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Determination of bond energies by mass spectrometry: some transition metal carbonyls

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Determination of bond energies by mass spectrometry. Some transition metal carbonyls

by

Gary Dean Michels

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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 anion[1].

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

$$R\text{-}S^{+,o,-}_{(g)} \rightarrow R^{+,o,-}_{(g)} + S_{(g)}. \qquad (1)$$

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.

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

[2] The 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, $\sum_i E_i^{+,o,-}$, is the enthalpy change for the reaction:

$$A_\ell B_m C_n \cdots {}_{(g)}^{+,o,-} \rightarrow A_{(g)}^{+,o,-} + (\ell-1)\, A_{(g)} + m\, B_{(g)} + n\, C_{(g)} + \cdots. \qquad (2)$$

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

$$A_\ell B_m C_n \cdots {}_{(g)}^{+,o,-} \rightarrow A_{(g)}^{*\,+,o,-} + (\ell-1)\, A_{(g)}^{*} + m\, B_{(g)}^{*} + n\, C_{(g)}^{*} + \cdots. \qquad (3)$$

The reactant molecule (molecular ion) dissociates from its ground state into its composite atoms (ion and atoms) in their <u>valence</u> 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:

$$\Delta H_{vs} = \Delta H_{atom} + \sum_j V_j. \tag{4}$$

By definition:

$$\Delta H_{vs} = \sum_i I_i^{+,o,-} \tag{5}$$

and:

$$\Delta H_{atom} = \sum_i E_i^{+,o,-} \tag{6}$$

so that:

$$\sum_i I_i^{+,o,-} = \sum_i E_i^{+,o,-} + \sum_j V_j. \tag{7}$$

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, $\cdots$, r_n and 3m-6-n bond angles α_1, α_2, $\cdots$, α_{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:

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

and:

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

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:

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

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

$$\alpha_i = \alpha_{io}$$

$$r_k = \gamma r_{ko} \tag{11}$$

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:

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

where L denotes the integration path defined previously.

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

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

where:

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

(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_{ko} 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:

$$\frac{\partial U}{\partial r_i} = 0 \quad \text{for } i \neq k$$

$$\frac{\partial U}{\partial \alpha_j} = 0 \quad \text{for all } \alpha_j\text{'s.} \tag{15}$$

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 kth bond can be compared directly. Performing this operation yields the result:

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

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 kth 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:

$$\Delta H_{atom} = \sum_{i=1}^{n} E_i. \tag{18}$$

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:

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

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:

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

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

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

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:

$$\begin{array}{l} AB_n \rightarrow AB_{n-1} + B \\ AB_{n-1} \rightarrow AB_{n-2} + B \\ \vdots \end{array}$$

$$AB \rightarrow A + B. \tag{22}$$

For the ith process (i=1, 2, •••, n):

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

The sum of the enthalpies of all of the processes:

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

is the energy of the atomization reaction:

$$AB_n \rightarrow A + nB. \tag{25}$$

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

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

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

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

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:

$$AB_n \rightarrow AB_{n-i} + i\ B \qquad (28)$$

for i = 1, 2,···, n. The enthalpy changes for these fragmentations are sums of the dissociation energies of the molecule. For the ith process:

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

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:

$$\begin{tikzcd} & A + nB \arrow[dr] & \\ AB_n \arrow[ur] & & AB_{n-i} + i\ B. \end{tikzcd} \qquad (30)$$

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:

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

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 ith fragmentation enthalpy:

$$\Delta H_i = i\ E(A\text{-}B) \tag{32}$$

for i=1, ···, 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:

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

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:

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

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 ith dissociation energy is $\sum_{j=i}^{n} j / \sum_{i=1}^{n} i^2$:

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

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 ith fragment of Eq. 28, O_i, is given by:

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

where by definition:

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

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

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

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

$$\Delta H_i = i\, E(A\text{-}B) + O_i \qquad (39)$$

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:

$$AB_{n-1}C \rightarrow AB_{n-1-i}C + i\ B \tag{40}$$

where i = 1, 2, ···, 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 jth process is:

$$AB_{n-1}C \rightarrow AB_{n-1-j} + j\ B + C \tag{41}$$

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:

$$\Delta H_i = i\ E(A-B)_c \qquad i = 1, 2, \cdots, n-1 \tag{42}$$

for the first collection of fragmentations and:

$$\Delta H_j = (n-1)E(A\text{-}B)_c + E(A\text{-}C) - (n-1-j)E(A\text{-}B) \qquad j=0,\ 1,\ \cdots,\ n-1 \tag{43}$$

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, $E(A\text{-}B)_c$; 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) ≠ E(A-B) and either $E(A\text{-}B)_c = E(A\text{-}B)$ or $E(A\text{-}B)_c \neq E(A\text{-}B)$). In other words the calculation allows for the determination of the energy terms <u>without</u> the constancy assumption.

To prove this contention it is necessary to show that a unique solution for E(A-C), $E(A\text{-}B)_c$, 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 $E(A\text{-}B)_c$ 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 $E(A\text{-}B)_c$ 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, $\bar{D}(A\overset{+,o,-}{\text{—}}R)$, would be 1/n times the heat of the reaction:

$$A\,R^{+,o,-}_{n(g)} \rightarrow A^{+,o,-}_{(g)} + nR_{(g)} \qquad (44)$$

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:

$$AR_{\ell}S_mT_n\cdots^{+,o,-}_{(g)} \rightarrow A^{+,o,-}_{(g)} + \ell R_{(g)} + mS_{(g)} + nT_{(g)} + \cdots. \qquad (45)$$

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:

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

and:

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

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 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 $\overline{D}(A\text{-}BC)$ by considering the fragmentation of $A(BC)_n$ as follows:

$$\begin{tikzcd} & A + nB + nC \arrow[dr] & \\ A(BC)_n \arrow[ur] \arrow[rr] & & A + nBC. \end{tikzcd} \qquad (48)$$

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

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

where:

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

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

and:

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

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

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

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

$$\begin{tikzcd} & A + nB + nC \arrow[dr] & \\ A(BC)_n \arrow[ur] \arrow[rr] & & A(BC)_{n-i} + iBC. \end{tikzcd} \tag{54}$$

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

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

where:

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

and:

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

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

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

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

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

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:

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

As expected $\hat{D}(A\text{-}BC)$ approximates $\bar{D}(A\text{-}BC)$ 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 $A_\ell B_m C_n \cdots$, $IP(A_\ell B_m C_n \cdots)$, 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:

$$A_\ell B_m C_n \cdots_{(g)} \rightarrow A_\ell B_m C_n \cdots_{(g)}^{+} + e^- . \qquad (61)$$

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:

$$A_\ell B_m C_n \cdots_{(g)} + e- \rightarrow A_\ell B_m C_n \cdots^{+}_{(g)} + 2e-. \qquad (62)$$

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

$$A_\ell B_m C_n \cdots^{-}_{(g)} \rightarrow A_\ell B_m C_n \cdots_{(g)} + e-. \qquad (63)$$

In a mass spectrometer the internal energy change of the reverse process is measured (i.e. $-EA(A_\ell B_m C_n \cdots)$). 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:

$$A_\ell B_m C_n \cdots_{(g)} + e^- \rightarrow A^{+}_{(g)} + 2e^- + \text{gaseous neutral product(s)} \qquad (64)$$

for the positive ion or:

$$A_\ell B_m C_n \cdots_{(g)} + e^- \rightarrow A^{-}_{(g)} + \text{gaseous neutral product(s)} \qquad (65)$$

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:

$$A_{\ell} B_m C_n \cdots {}^{+,-}_{(g)} \rightarrow A^{+,-}_{(g)} + \text{gaseous neutral product(s)}. \qquad (66)$$

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

$$\Delta E^+ = AP(A^+) - IP(A_{\ell} B_m C_n \cdots) \qquad (67)$$

for the cationic process or:

$$\Delta E^- = AP(A^-) + EA(A_{\ell} B_m C_n \cdots) \qquad (68)$$

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 Δ E can be equated with Δ H. Thus the Δ E's of Eqs. 67 and 68 can be replaced with Δ H'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 netural 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:

$$\begin{tikzcd}
 & A_\ell B_m C_n \cdots^{+,-} + (-)e^- \arrow[dr] & \\
A_\ell B_m C_n \cdots \arrow[ur] \arrow[dr] & & \begin{array}{l} A^{+,-} + (\ell-1)A + mB \\ + nC + \cdots + (-)e^-. \end{array} \\
 & \ell A + mB + nC + \cdots \arrow[ur] &
\end{tikzcd} \qquad (69)$$

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

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

or:

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

for the cation-neutral fragment relationship and:

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

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:

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

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

$$IP(R_1R_2) - IP(R_1) = D(R_1\text{-}R_2) - D(R_1^+\text{-}R_2), \tag{75}$$

$$EA(R_1) - EA(R_1R_2) = D(R_1\text{-}R_2) - D(R_1^-\text{-}R_2) \tag{76}$$

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 $n[E(I)(A\text{-}B) - E(I)(A^{+,-}\text{-}B)]$ 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 $\hat{D}$. 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:

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

and:

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

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:

$$\begin{tikzcd}
 & AR_n^{+,-} \; +/- \; e^- \arrow[dr] & \\
AR_n \arrow[ur] \arrow[dr] & & AR_{n-i}^{+,-} + iR +/- e^- \\
 & AR_{n-i} + i\,R \arrow[ur] &
\end{tikzcd} \qquad i = 1,n \qquad (79)$$

yields:

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

or:

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

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

$$\Delta H_i^{+,0,-} = i\,\hat{D}(A^{+,0,-} \text{---} B), \qquad (82)$$

Eqs. 80 and 81 can be rewritten as:

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

and:

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

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

$$\sum_{i=1}^{n} i\,[\mathrm{IP}(\mathrm{AR}_n) - \mathrm{IP}(\mathrm{AR}_{n-i})] = \sum_{i=1}^{n} i^2\,[\hat{D}(\mathrm{A\text{-}R}) - \hat{D}(\mathrm{A^+\text{-}R})] \qquad (85)$$

and:

$$\sum_{i=1}^{n} i\,[\mathrm{EA}(\mathrm{AR}_{n-i}) - \mathrm{EA}(\mathrm{AR}_n)] = \sum_{i=1}^{n} i^2\,[\hat{D}(\mathrm{A\text{-}R}) - \hat{D}(\mathrm{A^-\text{-}R})]. \qquad (86)$$

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, $\hat{D}(\mathrm{A\text{-}R})$ can be approximated from the equations:

$$\mathrm{IP}(\mathrm{AR}_n) - \mathrm{IP}(\mathrm{A}) = n\,[\hat{D}(\mathrm{A\text{-}R}) - \hat{D}(\mathrm{A^+\text{-}R})] \qquad (87)$$

or:

$$\mathrm{EA}(\mathrm{A}) - \mathrm{EA}(\mathrm{AR}_n) = n\,[\hat{D}(\mathrm{A\text{-}R}) - \hat{D}(\mathrm{A^-\text{-}R})]. \qquad (88)$$

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:

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

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 $\delta V'$ 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:

$$I_f = N\, I_i. \tag{90}$$

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

$$V_f = V_i + \Delta X. \tag{91}$$

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.

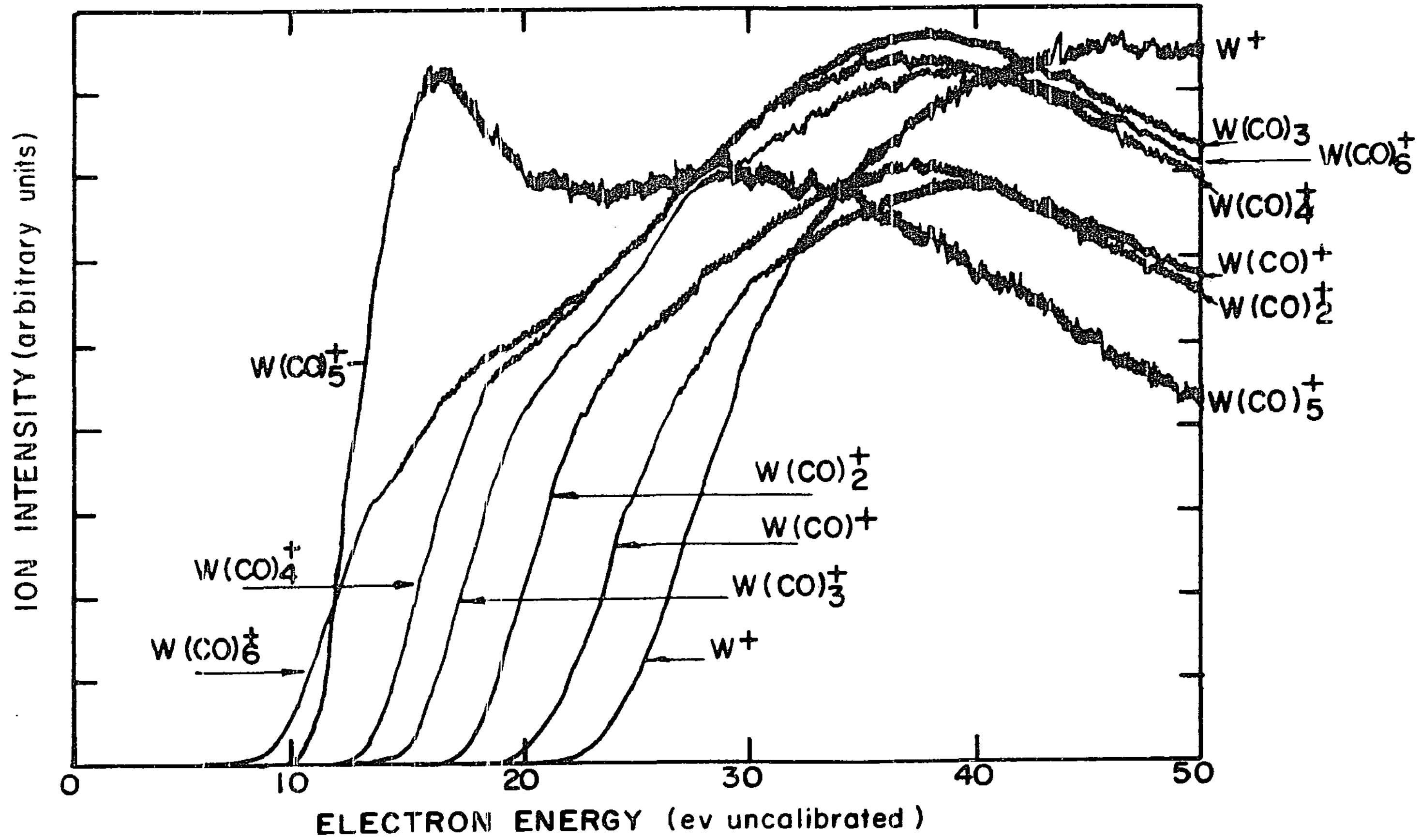


Figure 1. Ionization efficiency curves for the positive ions of $W(CO)_6$.

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 μs. 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 μs.

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 kΩ load is always across the DC-DC converter output.

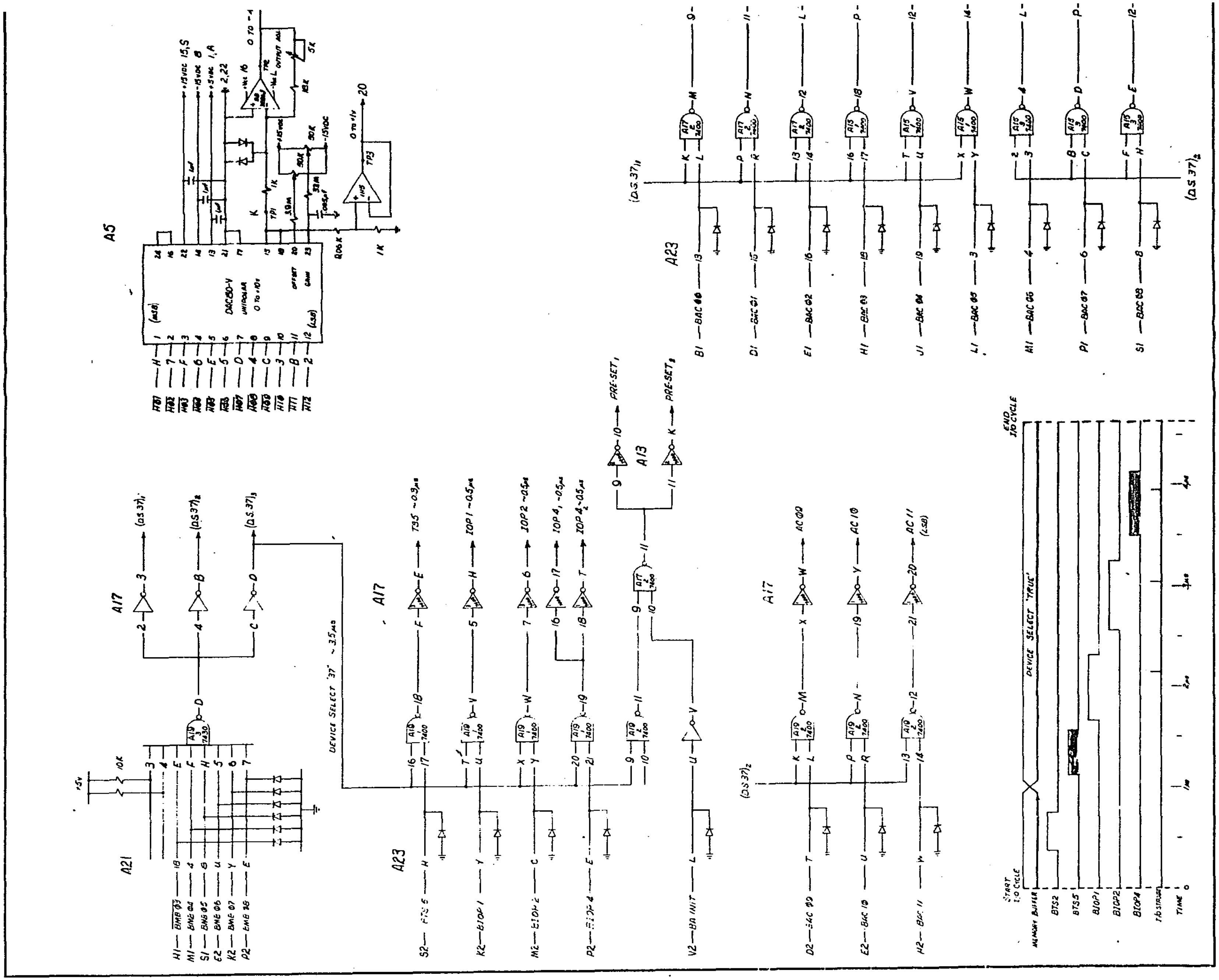
A 12-bit digital-to-analog converter, which was designed and built in the Ames Laboratory at Iowa State University, was used to supply the electron accelerating energy. A circuit diagram for the converter and its interface to the input/output bus of the PDP-12 are given in Figure 2. The converter is 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.

