                                /BASE REGISTERS
2551 12600 0000 B0.      0.
      12601 0000
      12602 0000
2552                                BASE B0
2553 12603 0000 B1.      0.
      12604 0000
      12605 0000
2554 12606 0000 B2.      0.
      12607 0000
      12610 0000
2555 12611 0000 B3.      0.
      12612 0000
      12613 0000
2556 12614 0000 B4.      0.
      12615 0000
      12616 0000
2557 12617 0000 B5.      0.
      12620 0000
      12621 0000
2560 12622 0000 B6.      0.
      12623 0000
      12624 0000
2561 12625 0000 B7.      0.
      12626 0000
      12627 0000
2562 12630 0000 B10.     0.
      12631 0000
      12632 0000
2563 12633 0000 B11.     0.
      12634 0000
      12635 0000
2564 12636 0000 B12.     0.
      12637 0000
      12640 0000
2565 12641 0000 B13.     0.
      12642 0000
      12643 0000
2566 12644 0000 B14.     0.
      12645 0000
      12646 0000
2567 12647 0000 B15.     0.
      12650 0000
      12651 0000
2570 12652 0000 B16.     0.
      12653 0000
      12654 0000
2571 12655 0000 B17.     0.
      12656 0000
      12657 0000
2572                                /FPP VARIABLES
2573 12660 0027 FIX.      27
2574 12661 0000          0

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2575	12662	0000	0
2576	12663	0000	SENGY, 0.
	12664	0000	
	12665	0000	
2577	12666	0000	INTVL, 0.
	12667	0000	
	12670	0000	
2600	12671	0000	RNGE, 0.
	12672	0000	
	12673	0000	
2601	12674	0000	ULIM, 0.
	12675	0000	
	12676	0000	
2602	12677	0000	LLIM, 0.
	12700	0000	
	12701	0000	
2603	12702	0000	RATIO, 0.
	12703	0000	
	12704	0000	
2604	12705	0000	DISPL, 0.
	12706	0000	
	12707	0000	
2605	12710	0000	HILOC, 0.
	12711	0000	
	12712	0000	
2606	12713	0000	LOLOC, 0.
	12714	0000	
	12715	0000	
2607	12716	0000	0.
	12717	0000	
	12720	0000	
2610	12721	0000	LOINT, 0.
	12722	0000	
	12723	0000	
2611	12724	0000	HIINT, 0.
	12725	0000	
	12726	0000	
2612	12727	0000	LOWINT, 0.
	12730	0000	
	12731	0000	
2613	12732	0000	INTFAC, 0.
	12733	0000	
	12734	0000	
2614	12735	0000	NUMPLT, 0.
	12736	0000	
	12737	0000	
2615	12740	0000	IROW, 0.
	12741	0000	
	12742	0000	
2616	12743	0000	JCOL, 0.
	12744	0000	
	12745	0000	
2617	12746	0000	BUFLOC, 0.
	12747	0000	
	12750	0000	
2620	12751	0000	SUMX, 0.
	12752	0000	
	12753	0000	
2621	12754	0000	SUMXX, 0.
	12755	0000	
	12756	0000	
2622	12757	0000	SUMW, 0.


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12760 0000
12761 0000
2623 12762 0000 SUMY, 0.
12763 0000
12764 0000
2624 12765 0000 SUMXY, 0.
12766 0000
12767 0000
2625 12770 0000 DENOM, 0.
12771 0000
12772 0000
2626 12773 0000 TEMP, 0.
12774 0000
12775 0000
2627 12776 0000 MIN, 0.
12777 0000
13000 0000
2630 13001 0000 NULNTH, 0.
13002 0000
13003 0000
2631 13004 0000 XFACTR, 0.
13005 0000
13006 0000
2632 13007 0000 YFACTR, 0.
13010 0000
13011 0000
2633 13012 0000 XVALUE, 0.
13013 0000
13014 0000
2634 13015 0000 KTRANS, 0.
13016 0000
13017 0000
2635 13020 0000 NOSPAC, 0.
13021 0000
13022 0000
2636 13023 0000 PUFLAG, 0.
13024 0000
13025 0000
2637 13026 0000 PLTFLG, 0.
13027 0000
13030 0000
2640 13031 0000 BYFLAG, 0.
13032 0000
13033 0000
2641 13034 0000 PTLOC, 0.
13035 0000
13036 0000
2642 13037 0000 WRDLOC, 0.
13040 0000
13041 0000
2643 13042 0000 BITLOC, 0.
13043 0000
13044 0000
2644 13045 0000 START, 0.
13046 0000
13047 0000
2645 13050 0000 ENDBIT, 0.
13051 0000
13052 0000
2646 13053 0000 LPOINT, 0.
13054 0000
13055 0000

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2647 13056 0000 LBIT, 0.
      13057 0000
      13060 0000
2650 13061 0000 UPOINT, 0.
      13062 0000
      13063 0000
2651 13064 0000 UBIT, 0.
      13065 0000
      13066 0000
2652 13067 0000 LLIMIT, 0.
      13070 0000
      13071 0000
2653 13072 0000 ULIMIT, 0.
      13073 0000
      13074 0000
2654 /FPP CONSTANTS
2655 13075 0012 XLNTH, 12:2640:0
      13076 2640
      13077 0000
2656 13100 0011 YLNTH, 11:3400:0
      13101 3400
      13102 0000
2657 13103 0004 NUMYDV, 4:2000:0
      13104 2000
      13105 0000
2660 13106 0012 K1000, 12:2000:0
      13107 2000
      13110 0000
2661 13111 0010 K377, 10:3770:0
      13112 3770
      13113 0000
2662 13114 0010 K200, 10:2000:0
      13115 2000
      13116 0000
2663 13117 0200 FCONST, 0200:0:0
      13120 0000
      13121 0000
2664 13122 0012 MAXIM, 999.
      13123 3716
      13124 0000
2665 13125 7773 DFACTR, .213618E-1
      13126 2567
      13127 7564
2666 /
2667 /** FPP ROUTINES **
2670 /
2671 /GET,CHECK,AND STORE ION MASS
2672 13130 1121 MASS, JSA GETNUM /ASSEMBLE NUMBER
      13131 6551
2673 13132 0010 ALN 0 /CHOP OFF FRACTION
2674 13133 0004 FNORM /FIX
2675 13134 6251 FSTA TEMP /STORE A SECOND
2676 13135 2401 FSUB FPPONE /GREATER THAN 1?
      13136 6511
2677 13137 1051 JLT MASSER /NO.ERROR
      13140 3160
2700 13141 2306 FSUB MAXIM /YES,LT 1000?
2701 13142 1011 JGE MASSER /NO.ERROR
      13143 3160
2702 13144 0400 FLDA (MASLOC /STORE
      13145 7400
2703 13146 6242 FSTA BUFLOC

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2704	13147	0400	FLDA NIE	
	13150	3005		
2705	13151	4400	FMUL (3.	
	13152	7403		
2706	13153	1121	JSA SETLOC	/IN
	13154	6447		
2707	13155	0251	FLDA TEMP	
2710	13156	6601	FSTA I B1	/MASS VECTOR
2711	13157	0000	FEXIT	
2712	13160	5000	MASSER, TRAP5 3	
	13161	0003		
2713			/GET,CHECK,AND STORE STARTING ENERGY	
2714	13162	1121	STRTEN, JSA GETNUM	/GET ENERGY
	13163	6551		
2715	13164	4400	FMUL (100.	/INTEGERIZE BY
	13165	7406		
2716	13166	1400	FADD (.5	/MULTIPLYING BY 100
	13167	7411		
2717	13170	0010	ALN 0	/ROUND AND CHOP
2720	13171	0004	FNORM	
2721	13172	6221	FSTA SENGY	/STORE FOR REFERENCE
2722	13173	1051	JLT STRTER	/LT 0,ERROR
	13174	3211		
2723	13175	2400	FSUB (4096.	/GE 40.96
	13176	7414		
2724	13177	1011	JGE STRTER	/ERROR
	13200	3211		
2725	13201	0400	FLDA (SENGY	/SAVE AS A
	13202	7417		
2726	13203	6201	FSTA B1	/SINGLE
2727	13204	0221	FLDA SENGY	/PRECISION
2730	13205	0010	ALN 0	
2731	13206	1121	JSA PUTWRD	/INTEGER
	13207	6354		
2732	13210	0000	FEXIT	
2733	13211	5000	STRTER, TRAP5 4	
	13212	0004		
2734			/GET,CHECK,AND SAVE ENERGY INTERVAL	
2735	13213	1121	ENTRVL, JSA GETNUM	/GET INTERVAL
	13214	6551		
2736	13215	4400	FMUL (100.	
	13216	7406		
2737	13217	1400	FADD (.5	/INTEGERIZE
	13220	7411		
2740	13221	0010	ALN 0	
2741	13222	0004	FNORM	
2742	13223	6222	FSTA INTVL	/SAVE FLOATING POINT
2743	13224	1021	JLE ENINER	/ERROR,LE 0
	13225	3242		
2744	13226	2400	FSUB (4096.	/LT 40.96?
	13227	7414		
2745	13230	1011	JGE ENINER	/NO,ERROR
	13231	3242		
2746	13232	0400	FLDA (ENIVL	/SINGLE
	13233	7422		
2747	13234	6201	FSTA B1	/PRECISION
2750	13235	0222	FLDA INTVL	/SAVE
2751	13236	0010	ALN 0	
2752	13237	1121	JSA PUTWRD	
	13240	6354		
2753	13241	0000	FEXIT	
2754	13242	5000	ENINER, TRAP5 5	

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13243 0005
2755          /GET,CHECK,SAVE ENERGY RANGE
2756          /CALCULATE NUMBER OF STEPS,CHECK,SAVE
2757 13244 1121 RANGE, JSA GETNUM      /GET RANGE
          13245 6551
2760 13246 4400          FMUL (100.
          13247 7406
2761 13250 1400          FADD (.5      /INTEGERIZE
          13251 7411
2762 13252 0010          ALN 0
2763 13253 0004          FNORM
2764 13254 6223          FSTA RNGE      /SAVE
2765 13255 0003          FNEG          /SUBTRACT FROM
2766 13256 1221          FADD SENG     /STARTING ENERGY
2767 13257 1051          JLT RANGER     /MUST BE GE 0
          13260 3307
2770 13261 0223          FLDA RNGE
2771 13262 2222          FSUB INTVL     /RANGE MUST BE
2772 13263 1051          JLT RANGER     /GE INTERVAI
          13264 3307
2773 13265 0400          FLDA (NSTEPS   /SET STEP SAVE
          13266 7425
2774 13267 6201          FSTA B1        /ADDRESS
2775 13270 0223          FLDA RNGE      /NSTEPS=RANGE/
2776 13271 3222          FDIV INTVL     /ENERGY INTERVAL
2777 13272 1401          FADD FPPONE    /+ONE
          13273 6511
3000 13274 0010          ALN 0          /SAVE IN A NICE
3001 13275 6251          FSTA TEMP      /FORM
3002 13276 1021          JLE STEPER     /MUST BE GT 0
          13277 3311
3003 13300 2302          FSUB K1000     /AND LT 512
3004 13301 1011          JGE STEPER
          13302 3311
3005 13303 0251          FLDA TEMP      /SAVE AWAY
3006 13304 1121          JSA PUTWRD     /AS A SINGLE PRECISION
          13305 6354
3007 13306 0000          FEXIT          /INTEGER
3010 13307 5000 RANGER, TRAPS 6
          13310 0006
3011 13311 5000 STEPER, TRAPS 7
          13312 0007
3012          /GET CHECK,SAVE NUMBER OF SCANS
3013 13313 1121 SCANS, JSA GETNUM      /ASSEMBLE IT
          13314 6551
3014 13315 0010          ALN 0          /STORE AS A
3015 13316 6251          FSTA TEMP      /WHOLE NUMBER
3016 13317 2401          FSUB FPPONE    /GE ONE?
          13320 6511
3017 13321 1051          JLT SCANER     /NO,ERROR
          13322 3336
3020 13323 2400          FSUB (7999.    /MUST BE LESS
          13324 7430
3021 13325 1011          JGE SCANER     /THAN 8000
          13326 3336
3022 13327 0400          FLDA (NSCANS   /SET SINGLE PRECISION
          13330 7433
3023 13331 6201          FSTA B1        /LOCATION
3024 13332 0251          FLDA TEMP      /GET NUMBER
3025 13333 1121          JSA PUTWRD     /SAVE AWAY
          13334 6354
3026 13335 0000          FEXIT

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3027	13336 5000	SCANNER, TRAPS 10	
	13337 0010		
3030		/NORMALIZE IE DATA	
3031	13340 0006	NORM, STARTD	/START IN DOUBLE PRECISION
3032	13341 0401	FLDA DTALOA	/GET ADDRESS OF IE DATA BUFFER
	13342 4012		
3033	13343 1121	JSA FLOAT	/FLOAT IT
	13344 6472		
3034	13345 6224	FSTA ULIM	/STORE AS UPPER LIMIT FOR POINTERS
3035	13346 0223	FLDA RNGE	
3036	13347 3222	FDIV INTVL	/(RANGE/ENERGY INTERVAL)*2=LENGTH OF
3037	13350 4401	FMUL FPPTWO	/DATA BUFFER
	13351 6514		
3040	13352 1224	FADD ULIM	/LENGTH + STARTING LIMIT=
3041	13353 6225	FSTA LLIM	/LOWER POINTER LIMIT
3042	13354 0400	FLDA NORANG	/CONVERT NORMALIZATION RANGE
	13355 3013		
3043	13356 4400	FMUL (100.	
	13357 7406		
3044	13360 1400	FADD (.5	
	13361 7411		
3045	13362 0010	ALN 0	
3046	13363 0004	FNORM	
3047	13364 3222	FDIV INTVL	/TO A NUMBER OF CORE LOCATIONS
3050	13365 6226	FSTA RATIO	/STORE TEMPORARILY
3051	13366 0010	ALN 0	/CHOP OFF AT DECIMAL POINT
3052	13367 0004	FNORM	/FIX
3053	13370 6227	FSTA DISPL	/STORE PARTIAL RESULT
3054	13371 0003	FNEG	/SUBTRACT TO GET
3055	13372 5226	FADDM RATIO	/FRACTIONAL PART
3056	13373 0227	FLDA DISPL	/MULTIPLY THE DISPLACEMENT
3057	13374 4401	FMUL FPPTWO	/BY TWO TO CONVERT TO A NUMBER OF CORE
	13375 6514		
3060	13376 0010	ALN 0	/LOCATIONS. STORE IT IN THIS FORM
3061	13377 6227	FSTA DISPL	
3062	13400 0006	STARTD	/GET INTO DOUBLE PRECISION
3063	13401 0401	FLDA DTALOA	/GET BUFFER ADDRESS AND
	13402 4012		
3064	13403 6230	FSTA HILOC	/INITIALIZE THE HIGH ENERGY POINTER TO
3065	13404 1227	FADD DISPL	/THE LIST TOP. SET LOW ENERGY POINTER
3066	13405 6231	FSTA LOLOC	/NORANG LOCATIONS AWAY.
3067	13406 1121	MAJADV, JSA CHECK	/CHECK POINTERS
	13407 4016		
3070	13410 0006	STARTD	/RETURN TO DOUBLE PRECISION MODE
3071	13411 0231	FLDA LOLOC	/SEND THE LOW POINTER ADDRESS
3072	13412 6202	FSTA B2	/TO THE INTERPOLATION ROUTINE
3073	13413 1121	JSA LINTRP	/TO GET LOW ENERGY INTENSITY
	13414 4100		
3074	13415 1061	JGT .+4	/GREATER THAN 2FR0?
	13416 3421		
3075	13417 5000	TRAPS 11	/NO,ERROR
	13420 0011		
3076	13421 6233	FSTA LOINT	/YES,SAVE AWAY
3077	13422 0230	FLDA HILOC	
3100	13423 6205	FSTA B5	/SAVE HERE OR ELSE ILLEGAL INDIRECT
3101	13424 0006	STARTD	/FIXED POINT AGAIN
3102	13425 0605	FLDA I B5	/TO GET THE HIGH ENERGY INTENSITY
3103	13426 1121	JSA FLOAT	/FLOAT IT
	13427 6472		
3104	13430 3233	FDIV LOINT	/DIVIDE BY LOW INTENSITY
3105	13431 2400	FSUB NORMUL	/COMPARE RESULT TO NORMALIZATION
	13432 3010		