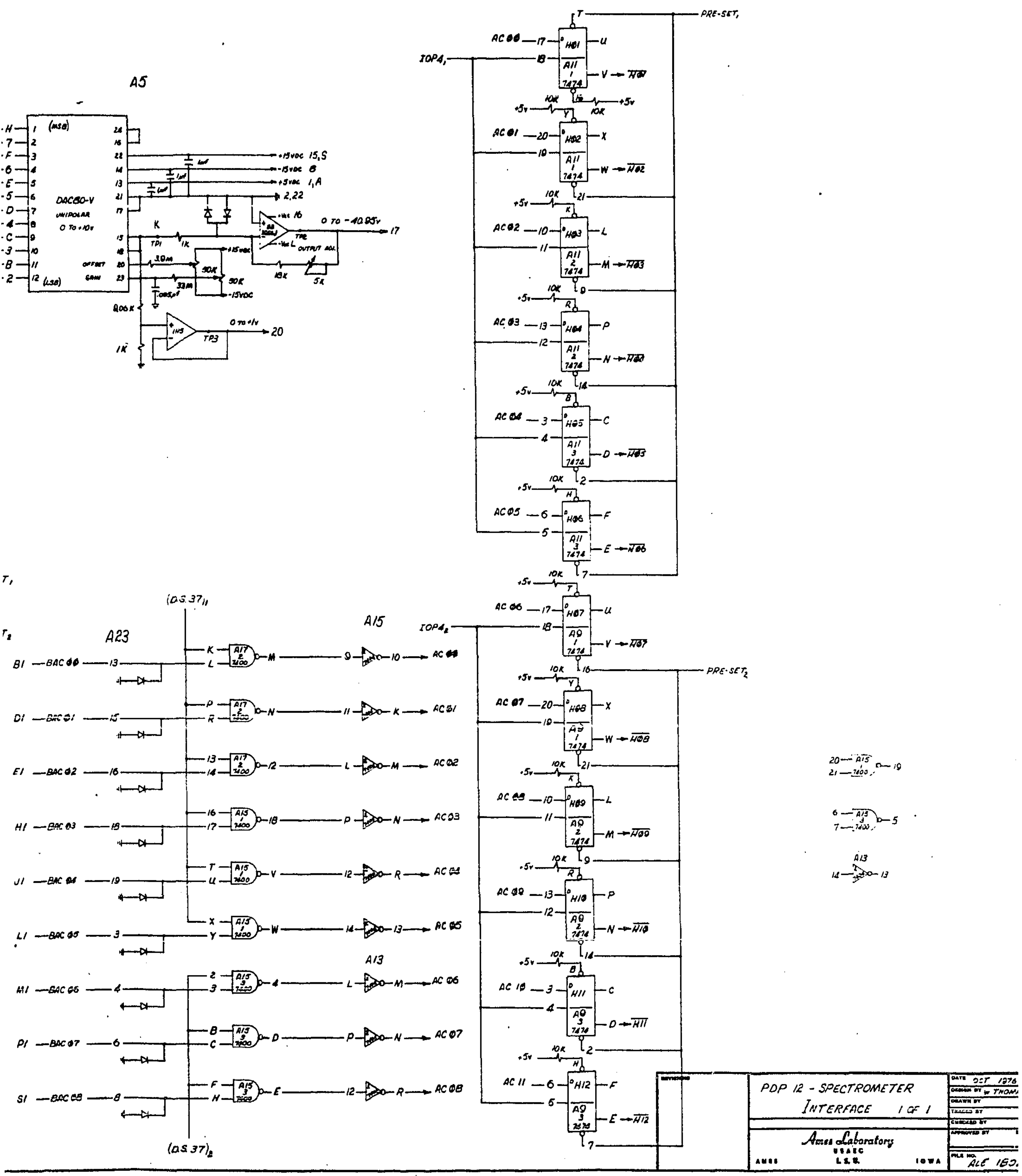
As far as the ionization efficiency experiment is concerned, the replacement of the electron energy potentiometer by the D-A converter produced one change. The electron accelerating voltage is no longer continuously variable. It must be incremented under program control. The voltage of the smallest increment 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

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).


A5
DAC80-V
UNIPOLAR
0 TO +10V
OFFSET
GAIN
(MSB)
(LSB)
0 TO -1
OUTPUT ADJ
5K
TP1
TP2
TP3
0 TO +1V
20
A17
A13
A19
A21
A23
7400
7430
10K
+5V
(D.S.37)1
(D.S.37)2
(D.S.37)3
DEVICE SELECT '37' ~3.5µs
T35 ~0.9µs
IOP1 ~0.5µs
IOP2 ~0.5µs
IOP4 ~0.5µs
PRE-SET1
PRE-SET2
AC 00
AC 10
AC 11 (LSB)
S2 — BTS 5
K2 — BIOP 1
M2 — BIOP 2
P2 — BIOP 4
V2 — BA INIT
D2 — BAC 09
E2 — BAC 10
H2 — BAC 11
H1 — BMB 03
M1 — BMB 04
S1 — BMB 05
E2 — BMB 06
K2 — BMB 07
P2 — BMB 08
B1 — BAC 00
D1 — BAC 01
E1 — BAC 02
H1 — BAC 03
J1 — BAC 04
L1 — BAC 05
M1 — BAC 06
P1 — BAC 07
S1 — BAC 08
START I/O CYCLE
END I/O CYCLE
MEMORY BUFFER
BTS2
BTS5
BIOP1
BIOP2
BIOP4
I/O STROBE
TIME
DEVICE SELECT 'TRUE'
0
1µs
2µs
3µs
4µs



PDP 12 - SPECTROMETER
INTERFACE 1 OF 1

REVISIONS

Ames Laboratory
USAEC
AMES I.S.U. IOWA

DATE OCT 1976
DESIGN BY W THOMA
DRAWN BY
TRACED BY
CHECKED BY
APPROVED BY
FILE NO. ALE 160

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	$1000 \leq$ ion mass < 1.
?4	$40.95 <$ starting energy < 0.
?5	$40.95 <$ energy increment ≤ 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	$8{,}000 \leq$ 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 sec ≤ delay time ≤ 0.01 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 ith 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 ith step, V_i, is related to the ith position of the acquisition vector:

$$V_i = SE - i(EI) \tag{92}$$

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

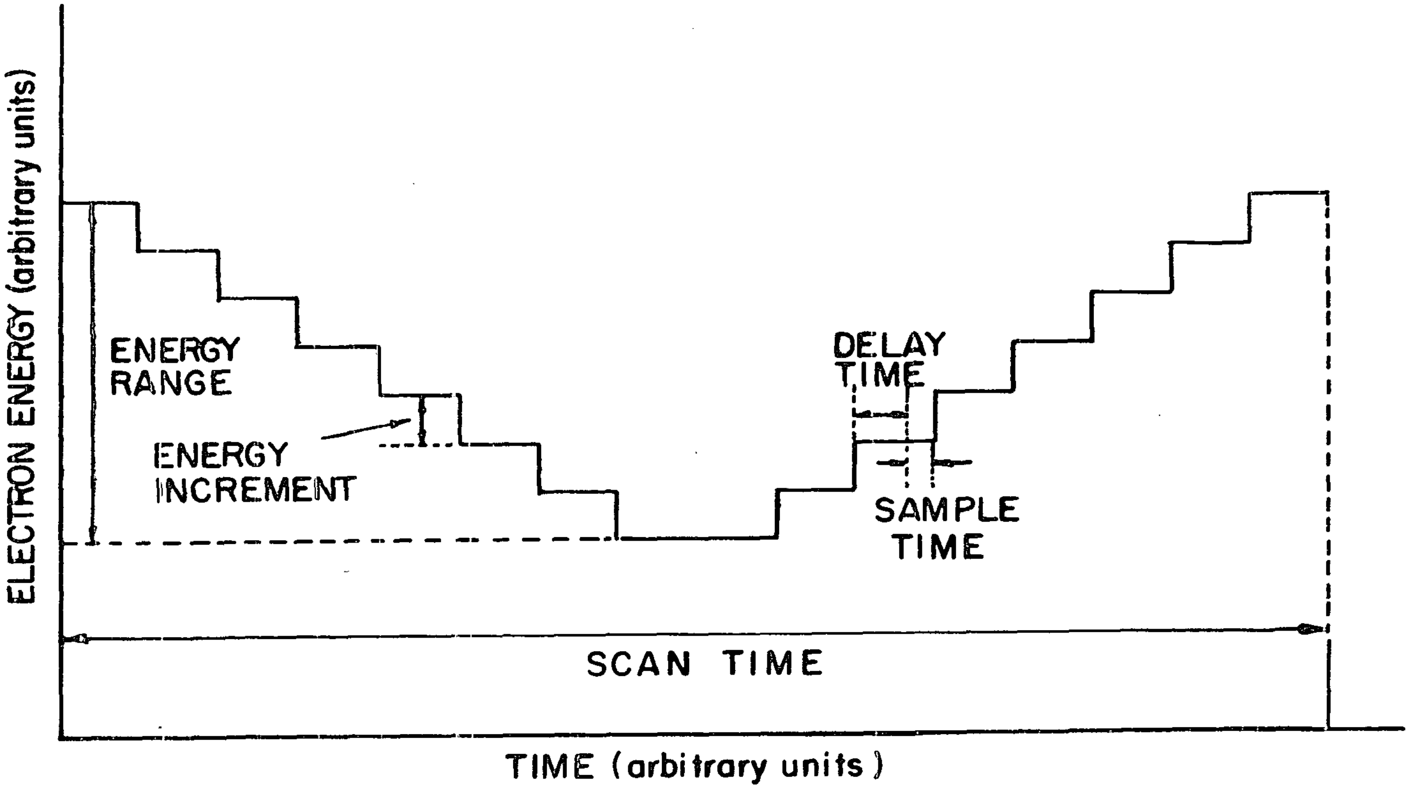


Figure 3. Timing cycle for the variation of electron energy during the acquisition of an ionization efficiency curve.

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 x1, x2, ···, xN 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 $Mo(CO)_6$ 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 $Mo(CO)_5^+$, $Mo(CO)_4^+$, $Mo(CO)_3^+$, $Mo(CO)_2^+$, $Mo(CO)^+$, 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 $Mo(CO)_5^+$, $Mo(CO)_4^+$, $Mo(CO)_3^+$, $Mo(CO)_2^+$, $Mo(CO)^+$, 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   13.46   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 labled. 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.

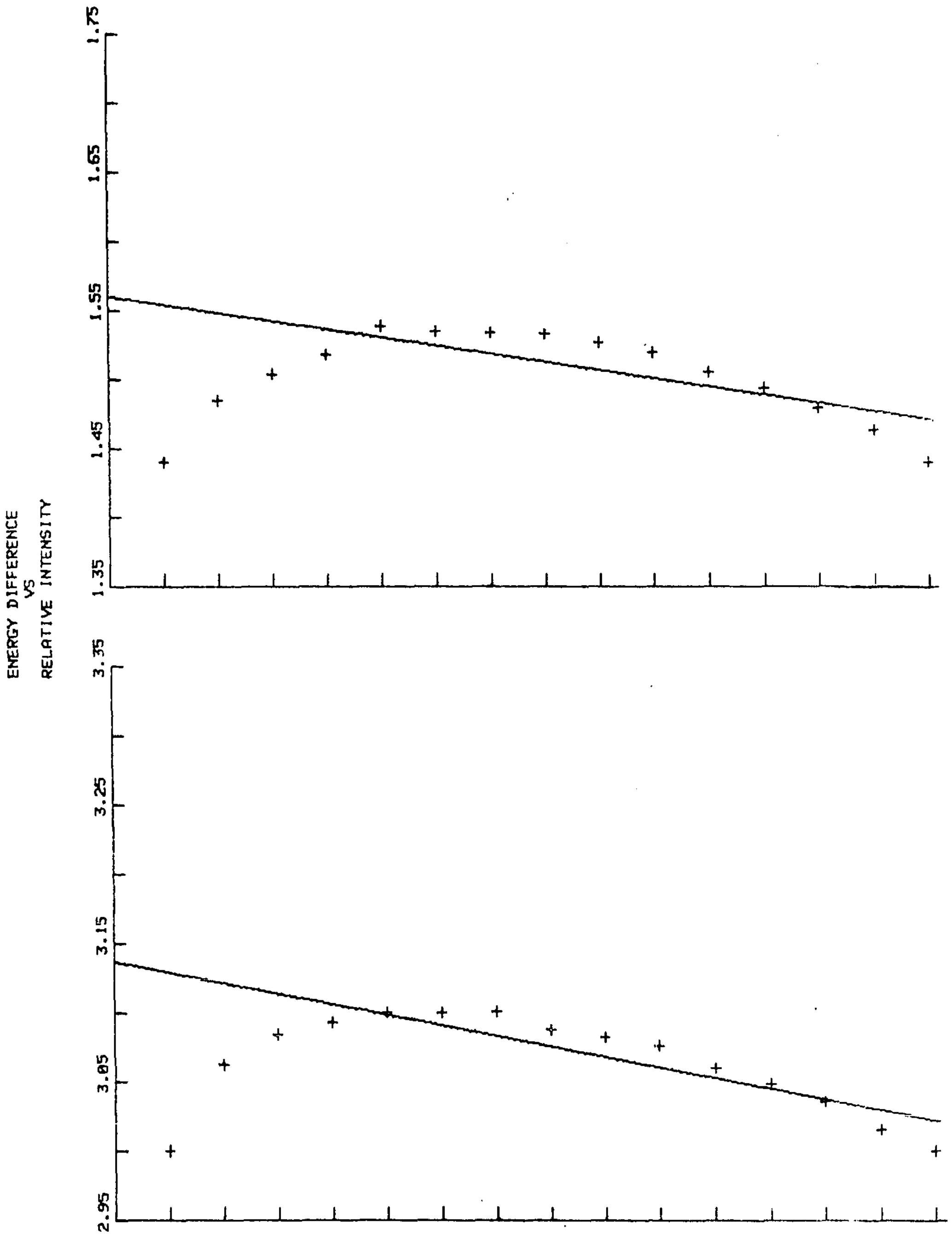


Figure 6. Printout of Warren's plots for the positive ions of $Mo(CO)_6$. $Mo(CO)_5^+$ (top), $Mo(CO)_4^+$ (bottom).

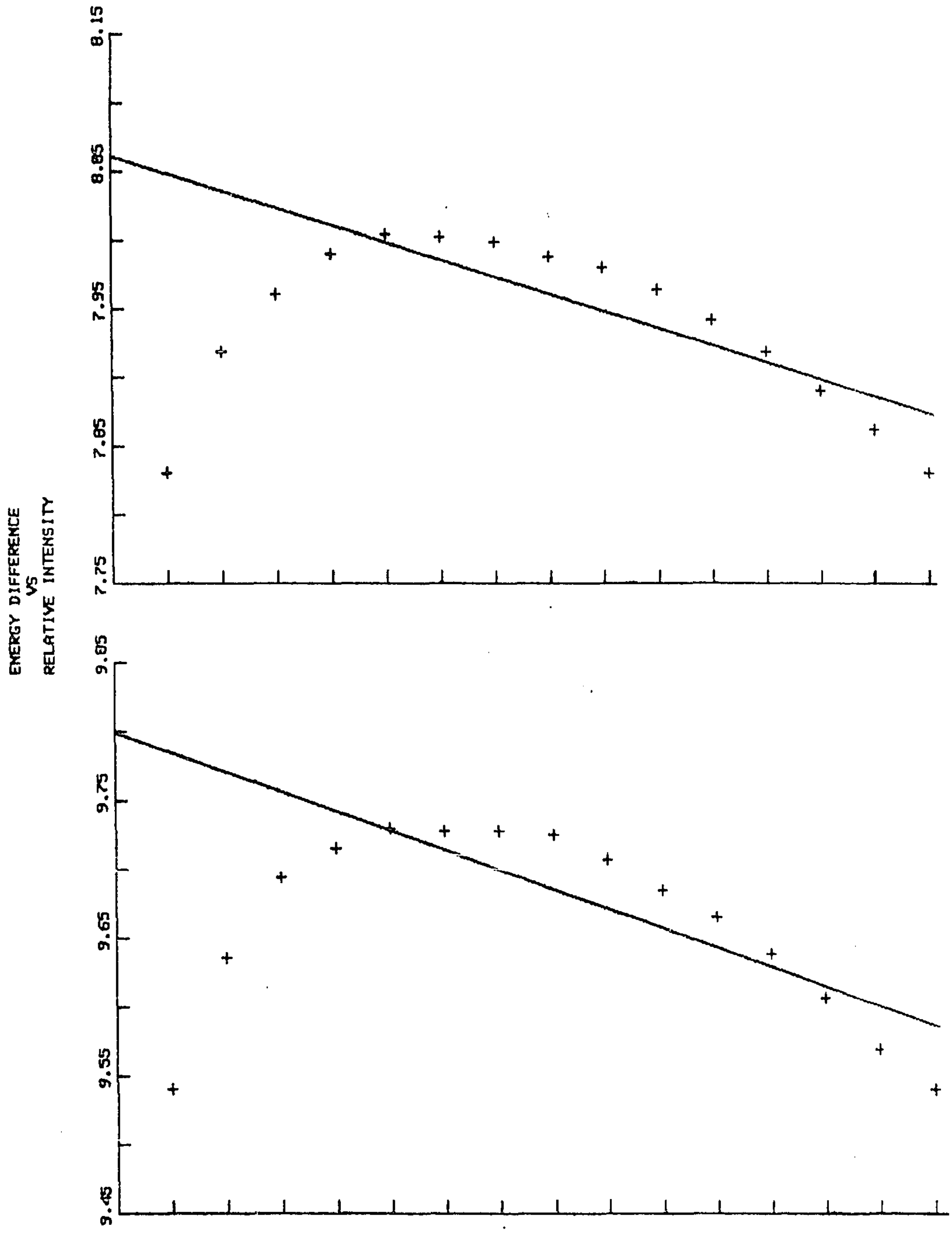


Figure 6. Continued. $Mo(CO)_3^+$ (top), $Mo(CO)_2^+$ (bottom).

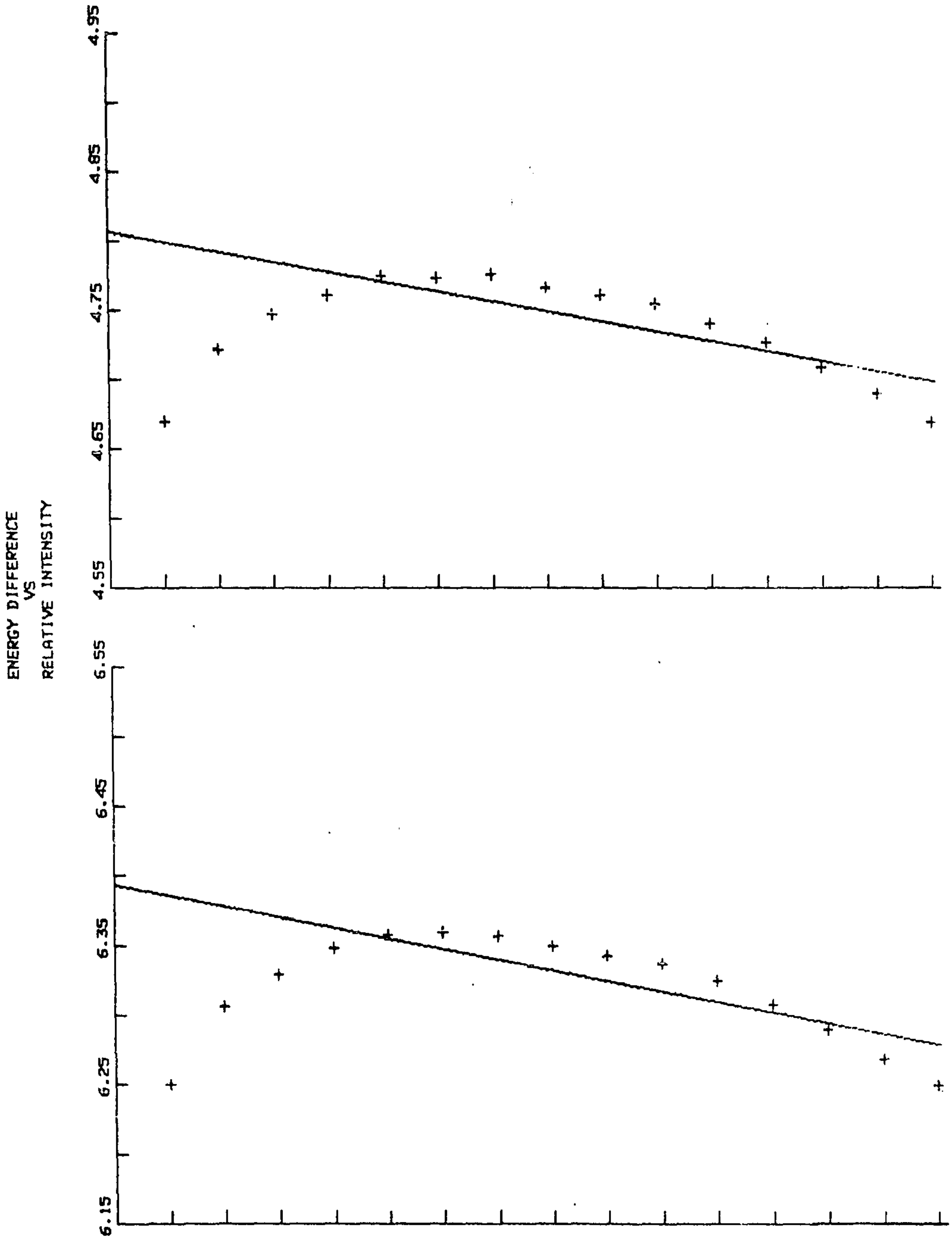


Figure 6. Continued. $Mo(CO)^+$ (top), Mo^+ (bottom).