3106	13433 1001	JEQ NORM1	/MULTIPLE. DONE WITH THIS STEP
	13434 3446		
3107	13435 1061	JGT NORM2	/BACK UP
	13436 3461		
3110	13437 0006	STARTD	/BACK TO FIXED POINT FOR THE LESS THAN
3111	13440 0401	FLDA FPPK2	/CONDITION. ADVANCE POINTERS TO THE NEXT
	13441 4014		
3112	13442 5230	FADDM HILOC	/INTENSITIES
3113	13443 5231	FADDM LOLOC	
3114	13444 1031	JA MAJADV	/TRY AGAIN TILL WE COME OUT GREATER THAN
	13445 3406		
3115	13446 0230	NORM1. FLDA HILOC	/NORMUL
3116	13447 6205	FSTA B5	
3117	13450 0006	STARTD	/FIXED POINT
3120	13451 0605	FLDA I B5	/GET THE HIGH ENERGY INTENSITY
3121	13452 1121	JSA FLOAT	/FLOAT IT
	13453 6472		
3122	13454 6234	FSTA HIINT	/STORE IT FOR LATER ON
3123	13455 0233	FLDA LOINT	/DO THE SAME FOR THE LOW ENERGY
3124	13456 6235	FSTA LOWINT	/INTENSITY
3125	13457 1031	JA DONADV	/WERE DONE HERE
	13460 3540		
3126	13461 0006	NORM2. STARTD	/GREATER THAN EXIT
3127	13462 0401	FLDA FPPK2	/DECREMENT THE BUFFER POINTERS
	13463 4014		
3130	13464 0003	FNEG	
3131	13465 5230	FADDM HILOC	
3132	13466 5231	FADDM LOLOC	
3133	13467 1121	JSA CHECK	/CHECK AGAINST THE LIMITS
	13470 4016		
3134	13471 0006	STARTD	
3135	13472 0231	FLDA LOLOC	
3136	13473 6202	FSTA B2	
3137	13474 1121	JSA LINTRP	/GET THE PREVIOUS LOW ENERGY INTENSITY
	13475 4100		
3140	13476 6232	FSTA LOINT-3	/STORE IT HERE
3141	13477 0222	FLDA INTVL	/SET MINOR ADVANCE
3142	13500 1401	FADD FPPONE	/INDEX REGISTER
	13501 6511		
3143	13502 0003	FNEG	
3144	13503 0027	ATX 7	/LOOP COUNTER
3145	13504 0037	MINADV. XTA 7	
3146	13505 1222	FADD INTVL	
3147	13506 1401	FADD FPPONE	/SET INTERPOLATION RATIO
	13507 6511		
3150	13510 3222	FDIV INTVL	
3151	13511 6226	FSTA RATIO	
3152	13512 1121	JSA GETINT	/GET HIGH AND LOW INTENSITIES RETURN
	13513 4050		
3153	13514 3235	FDIV LOWINT	/WITH HIGH IN FAC. COMPARE QUOTIENT TO
3154	13515 2400	FSUB NORMUL	/NORMALIZATION CONDITION
	13516 3010		
3155	13517 1001	JEQ DONADV	/DONE WITH THIS STEP
	13520 3540		
3156	13521 1061	JGT .+6	/CHECK CLOSENESS TO NORM CONDITION
	13522 3527		
3157	13523 0003	FNEG	/SAVE ABSOLUTE DIFFERENCE TEMPORARILY
3160	13524 6251	FSTA TEMP	
3161	13525 2171	JXN MINADV.7+	/LESS THAN TRY AGAIN
	13526 3504		
3162	13527 2251	FSUB TEMP	
3163	13530 1051	JLT DONADV	/THIS ONE IS CLOSER. DONE HERE NOW

13531	3540		
3164	13532 0037	XTA 7	/THE PREVIOUS ONE WAS CLOSER
3165	13533 1222	FADD INTVL	/RESET THE RATIO
3166	13534 3222	FDIV INTVL	
3167	13535 6226	FSTA RATIO	
3170	13536 1121	JSA GETINT	/AND GET THE INTENSITIES
	13537 4050		
3171	13540 0401	DONADV, FLDA TSTFLG	/ARE WE OPTIMIZING?
	13541 0052		
3172	13542 1041	JNE TSTEND	/YES, TAKE THIS ENDING
	13543 3706		
3173	13544 0400	FLDA NORMUL	/(HIGH INT-LOW INT)/NORMUL-1)
	13545 3010		
3174	13546 2401	FSUB FPPONE	
	13547 6511		
3175	13550 6251	FSTA TEMP	
3176	13551 0234	FLDA HIINT	
3177	13552 2235	FSUB LOWINT	
3200	13553 3251	FDIV TEMP	
3201	13554 6236	FSTA INTFAC	/INTENSITY INTERVAL
3202	13555 0006	STARTD	
3203	13556 0401	FLDA FPPK2	/RESET THE LOW ENERGY POINTER
	13557 4014		
3204	13560 5231	FADDM LOLOC	
3205	13561 5231	FADDM LOLOC	/TWO PLACES LOWER
3206	13562 0005	STARTF	/BACK TO FLOATING POINT
3207	13563 0235	FLDA LOWINT	/STORE LOWEST INTENSITY
3210	13564 6204	FSTA B4	/IN A HANDY BASE REGISTER
3211	13565 0400	FLDA (IELOC	/SET UP ENERGY STORAGE LOCATION
	13566 7436		
3212	13567 6242	FSTA BUFLOC	/IN IE MATRIX
3213	13570 0400	FLDA NIE	
	13571 3005		
3214	13572 6241	FSTA JCOL	/RIGHT COLUMN
3215	13573 0400	FLDA NORMUL	/INITIALIZE CONVERSION LOOP
	13574 3010		
3216	13575 0003	FNEG	
3217	13576 0027	ATX 7	
3220	13577 0037	INTOEN, XTA 7	/CONVERT INTENSITY TO ENERGY
3221	13600 1400	FADD NORMUL	/BUT FIRST FIND CORRECT ROW IN THE
	13601 3010		
3222	13602 6240	FSTA IROW	/MATRIX
3223	13603 1121	JSA ELMLOC	/SET LOCATION POINTER
	13604 6433		
3224	13605 0006	STARTD	
3225	13606 0231	FLDA LOLOC	/START THE SEARCH AT THE LOW ENERGY
3226	13607 6203	FSTA B3	/POINTER
3227	13610 0603	SEARCH, FLDA I B3	/GET THE INTENSITY
3230	13611 1121	JSA FLOAT	/FLOAT IT
	13612 6472		
3231	13613 2204	FSUB B4	/COMPARE IT WITH OURS
3232	13614 1011	JGE SRCH1	/ITS BIGGER GO CONVERT
	13615 3625		
3233	13616 0006	STARTD	
3234	13617 0401	FLDA FPPK2	/ITS SMALLER
	13620 4014		
3235	13621 0003	FNEG	
3236	13622 5203	FADDM B3	/DECREMENT POINTER
3237	13623 1031	JA SEARCH	/AND TRY AGAIN
	13624 3610		
3240	13625 1121	SRCH1, JSA INVTRP	/CALCULATE THE RATIO BY BACK
	13626 4123		

3241	13627	0006	STARTD	/INTERPOLATION AND CONVERT THE CORE
3242	13630	0401	FLDA DTALOA	/LOCATION TO AN ENERGY
	13631	4012		
3243	13632	0003	FNEG	
3244	13633	1203	FADD B3	
3245	13634	1121	JSA FLOAT	
	13635	6472		
3246	13636	3401	FDIV FPPTWO	
	13637	6514		
3247	13640	1226	FADD RATIO	
3250	13641	4222	FMUL INTVL	/STARTING ENERGY-(((HIGH POINTER-LOW
3251	13642	0003	FNEG	/POINTER)/2)+RATIO)*ENERGY INTERVAL)
3252	13643	1221	FADD SENGY	
3253	13644	3400	FDIV (100.	
	13645	7406		
3254	13646	6601	FSTA I B1	/STORE AWAY OUR INTENSITY
3255	13647	0236	FLDA INTFAC	/FORM NEXT INTENSITY
3256	13650	5204	FADDM B4	
3257	13651	7171	JXN INTOEN,7+	/GO CONVERT IT
	13652	3577		
3260	13653	0401	FLDA FPPONE	
	13654	6511		
3261	13655	5400	FADDM NIE	/BOP THE IE COUNT
	13656	3005		
3262	13657	0400	CHKBUF, FLDA NIE	
	13660	3005		
3263	13661	2400	FSUB (15.	/NUMBER OF IE CURVES GREATER THAN 15?
	13662	7441		
3264	13663	1061	JGT CHKER1	/YES.ERROR
	13664	3702		
3265	13665	0400	FLDA NIE	
	13666	3005		
3266	13667	1401	FADD FPPONE	/CALCULATE MATRIX LENGTH IN CORE
	13670	6511		
3267	13671	4400	FMUL NORMUL	/LOCATIONS
	13672	3010		
3270	13673	4400	FMUL (3.	
	13674	7403		
3271	13675	2400	FSUB (1024.	/IS IT GREATER THAN 1024 LOCATIONS FOR
	13676	7444		
3272	13677	1061	JGT CHKER2	/NEXT PASS? YES.ERROR
	13700	3704		
3273	13701	0000	FEXIT	
3274	13702	5000	CHKER1, TRAPS 14	
	13703	0014		
3275	13704	5000	CHKER2, TRAPS 15.	
	13705	0015		
3276	13706	0401	TSTEND, FLDA FPPTWO	
	13707	6514		
3277	13710	6210	FSTA B10	
3300	13711	0400	FLDA (7.	
	13712	7447		
3301	13713	1121	JSA FTYPE	/SET CONVERSION TO F7.2
	13714	7066		
3302	13715	0400	FLDA (CONLOC	/SET CONVERSION LOCATION
	13716	7452		
3303	13717	6200	FSTA B0	/FOR FCON
3304	13720	0006	STARTD	
3305	13721	0230	FLDA HILOC	/CONVERT THE HIGH ENERGY BUFFER POINTER
3306	13722	2401	FSUB DTALOA	/TO ITS ENERGY
	13723	4012		
3307	13724	1121	JSA FLOAT	

13725	6472		
3310	13726	3401	FDIV FPPTWO
	13727	6514	
3311	13730	1226	FADD RATIO
3312	13731	4222	FMUL INTVL
3313	13732	0003	FNEG
3314	13733	1221	FADD SENGY
3315	13734	3400	FDIV (100.
	13735	7406	
3316	13736	6207	FSTA B7 /STORE IT FOR LATER
3317	13737	1400	FADD (.005 /ROUND TO THE NEAREST HUNDRETH
	13740	7455	
3320	13741	1121	JSA FCON /CONVERT IT NOW
	13742	6760	
3321	13743	4001	TRAP4 PSTRA /STICK IN LP BUFFER
	13744	1472	
3322	13745	0400	FLDA (CONLOC /RESET CONVERSION POINTER
	13746	7452	
3323	13747	6200	FSTA B0
3324	13750	0234	FLDA HIINT /GET THE INTERCITY
3325	13751	1121	JSA FCON /CONVERT IT
	13752	6760	
3326	13753	4001	TRAP4 PSTRA1 /SAVE ONLY THE INTEGER PART IN THE LP
	13754	1477	
3327	13755	4001	TRAP4 PCRLF /BUFFER. CRLF TO END THE LINE
	13756	1537	
3330	13757	4001	TRAP4 BUTTY /DUMP THE LINE ON THE TTY
	13760	1427	
3331	13761	0400	FLDA (CONLOC /RESET POINTER
	13762	7452	
3332	13763	6200	FSTA B0
3333	13764	0207	FLDA B7 /GET THE HIGH ENERGY
3334	13765	2400	FSUB NORANG /SUBTRACT THE NORMALIZATION RANGE TO GET
	13766	3013	
3335	13767	1400	FADD (.005 /LOW ENERGY.ROUND
	13770	7455	
3336	13771	1121	JSA FCON /CONVERT IT
	13772	6760	
3337	13773	4001	TRAP4 PSTRA /SAVE IN LP BUFFER
	13774	1472	
3340	13775	0400	FLDA (CONLOC
	13776	7452	
3341	13777	6200	FSIA B0 /RESET CONVERSION POINTER
3342	14000	0235	FLDA LOWINT /GET LOW INTENSITY
3343	14001	1121	JSA FCON /CONVERT IT
	14002	6760	
3344	14003	4001	TRAP4 PSTRA1 /PUT OUT EVERYTHING BEFORE THE DECIMAL
	14004	1477	
3345	14005	4001	TRAP4 PCRLF /POINT. TERMINATE THE LINE
	14006	1537	
3346	14007	4001	TRAP4 BUTTY /PRINT ON TTY NOW
	14010	1427	
3347	14011	0000	FEXIT
3350	14012	0000	DTALOA. 0:5000
	14013	5000	
3351	14014	0000	FPPK2. 0:2
	14015	0002	
3352			/CHECK TO SEE THAT BUFFER POINTERS ARE
3353			/WITHIN MAXIMUM AND MINIMUM RANGE
3354			/ENTER IN FIXED EXIT IN FLOATING POINT
3355	14016	1031	CHECK. JA .
	14017	4016	