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 $Mo(CO)_5^+$, $Mo(CO)_4^+$, $\cdots$, 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. <u>Operation of the system</u> 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:

$$\text{function output file} = \text{input files.} \tag{93}$$

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

$$\text{IEAS LT1:} \quad \text{X.ext} = \text{Y.ext.} \tag{94}$$

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 1000_8 to any number divisible by two up to 10000_8.

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±0.008	12.456	0.126	1.01
Ne	20	9.482±0.004	9.434	0.048	0.51
Ar	40	3.673±0.005	3.629	0.044	1.21
Kr	84	1.897±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 $Cr(CO)_6$ 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 $Mo(CO)_6$ and $W(CO)_6$ also demonstrates

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

	$Cr(CO)_6$			$Mo(CO)_6$
Ion	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±0.02	1.70±0.02	1.76±0.03
3.18±0.02	3.62±0.02	3.68±0.03
4.85±0.02	5.46±0.01	5.50±0.03
6.44±0.04	7.69±0.03	7.92±0.02
8.16±0.04	9.76±0.05	10.02±0.05
9.94±0.05	12.41±0.04	12.41±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. $\hat{D}(M^+\text{-CO})$ (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 $Cr(CO)_6^+$ 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 $MnRe(CO)_{10}$, $MnTc(CO)_{10}$, and $TcRe(CO)_{10}$. The preparation and characterization of $ReMn(CO)_{10}$ have been described previously [41] De Jong and Wiles [42] speculated that $MnTc(CO)_{10}$ was formed in low yields (< 10%) when $^{99m}{\cdot}Tc(CO)_5$ produced from the β decay of $^{99}Mo(CO)_6$ reacted with photochemically produced $\cdot Mn(CO)_5$. 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, $M(CO)_5^-$, of one metal atom with the pentacarbonyl halide, $M'(CO)_5X$, of the other:

$$M(CO)_5^- + M'(CO)_5X \rightarrow MM'(CO)_{10} + X^-. \tag{95}$$

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:

$$M_2(CO)_{10} + 2Na/Hg \xrightarrow[N_2]{THF} 2M(CO)_5^- + 2Na^+, \tag{96}$$

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

$$M_2'(CO)_{10} + X_2 \rightarrow 2M'(CO)_5X. \tag{97}$$

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 ($\beta_{max} = 0.3$ MeV). When used on a small scale (< 50 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 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 $Tc_2(CO)_{10}$ 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 μl 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 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 $Mn_2(CO)_{10}$ (2.0 g, 5.13 mmol) in 40 ml of carbon disulfide was stirred while Br_2 (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 Br_2 (0.1 ml, 1.95 mmol) in carbon disulfide (40 ml) was added slowly (10 min) to a suspension of $Tc_2(CO)_{10}$ (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 $Re_2(CO)_{10}$ (1.0 g, 1.54 mmol) in 25 ml of carbon disulfide. After the solution was evaporated to dryness under reduced pressure, the white crystaline 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 $Tc_2(CO)_{10}$. 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 $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ 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 $Mn(CO)_5Br$ since $Re(CO)_5^-$ is the stronger nucleophile [45]. When this reaction was done, a gas chromatographic analysis of the product gave $Mn_2(CO)_{10}$ (22%), $ReMn(CO)_{10}$ (8%), and $Re_2(CO)_{10}$ (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 $Re(CO)_5Br$. The sublimate of this reaction contained $Mn_2(CO)_{10}$(11%) $MnRe(CO)_{10}$(77%), and $Re_2(CO)_{10}$(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, $Re(CO)_5^-$ will cleave it forming the more stable $Re_2(CO)_{10}$ molecule and $Mn(CO)_5^-$ which is oxidized to $Mn_2(CO)_{10}$ upon exposure to air. The nucleophilic strength of $Mn(CO)_5^-$ is insufficient to break the Mn-Re bond. The large percentage of $Re_2(CO)_{10}$ formed from the reaction with $Re(CO)_5^-$ provides additional evidence for this explanation. As a result, the optimum method for synthesizing the mixed-metal carbonyls is to react the <u>weakest</u> nucleophile with the corresponding bromide. Since the nucleophilic strength increases down the family, $MnTc(CO)_{10}$ and $TcRe(CO)_{10}$ were prepared by the following reactions:

$$Mn(CO)_5^- + Tc(CO)_5Br \rightarrow MnTc(CO)_{10} \qquad (98)$$

and:

$$Tc(CO)_5^- + Re(CO)_5Br \rightarrow TcRe(CO)_{10}. \qquad (99)$$

a. <u>$MnRe(CO)_{10}$</u> Manganese decacarbonyl (102 mg, 0.26 mmol) was reduced to $Mn(CO)_5^-$ 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 $Mn_2(CO)_{10}$(11%), $MnRe(CO)_{10}$(77%), and $Re_2(CO)_{10}$(12%).

b. $MnTc(CO)_{10}$ A solution of $Mn_2(CO)_{10}$ (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 $Mn_2(CO)_{10}$ (42%), $MnTc(CO)_{10}$ (55%), and $Tc_2(CO)_{10}$ (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 $Tc_2(CO)_{10}$ (37%), $TcRe(CO)_{10}$ (52%), and $Re_2(CO)_{10}$ (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 $MnTc(CO)_{10}$, $Tc_2(CO)_{10}$, $MnRe(CO)_{10}$, $TcRe(CO)_{10}$, and $Re_2(CO)_{10}$. 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, $Mn_2(CO)_{10}$ 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 $MM'(CO)_{10}$ and the $M_2(CO)_{10}$ and $M'_2(CO)_{10}$ 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

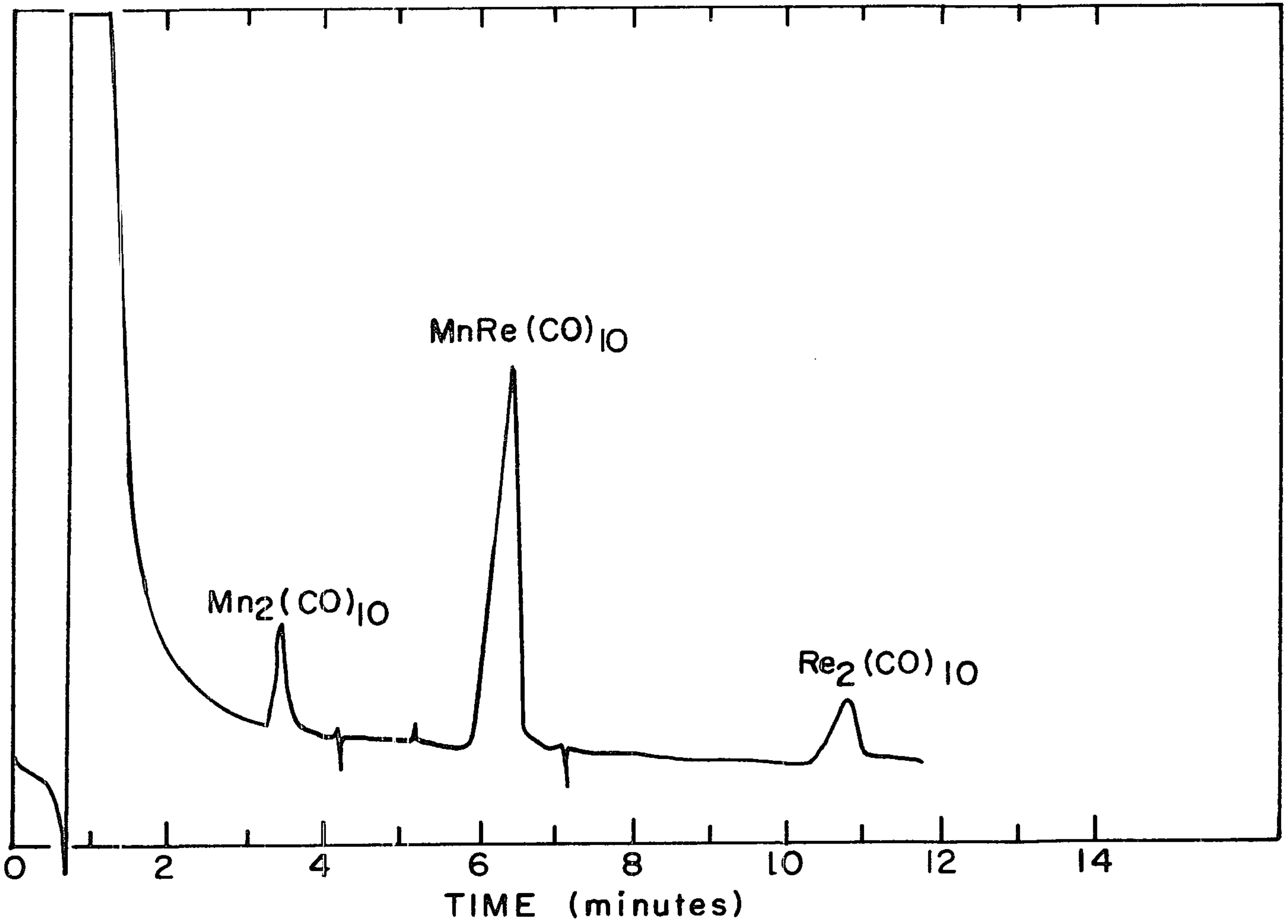


Figure 7. Gas chromatogram of a saturated pentane solution of the sublimate from a preparation of $MnRe(CO)_{10}$.

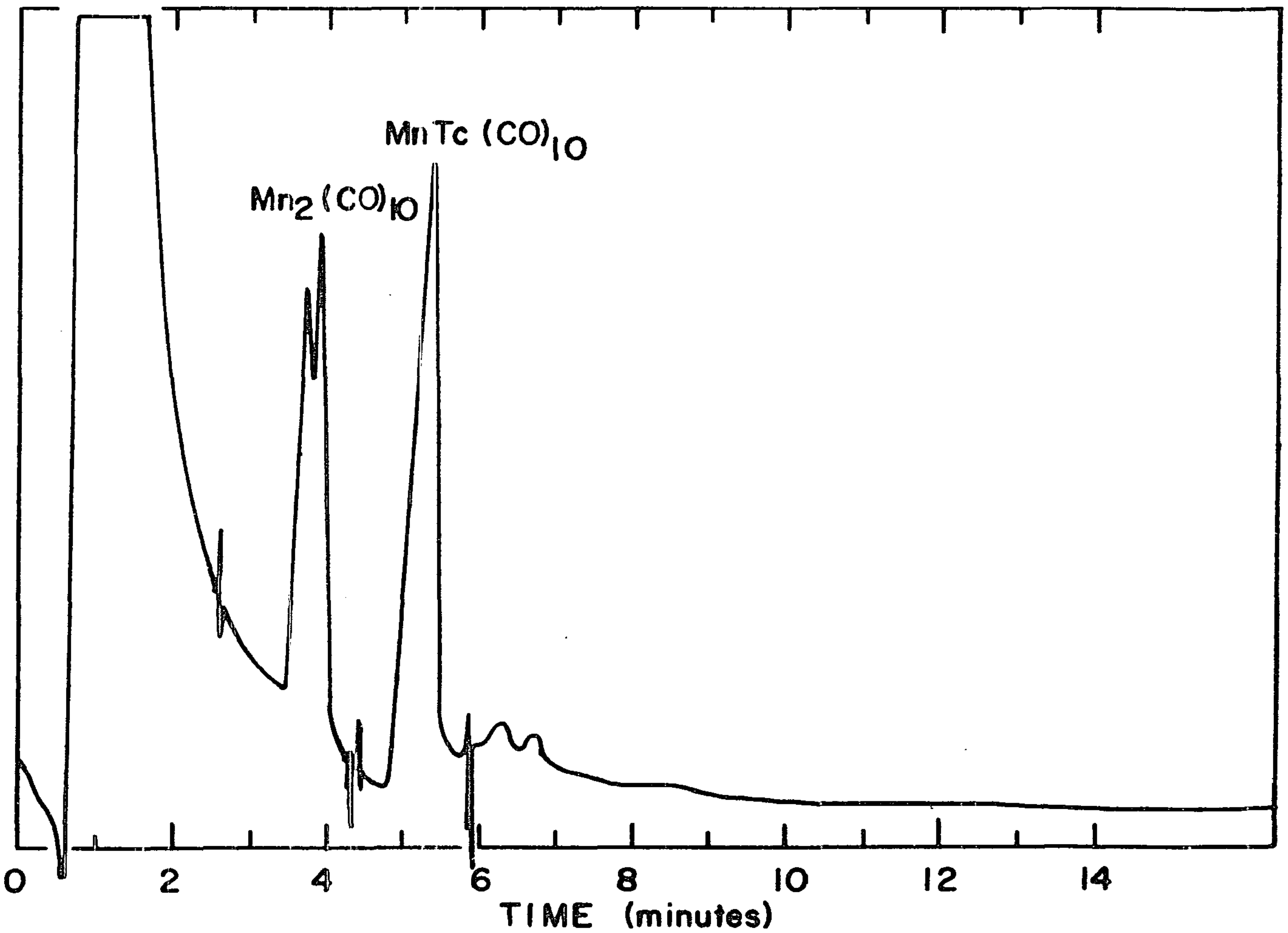


Figure 8. Gas chromatogram for two injections of a saturated pentane solution of the sublimate from a preparation of $MnTc(CO)_{10}$.

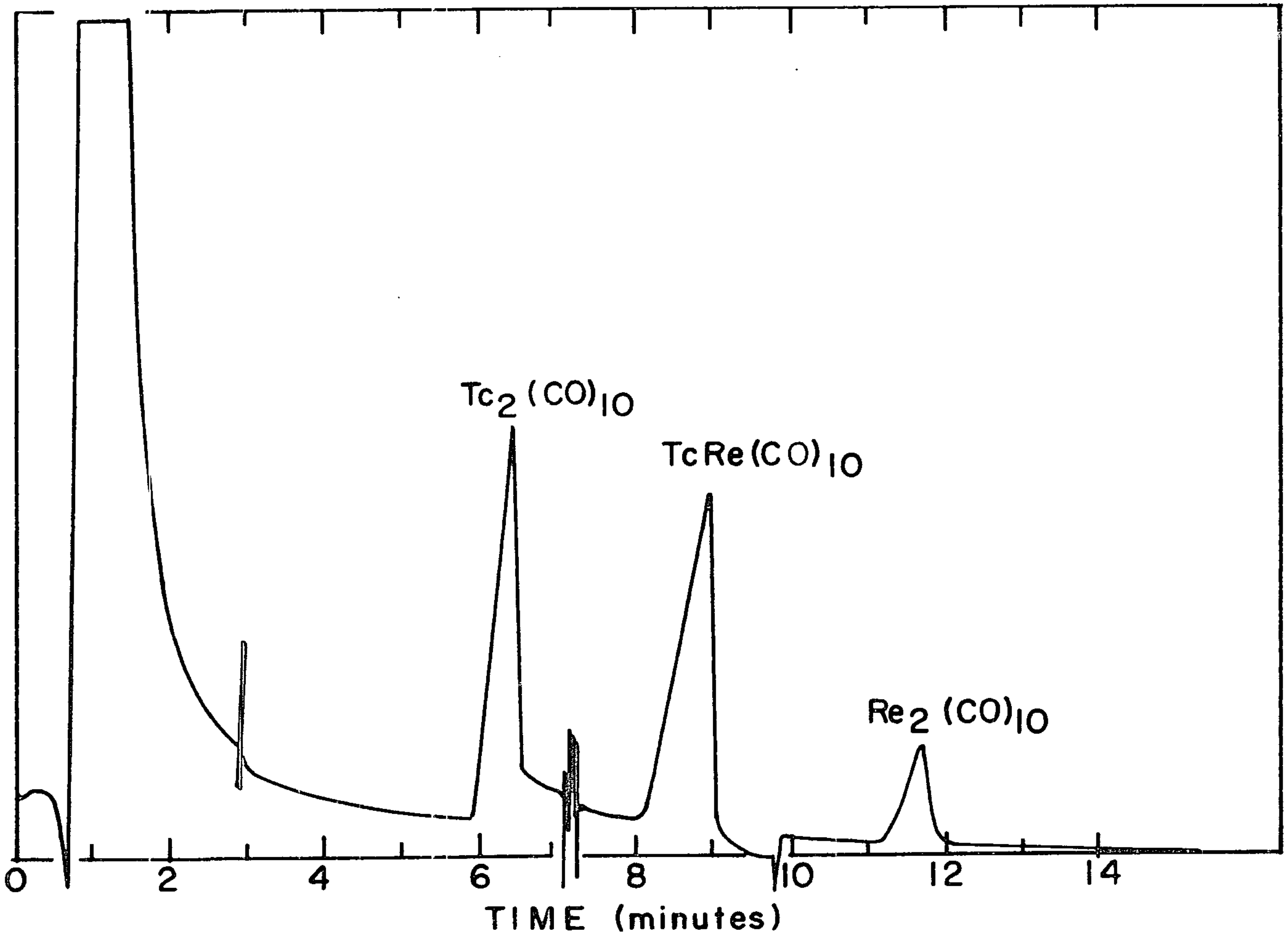


Figure 9. Gas chromatogram of a saturated pentane solution of the sublimate from a preparation of $TcRe(CO)_{10}$.

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 $MnRe(CO)_{10}$ and $TcRe(CO)_{10}$ (> 99%) were obtained in this manner. The Mn-Tc compound could not be separated from a small impurity of $Mn_2(CO)_{10}$ (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 $MnRe(CO)_{10}$ have been reported [43] and identification was made by direct comparison. The identification of $MnTc(CO)_{10}$ and $TcRe(CO)_{10}$ 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 $M_2(CO)_{10}$ 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 $MnRe(CO)_{10}$(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,

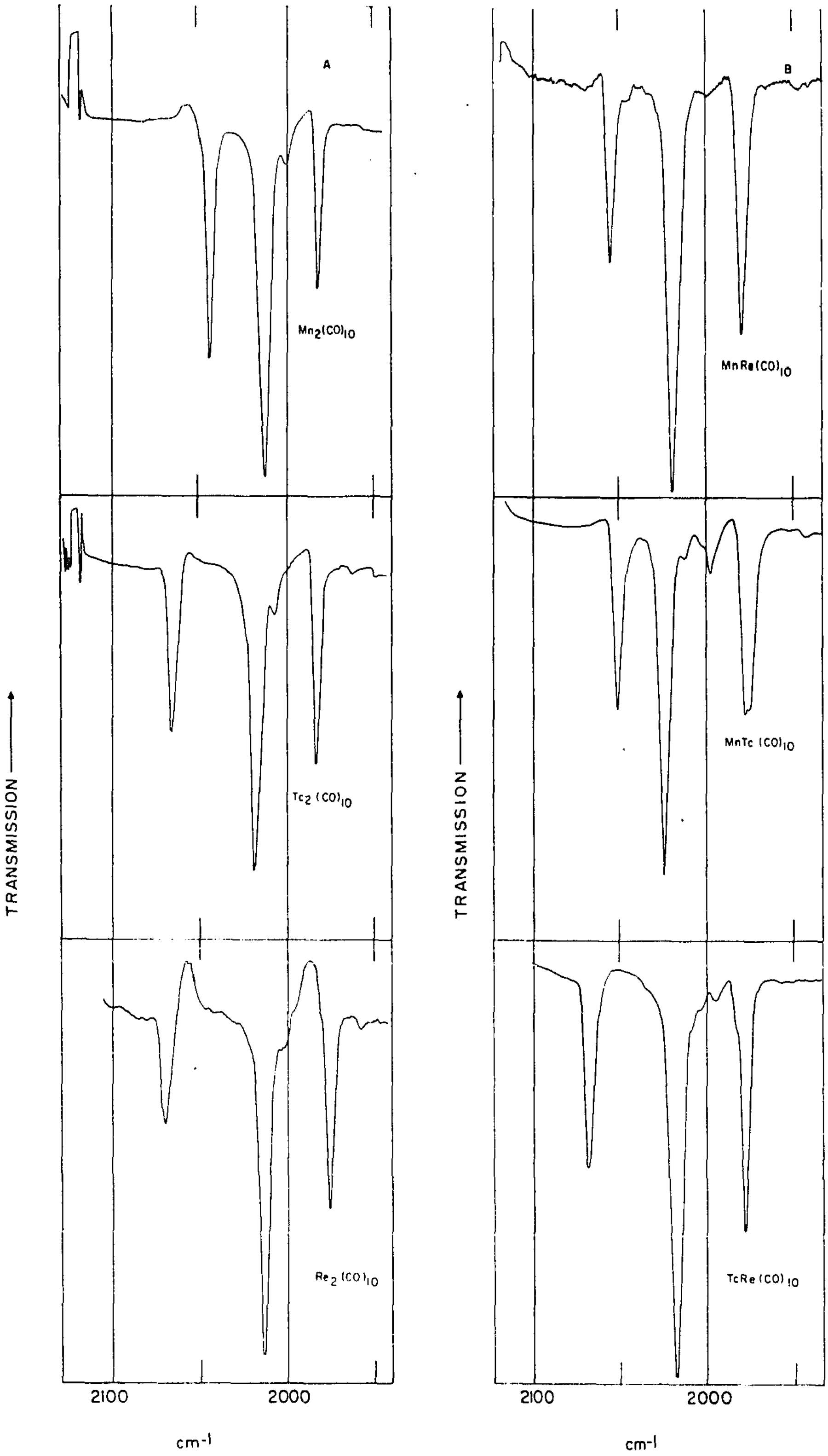


Figure 10. Carbonyl region of the infrared spectra of the Group VIIB dimetal (A) and mixed-metal (B) decacarbonyls.

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 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 arguement 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]		
$Mn_2(CO)_{10}$	2044	2013	1983	2044	2013	1983
$Tc_2(CO)_{10}$	2065	2017	1984	2064	2017	1984
$Re_2(CO)_{10}$	2070	2014	1976	2070	2014	1976
$MnRe(CO)_{10}$	2054	2017	1978	2054	2017	1978
$MnTc(CO)_{10}$	2051	2024	1979, 1975			
$TcRe(CO)_{10}$	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:

$$M(CO)_5L^+ \rightarrow M(CO)_{5-n}L^+ + nCO \qquad n = 1,2,\cdots,5 \qquad (100)$$

and:

$$M(CO)_5L^+ \rightarrow M(CO)_{5-n}^+ + nCO + L \qquad n = 0,1,\cdots,5. \qquad (101)$$

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 $\hat{D}(M^+\text{-CO})_H$, the metal-carbonyl bond energy in the hexacarbonyls; $\hat{D}(M^+\text{-CO})_T$, the metal-carbonyl bond energy in the thiocarbonyls; and $\hat{D}(M^+\text{-CS})$, the metal-thiocarbonyl bond energy. The fragmentation energies and average bond dissociation energies, $\bar{D}(M^+\text{-CO})_H$, 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 $\bar{D}(M^+\text{-CO})_H$ can be calculated (Eq. 77) from the thermochemical results for $\bar{D}(M\text{-CO})_H$ [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,···,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 $Mo(CO)_5CS$ contained 30-40% $Mo(CO)_6$. The magnitute of this impurity precluded obtaining any meaningful data for the $Mo(CO)_n^+$ ($n=0,1,\cdots,5$) 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 +/- 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 +/- mass spectrometer. The instrument was operated at 2000 V ion accelerating energy. A constant ionizing current of 2 μa was used for the Cr and Mo complexes. To compensate for their lower volatility, the data for the tungsten compounds were obtained with 8 μa 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 $Cr(CO)_5CS$ and $W(CO)_5CS$ were obtained graphically while those for $Mo(CO)_5CS$ 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 = Mn, Tc, Re; L = $M(CO)_5$) 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:

$$M(M')(CO)_{10}^{+} \rightarrow M(M')(CO)_{10-n}^{+} + nCO \qquad n = 0,1,\cdots,10 \qquad (102)$$

where the symbolism M(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 $S_5A((A')S_5)$. The former description implies that ten equivalent carbonyls are bonded to the central M(M') moiety. According to this interpretation one ionic bond energy, $\hat{D}(M(M')^{+}\text{-}CO)$, would be calculated from a least-squares treatment of the fragmentation data. The latter model distinguishes the M-C energies of the two $M(CO)_5$ groups. Two quantities would be calculated by the least-squares method, $\hat{D}(M(M')^{+}\text{-}CO)$ and $\hat{D}'(M(M')^{+}\text{-}CO)$. The energy of the M-(M') bond is calculated from the fragmentation energies of the processes:

$$(CO)_5M\text{-}(M')(CO)_5^+ \rightarrow \begin{matrix} (M)(CO)_{5-n}^+ + M(CO)_5 + nCO \\ \text{or} \\ M(CO)_{5-n}^+ + (M')(CO)_5 + nCO \end{matrix} \qquad n = 0,1,\cdots,5. \tag{103}$$

It must be emphasized that the energy of the first fragmentation process (n=0) is <u>not</u> the energy of the M-(M') bond. The energy of this process, as well as the energies of the remaining processes (n = 1,2,$\cdots$,5), reflects the difference between the M-C energies in the free and bound $M(CO)_5$ ($(M')(CO)_5$) ligand. In other words, the M^+-CO ($(M')^+$-CO) energy in the $M(CO)_5^+$ ($(M')(CO)_5^+$) ion is different from the M-CO ((M')-CO) energy in the $M(CO)_5$ ($(M')(CO)_5$) 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, $\hat{D}(M^+\text{-}(M'))$, $\hat{D}(M^+\text{-}CO)$ ($\hat{D}((M')^+\text{-}CO)$), and $\hat{D}(M\text{-}CO)$ ($\hat{D}((M')\text{-}CO)$). All M-C energies include the difference between the C-O energy in the bound and free carbonyl.

Samples of $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$ were obtained from commercial sources and were purified by vacuum sublimation before use. The mass spectrum of $Tc_2(CO)_{10}$ indicated a small impurity (< 10%) of a compound which was identified as $TcRe(CO)_{10}$. Pure $Tc_2(CO)_{10}$ was obtained by preparative gas chromatography. No impurities were noted in $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$. The mixed-metal decacarbonyls were synthesized and purified as described in Chapter 3. The small amount of $Mn_2(CO)_{10}$ 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 $Mn_2(CO)_{10}$ 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 $Re_2(CO)_{10}$. 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 $Mn_2(CO)_{10}^+$ to 654 for $Re_2(CO)_{10}^+$, 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 $Mn_2(CO)_{10}^+$ and $Re_2(CO)_{10}^+$ 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, $M(M')(CO)_{10-n}^{+}$ ($n = 0,1,\cdots,10$). 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 $Mn_2(CO)_{10}$,

$MnTc(CO)_{10}$, $Tc_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$. 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 $M(M')(CO)^{+}_{10-n}$ (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 μa 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 $Tc_2(CO)_{10}$. 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 that 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 thiocarbonyls 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 $Mo(CO)_n^+$ ($n = 0,1,\cdots,5$). 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 cyclopentadienylmanganese 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.

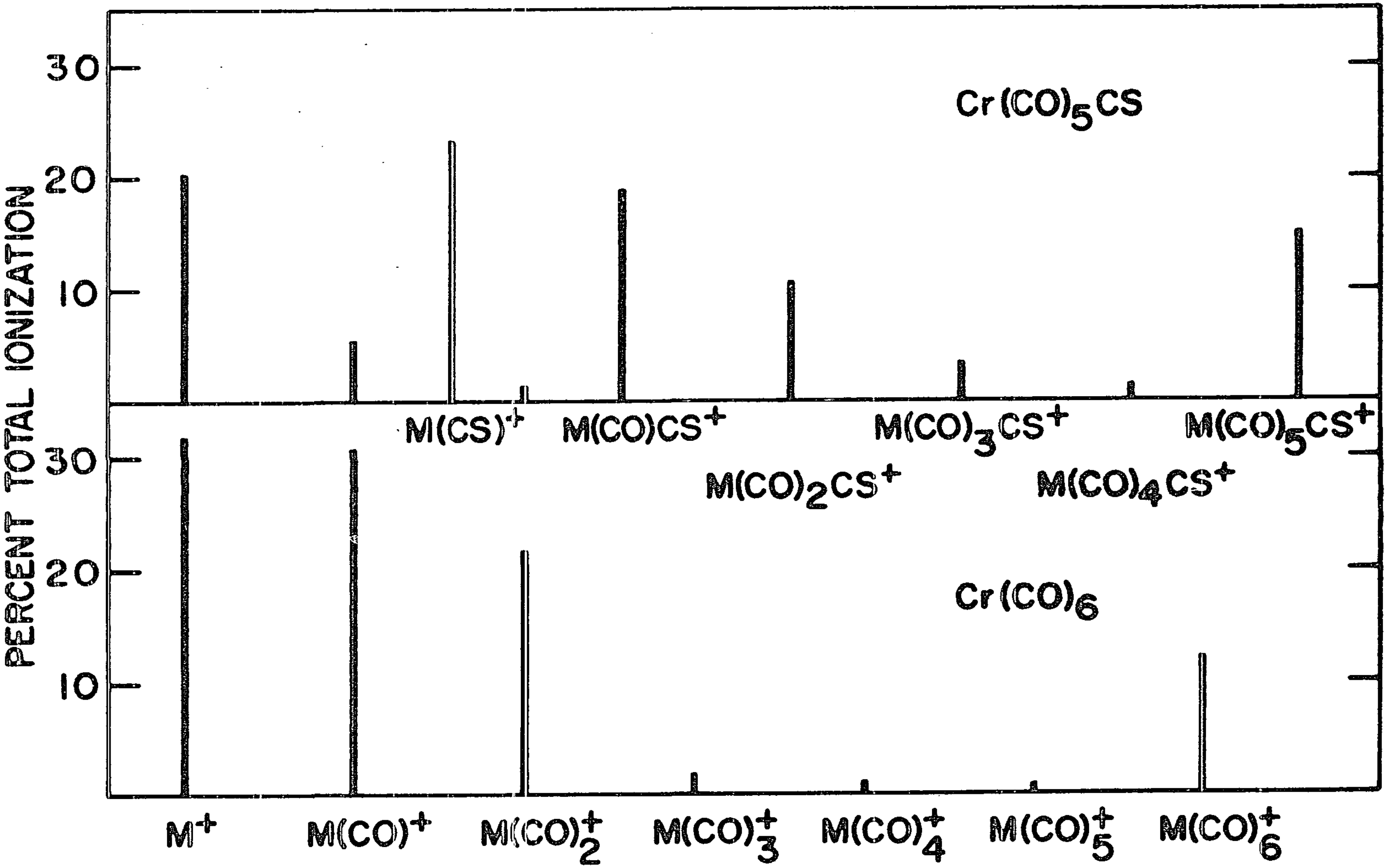


Figure 11. Monoisotopic mass spectra (50 eV) of $Cr(CO)_5CS$ and $Cr(CO)_6$.

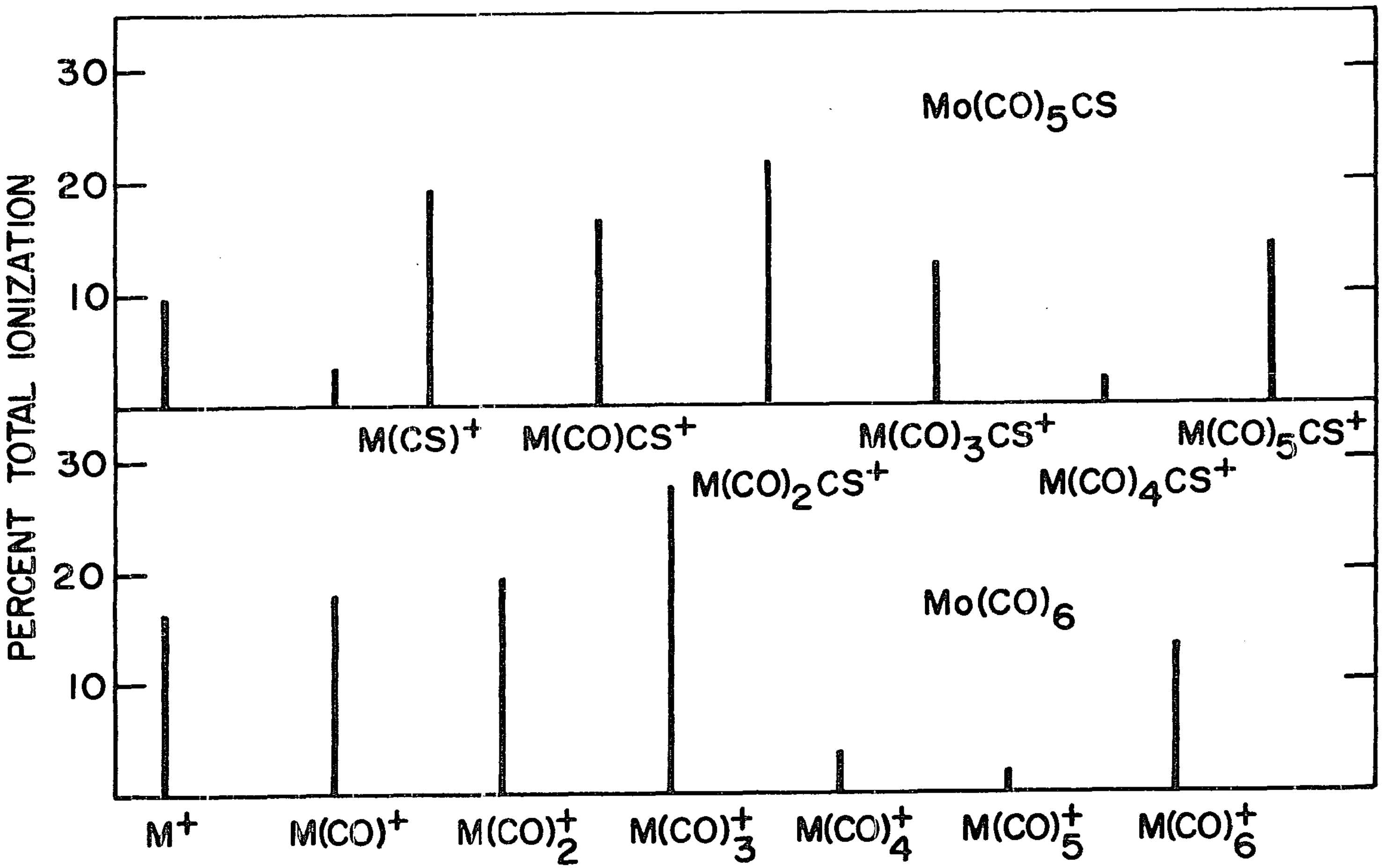


Figure 12. Monoisotopic mass spectra (50 eV) of Mo(CO)$_5$CS and Mo(CO)$_6$.

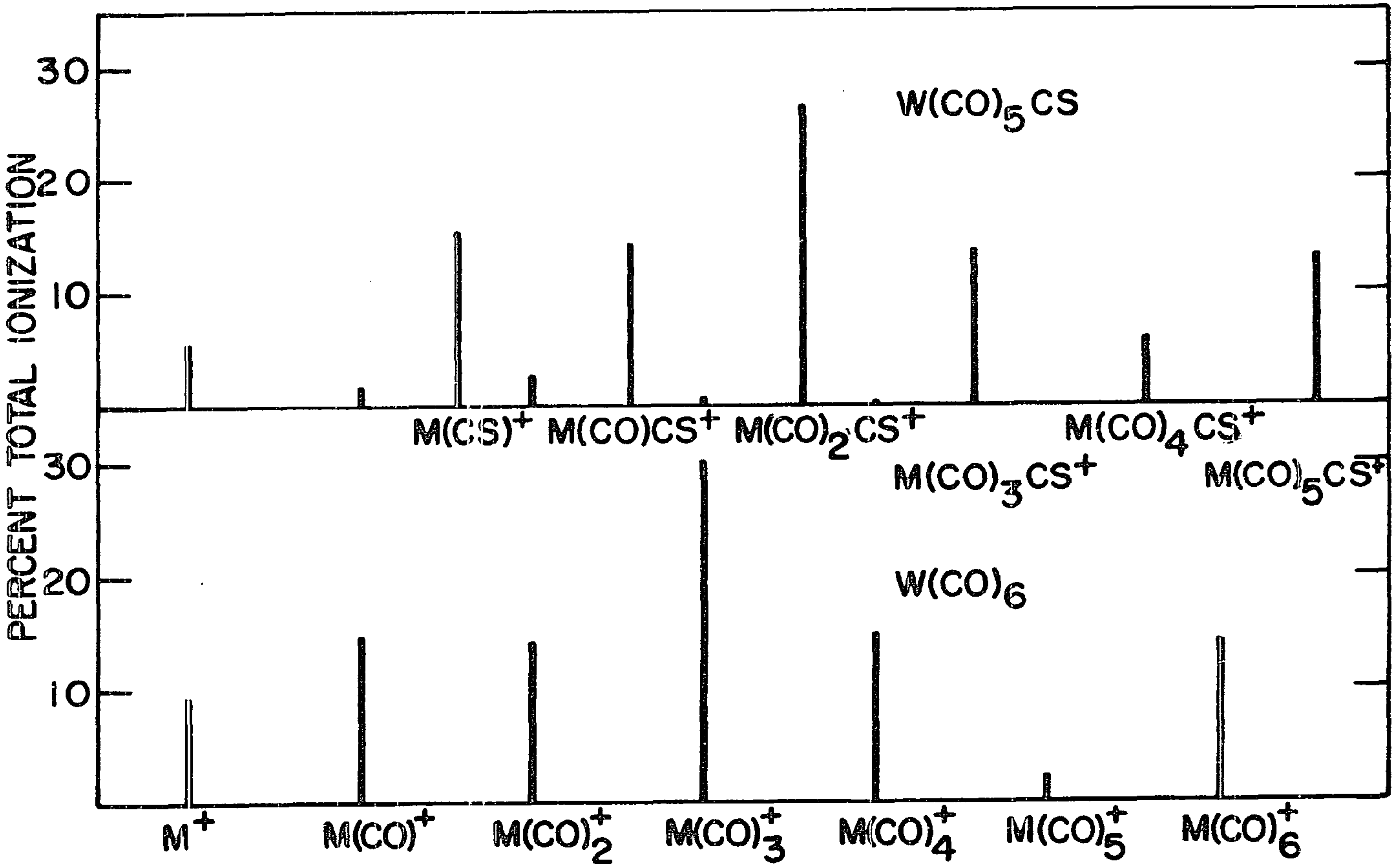


Figure 13. Monoisotopic mass spectra (50 eV) of $W(CO)_5CS$ and $W(CO)_6$.