3356	14020 0230	FLDA HILOC	/GET HIGH POINTER
3357	14021 1121	JSA FLOAT	/FLOAT IT
	14022 6472		
3360	14023 2224	FSUB ULIM	/GREATER THAN UPPER LIMIT?
3361	14024 1051	JLT NERR1	/NO, STARTING ENERGY IS TOO LOW
	14025 4046		
3362	14026 0006	STARTD	
3363	14027 0231	FLDA LOLOC	/GET LOW POINTER
3364	14030 1121	JSA FLOAT	/FLOAT IT
	14031 6472		
3365	14032 2225	FSUB LLIM	/LESS THAN LOWER LIMIT?
3366	14033 1061	JGT NERR2	/NO, ENERGY RANGE IS TOO SHORT
	14034 4044		
3367	14035 1001	JEQ .+4	/THEY ARE EQUAL, CHECK FOR INTERPOLATION
	14036 4041		
3370	14037 1031	JA CHECK	/WE ARE OK, RETURN
	14040 4016		
3371	14041 0226	FLDA RATIO	/DO WE HAVE TO INTERPOLATE
3372	14042 1001	IFQ -3	/NO, RETURN
	14043 4037		
3373	14044 5000 NERR2, TRAP5 12		
	14045 0012		
3374	14046 5000 NERR1, TRAP5 13		
	14047 0013		
3375		/GET THE LOW AND HIGH INTENSITIES	
3376	14050 1031	GETINT, JA .	
	14051 4050		
3377	14052 0400	FLDA (LOINT-3	/START OF LOW INTENSITY DATA
	14053 7460		
3400	14054 6202	FSTA B2	/SAVE FOR INTERPOLATION ROUTINE
3401	14055 0103	LDX -1,3	/INTERPOLATE
	14056 7777		
3402	14057 0732	FLDA I B2,3+	/TO FIND
3403	14060 6212	FSTA B12	
3404	14061 0732	FLDA I B2,3+	/OUR LOW
3405	14062 0003	FNEG	
3406	14063 1212	FADD B12	/INTENSITY
3407	14064 4226	FMUL RATIO	
3410	14065 0003	FNEG	
3411	14066 1212	FADD B12	
3412	14067 6235	FSTA LOWINT	/STORE
3413	14070 0006	STARTD	
3414	14071 0230	FLDA HILOC	/GET HIGH POINTER
3415	14072 6202	FSTA B2	/STORE HERE FOR LINTRP
3416	14073 1121	JSA LINTRP	/INTERPOLATE
	14074 4100		
3417	14075 6234	FSTA HIINT	/STORE HIGH INTENSITY
3420	14076 1031	JA GETINT	/RETURN TO MAIN LINE
	14077 4050		
3421		/LINEAR INTERPOLATION	
3422		/ENTER WITH UPPER ADDRESS IN B2	
3423		/FRACTION IN RATIO	
3424	14100 1031	LINTRP, JA .	
	14101 4100		
3425	14102 0103	LDX -1,3	/SET INDEX REGISTER FOR ADDRESS
	14103 7777		
3426	14104 0732	FLDA I B2,3+	/MODIFICATION, GET THE FIRST INTENSITY
3427	14105 1121	JSA FLOAT	/FLOAT IT
	14106 6472		
3430	14107 6212	FSTA B12	/STORE TEMPORARILY
3431	14110 0006	STARTD	
3432	14111 0732	FLDA I B2,3+	/GET SECOND (LOWER) INTENSITY

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3433 14112 1121      JSA FLOAT      /FLOAT IT
      14113 6472
3434 14114 0003      FNEG
3435 14115 1212      FADD B12
3436 14116 4226      FMUL RATIO      /INTERPOLATED INTENSITY=
3437 14117 0003      FNEG      /FIRST-(FIRST-SECOND)*RATIO
3440 14120 1212      FADD B12
3441 14121 1031      JA LINTRP      /RETURN WITH OUR INTENSITY IN FAC
      14122 4100
3442      /BACK INTERPOLATION
3443      /HIGH POINTER IN B3
3444      /INTENSITY IN B4
3445      /EXIT WITH FRACTION IN RATIO
3446 14123 1031      INTRP, JA .
      14124 4123
3447 14125 0103      LDX -1.3      /SET FOR ADDRESS MODIFICATION
      14126 7777
3450 14127 0006      STARTD
3451 14130 0733      FLDA I 03.31 /GET HIGH INTENSITY
3452 14131 1121      JSA FLOAT
      14132 6472
3453 14133 6212      FSTA B12      /STORE A SECOND
3454 14134 0006      STARTD
3455 14135 0733      FLDA I B3.3+ /GET LOW INTENSITY
3456 14136 1121      JSA FLOAT
      14137 6472
3457 14140 0003      FNEG
3460 14141 1212      FADD B12
3461 14142 6213      FSTA B13
3462 14143 0212      FLDA B12      /HI INT-X INT)/HI INT-LO INT)=
3463 14144 2204      FSUB B4
3464 14145 3213      FDIV B13
3465 14146 6226      FSTA RATIO    /THE RATIO
3466 14147 1031      JA INTRP      /RETURN
      14150 4123
0000      CHAIN "IEAS1"1
0001      /**CALCULATE AND PRINT DELTAS**
0002      /FIRST IE CURVE TAKEN AS THE REFERENCE
0003      /NORMALIZED ENERGIES OVERWRITTEN BY
0004      /DIFFERENCES
0005 14151 0400      DELTA, FLDA NIE      /GET THE NUMBER OF CURVES
      14152 3005
0006 14153 2401      FSUB FPPONE      /SUBTRACT ONE TO GET
      14154 6511
0007 14155 6237      FSTA NUMPLT      /THE NUMBER OF PLOTS
0010 14156 0401      FLDA FPPTWO
      14157 6514
0011 14160 6210      FSTA B10
0012 14161 0400      FLDA (7.
      14162 7447
0013 14163 1121      JSA FTYPE      /F7.2 CONVERSION SET
      14164 7066
0014 14165 0237      FLDA NUMPLT      /GET NUMBER OF PLOTS
0015 14166 4400      FMUL (4.      /MULT BY 8/2 TO GET HALF THE OUTPUT
      14167 7463
0016 14170 0003      FNEG      /WIDTH IN SPACES.
0017 14171 1400      FADD (66.      /SUBTRACT FROM 66 TO CENTER ON PAPER
      14172 7466
0020 14173 0023      ATX 3      /STORE THIS NUMBER OF SPACES HERE FOR
0021 14174 0400      FLDA (IELOC      /TBSPA
      14175 7436
0022 14176 6242      FSTA BUFLOC      /SET BUFFER LOCATION FOR DATA PICKUP

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0023	14177 0400	FLDA NORMUL	/SET THE OUTER LOOP COUNTER TO ADVANCE
	14200 3010		
0024	14201 0003	FNEG	/BY ROWS
0025	14202 0027	ATX 7	
0026	14203 4001 DEL1,	TRAP4 TBSPA	/SPACE NOW
	14204 1561		
0027	14205 0037	XTA 7	
0030	14206 1400	FADD NORMUL	/GET THE ROW WE ARE ON
	14207 3010		
0031	14210 6240	FSTA IROW	/STORE IT
0032	14211 0237	FLDA NUMPLT	
0033	14212 0003	FNEG	
0034	14213 0026	ATX 6	/SET THE INNER LOOP TO ADVANCE BY COLUMN
0035	14214 0240	FLDA IROW	/PICK UP THE FIRST ELEMENT OF THE FIRST
0036	14215 4400	FMUL (3.	/COLUMN.
	14216 7403		
0037	14217 1121	JSA SETLOC	
	14220 6447		
0040	14221 0001	FLDA I 01	/THE REFERENCE CURVE,
0041	14222 6202	FSTA B2	/SAVE IT HERE FOR LATER
0042	14223 0036 DEL2,	XTA 6	
0043	14224 1400	FADD NIE	
	14225 3005		
0044	14226 6241	FSTA JCOL	/GET THE CURRENT COLUMN AND STORE
0045	14227 0400	FLDA (CONLOC	
	14230 7452		
0046	14231 6200	FSTA B0	/INITIALIZE CONVERSION BUFFER POINTER
0047	14232 1121	JSA ELMLOC	
	14233 6433		
0050	14234 0601	FLDA I B1	/GET THE MATRIX ELEMENT
0051	14235 2202	/FSUB B2	/SUBTRACT THE REFERENCE ENERGY
0052	14236 6601	FSTA I B1	/STORE IT BACK IN THE SAME PLACE
0053	14237 1400	FADD (.005	/NOW ROUND IT
	14240 7455		
0054	14241 1121	JSA FCON	/CONVERT IT TO ASCII
	14242 6760		
0055	14243 4001	TRAP4 PSTRA	/PUT IT IN THE LP BUFFER
	14244 1472		
0056	14245 2161	JXN DEL2,6+	/REPEAT FOR THE NEXT COLUMN TILL DONE
	14246 4223		
0057	14247 4001	TRAP4 PCRLF	/TERMINATE THE SYNTHESIZED LINE
	14250 1537		
0060	14251 4001	TRAP4 PLPTR	/AND PRINT IT ON THE LINE PRINTER NOW
	14252 1440		
0061	14253 2171	JXN DEL1,7+	/GO TO THE NEXT ROW AND REPEAT TILL DONE
	14254 4203		
0062	14255 0000	FEXIT	
0063		/DECREMENT THE COUNT	
0064	14256 0400	ELIMIE, FLDA NIE	/IS THE BUFFER CLEARED?
	14257 3005		
0065	14260 1001	JEQ ELIMER	/YES.ERROR
	14261 4267		
0066	14262 2401	FSUB FPPONE	/NO.SUBTRACT ONE FROM
	14263 6511		
0067	14264 6400	FSTA NIE	/THE COUNT
	14265 3005		
0070	14266 0000	FEXIT	
0071	14267 5000	ELIMER, TRAP5 22	
	14270 0022		
0072		/PRINT UNNORMALIZED IE DATA ON THE TTY	
0073	14271 0105	IEPRIN, LDX -1,5	/SET INDEX 1 FOR ADDRESS MODIFICATION
	14272 7777		

0074	14273	0221	FLDA SENGY	/GET THE STARTING ENERGY
0075	14274	6204	FSTA B4	/STORE HERE SO IT CAN BE INCREMENTED AND
0076	14275	0401	FLDA FPPTWO	/USED LATER
	14276	6514		
0077	14277	6210	FSTA B10	
0100	14300	0400	FLDA (7.	
	14301	7447		
0101	14302	1121	JSA FTYPE	/F7.2 SET
	14303	7066		
0102	14304	0400	FLDA (CONLOC	
	14305	7452		
0103	14306	6200	FSTA B0	/CONVERSION POINTER SET
0104	14307	0204	FLDA B4	/GET THE ENERGY
0105	14310	3400	FDIV (100.	
	14311	7406		
0106	14312	1400	FADD (.005	/ROUND
	14313	7455		
0107	14314	1121	JSA FCON	/CONVERT TO ASCII
	14315	6760		
0110	14316	4001	TRAP4 PSTRA	/STORE CONVERTED NUMBER IN OUR BUFFER
	14317	1472		
0111	14320	0222	FLDA INTVL	/SUBTRACT THE ENERGY INTERVAL
0112	14321	0003	FNEG	
0113	14322	5204	FADDM B4	/TO THE OUR ENERGY
0114	14323	0002	FCLA	
0115	14324	6210	FSTA B10	
0116	14325	0400	FLDA (11.	
	14326	7471		
0117	14327	1121	JSA FTYPE	/F11.0
	14330	7066		
0120	14331	0400	FLDA (CONLOC	
	14332	7452		
0121	14333	6200	FSTA B0	/RESET CONVERSION POINTER
0122	14334	0006	STARTD	
0123	14335	0550	FLDA DTALOC.5+	/GET THE INTENSITY
	14336	5000		
0124	14337	1121	JSA FLOAT	
	14340	6472		
0125	14341	1121	JSA FCON	/FLOAT AND CONVERT
	14342	6760		
0126	14343	4001	TRAP4 PSTRA1	/PUT OUT EVERYTHING BEFORE THE DECIMAL
	14344	1477		
0127	14345	4001	TRAP4 PCRLF	/END THE LINE
	14346	1537		
0130	14347	4001	TRAP4 BUTTY	/AND PRINT ON TTY
	14350	1427		
0131	14351	2141	JXN IEP1.4+	/CONTINUE TILL DONE
	14352	4275		
0132	14353	0000	FEXIT	
0133			/CALCULATE A WEIGHTED LEAST-SQUARES	
0134			/FIT OF THE DELTAS FOR EACH ION IN	
0135			/THE TABLE.	
0136			/PRINT THE INTERCEPTS ON THE LINE	
0137			/PRINTER.	
0140	14354	0400	LSTSQ. FLDA NORMUL	
	14355	3010		
0141	14356	0003	FNEG	
0142	14357	0027	ATX 7	/SET A LOOP COUNTER TO MINUS THE NUMBER
0143	14360	0400	FLDA (WTLOC	/OF ROWS
	14361	7474		
0144	14362	6242	FSTA BUFLOC	/SET OUR POINTER TO THE WEIGHTING FACTOR
0145	14363	0037	SETWT. XTA 7	/VECTOR