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 $Cr(CO)_5CS$ and $W(CO)_5CS$ illustrates that results can be obtained quite precisely (i.e. to a few hundreths 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. IP(CO) = 14.01 eV, IP(CS) = 11.34 eV, and ΔIP(CO-CS) = 2.67 eV, hence $\Delta IP(M(CO)_6\text{-}M(CO)_5CS)$ 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]
$Cr(CO)_6$	8.42 ± 0.03	8.40 ± 0.02
$Cr(CO)_5CS$	8.31 ± 0.03	8.16 ± 0.02
$Mo(CO)_6$	8.46 ± 0.01	8.50 ± 0.02
$Mo(CO)_5CS$	8.18 ± 0.02	---
$W(CO)_6$	8.60 ± 0.02	8.56 ± 0.02
$W(CO)_5CS$	8.22 ± 0.01	8.30 ± 0.02[b]

[a] Hexacarbonyl results are taken from Ref. [69] and those for the thiocarbonyls from Ref. [66].

[b] Average 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:

$$\begin{tikzcd}
 & M(CO)_n^{+} + e^{-} \arrow[dr] & \\
M(CO)_n \arrow[ur] \arrow[dr] & & M^{+} + nCO + e^{-}. \\
 & M + nCO \arrow[ur] &
\end{tikzcd} \qquad (104)$$

It follows that:

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

where $\bar{D}(M^{+}\text{-}CO)$ and $\bar{D}(M\text{-}CO)$ 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 $\bar{D}(M^{+}\text{-}CO)$ and from the spectroscopic ionization potential of the central metal atom. This is not possible in general (e.g. $M(CO)_{n-1}L$) 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(C-O) = 11.14 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		
	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$
$M(CO)_6^+ \rightarrow M(CO)_5^+ + CO$	1.43 ± 0.01	1.56 ± 0.01	1.70 ± 0.02
$\rightarrow M(CO)_4^+ + 2CO$	2.03 ± 0.01	3.15 ± 0.01	3.62 ± 0.02
$\rightarrow M(CO)_3^+ + 3CO$	2.93 ± 0.01	4.83 ± 0.02	5.46 ± 0.01
$\rightarrow M(CO)_2^+ + 4CO$	4.09 ± 0.03	6.40 ± 0.02	7.69 ± 0.03
$\rightarrow M(CO)^+ + 5CO$	5.61 ± 0.02	8.06 ± 0.03	9.76 ± 0.05
$\rightarrow M^+ + 6CO$	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 $Cr(CO)_6$ [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 $D(W^+\text{-CO}) > D(Mo^+\text{-CO}) > D(Cr^+\text{-CO})$. 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, $\bar{D}(M^+\text{-CO})$. 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 $\bar{D}(M^+\text{-CO})$ 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 $\hat{D}(M^+\text{-CO})$. If the ith fragmentation is envisioned as occurring in the following manner:

$$M(CO)_6^+ \rightarrow M^+ + 6CO \rightarrow M(CO)_{6-i}^+ + iCO, \qquad (106)$$

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

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

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

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

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 $\bar{D}(M^+\text{-CO})$. 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 $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, respectively). As anticipated the electron impact and calorimetric dissociation energies do not agree. The differences between $\hat{D}(M^+-CO)$ and the calorimetric values for $\bar{D}(M^+-CO)$ 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 $Cr(CO)_6$ 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 $Cr(CO)_6$ 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 $\hat{D}(M^+\text{-CO})_T$, $\hat{D}(M^+\text{-CO})_H$, and $\hat{D}(M^+\text{-CS})$. 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

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

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

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

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

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	$\hat{D}(M^+\text{-CO})_H$	$\hat{D}(M^+\text{-CO})_T$	$\hat{D}(M^+\text{-CS})$
$Cr(CO)_5CS$	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-$W(CO)_4(CNC_6H_{11})CS$ [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 $\hat{D}(M^+\text{-}CO)_H$ 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 $\hat{D}'(M^+\text{-}CO)_T$ and $\hat{D}(M^+\text{-}CO)_T$ 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:

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

and:

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

for $Mo(CO)_5CS$. The calculated dissociation energies are tabulated in Table 14. There have been slight reductions in the M^+-CS dissociation energies, but more significantly the destabilizing effect of the CS ligand is limited to the weaker $M^{+\prime}$-CO bond. Dissociation energies of the remaining four carbonyls do not differ from those in the $M(CO)_6$ complexes. The relative energy ordering W > Mo > 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-$(^{13}CO)W(CO)_4CS$ 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	$\hat{D}(M^+\text{-CO})_H$	$\hat{D}(M^+\text{-CO})_T$	$\hat{D}'(M^+\text{-CO})_T$	$\hat{D}(M^+\text{-CS})$
$Cr(CO)_5CS$	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

$$(^{13}CO)W(CO)_4CS^+ \rightarrow W(CO)_4CS^+ + {}^{13}CO \qquad (112)$$

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 $W(CO)_4CS^+$ 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 $M(CO)_n$ were shown to be related according to Eq. 105. The analogous relationship for $M(CO)_5CS$ complexes is:

$$IP(M(CO)_5CS) - IP(M) = 5\hat{D}(M\text{-}CO)_T + \hat{D}(M\text{-}CS) - 5\hat{D}(M^+\text{-}CO)_T - \hat{D}(M^+\text{-}CS) \qquad (113)$$

where it has been assumed that the five carbonyls are equivalent and the substitution of $\hat{D}$ for $\bar{D}$ 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 $Cr(CO)_5CS$, $Mo(CO)_5CS$, and $W(CO)_5CS$, 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:

$$\hat{D}(M^{+}\text{-CO})_{H} - \hat{D}(M^{+}\text{-CO})_{T} = \hat{D}(M\text{-CO})_{H} - \hat{D}(M\text{-CO})_{T} \qquad (114)$$

(i.e. the difference between the M-CO dissociation energy in the hexacarbonyls and thiocarbonyls is the same in both the ion and molecule), $\hat{D}(M\text{-CO})_T$ and $\hat{D}(M\text{-CS})$ can be calculated. Approximate values for these quantities are listed in Table 15. The results for $\hat{D}(M\text{-CO})_T$ were obtained from Eq. 114 using the values of $\hat{D}(M^{+}\text{-CO})_H$ and $\hat{D}(M^{+}\text{-CO})_T$ from Table 13. For $Mo(CO)_5CS$ the calorimetric value of 1.35 ± 0.01 eV was used for $\hat{D}(M^{+}\text{-CO})_H$. Values for $\hat{D}(M\text{-CO})_H$ were given previously and were taken from Pilcher, Ware, and Pittam [55]. Substitution of $\hat{D}(M^{+}\text{-CO})_T$ and $\hat{D}(M^{+}\text{-CS})$ from Table 13 (and the results for $\hat{D}(M\text{-CO})_T$) into Eq. 113 yields the values for $\hat{D}(M\text{-CS})$ 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, ···,5) ions from thiocarbonyls gives six values for the energy of the substitution reaction:

$$\begin{array}{l} M(CO)_5CS \rightarrow M(CO)_n^{+} + (5-n)CO + CS \\ \underline{-M(CO)_6 \rightarrow M(CO)_n^{+} + (6-n)CO} \\ M(CO)_5CS + CO \rightarrow M(CO)_6 + CS. \end{array} \qquad (115)$$

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

Compound	$\hat{D}(M\text{-}CO)_T$	$\hat{D}(M\text{-}CS)$
$Cr(CO)_5CS$	0.94 ± 0.08	3.10 ± 0.50
$Mo(CO)_5CS$	1.50 ± 0.04	---
$W(CO)_5CS$	1.60 ± 0.10	4.10 ± 0.70

These energies are tabulated in Table 16. Known values for the heats of formation of gaseous $Cr(CO)_6$ and $W(CO)_6$, -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 $\Delta H_f^o(Cr(CO)_5CS,g) = -6.3 \pm 0.3$ eV and $\Delta H_f^o(W(CO)_5CS,g) = -6.2 \pm 0.3$ eV. These results are in agreement with gaseous heats of formation of $Cr(CO)_5CS$, -6.7 ± 0.3 eV, and $W(CO)_5CS$, -6.7 ± 0.3 eV, calculated directly from the appearance potentials of the metal ions:

$$M(CO)_5CS \rightarrow M^+ + 5CO + CS. \qquad (116)$$

Spectroscopic values of the ionization potentials of the metal atoms [75], $\Delta H_f(Cr) = 4.12$ eV, and $\Delta H_f(W) = 8.75$ 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^+	0.88	1.05
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.

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

Complex	M-M Distance (Å)[a]	Reduction Potentials $E_{\frac{1}{2}}$(volts)[b]	Electronic Transitions $\sigma \rightarrow \sigma^*$ (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

[a] $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$ Refs. [81-83]; $MnRe(CO)_{10}$ Ref. [84].

[b] Ref. [85].

[c] Ref. [86].

[d] Ref. [87].

[e] Ref. [88].

[f] Ref. [89].

[g] Ref. [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 $M(CO)_5CS$ 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:

$$M_2^{+}(CO)_{10} \rightarrow M^{+}(CO)_5 + M(CO)_5 \tag{117}$$

was incorrectly being associated with the energy of the M^{+}-M bond. For this to be true it has to be assumed that the dissociation energies $D(M_2^{+}\text{-CO})$, $D(M^{+}\text{-CO})$, and D(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 $D(M^{+}\text{-M})$ 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 $MnTc(CO)_{10}$ and $TcRe(CO)_{10}$ 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 $MnTc(CO)_{10}$ and $TcRe(CO)_{10}$ are very similar to those of $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$, respectively. The low abundance of the $M_2(CO)_9^+$ to $M_2(CO)_6^+$ ions from $MnTc(CO)_{10}$ is in agreement with the equally low intensities of these ions for $Mn_2(CO)_{10}$ and $MnRe(CO)_{10}$. This trend is undoubtedly related to the presence of manganese in the complexes, but is yet unexplained. The spectra of $Tc_2(CO)_{10}$, $Re_2(CO)_{10}$ and $TcRe(CO)_{10}$ show a similar trend in low abundances for the $M_2(CO)_9^+$ and $M_2(CO)_8^+$ ions.

2. Ionization potentials

Ionization potentials are recorded in Table 18 for all members of the Group VIIB decacarbonyls except $TcRe(CO)_{10}$. 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 $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. 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 $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, respectively) levels. The data appear to indicate that

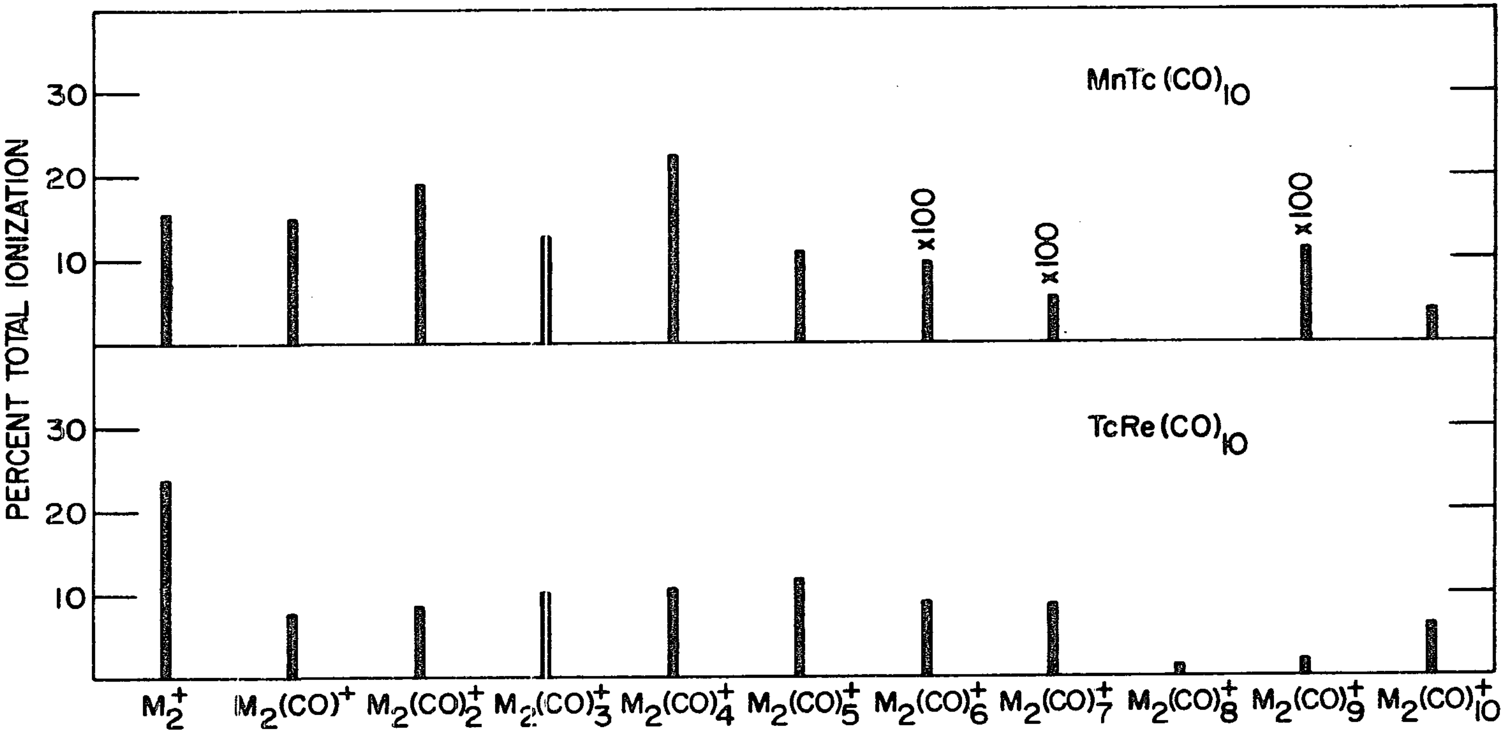


Figure 14. The 50 eV mass spectra of $MnTc(CO)_{10}$ and $TcRe(CO)_{10}$.

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

Compound	Electron Impact	Photoelectron[a]
$Mn_2(CO)_{10}$	8.32 ± 0.01	8.02
$Tc_2(CO)_{10}$	8.22 ± 0.01	--
$Re_2(CO)_{10}$	8.49 ± 0.02	8.07
$MnTc(CO)_{10}$	8.16 ± 0.02	--
$MnRe(CO)_{10}$	8.22 ± 0.01	--

[a] Ref. [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, $\hat{D}(M_2^+\text{-CO})$, is calculated from the first model. For this case the observational equations are:

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

	ΔH	
$Re_2(CO)_{10}$	$MnTc(CO)_{10}$	$MnRe(CO)_{10}$
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

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

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

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

where ΔH_n ($n = 9,8,\cdots,0$) 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

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

Complex	I	
	$\hat{D}(M_2^+\text{-CO})$	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. $\hat{D}'(M_2^+\text{-CO}) - \hat{D}(M_2^+\text{-CO})$) 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 $\hat{D}'(M_2^+\text{-CO})$ 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; $Mn(CO)_5$ <

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

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

$$\Delta H'_n = 5\hat{D}'(M_2^+\text{-CO}) + 5\hat{D}(M_2^+\text{-CO}) + \hat{D}(M^+\text{-M}) - 5\hat{D}(M\text{-CO}) - n\hat{D}(M^+\text{-CO}) \qquad (120)$$

where $\Delta H'_n$ is the fragmentation energy for $M(CO)_n^+$; $\hat{D}'(M_2^+\text{-CO})$ and $\hat{D}(M_2^+\text{-CO})$ are as defined previously for the five weak-five strong model; $\hat{D}(M^+\text{-M})$ is the least-squares dissociation energy for the ionic M-M bond; and $\hat{D}(M\text{-CO})$ and $\hat{D}(M^+\text{-CO})$ are the dissociation energies for the M-CO bonds in $M(CO)_5$ and $M(CO)_5^+$, respectively. When combined with the fragmentation data for the $M_2(CO)_n^+$ ions ($n = 9,8,\cdots,0$), the system cannot be solved because the coefficients of $\hat{D}(M^+\text{-M})$ and $\hat{D}(M\text{-CO})$ are linearly dependent. However results can be obtained for the combination $\hat{D}(M^+\text{-M}) - 5\hat{D}(M\text{-CO})$. In matrix form the observational equations are:

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & 0 \\ 3 & 0 & 0 & 0 \\ 4 & 0 & 0 & 0 \\ 5 & 0 & 0 & 0 \\ 5 & 1 & 0 & 0 \\ 5 & 2 & 0 & 0 \\ 5 & 3 & 0 & 0 \\ 5 & 4 & 0 & 0 \\ 5 & 5 & 0 & 0 \\ 5 & 5 & 1 & -5 \\ 5 & 5 & 1 & -4 \end{bmatrix} \begin{bmatrix} \hat{D}'(M_2^+\text{-CO}) \\ \hat{D}(M_2^+\text{-CO}) \\ \hat{D}(M^+\text{-M}) - 5\hat{D}(M\text{-CO}) \\ \hat{D}(M^+\text{-CO}) \end{bmatrix} = \begin{bmatrix} H_9 \\ H_8 \\ H_7 \\ H_6 \\ H_5 \\ H_4 \\ H_3 \\ H_2 \\ H_1 \\ H_0 \\ H'_5 \\ H'_4 \end{bmatrix}$$

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

Unfortunately $M(CO)_n^+$ 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 $\hat{D}'(M_2^+\text{-CO})$ and $\hat{D}(M_2^+\text{-CO})$ are unchanged from their values in Table 20 and are not listed.