0146	14364 1400	FADD NORMUL	/DETERMINE THE ELEMENT
	14365 3010		
0147	14366 6240	FSTA IROW	/STORE A SECOND
0150	14367 4400	FMUL (3.	/MULTIPLY TO FORM A CORE DISPLACEMENT
	14370 7403		
0151	14371 1121	JSA SETLOC	/AND SAVE ITS LOCATION IN B1
	14372 6447		
0152	14373 0240	FLDA IROW	
0153	14374 2401	FSUB FPPONE	/ARE WE ON THE FIRST TWO ELEMENTS?
	14375 6511		
0154	14376 1061	JGT .+6	/NO. SET WEIGHT TO ONE
	14377 4404		
0155	14400 0002	FCLA	/YES.
0156	14401 6601	FSTA I B1	/SET THE WEIGHTING FACTOR TO ZERO
0157	14402 1031	JA .+5	/JUMP OVER THE OTHER STUFF
	14403 4407		
0160	14404 0401	FLDA FPPONE	
	14405 6511		
0161	14406 6601	FSTA I A1	/SET FACTOR TO ONE
0162	14407 2171	JXN SETWT.7+	/LOOP TILL DONE
	14410 4363		
0163	14411 0002	FCLA	/CLEAR THE
0164	14412 6243	FSTA SUMX	/SUM OF THE RELATIVE INTENSITIES.
0165	14413 6244	FSTA SUMXX	/SUM OF THE INTENSITIES SQUARED.
0166	14414 6245	FSTA SUMW	/AND THE SUM OF THE WEIGHTS
0167	14415 0400	FLDA NORMUL	
	14416 3010		
0170	14417 0003	FNEG	
0171	14420 0027	ATX 7	/SET THE SUM LOOP COUNTER
0172	14421 0037 SUM1.	XTA 7	
0173	14422 1400	FADD NORMUL	/GET THE ELEMENT
	14423 3010		
0174	14424 6240	FSTA IROW	/STORE FOR FUTURE CALCULATIONS
0175	14425 4400	FMUL (3.	/CONVERT TO CORE DISPLACEMENT
	14426 7403		
0176	14427 1121	JSA SETLOC	/AND SET THE ABSOLUTE LOCATION
	14430 6447		
0177	14431 0601	FLDA I B1	/GET THE ELEMENT FROM OUR WEIGHT VECTOR
0200	14432 5245	FADDM SUMW	/ADD TO OUR SUMMING REGISTER
0201	14433 0240	FLDA IROW	/ADD ONE TO THE ELEMENT
0202	14434 1401	FADD FPPONE	/TO FORM THE INTENSITY
	14435 0511		
0203	14436 6251	FSTA TEMP	/STORE TEMPORARILY
0204	14437 0601	FLDA I B1	/GET THE WEIGHTING FACTOR
0205	14440 4251	FMUL TEMP	/MULTIPLY IT BY THE INTENSITY
0206	14441 5243	FADDM SUMX	/AND ADD TO THE INTENSITY SUM
0207	14442 0251	FLDA TEMP	
0210	14443 7251	FMULM TEMP	/FORM THE INTENSITY SQUARE
0211	14444 0601	FLDA I B1	/MULTIPLY IT BY THE WEIGHTING FACTOR
0212	14445 4251	FMUL TEMP	
0213	14446 5244	FADDM SUMXX	/AND ADD TO THE TOTAL
0214	14447 2171	JXN SUM1.7+	/CONTINUE FOR ALL ELEMENTS
	14450 4421		
0215	14451 4001	TRAP4 TBSPA	/PUT OUT OUR CENTERING SPACES AS
	14452 1561		
0216	14453 0237	FLDA NUMPLT	/CALCULATED BY DELTA
0217	14454 0003	FNEG	
0220	14455 0027	ATX 7	/SET COLUMN COUNTER
0221	14456 0037 LSTSQ1.	XTA 7	
0222	14457 1400	FADD NIE	/FORM THE CORRECT COLUMN
	14460 3005		
0223	14461 6241	FSTA JCOL	/AND STORE HERE

0224	14462	0002	FCLA	/CLEAR THE
0225	14463	6246	FSTA SUMY	/ENERGY SUM AND
0226	14464	6247	FSTA SUMXY	/ENERGY*INTENSITY CROSS SUM
0227	14465	0400	FLDA NORMUL	
	14466	3010		
0230	14467	0003	FNEG	
0231	14470	0026	ATX 6	/SET THE ROW COUNTER
0232	14471	0036	XTA 6	
0233	14472	1400	FADD NORMUL	/FORM THE CORRECT ROW
	14473	3010		
0234	14474	6240	FSTA IROW	/STORE IT
0235	14475	0400	FLDA (WTLOC	
	14476	7474		
0236	14477	6242	FSTA BUFLOC	/SET OUR VECTOR POINTER TO THE WIEGHT
0237	14500	0240	FLDA IROW	/BUFFER
0240	14501	4400	FMUL (3.	
	14502	7403		
0241	14503	1121	JSA SETLOC	/SET THE DISPLACEMENT
	14504	6447		
0242	14505	0601	FLDA I B1	/GET THE WEIGHT
0243	14506	6251	FSTA TEMP	/STORE TEMPORARILY
0244	14507	0400	FLDA (IELOC	
	14510	7436		
0245	14511	6242	FSTA BUFLOC	/SET VECTOR POINTER TO THE IE BUFFER
0246	14512	1121	JSA ELMLOC	/AND GET THE ELEMENT WE ARE DEALING WITH
	14513	6433		
0247	14514	0601	FLDA I B1	
0250	14515	4251	FMUL TEMP	/MULTIPLY IT BY THE WEIGHTING FACTOR
0251	14516	5246	FADDM SUMY	/ADD TO THE ENERGY SUM FOR THAT ION,
0252	14517	6251	FSTA TEMP	/COLUMN. STORE THE PRODUCT A SECOND
0253	14520	0240	FLDA IROW	
0254	14521	1401	FADD FPPONE	/FORM THE INTENSITY
	14522	6511		
0255	14523	4251	FMUL TEMP	/AND THE CROSS PRODUCT
0256	14524	5247	FADDM SUMXY	/ADD TO THE SUM
0257	14525	2161	JXN SUM2,6+	/FINISH SUMMING FOR THAT ION
	14526	4471		
0260	14527	0243	FLDA SUMX	/NOW CALCULATE THE SLOPE AND INTERCEPT
0261	14530	4243	FMUL SUMX	/BUT FIRST
0262	14531	6251	FSTA TEMP	
0263	14532	0245	FLDA SUMW	
0264	14533	4244	FMUL SUMXX	
0265	14534	2251	FSUB TEMP	
0266	14535	6250	FSTA DENOM	/DENOM=SW*SXX-(SX)**2.
0267	14536	0400	FLDA (SLOPE	
	14537	7477		
0270	14540	6242	FSTA BUFLOC	/SET POINTER FOR THE SLOPE VECTOR
0271	14541	0241	FLDA JCOL	
0272	14542	4400	FMUL (3.	/CALCULATE THE DISPLACEMENT
	14543	7403		
0273	14544	1121	JSA SETLOC	/SET THE ABSOLUTE LOCATION
	14545	6447		
0274	14546	0243	FLDA SUMX	/CALCULATE THE SLOPE
0275	14547	4246	FMUL SUMY	
0276	14550	6251	FSTA TEMP	
0277	14551	0245	FLDA SUMW	
0300	14552	4247	FMUL SUMXY	
0301	14553	2251	FSUB TEMP	
0302	14554	3250	FDIV DENOM	/SLOPE=(SW*SXY-SX*SY)/DENOM
0303	14555	0001	FSTA I B1	/STORE AWAY
0304	14556	0400	FLDA (INCEPT	
	14557	7502		

0305	14560	6242	FSTA BUFLOC	/SET INTERCEPT VECTOR POINTER
0306	14561	0241	FLDA JCOL	
0307	14562	4400	FMUL (3.	/CALCULATE THE DISPLACEMENT
	14563	7403		
0310	14564	1121	JSA SETLOC	/SET THE LOCATION
	14565	6447		
0311	14566	0400	FLDA (CONLOC	
	14567	7452		
0312	14570	6200	FSTA B0	/SET THE CONVERSION POINTER
0313	14571	0243	FLDA SUMX	/AND CALCULATE THE INTERCEPT
0314	14572	4247	FMUL SUMXY	
0315	14573	6251	FSTA TEMP	
0316	14574	0244	FLDA SUMXX	
0317	14575	4246	FMUL SUMY	
0320	14576	2251	FSUB TEMP	
0321	14577	3250	FDIV DENOM	/INTERCEPT=(SXX*SY-SX*SXY)/DENOM
0322	14600	6601	FSTA I B1	/STORE IT
0323	14601	1400	FADD (.005	/ROUND.
	14602	7455		
0324	14603	1121	JSA FCON	/CONVERT TO ASCII.
	14604	6760		
0325	14605	4001	TRAP4 PSTRA	/AND PUT IN PRINT BUFFER
	14606	1472		
0326	14607	2171	JXN LSTSQ1.7+	/REPEAT FOR ALL IONS
	14610	4456		
0327	14611	0000	FEXIT	
0330			/PRINT THE INFORMATION IN THE IE TABLE	
0331			/FOR A GIVEN ION ON THE TTY	
0332			/(PRINT ONE COLUMN)	
0333	14612	1121	MPRINT, JSA GETNUM	/GET THE MASS TO LOCATE WHICH ION
	14613	6551		
0334	14614	6251	FSTA TEMP	/(COLUMN) WE WANT. STORE FOR LATER
0335	14615	0400	FLDA NIE	
	14616	3005		
0336	14617	0003	FNEG	
0337	14620	0027	ATX 7	/SET SEARCH LOOP COUNTER
0340	14621	0106	LDX -1.6	/AND ADDRESS MODIFIER
	14622	7777		
0341	14623	0560	MP1, FLDA MASLOC.6+	/GET THE FIRST MASS IN THE LIST
	14624	3030		
0342	14625	2251	FSUB TEMP	/IS IT OURS?
0343	14626	1001	JEQ .+6	/YES, GO ON
	14627	4634		
0344	14630	2171	JXN MP1.7+	/NO, TRY AGAIN
	14631	4623		
0345	14632	5000	TRAP5 16	/THEY SENT US ON A BUM TRIP
	14633	0016		
0346	14634	0036	XTA 6	/GET WHICH COLUMN IT WAS IN
0347	14635	6241	FSTA JCOL	/STORE HERE
0350	14636	0400	FLDA (IELOC	
	14637	7436		
0351	14640	6242	FSTA BUFLOC	/VECTOR POINTER TO THE IE DATA
0352	14641	0400	FLDA NORMUL	
	14642	3010		
0353	14643	0003	FNEG	
0354	14644	0027	ATX 7	/SET THE ROW COUNTER
0355	14645	0002	MP2, FCLA	
0356	14646	6210	FSTA B10	
0357	14647	0400	FLDA (0.	
	14650	7505		
0360	14651	1121	JSA FTYPE	/F8.0
	14652	7066		

0361	14653	0400	FLDA (CONLOC	
	14654	7452		
0362	14655	6200	FSTA B0	/SET CONVERSION POINTER
0363	14656	0037	XTA 7	
0364	14657	1400	FADD NORMUL	
	14660	3010		
0365	14661	6240	FSTA IROW	/DETERMINE WHICH ROW(RELATIVE INTENSITY)
0366	14662	1401	FADD FPPONE	/FORM CORRECT INTENSITY
	14663	6511		
0367	14664	1121	JSA FCON	/CONVERT THE INTENSITY
	14665	6760		
0370	14666	4001	TRAP4 PSTRA1	/PUT EVERYTHING BEFORE THE DECIMAL
	14667	1477		
0371	14670	0400	FLDA (CONLOC	
	14671	7452		
0372	14672	6200	FSTA B0	/RESET
0373	14673	0401	FLDA FPPTWO	
	14674	6514		
0374	14675	6210	FSTA B10	
0375	14676	0400	FLDA (12.	
	14677	7510		
0376	14700	1121	JSA FTYPE	/F12.2
	14701	7066		
0377	14702	1121	JSA ELMLOC	/SET ABSOLUTE LOCATION IN TABLE
	14703	6433		
0400	14704	0601	FLDA I B1	/GET THE ENERGY
0401	14705	1400	FADD (.005	/ROUND
	14706	7455		
0402	14707	1121	JSA FCON	/CONVERT AND
	14710	6760		
0403	14711	4001	TRAP4 PSTRA	/PUT EVERYTHING
	14712	1472		
0404	14713	4001	TRAP4 PCRLF	/END THE LINE
	14714	1537		
0405	14715	4001	TRAP4 BUTTY	/PUT THE LINE ON THE TTY
	14716	1427		
0406	14717	2171	JXN MP2.7+	/REPEAT TILL ALL ARE DONE
	14720	4645		
0407	14721	0000	FEXIT	
0410			/GET AND STORE THE NORMALIZATION	
0411			/MULTIPLE	
0412	14722	1121	NMUL. JSA GETNUM	/CHANGE ASCII TO THE NEW NUMBER
	14723	6551		
0413	14724	0010	ALN 0	
0414	14725	0004	FNORM	/INTEGERIZE IT
0415	14726	1021	JLE .+5	/MAKE SURE ITS POSITIVE
	14727	4733		
0416	14730	6400	FSTA NORMUL	/STORE THE NEW MULTIPLE
	14731	3010		
0417	14732	0000	FEXIT	
0420	14733	5000	TRAP5 17	
	14734	0017		
0421			/GET AND STORE NORMALIZATION RANGE	
0422	14735	1121	NRANG. JSA GETNUM	/CONVERT TO FLOATING POINT
	14736	6551		
0423	14737	1021	JLE .+5	/CHECK TO SEE IF POSITIVE
	14740	4744		
0424	14741	6400	FSTA NORANG	/SAVE NEW RANGE
	14742	3013		
0425	14743	0000	FEXIT	
0426	14744	5000	TRAP5 20	
	14745	0020		