Numerical results for $\hat{D}(Tc^+\text{-CO})$ calculated from the data for $Tc_2(CO)_{10}$ and $MnTc(CO)_{10}$ are in agreement, as are those for $\hat{D}(Re^+\text{-CO})$ calculated from the data for $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$. Dissociation energies are in the expected order $\hat{D}(Mn^+\text{-CO}) < \hat{D}(Tc^+\text{-CO}) < \hat{D}(Re^+\text{-CO})$. Results for $\hat{D}(M^+\text{-M}) - 5\hat{D}(M\text{-CO})$ are not altogether satisfying because of large uncertainties. Values for $\hat{D}(M^+\text{-M})$ listed in the final column of the table were calculated from these data using the results for $\hat{D}(M\text{-CO})$ given in the fourth column. These quantities were calculated using Eq. 105 (n=5) and the results for $\hat{D}(M^+\text{-CO})$ 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 $\cdot Mn(CO)_5$ [93] (8.44 eV) and approximate values for the ionization potentials of $\cdot Tc(CO)_5$ and $\cdot Re(CO)_5$ (8.27 and 8.94 eV, respectively). These were calculated assuming:

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	---

[a] Charge remains on fragment containing Tc.

[b] Charge remains on fragment containing Re.

ΔH		
$Re_2(CO)_{10}$	$MnTc(CO)_{10}$[a]	$MnRe(CO)_{10}$[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] $M^+ = Re^+$.

$$\frac{IP(Mn(CO)_5)}{IP(Mn)} = \frac{IP(M(CO)_5)}{IP(M)} . \qquad (122)$$

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

$$\begin{array}{rl}
M_2{}^+{}_{(g)} + 10\ CO_{(g)} \rightarrow M_2(CO)_{10(g)} & -AP(M_2{}^+) \\
M_2(CO)_{10(g)} \rightarrow M_2(CO)_{10(s)} & -\Delta H_{sub}(M_2(CO)_{10}) \\
M_2(CO)_{10(s)} \rightarrow 2M_{(s)} + 10C_{(s)} + 5O_{2(g)} & -\Delta H_f{}^o(M_2(CO)_{10}) \\
10C_{(s)} + 5O_{2(g)} \rightarrow 10CO_{(g)} & 10\ \Delta H_f{}^o(CO) \\
2M_{(s)} \rightarrow 2M_{(g)} & 2\ \Delta H_{sub}(M) \\
M_{(g)} \rightarrow M^+{}_{(g)} & IP(M) \\
\hline
M_2{}^+ \rightarrow M^+ + M & D(M^+\text{-}M).
\end{array} \qquad (123)$$

Data required for the calculations are summarized in Table 23. In addition, the spectroscopic values for the ionization potentials of the metals and $\Delta H_f{}^o(CO) = -1.146 \pm 0.002$ eV were used. Since thermochemical information is available only for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, results are limited to $D(Mn^+\text{-}Mn)$ and $D(Re^+\text{-}Re)$. 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
$\Delta H_{sub}(M_2(CO)_{10})$	0.83 ± 0.02[a]	0.97 ± 0.01[a]
$\Delta H_f^o(M_2(CO)_{10})$	-17.39 ± 0.04[b]	-17.13 ± 0.22[c]
$\Delta H_{sub}(M)$	2.91 ± 0.04[d]	7.98 ± 0.07[d]

[a] Ref. [94].

[b] Ref. [95].

[c] Ref. [96].

[d] Ref. [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 $M_2(CO)_{10}$ and $M(CO)_5$ complexes, heats of formation cannot be calculated for these compounds. Energies of the substitution reactions:

$$Tc_2(CO)_{10} + Mn(CO)_5 \rightarrow MnTc(CO)_{10} + Tc(CO)_5$$

$$Re_2(CO)_{10} + Mn(CO)_5 \rightarrow MnRe(CO)_{10} + Re(CO)_5 \qquad (124)$$

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:

$$M_2^+(CO)_{10} \rightarrow M(CO)_5^+ + M(CO)_5. \qquad (125)$$

$D(Mn^+\text{-}Mn)$ and $D(Re^+\text{-}Re)$ 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 $\hat{D}(M^+\text{-CO})$. 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 $\hat{D}(M^+\text{-CO})$ and $\hat{D}(W^+\text{-CNCH}_3)$ from these data are 1.82 ± 0.02 and 3.95 ± 0.16 eV, respectively. Comparison of the corrected result for $\hat{D}(M^+\text{-CO})$,

Table 24. Fragmentation data (eV) for $W(CO)_5CNCH_3$

Process	Energy
$W(CO)_5CNCH_3 \rightarrow W(CO)_5CNCH_3^+$	7.98 ± 0.05[a]
$W(CO)_5CNCH_3^+ \rightarrow W(CO)_4CNCH_3 + CO$	9.60 ± 0.06
$\rightarrow W(CO)_3CNCH_3^+ + 2CO$	11.58 ± 0.06
$\rightarrow W(CO)_2CNCH_3^+ + 3CO$	13.31 ± 0.06
$\rightarrow W(CO)CNCH_3^+ + 4CO$	15.33 ± 0.06
$\rightarrow WCNCH_3^+ + 5CO$	17.14 ± 0.07
$\rightarrow W^+ + 5CO + CNCH_3$	21.02 ± 0.10

[a] Relative 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 that in either the hexacarbonyl or thiocarbonyl. Values for $\hat{D}(W^+\text{-}CNCH_3)$ and $\hat{D}(W^+\text{-}CS)$ 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.

VII. BIBLIOGRAPHY

1. R. T. Sanderson, Chemical Bonds and Bond Energy (Academic Press, New York, 1971).

2. T. L. Cottrell, The Strengths of Chemical Bonds (Butterworths Publications Ltd., London, 1958).

3. D. P. Stevenson, J. Chem. Phys. 10, 291 (1942).

4. D. P. Stevenson, Discuss. Faraday Soc. 10, 35 (1951).

5. F. H. Field and J. L. Franklin, Electron Impact Phenomena (Academic Press, New York, 1957).

6. G. A. Junk and H. J. Svec, Z. Naturforsch. 23b, 1 (1968).

7. B. E. Knox and R. E. Palmer, J. Chem. Educ. 38, 292 (1961).

8. S. W. Benson, J. Chem. Educ. 42, 502 (1965).

9. E. T. Butler and M. Polanyi, Trans. Faraday Soc. 39, 19 (1943).

10. D. A. Walsh, J. Chem. Soc., 398 (1948).

11. H. A. Skinner, Trans. Faraday Soc. 45, 20 (1949).

12. M. Szwarc, Q. Rev. Chem. Soc. 5, 22 (1951).

13. G. Glockler, J. Phys. Chem. 56, 289 (1952).

14. R. T. Sanderson, J. Am. Chem. Soc. 97, 1367 (1975).

15. S. Siegel and B. Siegel, J. Chem. Educ. 40, 143 (1963).

16. M. Szwarc, Chem. Rev. 47, 75 (1950).

17. D. A. Johnson, Some Thermodynamic Aspects of Inorganic Chemistry (Cambridge University Press, London, 1968).

18. M. Szwarc and M. G. Evans, J. Chem. Phys. 18, 618 (1950).

19. D. Brunt, The Combination of Observations (Cambridge University Press, London, 1931).

20. F. A. Cotton, A. K. Fischer, and G. Wilkinson, J. Am. Chem. Soc. 81, 800 (1956).

21. H. D. Smyth, Proc. R. Soc. London 102, 283 (1922).

22. J. J. Mitchell and F. F. Coleman, J. Chem. Phys. 17, 44 (1949).

23. P. T. Smith, Phys. Rev. 36, 1293 (1930).

24. R. E. Honig, J. Chem. Phys. 16, 105 (1948).

25. J. W. Warren, Nature (London) 165, 810 (1950).

26. F. P. Lossing, A. W. Tickner, and W. A. Bryce, J. Chem. Phys. 19, 1254 (1951).

27. R. W. Kiser and E. J. Gallegos, J. Phys. Chem. 66, 947 (1962).

28. R. E. Winters, J. H. Collins, and W. L. Courchene, J. Chem. Phys. 45, 1931 (1966).

29. F. H. Dorman, J. Chem. Phys. 43, 3507 (1965).

30. J. D. Morrison, J. Chem. Phys. 39, 200 (1963).

31. G. D. Flesch and H. J. Svec, J. Chem. Phys. 54, 2681 (1971).

32. J. A. Hipple, R. E. Fox, and E. U. Condon, Phys. Rev. 69, 347 (1946).

33. G. D. Flesch, R. M. White, and H. J. Svec, Int. J. Mass Spectrom. Ion Phys. 3, 339 (1969).

34. G. D. Flesch and H. J. Svec, J. Chem. Phys. 54, 2681 (1971).

35. G. D. Flesch and H. J. Svec, J. Chem. Phys. 55, 4310 (1971).

36. G. D. Flesch and H. J. Svec, Int. J. Mass Spectrom. Ion Phys. 9, 106 (1972).

37. K. A. G. MacNeil and J. C. J. Thynne, Int. J. Mass Spectrom. Ion Phys. 3, 35 (1969).

38. G. D. Flesch and H. J. Svec, Int. J. Mass Spectrom. Ion Phys. 1, 41 (1968).

39. W. A. Rhinehart, D. Van Zuuk, and L. Mourlam, USAEC Report IS-1773, Ames, Iowa, 1968.

40. AIPOS User's Manual DEC-12-SQ1A-D, Digital Equip. Corp., Maynard Mass., 1971.

41. N. Flitcroft, D. K. Huggins, and H. D. Kaesz, Inorg. Chem. 3, 1123 (1964).

42. I. G. deJong and D. R. Wiles, Inorg. Chem. 12, 2519 (1973).

43. E. W. Abel and G. Wilkinson, J. Chem. Soc., 1501 (1959).

44. R. D. Peacock, The Chemistry of Technetium and Rhenium (Elsevier Publishing Co., Amsterdam, 1966).

45. R. E. Dessy, R. L. Pohl, and R. B. King, J. Am. Chem. Soc. 88, 5121 (1966).

46. R. E. Dessy and P. M. Weissman, J. Am. Chem. Soc. 88, 5125 (1966).

47. J. C. Hileman, D. K. Huggins, and H. D. Kaesz, Inorg. Chem. 1, 933 (1962).

48. A. Foffani and S. Pignataro, B. Cantone, and F. Grasso, Z. Phys. Chem. (Frankfurt am Main) 45, 79 (1965).

49. R. E. Winters and R. W. Kiser, Inorg. Chem. 4, 157 (1965).

50. D. R. Bidinosti and N. S. McIntyre, Can. J. Chem. 45, 641 (1967).

51. F. A. Cotton, A. K. Fischer, and G. Wilkinson, J. Am. Chem. Soc. 78, 5168 (1956).

52. D. S. Barnes, G. Pilcher, D. A. Pittam, H. A. Skinner, D. Todd, and Y. Virmani, J. Less-Common Met. 36, 177 (1974).

53. D. S. Barnes, G. Pilcher, D. A. Pittam, H. A. Skinner, and D. Todd, J. Less-Common Met. 38, 53 (1974).

54. D. A. Pittam, G. Pilcher, D. S. Barnes, H. A. Skinner, and D. Todd, J. Less-Common Met. 42, 217 (1975).

55. G. Pilcher, M. J. Ware, and D. A. Pittam, J. Less-Common Met. 42, 223 (1975).

56. B. D. Dombek and R. J. Angelici, J. Am. Chem. Soc. 95, 7516 (1973).

57. B. D. Dombek and R. J. Angelici, Inorg. Chem. 15, 1089 (1976).

58. G. A. Junk and H. J. Svec, Inorg. Chem. 7, 1688 (1968).

59. I. S. Butler and A. E. Fenster, J. Organomet. Chem. 66, 161 (1974).

60. B. D. Dombek and R. J. Angelici, Inorg. Chem. 15, 2397 (1976).

61. B. D. Dombek and R. J. Angelici, Inorg. Chem. 15, 2403 (1976).

62. M. Poliakoff, Inorg. Chem. 15, 2022 (1976).

63. M. Poliakoff, Inorg. Chem. 15, 2892 (1976).

64. I. S. Butler, A. Garcia-Rodriquez, K. R. Plowman, and C. F. Shaw III, Inorg. Chem. 15, 2602 (1976).

65. W. G. Richards, Trans. Faraday Soc. 63, 257 (1967).

66. D. L. Lichtenberger and R. F. Fenske, Inorg. Chem. 15, 2015 (1976).

67. N. J. Coville and I. S. Butler, J. Organomet. Chem. 64, 101 (1974).

68. A. Efraty, M. H. A. Huang, and C. A. Weston, Inorg. Chem. 14, 2796 (1975).

69. B. R. Higginson, D. R. Lloyd, P. Burroughs, D. M. Gibson, and A. F. Orchard, J. Chem. Soc. Faraday Trans. II 69, 1659 (1974).

70. G. A. Junk, H. J. Svec, and R. J. Angelici, J. Am. Chem. Soc. 90, 5758 (1968).

71. W. A. Graham, Inorg. Chem. 7, 315 (1968).

72. G. A. Junk, F. J. Preston, H. J. Svec, and D. T. Thompson, J. Chem. Soc. (A), 3171 (1970).

73. J. R. Reeher, G. D. Flesch, and H. J. Svec, Int. J. Mass Spectrom. Ion Phys. 19, 351 (1976).

74. W. Deissler, unpublished results.

75. C. E. Moore, Natl. Bur. Std. (U.S.) Circ., No. 467 (1949).

76. D. Okey, M.S. Thesis, Iowa State University, 1974 (unpublished).

77. S. S. Woodard, R. A. Jacobson, and R. J. Angelici, J. Organomet. Chem. 117, C75 (1976).

78. M. A. Andrews, Inorg. Chem. 16, 496 (1977).

79. JANAF Thermochemical Tables, NSRDS.-NBS, 2nd edn., 37 (1971).

80. H. A. Skinner and G. Pilcher, Q. Rev. Chem. Soc. 17, 264 (1963).

81. L. F. Dahl and R. E. Rundle, Acta Cryst. 16, 419 (1963).

82. M. F. Bailey and L. F. Dahl, Inorg. Chem. 4, 1140 (1965).

83. L. F. Dahl, E. Ishishi, and R. E. Rundle, J. Chem. Phys. 26, 1750 (1957).

84. A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and I. S. Kolomniker, Invest. Akad. Nauk SSSR, Ger. Khim., 194 (1963).

85. P. Lemoine and J. Bousquet, J. Organomet. Chem. 112, 79 (1976).

86. R. A. Levenson and H. B. Gray, J. Am. Chem. Soc. 97, 6042 (1975).

87. C. O. Quicksall and T. G. Spiro, Inorg. Chem. 8, 2363 (1969).

88. G. A. Junk and H. J. Svec, J. Chem. Soc. (A), 2102 (1970).

89. D. A. Brown, W. J. Chambers, N. J. Fitzpatrick, and Sister R. M. Rawlinson, J. Chem. Soc. (A), 720 (1971).

90. L. I. B. Haines and A. J. Poe, J. Chem. Soc. (A), 2826 (1969).

91. H. J. Svec and G. A. Junk, J. Am. Chem. Soc. 89, 2836 (1967).

92. B. R. Higginson, D. R. Lloyd, S. Evans, and A. F. Orchard, J. Chem. Soc. Faraday Trans. II 71, 1913 (1975).

93. B. R. Bidinosti and N. S. McIntyre, Chem. Comm., 555 (1966).

94. D. L. S. Brown, J. A. Connor, and H. A. Skinner, J. Organomet. Chem. 81, 403 (1974).

95. J. A. Connor, Y. Virmani, and H. A. Skinner, J. Chem. Soc. Faraday Trans. I 68, 1754 (1972).

96. J. A. Connor, H. A. Skinner, and Y. Virmani, Faraday Symp. Chem. Soc. 8, 18 (1974).

97. D. D. Wagman, Nat. Bur. Stand. Tec. Notes, 270-1 to 270-5, U.S. Gov. Printing Office, Washington, D.C., 1965-1971.

98. G. A. Junk, H. J. Svec, and R. J. Angelici, J. Am. Chem. Soc. 90, 5758 (1968).

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:

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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)

```
            *20
            /************************************
            /
            /
            /               DATST1
            /
            /
            /DIGITAL TO ANALOG TEST ONE
            /
            /
            /WRITTEN BY GARY MICHELS
            /
            /
            /FEBRUARY 1977
            /
            /
            /************************************
                    PMODE
                    DAC=6374        /DA INST CODE
                    *100
            /
            /VARIABLES
            /
0100  0000  TMP1,   0
0101  0000  TMP2,   0
0102  0000  TMP3,   0
0103  0001  CONST,  1
0104  0007  K7,     7
0105  7776  M2,     -2
0106  7774  M4,     -4
0107  0600  PTRNAD, PATTRN
            /
            /SUBROUTINE LINKS
            /
                    KEEP=4000 400 .
0110  0330          KEEPA
                    DISPLY=4000 400 .
0111  0400          DSPLAY
                    UNPACK=4000 400 .
0112  0262          UNPAKA
                    *200
            /
            /MAIN PROGRAM
            /
0200  7300  START,  CLA CLL         /CLEAR AC AND LINK
0201  1105          TAD M2          /SET THE UP
0202  3254          DCA TSTCNT      /AND DOWN COUNT
0203  1103          TAD CONST       /SET THE D TO A
0204  3255          DCA INCR        /INPUT
0205  1103          TAD CONST       /SET THE STEP
0206  3256          DCA STEP        /COUNTER
0207  3261          DCA DIGVAL      /CLEAR THE D TO A INPUT
0210  1261  TEST,   TAD DIGVAL      /GET THE INPUT
0211  6374          DAC             /CONVERT IT
0212  4512          UNPACK          /DIGITIZE AND STORE
0213  0515          DIGAD           /PATTERN FOR DISPLAY
0214  6141          LINC
                    LMODE           /SAMPLE D TO A
0215  0110          SAM 10          /OUTPUT
0216  0002          PDP
                    PMODE
0217  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 K7         /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  1105          TAD M2         /SET COUNT FOR
0173    0312  3327          DCA COUNT      /BOTH HALVES OF PATTERN
0174    0313  1726  AGAIN,  TAD I POINTR   /STORE THE
```

```
0314  3725           DCA I DSPBUF    /FIRST HALF
0315  2326           ISZ POINTR      /IN THE DISPLAY
0316  2325           ISZ DSPBUF      /BUFFER
0317  2327           ISZ COUNT       /DONE YET?
0320  5313           JMP AGAIN       /NO,DO SECOND HALF
0321  2324           ISZ DIGCTR      /DONE WITH 4 DIGITS?
0322  5274           JMP UNPAK       /NO,CONTINUE
0323  5662           JMP I UNPAKA    /YES,RETURN TO MAINLINE
0324  0000  DIGCTR,  0
0325  0000  DSPBUF,  0
0326  0000  POINTR,  0
0327  0000  COUNT,   0
            /
            /REFRESHER SUBROUTINE
            /
0330  0000  KEEPA,   0
0331  4511           DISPLY          /DISPLAY THE
0332  0433           HEADA-1         /HEADING
0333  0100           100
0334  4511           DISPLY          /DISPLAY THE D TO A
0335  0504           INFO-1          /INPUT AND OUTPUT
0336  0000           0
0337  5730           JMP I KEEPA     /RETURN
                     PAGE
            /
            /DISPLAY SUBROUTINE
            /
0400  0000  DSPLAY,  0
0401  1600           TAD I DSPLAY    /GET AND SAVE THE
0402  3214           DCA BUFA        /ADDRESS
0403  2200           ISZ DSPLAY      /GET THE VERTICAL
0404  1600           TAD I DSPLAY    /LOCATION
0405  3232           DCA YVALUE
0406  2200           ISZ DSPLAY      /BOP FOR THE RETURN
0407  6141           LINC            /GET INTO LINC
                     LMODE           /MODE
0410  0011           CLR             /CLEAR AC,MQ,AND LINK
0411  0061           SET I 1         /SET THE HORIZONTAL
0412  0000           0               /COORDINATE
0413  0063           SET I 3         /GET THE
0414  0000  BUFA,    0               /BUFFER
0415  1003           LDA 3           /COUNT
0416  0017           COM             /NEGATE IT
0417  4421           STC .+2         /STORE IT
0420  0062           SET I 2         /SET THE LOOP
0421  0000           0               /COUNTER
0422  2432           ADD YVALUE      /GET THE Y LOCATION
0423  1763  REPEAT,  DSC I 3         /DISPLAY THE
0424  1763           DSC I 3         /PATTERN
0425  0222           XSK I 2         /DONE WITH THE BUFFER?
0426  6423           JMP REPEAT      /NO,CONTINUE
0427  0002           PDP             /YES,RETURN
                     PMODE
0430  7300           CLA CLL         /TO CALLING
0431  5600           JMP I DSPLAY    /ROUTINE
0432  0000  YVALUE,  0
            /HEADING BUFFER
0433  0024           24              /HEADING COUNT
0434  0000  HEADA,   0
0435  0000           0
0436  0000           0
0437  0000           0
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          /O
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          /O
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
ANLAD  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
HEADA  0434
INCR   0255
INFO   0505
KEEP   4510
KEEPA  0330
K7     0104
M2     0105
M4     0106
PATTRN 0600
POINTR 0326
PTRNAD 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)