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0427          /DUMP THE IE TABLE
0430 14746 0401 PTABL, FLDA FPPTWO
      14747 6514
0431 14750 6210          FSTA B10
0432 14751 0400          FLDA (7.
      14752 7447
0433 14753 1121          JSA FTYPE          /F7.2
      14754 7066
0434 14755 0400          FLDA (IELOC
      14756 7436
0435 14757 6242          FSTA BUFLOC      /SET VECTOR POINTER
0436 14760 0400          FLDA NIE
      14761 3005
0437 14762 4400          FMUL (4.          /CALCULATE THE NUMBER OF SPACES NEEDED
      14763 7463
0440 14764 0003          FNEG              /TO CENTER ON LP
0441 14765 1400          FADD (66.
      14766 7466
0442 14767 0023          ATX 3              /STORE HERE FOR OUR TAB SPACE ROUTINE
0443 14770 0400          FLDA NORMUL
      14771 3010
0444 14772 0003          FNEG
0445 14773 0027          ATX 7              /SET ROW COUNTER
0446 14774 4001 PTABL2, TRAP4 TBSPA      /PUT THE CENTERING SPACES NOW
      14775 1501
0447 14776 0037          XTA 7
0450 14777 1400          FADD NORMUL      /DETERMINE THE ROW
      15000 3010
0451 15001 6240          FSTA IROW        /STORE FOR REFERENCE
0452 15002 0400          FLDA NIE
      15003 3005
0453 15004 0003          FNEG
0454 15005 0026          ATX 6              /SET COLUMN COUNTER
0455 15006 0036 PTABL1, XTA 6
0456 15007 1400          FADD NIE          /DETERMINE WHICH COLUMN
      15010 3005
0457 15011 6241          FSTA JCOL        /STORE FOR LOCATION REFERENCE
0460 15012 0400          FLDA (CONLOC
      15013 7452
0461 15014 6200          FSTA B0          /SET CONVERSION POINTER
0462 15015 1121          JSA ELMLOC      /CALCULATE THE CORE LOCATION OF THE
      15016 6433
0463 15017 0601          FLDA I B1        /TABLE ELEMENT. GET THE ELEMENT LIKE
0464 15020 1400          FADD (.005      /THIS. ROUND IT
      15021 7455
0465 15022 1121          JSA FCON          /CONVERT
      15023 6760
0466 15024 4001          TRAP4 PSTRA      /PUT IT IN BUFFER
      15025 1472
0467 15026 2161          JXN PTABL1.6+    /FINISH THE ROW
      15027 5006
0470 15030 4001          TRAP4 PCRI F      /TERMINATE OUR LINE
      15031 1537
0471 15032 4001          TRAP4 PLFTR      /LET IT GO
      15033 1440
0472 15034 2171          JXN PTABL2.7+    /DO ANOTHER ROW TILL THE TABLE IS
      15035 4774
0473 15036 0000          FEXIT            /FINISHED
0474          /GET A DELAY TIME IN SECONDS AND CONVERT
0475          /TO THE RIGHT LOOP COUNTER VALUE
0476 15037 1121 DELTIM, JSA GETNUM      /ASSEMBLE THE NUMBER
      15040 6551

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0477	15041	3307	FDIV DFACTR	/TO CONVERT JUST DIVIDE BY OUR FACTOR
0500	15042	1400	FADD (.5	/ROUND IT
	15043	7411		
0501	15044	0010	ALN 0	
0502	15045	0004	FNORM	/REMOVE THE FRACTIONAL PART AND REFIX
0503	15046	6251	FSTA TEMP	/STORE FOR A SECOND
0504	15047	2401	FSUB FPPONE	/IS IT GREATER THAN 1?
	15050	6511		
0505	15051	1051	JLT TERR	/NO.ERROR
	15052	5070		
0506	15053	2400	FSUB (4095.	/LESS THAN 4095?
	15054	7513		
0507	15055	1061	JGT TERR	/BAD NEWS,WE CANNOT DELAY THAT LONG
	15056	5070		
0510	15057	0400	FLDA (DCONST	/GET THE SINGLE PRECISION ADDRESS
	15060	7516		
0511	15061	6201	FSTA B1	/STORE HERE FOR PUTWRD
0512	15062	0251	FLDA TEMP	/GET THE LOOP COUNT
0513	15063	0003	FNCG	/FORM ITS TWO'S COMPLIMENT
0514	15064	0010	ALN 0	/MAKE IT IN INTEGER FORM IN THE LSW OF
0515	15065	1121	JSA PUTWRD	/THE FAC. STORE IT NOW
	15066	6354		
0516	15067	0000	FEXIT	
0517	15070	5000	TERR, TRAPS 21	
	15071	0021		
0520			/*****PLOT WARRENS PLOTS*****/	
0521	15072	0237	WARPLT, FLDA NUMPLT	
0522	15073	0003	FNEG	
0523	15074	0027	ATX 7	/SET LOOP COUNTER TO MINUS THE NUMBER OF
0524	15075	0037	MNCAL1, XTA 7	/PLOTS
0525	15076	1400	FADD NIE	/GET THE COLUMN
	15077	3005		
0526	15100	6241	FSTA JCOL	/STORE IT
0527	15101	0400	FLDA (IELOC	
	15102	7436		
0530	15103	6242	FSTA BUFLOC	/SET OUR POINTER TO THE IE BUFFER
0531	15104	0002	FCLA	
0532	15105	6240	FSTA IROW	/START AT THE FIRST ROW
0533	15106	1121	JSA ELMLOC	/DETERMINE THE LOCATION IN CORE
	15107	6433		
0534	15110	0601	FLDA I B1	/GET THE ENERGY
0535	15111	6252	FSTA MIN	/INITIALIZE THE MINIMUM DELTA TO THE
0536	15112	0400	FLDA NORMUL	/FIRST ELEMENT
	15113	3010		
0537	15114	2401	FSUB FPPONE	
	15115	6511		
0540	15116	0003	FNEG	
0541	15117	0026	ATX 6	/SET UP A LOOP COUNTER FOR THE REST OF
0542	15120	0036	MNCAL2, XTA 6	/THE ROWS. GET THE COUNT
0543	15121	1400	FADD NORMUL	/CONVERT IT TO THE ROW WE ARE ON
	15122	3010		
0544	15123	6240	FSTA IROW	/STORE IT
0545	15124	1121	JSA ELMLOC	/SET CORE LOCATION IN B1
	15125	6433		
0546	15126	0601	FLDA I B1	/GET THE ENERGY
0547	15127	2252	FSUB MIN	/IS IT SMALLER THAN OUR CURRENT MINIMUM?
0550	15130	1011	JGE .+4	/NO,TRY AGAIN
	15131	5134		
0551	15132	0601	FLDA I B1	/IT IS,GET IT
0552	15133	6252	FSTA MIN	/STORE IT AS OUR MINIMUM
0553	15134	2161	JXN MNCAL2,6+	
	15135	5120		

0554	15136	0400	FLDA (MINLOC	
	15137	7521		
0555	15140	6242	FSTA BUFLOC	/SET OUR POINTER TO THE MINIMUM VECTOR
0556	15141	0241	FLDA JCCL	/AND
0557	15142	4400	FMUL (3.	
	15143	7403		
0560	15144	1121	JSA SETLOC	/SET THE CORE LOCATION FOR OUR ENTRY
	15145	6447		
0561	15146	0252	FLDA MIN	/GET THE ENTRY
0562	15147	4400	FMUL (10.	
	15150	7524		
0563	15151	0010	ALN 0	
0564	15152	0004	FNORM	
0565	15153	3400	FDIV (10.	/FIX IT UP A BIT
	15154	7524		
0566	15155	2400	FSUB (.05	/ROUND IT
	15156	7527		
0567	15157	6601	FSTA I B1	/STORE AWAY
0570	15160	2171	JXN MNCAL1.7+	/REPEAT FOR THE REST OF THE IONS
	15161	5075		
0571	15162	0277	DIVXAX. FLDA XLNTH	/GET THE X AXIS LENGTH
0572	15163	6253	FSTA NULNTH	/STORE IT HERE FOR AWHILE
0573	15164	3400	FDIV NORMUL	/AND CALCULATE THE LENGTH PER DIVISION
	15165	3010		
0574	15166	0010	ALN 0	
0575	15167	0004	FNORM	/INTEGERIZE IT
0576	15170	6254	FSTA XFACTR	/AND STORE AS THE X AXIS FACTOR
0577	15171	0400	FLDA NORMUL	
	15172	3010		
0600	15173	6210	FSTA B10	/NOW FIND THE REMAINDER THROUGH THE
0601	15174	0277	FLDA XLNTH	/MODULUS ROUTINE
0602	15175	1121	JSA AMOD	/REMAINDER IN THE FAC
	15176	6530		
0603	15177	1001	JEQ .+11	/IF IT IS ZERO WE DONT HAVE TO FUDGE
	15200	5210		
0604	15201	0003	FNEG	
0605	15202	1210	FADD B10	
0606	15203	1277	FADD XLNTH	/INCREASE THE LENGTY TO THE NEXT EVEN
0607	15204	6253	FSTA NULNTH	/MULTIPLE AND STORE AS OUR AXIS LENGTH
0610	15205	0401	FLDA FPPONE	
	15206	6511		
0611	15207	5254	FADDM XFACTR	/BOP THE XFACTOR
0612	15210	0400	FLDA (5.	
	15211	7532		
0613	15212	5253	FADDM NULNTH	/AND ADD 5 TO THE LENGTH FOR THE LAST
0614	15213	0300	DIVYAX. FLDA YLNTH	/PLUS SIGN. DO THE SAME THING FOR THE Y
0615	15214	6276	FSTA ULIMIT	/AXIS BUT STORE THE LENGTH HERE
0616	15215	3301	FDIV NUMYDV	
0617	15216	0010	ALN 0	
0620	15217	0004	FNORM	
0621	15220	6255	FSTA YFACTR	
0622	15221	0301	FLDA NUMYDV	
0623	15222	6210	FSTA B10	
0624	15223	0300	FLDA YLNTH	
0625	15224	1121	JSA AMOD	
	15225	6530		
0626	15226	1001	JEQ .+11	
	15227	5237		
0627	15230	0003	FNEG	
0630	15231	1210	FADD B10	
0631	15232	1300	FADD YLNTH	
0632	15233	6276	FSTA ULIMIT	

0633	15234	0401	FLDA FPPONE	
	15235	6511		
0634	15236	5255	FADDM YFACTR	/NOW EVERYTHING IS OK WITH THE Y AXIS
0635	15237	0002	FCLA	
0636	15240	6262	FSTA PLTFLG	/CLEAR THE PLOT FLAG
0637	15241	6240	FSTA IROW	/AND THE ROW
0640	15242	0401	FLDA FPPONE	
	15243	6511		
0641	15244	6241	FSTA JCOL	/SET FOR THE SECOND COLUMN
0642	15245	0237	FLDA NUMPLT	/GET THE NUMBER OF PLOTS
0643	15246	3401	FDIV FPPTWO	/DIVIDE BY 2, SINCE THERE ARE TWO PLOTS
	15247	6514		
0644	15250	0010	ALN 0	/PER PAGE
0645	15251	0004	FNORM	/INTEGERIZE
0646	15252	0003	FNEG	
0647	15253	0026	ATX 6	/AND SAVE AS OUR PLOT LOOP COUNTER
0650	15254	0401	FLDA FPPTWO	
	15255	6514		
0651	15256	6210	FSTA B10	
0652	15257	0237	FLDA NUMPLT	
0653	15260	1121	JSA AMOD	/GET THE REMAINDER OF THE DIVISION BY 2
	15261	6530		
0654	15262	1001	JEQ .+5	/IT WAS ZERO, THERE IS NOT AN ODD PLOT
	15263	5267		
0655	15264	6262	FSTA PLTFLG	/SET THE ODD PLOT FLAG
0656	15265	0116	ADDX -1.6	/AND INCREASE THE LOOP COUNT
	15266	7777		
0657	15267	0253	OUTLOP, FLDA NULNTH	/WE WILL DO THE PLOTS ONE X POINT AT A
0660	15270	0003	FNEG	/TIME
0661	15271	0027	ATX 7	/SET THE POINT LOOP COUNTER
0662	15272	0254	FLDA XFACTR	
0663	15273	6203	FSTA B3	/SAVE THE X FACTOR IN A HANDY BASE
0664	15274	0002	FCLA	/REGISTER
0665	15275	6263	FSTA BYFLAG	/CLEAR THE BYPASS FLAG
0666	15276	0036	XTA 6	
0667	15277	1401	FADD FPPONE	/ARE WE ON THE LAST PLOT PAGE?
	15300	6511		
0670	15301	1041	JNE .+10	/NO, SKIP PAST
	15302	5311		
0671	15303	0262	FLDA PLTFLG	/YES WE ARE, CHECK THE PLOT FLAG
0672	15304	1001	JEQ .+5	/THERE ARE TWO PLOTS ON THE LAST PAGE
	15305	5311		
0673	15306	0401	FLDA FPPONE	/ONLY ONE PLOT ON THE LAST PAGE
	15307	6511		
0674	15310	6263	FSTA BYFLAG	/SET THE BYPASS FLAG
0675	15311	1121	JSA AXLABL	/NOW LABEL THE PLOT AND Y AXIS
	15312	5625		
0676	15313	0400	INLOP, FLDA (LPBUF	
	15314	7535		
0677	15315	6242	FSTA BUFLOC	/SET OUR POINTER TO THE PLOT BUFFER
0700	15316	1121	JSA ZROBUF	/AND CLEAR THE BUFFER
	15317	6372		
0701	15320	0037	XTA 7	
0702	15321	1253	FADD NULNTH	
0703	15322	6256	FSTA XVALUE	/GET THE X VALUE FROM THE LOOP COUNTER
0704	15323	0263	FLDA BYFLAG	/CHECK THE BYPASS FLAG
0705	15324	1041	JNE .+5	/ONLY ONE PLOT, DO NOT SET THE PUT FLAG
	15325	5331		
0706	15326	0401	FLDA FPPONE	/IT IS SET
	15327	6511		
0707	15330	6261	FSTA PUFLAG	/SET THE PUT FLAG FOR THE FIRST PLOT
0710	15331	0302	FLDA K1000	

0711 15332 6257	FSTA KTRANS	/SET THE TRANSLATION CONSTANT
0712 15333 0256 AGAIN.	FLDA XVALUE	/IS THE X VALUE 0?
0713 15334 1041	JNE .+4	/NO, WE DONT HAVE TO
15335 5340		
0714 15336 1121	JSA PUTYAX	/PLOT THE Y AXIS
15337 6407		
0715 15340 1121	JSA PUTXPT	/PLOT THE X AXIS POINT
15341 6423		
0716 15342 0256	FLDA XVALUE	
0717 15343 2400	FSUB (10.	/ARE WE DONE MARKING THE Y DIVISIONS?
15344 7524		
0720 15345 1061	JGT .+4	/YES, SKIP
15346 5351		
0721 15347 1121	JSA PUYDV	/PLOT THE Y DIVISIONS
15350 6025		
0722 15351 0400	FLDA (MINLOC	
15352 7521		
0723 15353 6242	FSTA BUFLOC	/SET OUR POINTER TO THE MINIMUM VECTOR
0724 15354 0241	FLDA JCOL	
0725 15355 4400	FMUL (3.	
15356 7403		
0726 15357 1121	JSA SETLOC	/AND SET THE CORE LOCATION TO BE
15360 6447		
0727 15361 0601	FLDA I B1	/ACCESSED. GET THE MINIMUM
0730 15362 6251	FSTA TEMP	/STORE TEMPORARILY
0731 15363 0400	FLDA (INCEPT	
15364 7502		
0732 15365 6242	FSTA BUFLOC	/SET OUR POINTER TO THE INTERCEPT VECTOR
0733 15366 0241	FLDA JCOL	
0734 15367 4400	FMUL (3.	
15370 7403		
0735 15371 1121	JSA SETLOC	/AND SET THE LOCATION WE WANT
15372 6447		
0736 15373 0601	FLDA I B1	/GET THE INTERCEPT
0737 15374 2251	FSUB TEMP	/AND SUBTRACT OFF THE MINIMUM
0740 15375 6251	FSTA TEMP	/RESTORE HERE
0741 15376 0400	FLDA (SLOPE	
15377 7477		
0742 15400 6242	FSTA BUFLOC	/SET UP THE SLOPE VECTOR
0743 15401 0241	FLDA JCOL	
0744 15402 4400	FMUL (3.	
15403 7403		
0745 15404 1121	JSA SETLOC	/DETERMINE THE LOCATION OF THE ELEMENT
15405 6447		
0746 15406 0601	FLDA I B1	/GET THE SLOPE
0747 15407 4256	FMUL XVALUE	/MULTIPLY IT BY X (GRAPH UNITS)
0750 15410 3254	FDIV XFACTOR	/CONVERT TO DATA COORDINATE UNITS
0751 15411 1251	FADD TEMP	/ADD IN THE TRANSLATED INTERCEPT
0752 15412 4255	FMUL YFACTOR	/CONVERT THE Y VALUE TO GRAPH UNITS BY
0753 15413 3400	FDIV (.05	/MULTIPLYING BY THE Y FACTOR AND
15414 7527		
0754 15415 6251	FSTA TEMP	/DIVIDING BY OUR Y UNIT. STORE TILL WE
0755 15416 0400	FLDA (LPBUF	/ARE READY
15417 7535		
0756 15420 6242	FSTA BUFLOC	/SET OUR POINTER TO THE PLOT BUFFER
0757 15421 0251	FLDA TEMP	/NOW GET IT
0760 15422 1257	FADD KTRANS	/ADD IN THE TRANSLATION FOR WHICH GRAPH
0761 15423 1121	JSA PTPUT	/PUT THE POINT IN THE BUFFER
15424 6063		
0762 15425 0256	FLDA XVALUE	
0763 15426 2203	FSUB B3	
0764 15427 1400	FADD (4.	/START PRINTING THE PLUS(DELTA POINT)?