```
            *20
            /************************************
            /
            /
            /          DATST2
            /
            /
            /DIGITAL TO ANALOG TEST TWO
            /
            /
            /WRITTEN BY GARY MICHELS
            /
            /
            /FEBRUARY 1977
            /
            /
            /************************************
            /
            /MAIN PROGRAM
            /
                      PMODE
                      DAC=6374          /DA INST CODE
                      *200
0200  7300  START,    CLA CLL           /CLEAR AC AND LINK
0201  1221            TAD BUFA          /STORE BUFFER ADDRESS
0202  3017            DCA 17            /IN AUTO REGISTER
0203  3222            DCA DIGVAL        /CLEAR THE DA INPUT
0204  6374  AGAIN,    DAC               /CONVERT THE AC
0205  3222            DCA DIGVAL        /SAVE THE INPUT
0206  4225            JMS DISPLY        /DISPLAY THE BUFFER
0207  6141            LINC
                      LMODE             /GET INTO LINC MODE
0210  0110            SAM 10            /CONVERT THE OUTPUT
0211  0002            PDP
                      PMODE             /BACK TO 8 MODE
0212  1224            TAD K400          /ADJUST CONVERTED NUM FOR SCREEN
0213  3417            DCA I 17          /STORE IN BUFFER
0214  1222            TAD DIGVAL        /GET THE INPUT
0215  1223            TAD K10           /INCREMENT BY 8
0216  7440            SZA               /IS IT ZERO?
0217  5204            JMP AGAIN         /NO,REPEAT
0220  5200            JMP START         /YES,START AGAIN
0221  5777  BUFA,     BUFFR-1
0222  0000  DIGVAL,   0
0223  0010  K10,      10
0224  0400  K400,     400
            /
            /DISPLAY SUBROUTINE
            /
0225  0000  DISPLY,   0
0226  6141            LINC
                      LMODE             /INTO L MODE
0227  0011            CLR               /CLEAR AC,MQ,AND LINK
0230  0062            SET I 2           /SET HORIZONTAL
0231  1777            1777              /AXIS
0232  0063            SET I 3           /SET BUFFER
0233  3777            3777              /ADDRESS
0234  0064            SET I 4           /SET THE
0235  6777            -1000             /COUNT
0236  1023            LDA I 3           /GET CONVERTED DA OUTPUT
0237  0162            DIS I 2           /DISPLAY
0240  0162            DIS I 2           /TWICE
```

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

```
NO ERRORS
```

```
AGAIN  0204
BUFA   0221
BUFFR  6000
DAC    6374
DIGVAL 0222
DISPLY 0225
K10    0223
K40A   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.

```
                               LISTON
           /****************************************
           /
           /
           /                 I E A S
           /
           /
           /IONIZATION EFFICIENCY ACQUISITION
           /SYSTEM
           /
           /
           /WRITTEN BY GARY MICHELS
           /
           /
           /MARCH 1976
           /
           /
           /****************************************
           /
           /          FIELD 0
           /
           /HEADER AND IE TABLE
                   ORG 03000
03000 0001 HEADR,  1                /NUMBER OF HEADER BLOCKS
03001 0003         3                /NUMBER OF DATA BLOCKS
03002 0000         0                /DATA FORMAT
03003 0000         0
03004 0000         0
03005 0000 NIE,    0.               /NUMBER OF IE CURVES
03006 0000
03007 0000
03010 0004 NORMUL, 15.              /NUMBER OF POINTS/CURVE
03011 3600
03012 0000
03013 0001 NORANG, 1.5              /NORMALIZATION RANGE
03014 3000
03015 0000
           /MASS VECTOR
                   ORG 03030
03030 0000 MASLOC, 0
           /LSTSQ INTERCEPTS
                   ORG 03110
03110 0000 INCEPT, 0
           /LSTSQ SLOPES
                   ORG 03170
03170 0000 SLOPE,  0
           /LSTSQ WEIGHTING FACTORS
                   ORG 03250
03250 0000 WTLOC,  0
           /MINIMUM DELTA FOR EACH ION
                   ORG 03330
03330 0000 MINLOC, 0
           /
           /IE TABLE
           /
                   ORG 03400
03400 0000 IELOC,  0
           /
           /INTENSITY VECTOR
           /
                   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 PAMAMETER
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                        PUSTR=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                     SAM11=0111
0363                     PDP=0002
0364                     PAGE
```

```
                           EJECT
                   /
                   /COMMAND OVERLORD DISPATCHER
                   /
10200 6201 COMAND, CDF 0
10201 1063         TAD CNTRLA       /INITIALIZE CONTROL
10202 3464         DCA I CNTRLH     /CHARACTER HANDLER
10203 1440         TAD I READ       /INITIALIZE AIPOS
10204 3040         DCA READ         /MONITOR
10205 1441         TAD I WRITE      /I/O LINKS
10206 3041         DCA WRITE
10207 1442         TAD I RETURN
10210 3042         DCA RETURN
10211 6211         CDF 10
10212 1146         TAD K4704        /INITIALIZE ELECTRON
10213 6374         DAC              /ENERGY
10214 7300 COMND1, CLA CLL
10215 3050         DCA BKGFLG       /CLEAR
10216 3051         DCA CHNFLG       /ALL
10217 3054         DCA TSTFLG+2     /FLAGS
10220 6201         CDF 0
10221 3455         DCA I CNTRFA
10222 6211         CDF 10
10223 1057         TAD PBUFA        /INITIALIZE
10224 3010         DCA AUX0         /PUT STRING
10225 3456         DCA I PUCNTA     /ROUTINES
10226 4525         LPCTL            /SET LP TO
10227 0006         PRNT             /PRINT MODE
10230 4531         PUTTY
10231 2347         ASTER            /PRINT ASTERISK
10232 4523         GETTY            /GET
10233 0100         CHAR             /COMMAND
10234 0002         2                /CHARACTER
10235 1100 COMND2, TAD CHAR         /IT MUST
10236 1152         TAD M301
10237 7510         SPA
10240 5304         JMP CNTERR       /BE
10241 1150         TAD M32
10242 7700         SMA CLA
10243 5304         JMP CNTERR       /ALPHABETIC
10244 1100         TAD CHAR         /FORM
10245 0142         AND K77          /CORRECT
10246 1251         TAD TTYJMP       /JUMP
10247 3250         DCA .+1
10250 0000         0
10251 5651 TTYJMP, JMP I .+0        /DISPATCH
10252 0310         ACQUIR           /A
10253 0315         BCKSUB           /B
10254 0330         CAIN             /C
10255 0400         DELSQ            /D
10256 0423         ELIM             /E
10257 0426         FILSAV           /F
10260 0306         CMNDER           /G
10261 0306         CMNDER           /H
10262 0465         IEPRNT           /I
10263 0306         CMNDER           /J
10264 0306         CMNDER           /K
10265 0306         CMNDER           /L
10266 0475         MASPRT           /M
10267 0505         NORPRM           /N
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                / ACQURIE 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
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10352 1364         TAD CHARA       /RESET CHARACTER
10353 3017         DCA AUX7        /POINTER
10354 1417         TAD I AUX7      /GET COMMAND CHARACTER
10355 3100         DCA CHAR        /STORE
10356 5765         JMP I CMND2A    /DISPATCH
10357 2366 CHN1,   ISZ CARCNT      /CHAIN DONE?
10360 5354         JMP .-4         /NOPE
10361 7300         CLA CLL         /YEP,CLEAR
10362 3051         DCA CHNFLG      /CHAIN FLAG
10363 5465         JMP I XIT       /RETURN
10364 0077 CHARA,  CHAR-1
10365 0235 CMND2A, COMND2
10366 0000 CARCNT, 0
                   PAGE
           /CALCULATE THE DELTAS AND LEAST-SQUARE
           /INTERCEPTS
           /PRINT ON LINE PRINTER
10400 4533 DELSQ,  TABSP           /CENTER
10401 0074         74              /HEADING
10402 4527         PUSTR           /PRINT
10403 1777         DELHED-1        /HEADING
10404 4530         PUTLP
10405 4521         FPPGO           /CALCULATE AND
10406 4151         DELTA           /PRINT DELTAS
10407 4533         TABSP
10410 0066         66              /CENTER AND
10411 4527         PUSTR           /PRINT
10412 2132         LSQHED-1        /HEADING
10413 4530         PUTLP
10414 4521         FPPGO
10415 4354         LSTSQ           /CALCULATE INTERCEPTS
10416 4526         PUCRLF          /END THE LINE
10417 4530         PUTLP           /PRINT ON LP
10420 4525         LPCTL           /END
10421 0004         REOT            /TRANSMISSION
10422 5465         JMP I XIT       /RETURN
           /ELIMINATE CURRENT IE DATA FROM TABLE
10423 4521 ELIM,   FPPGO           /DO IT THIS
10424 4256         ELIMIE          /WAY
10425 5465         JMP I XIT       /RETURN
           /SAVE HEADER AND DELTA TABLE
10426 6201 FILSAV, CDF 0
10427 1144         TAD K304        /DATA FORMAT
10430 3660         DCA I HEADA
10431 1443         TAD I UNIT      /CHECK BIT 0
10432 7104         CLL RAL         /OF UNIT NUMBER
10433 7430         SZL
10434 5261         JMP FILERR      /EXISTING FILE
10435 7030         CML RAR         /NEW FILE, SET
10436 3443         DCA I UNIT      /BIT 0
10437 1137         TAD K4          /FILE LENGTH
10440 3445         DCA I NBLK      /SET
10441 1443         TAD I UNIT      /SET UNIT FROM
10442 0142         AND K77         /JOB CONTROL
10443 3110         DCA TPARM       /TO PARMETER LIST
10444 1444         TAD I STBLK     /STARTING BLOCK
10445 3114         DCA TBLK        /TO PARMETER LIST
10446 6211         CDF 10
10447 6224         RIF             /STARDARD
10450 6202         CIF 0           /MONITOR
10451 4441         JMS I WRITE     /I/O CALL
10452 0110         TPARM
```

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10453 1110          TAD TPARM       /AND
10454 7710          SPA CLA
10455 5253          JMP .-2         /WAIT TILL DONE
10456 6202          CIF 0
10457 5442          JMP I RETURN    /EXIT TO AIPOS
10460 3002 HEADA,   HEADR+2
10461 7300 FILERR,  CLA CLL         /ATTEMPT TO SAVE
10462 6211          CDF 10
10463 1135          TAD K2          /DATA IN A PRE-
10464 5460          JMP I ERRA      /EXISTING FILE
           /PRINT RAW IE DATA ON TTY
10465 4531 IEPRNT,  PUTTY           /PRINT
10466 2026          IEHED           /HEADING
10467 1073          TAD NSTEPS      /SET INDEX
10470 7041          CIA             /COUNTER
10471 3024          DCA FXR4        /FOR FPP
10472 4521          FPPGO           /PRINT ENERGIES
10473 4271          IEPRIN          /AND INTENSITIES
10474 5465          JMP I XIT       /RETURN
           /PRINT NORM ENERGIES FOR A GIVEN MASS
           /ON THE TTY
10475 4531 MASPRT,  PUTTY           /GET
10476 2230          MMS1            /THE
10477 4524          GNUMB           /MASS
10500 4531          PUTTY           /PRINT
10501 2200          MASHED          /HEADING
10502 4521          FPPGO           /AND
10503 4612          MPRINT          /ENERGIES
10504 5465          JMP I XIT       /RETURN
           /RESET NORMALIZATION PARAMETERS
10505 4531 NORPRM,  PUTTY           /GET THE
10506 2237          NMS1            /INTENSITY
10507 4524          GNUMB           /MULTIPLE
10510 4521          FPPGO
10511 4722          NMUL            /CHANGE IT
10512 4531          PUTTY           /GET THE
10513 2264          NMS2            /ENERGY
10514 4524          GNUMB           /RANGE
10515 4521          FPPGO
10516 4735          NRANG           /CHANGE IT
10517 5465          JMP I XIT       /RETURN
                    PAGE
           /OPTIMIZE GAIN AND ENERGY LIMITS
           /ACQUISITION 1 PASS
           /RECYCLE TILL CONTROL R
10600 7001 OPTMIZ,  IAC
10601 3054          DCA TSTFLG+2    /SET TEST FLAG
10602 4531 OPTM1,   PUTTY           /GET
10603 1700          AMS2            /STARTING
10604 4524          GNUMB           /ENERGY
10605 4521          FPPGO
10606 3162          STRTEN
10607 4531          PUTTY           /GET
10610 1705          AMS3            /ENERGY
10611 4524          GNUMB           /INTERVAL
10612 4521          FPPGO
10613 3213          ENTRVL
10614 4531          PUTTY           /GET
10615 1712          AMS4            /ENERGY
10616 4524          GNUMB           /RANGE
10617 4521          FPPGO
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 READTA, 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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10710 7012         RTR
10711 7010         RAR               /FIRST
10712 0140         AND K7            /DIGIT
10713 1143         TAD K260          /MAKE ASCII
10714 3461         DCA I DIGA        /AND SAVE
10715 1067         TAD ERRNUM        /GET
10716 0140         AND K7            /SECOND DIGIT
10717 1143         TAD K260          /MAKE ASCII
10720 3462         DCA I DIG1A       /SAVE
10721 4531         PUTTY             /PRINT
10722 2337         ERRMS             /ERROR MESSAGE
10723 1054         TAD TSTFLG+2      /OPTIMIZATION?
10724 7640         SZA CLA
10725 5734         JMP I OPTMA       /YES,RECYCLE
10726 5466         JMP I CMND1A      /NO, RETURN
           /ROUTINES EXIT HERE
10727 7300 EXIT,   CLA CLL
10730 1051         TAD CHNFLG        /CHAINING?
10731 7640         SZA CLA
10732 5735         JMP I CHNA        /YES,CONTINUE
10733 5466         JMP I CMND1A      /NO,TO OVERLORD
10734 0602 OPTMA,  OPTM1
10735 0357 CHNA,   CHN1
           /
           /
           /**********SUBROUTINES**********
           /
           /
           /GET AQUISITION PARAMETERS
10736 0000 GPARM,  0
10737 4531         PUTTY             /GET
10740 1673         AMS1              /ION
10741 4524         GNUMB             /MASS
10742 4521         FPPGO
10743 3130         MASS
10744 4531         PUTTY             /GET
10745 1700         AMS2              /STARTING
10746 4524         GNUMB             /ENERGY
10747 4521         FPPGO
10750 3162         STRTEN
10751 4531         PUTTY             /GET
10752 1705         AMS3              /ENERGY
10753 4524         GNUMB             /INTERVAL
10754 4521         FPPGO
10755 3213         ENTRVL
10756 4531         PUTTY             /GET
10757 1712         AMS4              /ENERGY
10760 4524         GNUMB             /RANGE
10761 4521         FPPGO
10762 3244         RANGE
10763 4531         PUTTY             /GET
10764 1716         AMS5              /NUMBER OF
10765 4524         GNUMB             /SCANS
10766 4521         FPPGO
10767 3313         SCANS
10770 5736         JMP I GPARM
           /CHECK FOR CONTROL R
10771 0000 CKFLG,  0
10772 6201         CDF 0
10773 1455         TAD I CNTRFA      /GET FLAG
10774 6211         CDF 10
10775 7640         SZA CLA           /CONTROL R?
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1150 10776 5466          JMP I CMND1A    /YES.OVRELORD 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 A
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
```

```
11051 1061          TRP7
11052 0000 TRPIN,   0
11053 5631 TRP3,    JMP I TRP         /UNDEFINED
11054 4434 TRP4,    JMS I OPR         /SUBROUTINE EXIT
11055 5631          JMP I TRP         /RETURN
11056 1034 TRP5,    TAD OPR           /GET ERROR CODE
11057 5460          JMP I ERRA        /ERROR EXIT
11060 5631 TRP6,    JMP I TRP         /UNDEFINED
11061 5631 TRP7,    JMP I TRP         /UNDEFINED
           /IE AQUISITION
11062 0000 ACQ,     0
11063 1050          TAD BKGFLG
11064 7640          SZA CLA           /ZERO BUFFER?
11065 5277          JMP .+12          /NO,SKIP
11066 1154          TAD M2000         /ZERO
11067 3070          DCA COUNTL
11070 1367          TAD DATLOA
11071 3011          DCA AUX1          /DATA
11072 6201          CDF 0
11073 3411          DCA I AUX1
11074 2070          ISZ COUNTL        /BUFFER
11075 5273          JMP .-2
11076 6211          CDF 10
11077 1370          TAD DATAD         /SET HIGH
11100 3076          DCA HWPTR         /WORD POINTER
11101 1076          TAD HWPTR         /SET LOW
11102 7001          IAC               /WORD
11103 3077          DCA LWPTR         /POINTER
11104 1071          TAD SENRGY        /SAVE
11105 3075          DCA ENERGY        /STARTING ENERGY
11106 1075          TAD ENERGY        /AND
11107 6374          DAC               /SEND IT OUT
11110 7300          CLA CLL
11111 4523          GETTY             /WAIT FOR
11112 0100          CHAR              /GO
11113 0001          1                 /COMMAND
11114 1100          TAD CHAR          /IS IT A G?
11115 1153          TAD M307
11116 7640          SZA CLA
11117 5466          JMP I CMND1A      /NO,RETURN
11120 1074          TAD NSCANS        /YES,SET SCAN
11121 7041          CIA
11122 3365          DCA SCANL         /LOOP
11123 1073 ACQ1,    TAD NSTEPS        /SET STEP
11124 7041          CIA
11125 3366          DCA STEPL         /LOOP
11126 4532 ACQ2,    SAMPLE            /SAMPLE ION INTENSITY
11127 4520          CHKFLG            /CONTROL R?
11130 2076          ISZ HWPTR         /INCREMENT HIGH
11131 2076          ISZ HWPTR         /POINTER BY 2
11132 2077          ISZ LWPTR         /INCREMENT LOW
11133 2077          ISZ LWPTR         /POINTER BY 2
11134 1072          TAD ENIVL         /GET INTERVAL
11135 7041          CIA               /NEGATE
11136 1075          TAD ENERGY        /DECREMENT
11137 3075          DCA ENERGY        /ELECTRON ENERGY
11140 2366          ISZ STEPL         /STEP DOWN DONE?
11141 5326          JMP ACQ2          /NO,REPEAT
11142 1073          TAD NSTEPS        /YES,
11143 7041          CIA               /RESET STEP
11144 3366          DCA STEPL         /LOOP
11145 1147 ACQ3,    TAD M2            /DECREMENT
```