15430 7463		
0765 15431 1051	JLT .+102	/NO,SKIP OVER THIS PLUS SIGN STUFF
15432 5533		
0766 15433 0256	FLDA XVALUE	
0767 15434 2203	FSUB B3	/DO WE HAVE TO PLOT THE X AXIS DIVISION?
0770 15435 1041	JNE .+26	/NO,SKIP AND CHECK IF DONE
15436 5463		
0771 15437 0400	FLDA (LPBUF	
15440 7535		
0772 15441 6242	FSTA BUFLOC	/SET OUR POINTER
0773 15442 1121	JSA PUXDV	/AND PUT OUT THE AXIS DIVISION
15443 6046		
0774 15444 1121	JSA DELPT	/LOCATE THE DELTA POINTS POSITION
15445 5574		
0775 15446 1400	FADD (4.	
15447 7463		
0776 15450 6270	FSTA ENDBIT	
0777 15451 2400	FSUB (8.	
15452 7505		
1000 15453 6267	FSTA START	/AND SET OUR VARIABLES TO PUT OUT
1001 15454 0400	FLDA (LPBUF	/VERTICAL PART OF +
15455 7535		
1002 15456 6242	FSTA BUFLOC	/SET THE BUFFER POINTER
1003 15457 1121	JSA LINPUT	/AND PUT IT OUT NOW
15460 6133		
1004 15461 1031	JA .+52	/SKIP OVER THE REST OF THE + CHECKS
15462 5533		
1005 15463 0256	FLDA XVALUE	
1006 15464 2203	FSUB B3	
1007 15465 2400	FSUB (4.	/FINISHED WITH + YET?
15466 7463		
1010 15467 1061	JGT .+44	/YES
15470 5533		
1011 15471 1051	JLT .+27	/NO,BUT WE ARE NOT ON THE LAST POINT EIT
15472 5520		
1012 15473 1121	JSA DELPT	/GET WHERE TO PUT THE DELTA
15474 5574		
1013 15475 6401	FSTA PUBLK	/SAVE A SECOND
15476 6467		
1014 15477 0400	FLDA (LPBUF	
15500 7535		
1015 15501 6242	FSTA BUFLOC	/SET THE POINTER
1016 15502 0401	FLDA PUBLK	/GET THE LOCATION
15503 6467		
1017 15504 1121	JSA PTPUT	/AND PUT THE POINT IN THE BUFFER
15505 6063		
1020 15506 0261	FLDA PUFLAG	/FIRST OR SECOND PLOT?
1021 15507 1041	JNE .+27	/WE ARE ON THE FIRST, SET FOR THE SECOND
15510 5536		
1022 15511 0254	FLDA XFACTR	/FINISHED THIS DELTA FOR THE SECOND
1023 15512 5203	FADDM B3	/BOP THE DIVISION INDICATOR
1024 15513 0401	FLDA FPPONE	
15514 6511		
1025 15515 5240	FADDM IROW	/BOP TO THE NEXT DELTA
1026 15516 1031	JA .+30	/PUT THIS LINE OUT ON THE LP NOW
15517 5546		
1027 15520 1121	JSA DELPT	/NOT FINISHED WITH THE PLUS GET THE
15521 5574		
1030 15522 6401	FSTA PUBLK	/LOCATION. STORE TEMPORARILY
15523 6467		
1031 15524 0400	FLDA (LPBUF	
15525 7535		

1032	15526 6242	FSTA BUFLOC	/SET THE BUFFER LOCATOR
1033	15527 0401	FLDA PUBLK	
	15530 6467		
1034	15531 1121	JSA PTPUT	/AND SEND OUT THE DELTA POINT
	15532 6063		
1035	15533 0261	FLDA PUFLAG	/WHICH PLOT?
1036	15534 1001	JEQ .+12	/THE SECOND, SKIP
	15535 5546		
1037	15536 0002	FCLA	
1040	15537 6261	FSTA PUFLAG	/CLEAR THE PUT FLAG FOR THE SECOND PLOT
1041	15540 6257	FSTA KTRANS	/CLEAR THE TRANSLATION CONSTANT
1042	15541 0401	FLDA FPPONE	
	15542 6511		
1043	15543 5241	FADDM JCOL	/BOP TO THE NEXT IE CURVE
1044	15544 1031	JA AGAIN	/GO DO THE SECOND PLOT ON THE PAGE
	15545 5333		
1045	15546 0305	FLDA PCONST	
1046	15547 6401	FSTA PCNT	/SET THE PARAMETER LIST COUNT
	15550 1460		
1047	15551 4001	TRAP4 PLPTR	/PUT THE LINE ON THE PRINTER NOW
	15552 1440		
1050	15553 0263	FLDA BYFLAG	/DID WE BYPASS THE SECOND PLOT
1051	15554 1041	JNE .+6	/YES
	15555 5562		
1052	15556 0241	FLDA JCOL	/NO, RESET TO THE FIRST IE CURVE
1053	15557 2401	FSUB FPPONE	
	15560 6511		
1054	15561 6241	FSTA JCOL	
1055	15562 2171	JXN INLOP, 7+	/LOOP TO FINISH THE TWO PLOTS
	15563 5313		
1056	15564 0401	FLDA FPPTWO	
	15565 6514		
1057	15566 5241	FADDM JCOL	/BOP TO THE NEXT IE SET
1060	15567 0002	FCLA	
1061	15570 6240	FSTA IROW	/START WITH THE FIRST DELTA
1062	15571 2161	JXN OUTLOP, 6+	/LOOP TILL ALL PLOT PAGES ARE DONE
	15572 5267		
1063	15573 0000	FEXIT	
1064		/DETERMINE WHERE TO PUT THE DELTA POINT	
1065	15574 1031	DELPT, JA	
	15575 5574		
1066	15576 0400	FLDA (MINLOC	
	15577 7521		
1067	15600 6242	FSTA BUFLOC	/SET THE POINTER TO THE MINIMUM VECTOR
1070	15601 0241	FLDA JCOL	
1071	15602 4400	FMUL (3.	
	15603 7403		
1072	15604 1121	JSA SETLOC	/DETERMINE THE ADDRESS
	15605 6447		
1073	15606 0601	FLDA I B1	/GET THE MINIMUM
1074	15607 6251	FSTA TEMP	/STORE A SECOND
1075	15610 0400	FLDA (IELOC	
	15611 7436		
1076	15612 6242	FSTA BUFLOC	/RESET TO IE TABLE
1077	15613 1121	JSA ELMLOC	/LOCATE THE ELEMENT WE WANT
	15614 0433		
1100	15615 0601	FLDA I B1	/GET THE DELTA
1101	15616 2251	FSUB TEMP	/SUBTRACT THE MINIMUM
1102	15617 4255	FMUL YFACTR	
1103	15620 3400	FDIV (.05	/AND CONVERT THIS ENERGY TO DISPLACEMENT
	15621 7527		
1104	15622 1257	FADD KTRANS	/ON THE GRAPH. ADD TRANSLATION CONSTANT

1105	15623 1031	JA DELPT	/RETURN WITH VALUE IN FAC
	15624 5574		
1106		/PRINT PAGE HEADING AND LABEL THE Y AXES	
1107	15625 1031	AXLABEL, JA	
	15626 5625		
1110	15627 4001	TRAP4 LABEL	/PRINT THE HEADING
	15630 1646		
1111	15631 0401	FLDA FPPTWO	
	15632 6514		
1112	15633 6210	FSTA B10	
1113	15634 0400	FLDA (5.	
	15635 7532		
1114	15636 1121	JSA FTYPE	/F5.2
	15637 7066		
1115	15640 0263	FLDA BYFLAG	/HOW MANY PLOTS ON THE PAGE?
1116	15641 1001	JEQ .+10	/TWO
	15642 5651		
1117	15643 0103	LDX 100.3	/ONLY ONE
	15644 0100		
1120	15645 4001	TRAP4 TBSPA	/SPACE TO THE RIGHT POINT
	15646 1561		
1121	15647 1031	JA .+7	/DO NOT RESET THE COLUMN OR LOOP COUNT
	15650 5656		
1122	15651 0105	LDX -2.5	/SET THE LOOP COUNT TO MINUS TWO
	15652 7776		
1123	15653 0401	FLDA FPPONE	
	15654 6511		
1124	15655 5241	FADDM JCOL	/BOP TO THE NEXT COLUMN
1125	15656 0255	FLDA YFACTR	/CALCULATE THE LABEL SPACING
1126	15657 4401	FMUL FPPTWO	/LABEL EVERY TWO DIVISIONS
	15660 6514		
1127	15661 3400	FDIV (8.	/ONE SPACE PER 8 POINTS
	15662 7505		
1130	15663 2400	FSUB (5.	/THE LABEL TAKES 5 SPACES
	15664 7532		
1131	15665 0010	ALN 0	
1132	15666 0004	FNORM	/FIX IT UP
1133	15667 6260	FSTA NOSPACE	/STORE OUR SPACING FACTOR
1134	15670 0301	AXLOOP, FLDA NUMYDV	/DETERMINE THE NUMBER OF LABELS WE HAVE
1135	15671 3401	FDIV FPPTWO	/TO MAKE
	15672 6514		
1136	15673 0010	ALN 0	
1137	15674 0004	FNORM	
1140	15675 1401	FADD FPPONE	
	15676 6511		
1141	15677 0003	FNEG	
1142	15700 0024	ATX 4	/AND STORE IN OUR LOOP COUNTER
1143	15701 0400	FLDA (MINLOC	
	15702 7521		
1144	15703 6242	FSTA BUFLOC	
1145	15704 0241	FLDA JCOL	
1146	15705 4400	FMUL (3.	
	15706 7403		
1147	15707 1121	JSA SETLOC	
	15710 6447		
1150	15711 0601	FLDA I B1	/GET THE MINIMUM DELTA (FIRST LABEL)
1151	15712 6252	FSTA MIN	/STORE
1152	15713 1121	JSA PRNTDV	/AND SEND IT TO THE LP BUFFER
	15714 6004		
1153	15715 0034	XTA 4	
1154	15716 1401	FADD FPPONE	/ARE WE ON THE LAST LABEL?
	15717 6511		

1155	15720 1001	JEQ .+6	/YES,CONTINUE WITH THE NEXT GRAPH
	15721 5726		
1156	15722 0260	FLDA NOSPAC	
1157	15723 0023	ATX 3	
1160	15724 4001	TRAP4 TBSPA	/SPACE FOR THE NEXT LABEL
	15725 1561		
1161	15726 2141	JXN .-13,4+	/FINISH THE FIRST GRAPH
	15727 5713		
1162	15730 0263	FLDA BYFLAG	/BYPASS SET?
1163	15731 1041	JNE .+43	/YES,DONE LABELING PUT IT OUT
	15732 5774		
1164	15733 0035	XTA 5	/NO,DO THE NEXT ONE
1165	15734 1401	FADD FPPONE	/HAVE WE DONE THE LAST ONE?
	15735 6511		
1166	15736 1001	JEQ .+34	/YES,PRINT OUT THE LABELS
	15737 5772		
1167	15740 0241	FLDA JCOL	/NO,RESET TO THE NEXT IE CURVE
1170	15741 2401	FSUB FPPONE	
	15742 6511		
1171	15743 6241	FSTA JCOL	
1172	15744 0301	FLDA NUMYDV	/CALCULATE THE NUMBER OF SPACES
1173	15745 3401	FDIV FPPTWO	/BETWEEN THE TWO GRAPH LABELS
	15746 6514		
1174	15747 0010	ALN 0	
1175	15750 0004	FNORM	
1176	15751 6251	FSTA TEMP	
1177	15752 1401	FADD FPPONE	
	15753 6511		
1200	15754 4400	FMUL (5.	
	15755 7532		
1201	15756 6401	FSTA PUBLK	
	15757 6467		
1202	15760 0251	FLDA TEMP	
1203	15761 4260	FMUL NOSPAC	
1204	15762 1401	FADD PUBLK	
	15763 6407		
1205	15764 0003	FNEG	
1206	15765 1400	FADD (64.	
	15766 7540		
1207	15767 0023	ATX 3	/DONE HERE,SAVE AND
1210	15770 4001	TRAP4 TBSPA	/PUT OUT THE REQUIRED NUMBER OF SPACES
	15771 1561		
1211	15772 2151	JXN AXLOOP,5+	/LOOP TO FINISH LABELING THE SECOND GRAP
	15773 5670		
1212	15774 4001	TRAP4 PCRLF	/TERMINATE THE LINE
	15775 1537		
1213	15776 4001	TRAP4 PLPTR	/LET THE LINE GO
	15777 1440		
1214	16000 4001	TRAP4 STPLOT	/SET THE LP TO THE PLOT MODE
	16001 1642		
1215	16002 1031	JA AXLABL	/RETURN
	16003 5625		
1216		/CONVERT THE ENERGY LABEL TO ASCII	
1217		/PUT IN BUFFER	
1220		/BOP THE LABEL	
1221	16004 1031	PRNTDV, JA .	
	16005 6004		
1222	16006 0400	FLDA (CONLOC	
	16007 7452		
1223	16010 6200	FSTA B0	/SET CONVERSION POINTER
1224	16011 0252	FLDA MIN	/GET THE ENERGY LABEL
1225	16012 1400	FADD (.005	/ROUND IT

1226	16013 7455		
	16014 1121	JSA FCON	/CONVERT IT
	16015 6760		
1227	16016 4001	TRAP4 PSTRA	/PUT IT IN THE BUFFER
	16017 1472		
1230	16020 0400	FLDA (.1	
	16021 7543		
1231	16022 5252	FADDM MIN	/BOP FOR THE NEXT LABEL
1232	16023 1031	JA PRNTDV	/RETURN
	16024 6004		
1233		/PLOT THE Y AXIS DIVISIONS	
1234	16025 1031	PUYDV, JA	
	16026 6025		
1235	16027 0301	FLDA NUMYDV	
1236	16030 0003	FNEG	
1237	16031 0022	ATX 2	/SET THE COUNT
1240	16032 0255	FLDA YFACTR	
1241	16033 1257	FADD KTRANS	/FORM THE INITIAL DISPLACEMENT
1242	16034 6202	FSTA B2	/STORE FOR FUTURE INCREMENTATION
1243	16035 0202	FLDA B2	/GET THE DISPLACEMENT
1244	16036 1121	JSA PTPUT	/SET THE CORRECT POINT IN THE PLOTTER
	16037 6063		
1245	16040 0255	FLDA YFACTR	/BUFFER
1246	16041 5202	FADDM B2	/BOP THE DISPLACEMENT
1247	16042 2121	JXN .-5,2+	/LOOP TILL ALL DIVISIONS ARE DONE
	16043 6035		
1250	16044 1031	JA PUYDV	/RETURN
	16045 6025		
1251		/PLOT AN X AXIS DIVISION	
1252	16046 1031	PUXDV, JA	
	16047 6046		
1253	16050 0002	FCLA	
1254	16051 1257	FADD KTRANS	
1255	16052 6267	FSTA START	/SET THE STARTING POINT
1256	16053 0400	FLDA (10.	
	16054 7524		
1257	16055 1257	FADD KTRANS	
1260	16056 6270	FSTA ENDBIT	/SET THE ENDING POINT
1261	16057 1121	JSA LINPUT	/PUT THE LINE INTO THE BUFFER
	16060 6133		
1262	16061 1031	JA PUXDV	/RETURN
	16062 6046		
1263		/SET A BIT TO PUT A POINT ON THE LP	
1264		/ENTER WITH THE DISPLACEMENT IN FAC	
1265	16063 1031	PTPUT, JA	
	16064 6063		
1266	16065 1121	JSA ROUND	/ROUND THE DISPLACEMENT
	16066 6313		
1267	16067 1121	JSA LIMCK	/CHECK THAT IT DOESNT EXCEED THE GRAPH
	16070 6330		
1270	16071 6264	FSTA PTLOC	/LIMITS. STORE IT HERE
1271	16072 0400	FLDA (8.	
	16073 7505		
1272	16074 6210	FSTA B10	/DIVISOR FOR MODULUS FUNCTION
1273	16075 0264	FLDA PTLOC	/GET OUR DISPLACEMENT
1274	16076 3210	FDIV B10	/DIVIDE BY 8 TO GET THE CORRECT
1275	16077 6265	FSTA WRDLOC	/WORD LOCATION IN THE BUFFER
1276	16100 0264	FLDA PTLOC	
1277	16101 1121	JSA AMOD	/USE THE REMAINDER TO SET THE
	16102 6530		
1300	16103 6266	FSTA BITLOC	/CORRECT BIT
1301	16104 0265	FLDA WRDLOC	

1302	16105 1121	JSA SETLOC	/SET THE ABSOLUTE CORE LOCATION
	16106 6447		
1303	16107 0266	FLDA BITLOC	/GET OUR BIT LOCATOR
1304	16110 0003	FNEG	/NEGATE
1305	16111 1001	JEQ .+12	/IT IS ZERO,NO ROTATION NECESSARY
	16112 6123		
1306	16113 0021	ATX 1	/SET THE ROTATION COUNTER
1307	16114 0304	FLDA K200	/FIRST BIT SET
1310	16115 3401	FDIV FPPTWO	/ROTATE
	16116 6514		
1311	16117 2111	JXN .-2,1+	/TILL DONE
	16120 6115		
1312	16121 1031	JA .+3	/SKIP THE NEXT INSTRUCTION
	16122 6124		
1313	16123 0304	FLDA K200	/NO ROTATION,SET FIRST BIT
1314	16124 0010	ALN 0	/ALIGN OUR NUMBER
1315	16125 4001	TRAP4 OR	/DO AN INCLUSIVE OR WITH WHAT IS ALREADY
	16126 1626		
1316	16127 1121	JSA PUTWRD	/THREF. PUT THE RESULT IN THE BUFFER
	16130 6354		
1317	16131 1031	JA PTPUT	/RETURN
	16132 6063		
1320		/PUT A LINE ON THE LP	
1321		/STARTING LOCATION IN START	
1322		/ENDING LOCATION IN ENDBIT	
1323		/SET ALL THE BITS BETWEEN IN THE BUFFER	
1324	16133 1031	LINPUT, JA .	
	16134 6133		
1325	16135 0267	FLDA START	/GET THE STARTING LOCATION
1326	16136 1121	JSA ROUND	/ROUND IT
	16137 6313		
1327	16140 1121	JSA LIMCK	/WITHIN OUR LIMITS?
	16141 6330		
1330	16142 6267	FSTA START	/STORE HERE AGAIN
1331	16143 0270	FLDA ENDBIT	/DO THE SAME FOR THE ENDING LOCATION
1332	16144 1121	JSA ROUND	
	16145 6313		
1333	16146 1121	JSA LIMCK	
	16147 6330		
1334	16150 6270	FSTA ENDBIT	
1335	16151 2267	FSUB START	/GET THE DIFFERENCE
1336	16152 1051	JLT LPTERR	/AND MAKE SURE WE ARE NOT MESSED UP
	16153 6311		
1337	16154 0400	FLDA (0.	
	16155 7505		
1340	16156 6210	FSTA B10	/SET MODULUS DIVISOR
1341	16157 0267	FLDA START	/GET THE STARTING DISPLACEMENT
1342	16160 3210	FDIV B10	
1343	16161 6271	FSTA LPOINT	/AND FIND THE STARTING WORD
1344	16162 0267	FLDA START	
1345	16163 1121	JSA AMOD	
	16164 6530		
1346	16165 6272	FSTA LBIT	/THE REMAINDER SETS THE CORRECT STARTING
1347	16166 0270	FLDA ENDBIT	/BIT
1350	16167 3210	FDIV B10	
1351	16170 6273	FSTA UPOINT	/DETERMINE THE UPPER WORD
1352	16171 0270	FLDA ENDBIT	
1353	16172 1121	JSA AMOD	
	16173 6530		
1354	16174 6274	FSTA UBIT	/AND THE REMAINDER FOR SETTING THE UPPER
1355	16175 0271	FLDA LPOINT	/BIT
1356			/GET THE LOWER WORD POINTER

1357	16176	0010	ALN 0	
1360	16177	0004	FNORM	/FIX IT UP A BIT
1361	16200	6251	FSTA TEMP	/SAVE TEMPORARILY
1362	16201	0273	FLDA UPOINT	/GET THE UPPER WORD POINTER
1363	16202	0010	ALN 0	
1364	16203	0004	FNORM	/FIX IT UP TOO
1365	16204	2251	FSUB TEMP	/FORM THEIR DIFFERENCE
1366	16205	1001	JEQ UWORD	/THE BITS TO BE SET ARE IN THE SAME WORD
	16206	6263		
1367	16207	2401	FSUB FPPONE	
	16210	6511		
1370	16211	1001	JEQ LWORD	/THE BITS TO BE SET ARE IN CONSECUTIVE
	16212	6233		
1371	16213	0003	FNEG	/WORDS
1372	16214	0021	ATX 1	/SET THE FINAL DIFFERENCE TO A LOOP
1373	16215	0271	FLDA LPOINT	/COUNTER
1374	16216	1121	JSA SETLOC	/START AT THE LOWER WORD
	16217	6447		
1375	16220	0006	STARTD	
1376	16221	0401	FLDA FPPPI2-1	/"00000001"
	16222	6516		
1377	16223	5201	FADDM B1	/PLUS ONE
1400	16224	0005	STARTF	
1401	16225	0303	FLDA K377	/SET ALL BITS
1402	16226	0010	ALN 0	
1403	16227	1121	JSA PUTWRD	/OF ALL WORDS
	16230	6354		
1404	16231	2111	JXN .-11,1+	/BETWEEN THE LIMITS.
	16232	6220		
1405	16233	0271	LWORD, FLDA LPOINT	/SET THE BUFFER LOCATION OF THE LOWER
1406	16234	1121	JSA SETLOC	/WORD
	16235	6447		
1407	16236	0401	FLDA FPPONE	/INITIAL BIT SET
	16237	6511		
1410	16240	6251	FSTA TEMP	/STORE FOR ROTATION
1411	16241	0272	FLDA LBIT	
1412	16242	2400	FSUB (7.	
	16243	7447		
1413	16244	1001	JEQ .+11	/WE DO NOT HAVE TO ROTATE
	16245	6255		
1414	16246	0021	ATX 1	/ROTATION COUNT
1415	16247	0251	FLDA TEMP	
1416	16250	4401	FMUL FPPTWO	/ROTATE TO THE LEFT ONE PLACE BY
	16251	6514		
1417	16252	5251	FADDM TEMP	/MULTIPLYING AND ADD TO THE PREVIOUS
1420	16253	2111	JXN .-3,1+	/RESULT. PERFORM THE REQUISITE ARITHMETI
	16254	6250		
1421	16255	0251	FLDA TEMP	/SHIFT LEFT. FINAL "PRODUCT"
1422	16256	0010	ALN 0	/STICK IN LSW OF FAC
1423	16257	4001	TRAP4 OR	/DO AN INCLUSIVE OR WITH WHAT IS THERE
	16260	1626		
1424	16261	1121	JSA PUTWRD	/PUT THE RESULT INTO THE BUFFER
	16262	6354		
1425	16263	0273	UWORD, FLDA UPOINT	
1426	16264	1121	JSA SETLOC	/SET THE BUFFER LOCATION OF THE UPPER
	16265	6447		
1427	16266	0304	FLDA K200	/WORD. INITIAL BIT SET
1430	16267	6251	FSTA TEMP	/STORE FOR THE ROTATION RESULT
1431	16270	0274	FLDA UBIT	
1432	16271	0003	FNEG	/ROTATION COUNT
1433	16272	1001	JEQ .+11	/IT IS ZERO, DONT ROTATE
	16273	6303		

1434	16274 0021	ATX 1	/SET THE COUNT LOOP
1435	16275 0251	FLDA TEMP	/GET RESULT
1436	16276 3401	FDIV FPPTWO	/ROTATE ONE PLACE RIGHT BY DIVIDING
	16277 6514		
1437	16300 5251	FADDM TEMP	/ADD BACK ON
1440	16301 2111	JXN .-3,1+	/CONTINUE TILL THE ARITHMETIC SHIFT IS
	16302 6276		
1441	16303 0251	FLDA TEMP	/DONE. GET THE FINAL RESULT
1442	16304 0010	ALN 0	/ALIGN IT TO THE LSW OF THE FAC
1443	16305 4001	TRAP4 OR	/INCLUSIVE OR
	16306 1626		
1444	16307 1121	JSA PUTWRD	/PUT THE ORED RESULT INTO THE BUFFER
	16310 6354		
1445	16311 1031	LPTRR, JA LINPUT	/RETURN
	16312 6133		
1446		/ROUND THE DISPLACEMENT TO THE NEAREST	
1447		/UNIT	
1450		/CHOP OFF FRACTION	
1451	16313 1031	ROUND, JA .	
	16314 6313		
1452	16315 1400	FADD (.5	/ROUND UP
	16316 7411		
1453	16317 1071	JAL RNDERR	/IF WE CANT ALIGN IT ITS NO GOOD
	16320 6325		
1454	16321 0010	ALN 0	
1455	16322 0004	FNORM	/CHOP OFF FRACTION AND FIX
1456	16323 1031	JA ROUND	/RETURN
	16324 6313		
1457	16325 0002	RNDERR, FCLA	/RETURN WITH ZERO
1460	16326 1031	JA ROUND	
	16327 6313		
1461		/LIMIT CHECK	
1462	16330 1031	LIMCK, JA .	
	16331 6330		
1463	16332 1051	JLT LIMERR	/ITS NEGATIVE????
	16333 6351		
1464	16334 6251	FSTA TEMP	/SAVE IN OUR TEMPORARY LOCATION
1465	16335 2275	FSUB LLIMIT	
1466	16336 2257	FSUB KTRANS	/IS IT LESS THAN THE LOWER LIMIT?
1467	16337 1051	JLT LIMERR	/YES,ERROR
	16340 6351		
1470	16341 0251	FLDA TEMP	
1471	16342 2276	FSUB ULIMIT	
1472	16343 2257	FSUB KTRANS	/GREATER THAN UPPER LIMIT?
1473	16344 1061	JGT LIMERR	/YES,ERROR
	16345 6351		
1474	16346 0251	FLDA TEMP	
1475	16347 1031	JA LIMCK	/RETURN AS IF NOTHING HAPPENED
	16350 6330		
1476	16351 0002	LIMERR, FCLA	/CLEAR THE FAC
1477	16352 1031	JA LIMCK	/AND RETRUN IF OUTSIDE THE LIMITS
	16353 6330		
1500		/PUT THE LSW OF THE FAC INTO THE	
1501		/LOCATION SPECIFIED BY B1	
1502		/ENTER WITH FLOATING POINT WORD IN FAC	
1503	16354 1031	PUTWRD, JA .	
	16355 6354		
1504	16356 6251	FSTA TEMP	/SAVE A SECOND
1505	16357 0601	FLDA I B1	/GET WHAT IS ALREADY THERE
1506	16360 6401	FSTA PUBLK	/STORE IT IN OUR PUTTER BLOCK
	16361 6467		
1507	16362 0251	FLDA TEMP	/PICK IT UP NOW

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1510 16363 6401      FSTA PUBLK-2      /STORE AND OVERLAY ONLY ONE LOCATION
      16364 6465
1511 16365 0401      FLDA PUBLK      /GET THE ALTERED RESULT
      16366 6467
1512 16367 6601      FSTA I B1      /AND STORE IT BACK AGAIN
1513 16370 1031      JA PUTWRD      /RETURN
      16371 6354
1514                /ZERO THE PLOT BUFFER
1515 16372 1031      ZROBUF, JA .
      16373 6372
1516 16374 0101      LDX -100,1      /LOOP COUNTER AND ADDRESS MODIFIER
      16375 7700
1517 16376 0002      FCLA            /CLEAR THE FAC TO BE SURE
1520 16377 0006      STARTD          /GET IN FIXED POINT
1521 16400 6417      FSTA LPBUF+200-20000,1
      16401 2600
1522 16402 2111      JXN .-2,1+      /CLEAR TILL DONE
      16403 6400
1523 16404 0005      CTARTF          /RETURN TO FLOATING POINT
1524 16405 1031      JA ZROBUF      /RETURN
      16406 6372
1525                /FORM THE Y AXIS
1526 16407 1031      PUTYAX, JA .
      16410 6407
1527 16411 0002      FCLA
1530 16412 1257      FADD KTRANS
1531 16413 6267      FSTA START      /SET THE STARTING POINT
1532 16414 0276      FLDA ULIMIT
1533 16415 1257      FADD KTRANS
1534 16416 6270      FSTA ENDBIT      /SET THE ENDING POINT
1535 16417 1121      JSA LINPUT      /SET ALL BITS IN BETWEEN
      16420 6133
1536 16421 1031      JA PUTYAX      /RETURN
      16422 6407
1537                /PUT A POINT AT Y=0(THE X AXIS)
1540 16423 1031      PUTXPT, JA .
      16424 6423
1541 16425 0002      FCLA
1542 16426 1257      FADD KTRANS      /SET THE CORRECT POINT(DEPENDING ON THE
1543 16427 1121      JSA PTPUT      /PLOT). PUT IT OUT
      16430 6063
1544 16431 1031      JA PUTXPT      /RETURN
      16432 6423
1545                /DETERMINE THE ABSOLUTE LOCATION OF AN
1546                /ELEMENT IN A 2 DIMENSIONAL MATRIX
1547                /AS STORED IN A VECTOR
1550                /A(G)=A(I,J)
1551 16433 1031      ELMLOC, JA .
      16434 6433
1552 16435 0241      FLDA JCOL
1553 16436 4400      FMUL NORMUL
      15437 3010
1554 16440 1240      FADD IROW
1555 16441 4400      FMUL (3,        /G=I+ROWMAX*J
      16442 7403
1556 16443 1121      JSA SETLOC      /SET THE LOCATION NOW THAT WE HAVE THE
      16444 6447
1557 16445 1031      JA ELMLOC      /DISPLACEMENT. RETURN
      16446 6433
1560                /GIVEN A DISPLACEMENT FROM AN INITIAL
1561                /LOCATION SET THE CORE LOCATION
1562                /ENTER WITH DISPLACEMENT IN FAC

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1563          /INITIAL LOCATION IN BUFLOC
1564          /LEAVE THE RESULT IN B1
1565 16447 1031 SETLOC, JA .
          16450 6447
1566 16451 0010      ALN 0          /ALIGN THE DISPLACEMENT
1567 16452 6201      FSTA B1        /AND STORE IN B1
1570 16453 0242      FLDA BUFLOC    /GET THE INITIAL POINTER
1571 16454 6401      FSTA PUBLK     /STORE HERE
          16455 6467
1572 16456 0006      STARTD         /GET INTO FIXED POINT
1573 16457 0401      FLDA PUBLK+1    /AND PICK UP THE LAST TWO WORDS OF THE
          16460 6470
1574 16461 5201      FADDM B1       /POINTER. ADD TO THE DISPLACEMENT
1575 16462 0005      STARTF         /RETURN TO FLOATING POINT
1576 16463 1031      JA SETLOC      /RETURN
          16464 6447
1577 16465 0000      0
1600 16466 0000      0
1601 16467 0000 PUBLK. 0
1602 16470 0000      0
1603 16471 0000      0
1604          /FLOAT THE FAC
1605          /ENTER FIXED POINT EXIT FLOATING POINT
1606 16472 1031 FLOAT, JA .
          16473 6472
1607 16474 6220      FSTA FIX+1     /SAVE IN OUR HANDY FIXER UPPER LOCATION
1610 16475 0005      STARTF         /GET INTO FLOATING POINT
1611 16476 0220      FLDA FIX       /PICK UP THE RESULT
1612 16477 0004      FNORM          /NORMALIZE IT
1613 16500 1031      JA FLOAT       /RETURN
          16501 6472
1614          /PASS AN ASCII CHARACTER TO GETNUM
1615 16502 1031 GETC, JA .
          16503 6502
1616 16504 4001      TRAP4 GCHAR    /GET THE CHARACTER
          16505 1622
1617 16506 0034      XTA 4          /LOAD IT INTO THE FAC
1620 16507 1031      JA GETC        /RETURN
          16510 6502
CHAINING TO FPPLB1
0000 ERRORS

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ACHI	11303
ACLO	11304
ACQ	11062
ACQUI	14517
ACQUIR	10310
ACQ1	11123
ACQ2	11126
ACQ3	11145
AGAIN	15333
AMDD	16530
AMS1	11673
AMS2	11700
AMS3	11705
AMS4	11712
AMS5	11716
APT	10030
APTA	11030
ASTER	12347
AUX0	10010
AUX1	10011
AUX2	10012
AUX3	10013
AUX4	10014
AUX5	10015
AUX6	10016
AUX7	10017
AXLABL	15625
AXLOOP	15670
BAS1A	11640
BCKSUB	10315
BITLOC	13042
BKGFLG	10050
BUFLOC	12746
BUTTY	11427
BYFLAG	13031
B0	12600
B1	12603
B10	12630
B11	12633
B12	12636
B13	12641
B14	12644
B15	12647
B16	12652
B17	12655
B2	12606
B3	12611
B4	12614
B5	12617
B6	12622
B7	12625
CAIN	10330
CARCNT	10366
CCOUNT	07035
CHAR	10100
CHARA	10364
CHECK	14016
CHKBUF	13657
CHKER1	13702
CHKER2	13704
CHKFLG	14520

CHNA	10735
CHNFLG	10051
CHN1	10357
CKFLG	10771
CLAR	00001
CMNDR	10306
CMND1A	10066
CMND2A	10365
CMS	11723
CNTABA	07036
CNTABL	07031
CNTERR	10304
CNTRFA	10055
CNTRL	07000
CNTRLA	10063
CNTRLH	10064
CNTRL1	07005
CNTRL2	07025
CNTRL3	07027
COMAND	10200
COMND1	10214
COMND2	10235
CONLOA	11535
CONLOC	12353
COUNTL	10070
CR	11550
CTLFLG	07037
DAC	06374
DATAD	11170
DATLOA	11167
DCONST	11305
DELHED	12000
DELPT	15574
DELSQ	10400
DELTA	14151
DELTIM	15037
DEL1	14203
DEL2	14223
DENOM	12770
DFACTR	13125
DIG	12343
DIGA	10061
DIG1A	10062
DISPL	12705
DIVXAX	15162
DIVYAX	15213
DONADV	13540
DTALDA	14012
DTALOC	05000
ELIM	10423
ELIMER	14267
ELIMIE	14256
ELMLOC	16433
EMS	12016
ENDBIT	13050
ENERGY	10075
ENTNER	13242
ENIVL	10072
ENTRVL	13213
ERR	10706
ERRA	10060
ERRMS	12337

ERRNUM	10067
EXIT	10727
FCON	16760
FILERR	10461
FILSAV	10426
FIX	12660
FLOAT	16472
FPC	10031
FPPG	11006
FPPGO	14521
FPPG1	11016
FPPK2	14014
FPPNXT	17760
FPPONE	16511
FPPPI	16522
FPPPI2	16517
FPPTWO	16514
FPP2PI	16525
FTYPE	17066
FXR0	10020
FXR1	10021
FXR2	10022
FXR3	10023
FXR4	10024
FXR5	10025
FXR6	10026
FXR7	10027
GBUFA	11422
GBUFL	11423
GCHAR	11622
GETC	16502
GETINT	14050
GETNUM	16551
GETPRM	14522
GETTY	14523
GNUM	11600
GNUMB	14524
GPARM	10736
GTFARM	11420
GTTY	11400
HEADA	10460
HEHDR	03000
HIINT	12724
HILOC	12710
HUPTR	10076
IEHD	12026
IELOC	03400
IEPRIN	14271
IEPRNT	10465
IEP1	14275
INCEPT	03110
INLOP	15313
INRL	11307
INTFAC	12732
INTOEN	13577
INTVL	12666
INVTRP	14123
IROW	12740
ISTBLK	10047
IUNIT	10046
JCOL	12743
KTRANS	13015

K1000	13106
K11	10141
K2	10135
K200	13114
K260	10143
K3	10136
K304	10144
K377	13111
K4	10137
K4704	10146
K7	10140
K77	10142
K777	10145
LABEL	11646
LABL1	12053
LABL2	12077
LABL3	12104
LBIT	13056
LF	11551
LIMCK	16330
LINERR	16351
LINC	06141
LINPUT	16133
LINTRP	14100
LISTP	11335
LLIM	12677
LLIMIT	13067
LOINT	12721
LOLOC	12713
LOWINT	12727
LPARM	11455
LPBUF	12400
LPCTL	14525
LPOINT	13053
LPTRR	16311
LPTRC	11000
LSAVE	11312
LSQHD	12133
LSTSQ	14354
LSTSQ1	14456
LWORD	16233
LWPTR	10077
MAJADV	13406
MASHED	12200
MASLOC	03030
MASPR	10475
MASS	13130
MASSER	13160
MAXIM	13122
MCCPMS	17515
MCDIGC	17140
MCGFTD	17313
MCLBLK	17423
MCPDOT	17505
MCPEXP	17441
MCPRTD	17527
MCPUTC	17354
MCRTPB	77000
MCRTP1	77030
MCRTP2	77033
MCRTP3	77036
MCRTP4	77041

MCRTPS 77044
 MCRTPE 77047
 MCRTPE 77052
 MCRTPE 77055
 MCSTAR 17405
 MC1TAB 17545
 MC2TAB 17603
 MC260 17730
 MC3TAB 17541
 MC4TAB 17677
 MIN 12776
 MINADV 13504
 MINLOC 03330
 MNS1 12230
 MNCAL1 15075
 MNCAL2 15120
 MPCD 06644
 MPRINT 14612
 MP1 14623
 MP2 14645
 MYCRLF 11547
 M2 10147
 M2000 10154
 M251 10151
 M256 11517
 M301 10152
 M307 10153
 M32 10150
 NBLK 10045
 NERR1 14046
 NERR2 14044
 NIE 03005
 NMS1 12237
 NMS2 12264
 NMUL 14722
 NORANG 03013
 NORM 13340
 NORMUL 03010
 NORM1 13446
 NORM2 13461
 NORPRM 10505
 NOSFAC 13020
 NRANG 14735
 NSAM 11301
 NSCANS 10074
 NSHIFT 11310
 NSTEPS 10073
 NTIMES 11311
 NULNTH 13001
 NUMA 11607
 NUML 11610
 NUMPI T 12735
 NUMYDV 13103
 OPR 10034
 OPTMA 10734
 OPTMIZ 10600
 OPTM1 10602
 OR 11626
 ORPTR 11641
 OTRL 11306
 OUTLOP 15267
 PBUFA 10057
 PBUFL 11341
 PBUFRA 11340

PCNT 11460
 PCNST 13117
 PCRLF 11537
 PDP 00002
 PLPTR 11440
 PLT 00007
 PLTFLG 13026
 PRNT 00006
 PRNTAB 10627
 PRHTDV 16004
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 PSTRA 11472
 PSTRA1 11477
 PSTRG0 11526
 PSTR1 11502
 PTABL 14746
 PTABL1 15006
 PTABL2 14774
 PTLOC 13034
 PTPUT 16063
 PTTY 11313
 PUBLK 16467
 PUCNTA 10056
 PUCRLF 14526
 PUFLAG 13023
 PUPARM 11336
 PUSAV 11516
 PUSTR 14527
 PUTCTR 11536
 PUTLP 14530
 PUTTY 14531
 PUTWRD 16354
 PUTXPT 16423
 PUTYAX 16407
 PUXDV 16046
 PUYDV 16025
 RANGE 13244
 RANGER 13307
 RATIO 12702
 READ 10040
 READTA 10641
 REOT 00004
 RESET 00005
 RESFP 00011
 RETURN 10042
 RFFED 00003
 RLTER 00002
 RNDERR 16325
 RNGE 12671
 ROUND 16313
 SAML 11302
 SMT'L 11200
 SAMPLE 14532
 SAMPL1 11217
 SAMPL2 11264
 SAN11 00111
 SCANNER 13336
 SCANL 11165
 SCANS 13313
 SEARCH 13610

SENGY 12663
 SENRGY 10071
 SETEE 10660
 SETLOC 16447
 SETPTR 11520
 SETWT 14363
 SLOPE 03170
 SP 11576
 SPP 00010
 SRCH1 13625
 START 13045
 STBLK 10044
 STEPER 13311
 STEPL 11166
 STPLOT 11642
 STRTEN 13162
 STRTER 13211
 SUMW 12757
 SUMX 12751
 SUMXX 12754
 SUMXY 12765
 SUMY 12762
 SUM1 14421
 SUM2 14471
 TAGHED 12301
 TABSP 14533
 TBLK 10114
 TBSP 11552
 TBSPA 11561
 TBSPGO 11567
 TEMP 12773
 TEMP1 07040
 TEMP2 07041
 TERR 15070
 TIME 10671
 TMS 12314
 TPARM 10110
 TRAP 14534
 TRP 11031
 TRPIN 11052
 TRPJ 11044
 TRP3 11053
 TRP4 11054
 TRP5 11056
 TRP6 11060
 TRP7 11061
 TSTEND 13706
 TSTFLG 10052
 TTYJMP 10251
 UBIT 13064
 ULIM 12674
 ULINIT 13072
 UNIT 10043
 UPOINT 13061
 UWORD 16263
 WARFLT 15072
 WRDLOC 13037
 WRITE 10041
 WRPLT 10677
 WTLOC 03250
 XFACTR 13004
 XIT 10065

XLNTH 13075
XVALUE 13012
YFACTR 13007
YLNTH 13100
ZROBUE 16372