```
11146 1076          TAD HWPTR       /HIGH POINTER
11147 3076          DCA HWPTR
11150 1147          TAD M2          /DECREMENT
11151 1077          TAD LWPTR       /LOW POINTER
11152 3077          DCA LWPTR
11153 1072          TAD ENIVL       /INCREMENT
11154 1075          TAD ENERGY      /ELECTRON
11155 3075          DCA ENERGY      /ENERGY
11156 4532          SAMPLE          /SAMPLE ION INTENSITY
11157 4520          CHKFLG          /CONTROL R?
11160 2366          ISZ STEPL       /STEP UP DONE?
11161 5345          JMP ACQ3        /NO,REPEAT
11162 2365          ISZ SCANL       /SCAN DONE?
11163 5323          JMP ACQ1        /NO,DO NEXT SCAN
11164 5662          JMP I ACQ       /YES,RETURN
11165 0000 SCANL,   0
11166 0000 STEPL,   0
11167 4777 DATLOA,  DTALOC-1
11170 5000 DATAD,   DTALOC
                    PAGE
           /SET ELECTRON ENERGY,DELAY,SAMPLE
           /ION INTENSITY
11200 0000 SAMPL,   0
11201 1301          TAD NSAM        /SET SAMPLE
11202 7041          CIA             /COUNTER
11203 3302          DCA SAML
11204 3303          DCA ACHI        /CLEAR DOUBLE
11205 3304          DCA ACLO        /PRECISION AC
11206 1075          TAD ENERGY      /SEND OUT
11207 6374          DAC             /ELECTRON ENERGY
11210 7300          CLA CLL
11211 1305          TAD DCONST      /DELAY
11212 3306          DCA OTRL        /BY DOING
11213 2307          ISZ INRL        /NOTHING
11214 5213          JMP .-1
11215 2306          ISZ OTRL
11216 5213          JMP .-3
11217 6141 SAMPL1,  LINC            /LINC MODE SET
11220 0111          SAM11           /SAMPLE SIGNAL
11221 0002          PDP             /8 MODE SET
11222 7510          SPA             /POSITIVE?
11223 7200          CLA             /NO,SET TO ZERO
11224 7100          CLL
11225 1304          TAD ACLO        /ADD INTENSITY TO
11226 3304          DCA ACLO        /DPAC
11227 7004          RAL
11230 1303          TAD ACHI
11231 3303          DCA ACHI
11232 2302          ISZ SAML        /DONE SAMPLING?
11233 5217          JMP SAMPL1      /NO,REPEAT
11234 1310          TAD NSHIFT      /YES,AVERAGE INTENSITY
11235 7041          CIA
11236 3311          DCA NTIMES      /DIVIDE
11237 1303          TAD ACHI        /BY
11240 7110          CLL RAR         /ROTATING
11241 3303          DCA ACHI
11242 1304          TAD ACLO
11243 7010          RAR             /DPAC
11244 3304          DCA ACLO
11245 2311          ISZ NTIMES      /DIVISION DONE?
11246 5237          JMP .-7         /NO,ROTATE AGAIN
11247 6201          CDF 0
```

```
11250 1050         TAD BKGFLG       /YES.CHECK FOR
11251 7640         SZA CLA          /BACKGROUND SUBTRACTION
11252 5264         JMP SAMPL2       /SUBTRACT
11253 7100         CLL              /ADD SAMPLED
11254 1304         TAD ACLO         /INTENSITY
11255 1477         TAD I LWPTR      /TO
11256 3477         DCA I LWPTR      /BUFFER
11257 7004         RAL
11260 1476         TAD I HWPTR
11261 3476         DCA I HWPTR
11262 6211         CDF 10
11263 5600         JMP I SAMPL      /RETURN
11264 7100 SAMPL2, CLL              /SUBTRACT
11265 1304         TAD ACLO         /SAMPLED INTENSITY
11266 7041         CIA
11267 1477         TAD I LWPTR      /FROM BUFFER
11270 3477         DCA I LWPTR
11271 7004         RAL
11272 3312         DCA LSAVE
11273 7040         CMA
11274 1476         TAD I HWPTR
11275 1312         TAD LSAVE
11276 3476         DCA I HWPTR
11277 6211         CDF 10
11300 5600         JMP I SAMPL      /RETURN
11301 1000 NSAM,   1000
11302 0000 SAML,   0
11303 0000 ACHI,   0
11304 0000 ACLO,   0
11305 7764 DCONST, -14              /.25 SEC
11306 0000 OTRL,   0
11307 0000 INRL,   0
11310 0011 NSHIFT, 11
11311 0000 NTIMES, 0
11312 0000 LSAVE,  0
           /
           /**I/O SUBROUTINES**
           /
           /OUTPUT A LIST TO THE TTY
           /LIST ADDRESS IN CALL+1
           /LIST IN FIELD 1
11313 0000 PTTY,   0
11314 1713         TAD I PTTY       /GET ARGUEMENT
11315 3335         DCA LISTP        /SAVE
11316 2313         ISZ PTTY         /BOP THE POINTER
11317 1735         TAD I LISTP      /GET THE COUNT
11320 3341         DCA PBUFL        /PARAMETER COUNT
11321 1335         TAD LISTP        /BOP LIST
11322 7001         IAC              /POINTER AND
11323 3340         DCA PBUFRA       /SAVE AS ADDRESS
11324 6224         RIF              /STANDARD
11325 6202         CIF 0            /MONITOR
11326 4441         JMS I WRITE      /I/O CALL
11327 1336         PUPARM
11330 1336         TAD PUPARM       /STANDARD WAIT
11331 7710         SPA CLA          /TILL DONE
11332 5330         JMP .-2
11333 4520         CHKFLG           /CONTROL R?
11334 5713         JMP I PTTY       /DONE.RETURN
11335 0000 LISTP,  0
11336 0040 PUPARM, 40               /PARAMETER
11337 6211         CDF 10           /LIST
```

```
11340 0000 PBUFRA, 0
11341 0000 PBUFL,  0
11342 0000         0
11343 0000         0
11344 0000         0
                   PAGE
           /GET A LIST FROM THE TTY
           /CALL+1=STORAGE LOCATION IN FIELD 1
           /CALL+2=LIST LENGTH
11400 0000 GTTY,   0
11401 1600         TAD I GTTY       /GET BUFFER ADDRESS
11402 3222         DCA GBUFA        /SAVE IN PARMETER LIST
11403 2200         ISZ GTTY         /BOP POINTER
11404 1600         TAD I GTTY       /GET LIST LENGTH
11405 3223         DCA GBUFL        /SAVE IN PARAMETER LIST
11406 2200         ISZ GTTY         /BOP FOR RETURN
11407 6224         RIF              /STANDARD
11410 6202         CIF 0            /MONITOR
11411 4440         JMS I READ       /CALL
11412 1420         GTPARM
11413 1220         TAD GTPARM       /STANDARD
11414 7710         SPA CLA          /WAIT
11415 5213         JMP .-2
11416 4520         CHKFLG           /CONTROL R?
11417 5600         JMP I GTTY       /DONE,RETURN
11420 0040 GTPARM, 40               /PARAMETER
11421 6211         CDF 10           /LIST
11422 0000 GBUFA,  0
11423 0000 GBUFL,  0
11424 0000         0
11425 0000         0
11426 0000         0
           /PUT A LIST CREATED THROUGH PUT STRING
           /ON THE TTY
11427 0000 BUTTY,  0
11430 1260         TAD PCNT         /GET LIST LENGTH
11431 3457         DCA I PBUFA      /AND STORE HERE
11432 4531         PUTTY            /SO WE CAN USE
11433 2377         LPBUF-1          /OUR TTY PUTTER
11434 1057         TAD PBUFA        /RESET BUFFER
11435 3010         DCA AUX0         /POINTER
11436 3260         DCA PCNT         /CLEAR COUNT
11437 5627         JMP I BUTTY      /RETURN
           /OUTPUT TO LINE PRINTER
11440 0000 PLPTR,  0
11441 6224         RIF
11442 6202         CIF 0            /STANDARD
11443 4441         JMS I WRITE      /I/O
11444 1455         LPARM            /CALL
11445 1255         TAD LPARM
11446 7710         SPA CLA          /DONE?
11447 5245         JMP .-2          /NO.CHECK AGAIN
11450 4520         CHKFLG           /CONTROL R?
11451 1057         TAD PBUFA        /YES,RESET
11452 3010         DCA AUX0         /BUFFER POINTER
11453 3260         DCA PCNT         /CLEAR COUNT
11454 5640         JMP I PLPTR      /RETURN
11455 0050 LPARM,  50               /PARAMETER LIST
11456 6211         CDF 10
11457 2400         LPBUF
11460 0000 PCNT,   0
11461 0000         0
```

```
11462 0000         0
11463 0000         0
           /PUT STRING ROUTINES
11464 0000 PSTR,   0                /CALLED IN 8 MODE
11465 1664         TAD I PSTR       /GET STRING ADDRESS
11466 2264         ISZ PSTR         /BOP POINTER
11467 4320         JMS SETPTR       /INITIALIZE
11470 4326         JMS PSTRGO       /SEND IT OUT
11471 5664         JMP I PSTR       /RETURN
11472 0000 PSTRA,  0                /FPP ENTRY
11473 1335         TAD CONLOA       /GET ADDRESS
11474 4320         JMS SETPTR       /INITIALIZE
11475 4326         JMS PSTRGO       /SEND TO BUFFER
11476 5672         JMP I PSTRA      /RETURN TO FPP
11477 0000 PSTRA1, 0                /SAME AS PSTRA
11500 1335         TAD CONLOA       /BUT PURGES
11501 4320         JMS SETPTR       /DECIMAL POINT
11502 1411 PSTR1,  TAD I AUX1
11503 3316         DCA PUSAV
11504 1316         TAD PUSAV
11505 1317         TAD M256
11506 7650         SNA CLA          /DECIMAL POINT?
11507 5677         JMP I PSTRA1     /YES,RETURN
11510 1316         TAD PUSAV        /NO,STORE AWAY
11511 3410         DCA I AUX0
11512 2260         ISZ PCNT
11513 2336         ISZ PUTCTR
11514 5302         JMP PSTR1
11515 5677         JMP I PSTRA1     /RETURN
11516 0000 PUSAV,  0
11517 7522 M256,   -256
11520 0000 SETPTR, 0
11521 3011         DCA AUX1         /SAVE ADDRESS
11522 1411         TAD I AUX1       /GET LENGTH
11523 7041         CIA              /AND
11524 3336         DCA PUTCTR       /SET THE COUNT
11525 5720         JMP I SETPTR     /RETURN
11526 0000 PSTRGO, 0
11527 1411         TAD I AUX1       /GET A CHARACTER
11530 3410         DCA I AUX0       /STORE IN PBUF
11531 2260         ISZ PCNT         /BOP PARAMETER COUNT
11532 2336         ISZ PUTCTR       /STRING DONE?
11533 5327         JMP .-4          /NO,REPEAT
11534 5726         JMP I PSTRGO     /YES,RETURN
11535 2352 CONLOA, CONLOC-1
11536 0000 PUTCTR, 0
           /PUT OUT CRLF AT AUX0
11537 0000 PCRLF,  0
11540 1350         TAD CR           /GET RETURN
11541 3410         DCA I AUX0       /SAVE AWAY
11542 1351         TAD LF           /GET LINE FEED
11543 3410         DCA I AUX0       /SAVE AWAY
11544 2260         ISZ PCNT         /BOP PARAMETER
11545 2260         ISZ PCNT         /COUNT BY 2
11546 5737         JMP I PCRLF      /RETURN
11547 0002 MYCRLF, 2
11550 0215 CR,     215
11551 0212 LF,     212
           /TAB SPACE ROUTINES
11552 0000 TBSP,   0                /CALLED IN 8 MODE
11553 1752         TAD I TBSP       /GET SPACE COUNT
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 A 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
2020 11632 1641          TAD I ORPTR     /GET A
2021 11633 7040          CMA             /COMPLIMENT A
2022 11634 0037          AND APT+7       /INTERSECT B
2023 11635 1641          TAD I ORPTR     /ADD A
2024 11636 3037          DCA APT+7       /STORE RESULT
2025 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             /Q
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           /(
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
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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
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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
```

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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             /(
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 PCONST, 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 **
2570            /
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, TRAPS 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 (SENRGY    /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, TRAPS 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, TRAPS 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 SENGY      /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 INTERVAL
     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 SCANER, TRAP5 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 ZERO?
     13416 3421
3075 13417 5000         TRAP5 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
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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 6702          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
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     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    /INTERSITY 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
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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 2171          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
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     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 INTERSITY
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           FSTA 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
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14020 0230        FLDA HILOC      /GET HIGH POINTER
14021 1121        JSA FLOAT       /FLOAT IT
14022 6472
14023 2224        FSUB ULIM       /GREATER THAN UPPER LIMIT?
14024 1051        JLT NERR1       /NO.STARTING ENERGY IS TOO LOW
14025 4046
14026 0006        STARTD
14027 0231        FLDA LOLOC      /GET LOW POINTER
14030 1121        JSA FLOAT       /FLOAT IT
14031 6472
14032 2225        FSUB LLIM       /LESS THAN LOWER LIMIT?
14033 1061        JGT NERR2       /NO,ENERGY RANGE IS TOO SHORT
14034 4044
14035 1001        JEQ .+4         /THEY ARE EQUAL,CHECK FOR INTERPOLATION
14036 4041
14037 1031        JA CHECK        /WE ARE OK,RETURN
14040 4016
14041 0226        FLDA RATIO      /DO WE HAVE TO INTERPOLATE
14042 1001        JEQ .-3         /NO.RETURN
14043 4037
14044 5000 NERR2, TRAP5 12
14045 0012
14046 5000 NERR1, TRAP5 13
14047 0013
           /GET THE LOW AND HIGH INTENSITIES
14050 1031 GETINT, JA .
14051 4050
14052 0400        FLDA (LOINT-3   /START OF LOW INTENSITY DATA
14053 7460
14054 6202        FSTA B2         /SAVE FOR INTERPOLATION ROUTINE
14055 0103        LDX -1.3        /INTERPOLATE
14056 7777
14057 0732        FLDA I B2.3+    /TO FIND
14060 6212        FSTA B12
14061 0732        FLDA I B2.3+    /OUR LOW
14062 0003        FNEG
14063 1212        FADD B12        /INTENSITY
14064 4226        FMUL RATIO
14065 0003        FNEG
14066 1212        FADD B12
14067 6235        FSTA LOWINT     /STORE
14070 0006        STARTD
14071 0230        FLDA HILOC      /GET HIGH POINTER
14072 6202        FSTA B2         /STORE HERE FOR LINTRP
14073 1121        JSA LINTRP      /INTERPOLATE
14074 4100
14075 6234        FSTA HIINT      /STORE HIGH INTENSITY
14076 1031        JA GETINT       /RETURN TO MAIN LINE
14077 4050
           /LINEAR INTERPOLATION
           /ENTER WITH UPPER ADDRESS IN B2
           /FRACTION IN RATIO
14100 1031 LINTRP, JA .
14101 4100
14102 0103        LDX -1,3        /SET INDEX REGISTER FOR ADDRESS
14103 7777
14104 0732        FLDA I B2,3+    /MODIFICATION. GET THE FIRST INTENSITY
14105 1121        JSA FLOAT       /FLOAT IT
14106 6472
14107 6212        FSTA B12        /STORE TEMPORARILY
14110 0006        STARTD
14111 0732        FLDA I B2,3+    /GET SECOND(LOWER) INTENSITY
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14112 1121          JSA FLOAT       /FLOAT IT
14113 6472
14114 0003          FNEG
14115 1212          FADD B12
14116 4226          FMUL RATIO      /INTERPOLATED INTENSITY=
14117 0003          FNEG            /FIRST-(FIRST-SECOND)*RATIO
14120 1212          FADD B12
14121 1031          JA LINTRP       /RETURN WITH OUR INTENSITY IN FAC
14122 4100
           /BACK INTERPOLATION
           /HIGH POINTER IN B3
           /INTENSITY IN B4
           /EXIT WITH FRACTION IN RATIO
14123 1031 INVTRP, JA .
14124 4123
14125 0103          LDX -1,3        /SET FOR ADDRESS MODIFICATION
14126 7777
14127 0006          STARTD
14130 0733          FLDA I B3,3+    /GET HIGH INTENSITY
14131 1121          JSA FLOAT
14132 6472
14133 6212          FSTA B12        /STORE A SECOND
14134 0006          STARTD
14135 0733          FLDA I B3,3+    /GET LOW INTENSITY
14136 1121          JSA FLOAT
14137 6472
14140 0003          FNEG
14141 1212          FADD B12
14142 6213          FSTA B13
14143 0212          FLDA B12        /(HI INT-X INT)/(HI INT-LO INT)=
14144 2204          FSUB B4
14145 3213          FDIV B13
14146 6226          FSTA RATIO      /THE RATIO
14147 1031          JA INVTRP       /RETURN
14150 4123
                    CHAIN "IEAS1"1
           /**CALCULATE AND PRINT DELTAS**
           /FIRST IE CURVE TAKEN AS THE REFERENCE
           /NORMALIZED ENERGIES OVERWRITTEN BY
           /DIFFERENCES
14151 0400 DELTA,   FLDA NIE        /GET THE NUMBER OF CURVES
14152 3005
14153 2401          FSUB FPPONE     /SUBTRACT ONE TO GET
14154 6511
14155 6237          FSTA NUMPLT     /THE NUMBER OF PLOTS
14156 0401          FLDA FPPTWO
14157 6514
14160 6210          FSTA B10
14161 0400          FLDA (7.
14162 7447
14163 1121          JSA FTYPE       /F7.2 CONVERSION SET
14164 7066
14165 0237          FLDA NUMPLT     /GET NUMBER OF PLOTS
14166 4400          FMUL (4.        /MULT BY 8/2 TO GET HALF THE OUTPUT
14167 7463
14170 0003          FNEG            /WIDTH IN SPACES.
14171 1400          FADD (66.       /SUBTRACT FROM 66 TO CENTER ON PAPER
14172 7406
14173 0023          ATX 3           /STORE THIS NUMBER OF SPACES HERE FOR
14174 0400          FLDA (IELOC     /TBSPA
14175 7436
14176 6243          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 0601        FLDA I B1       /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 IO ASCII
     14242 5760
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
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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 IEP1,   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
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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 B1       /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 6511
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
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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 SUM2,  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 6601        FSTA I B1        /STORE AWAY
0304 14556 0400        FLDA (INCEPT
     14557 7502
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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 6700
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 (8.
     14650 7505
0360 14651 1121         JSA FTYPE       /F8.0
     14652 7066
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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 CERTERING SPACES NOW
     14775 1561
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 PCRLF     /TERMINATE OUR LINE
     15031 1537
0471 15032 4001         TRAP4 PLPTR     /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         FNEG             /FORM ITS TWOS 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,   TRAP5 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 MINUMUM 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
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0554 15136 0400         FLDA (MINLOC
     15137 7521
0555 15140 6242         FSTA BUFLOC     /SET OUR POINTER TO THE MINIMUM VECTOR
0556 15141 0241         FLDA JCOL       /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
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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
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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 XFACTR     /CONVERT TO DATA COORDINATE UNITS
0751 15411 1251         FADD TEMP       /ADD IN THE TRANSLATED INTERCEPT
0752 15412 4255         FMUL YFACTR     /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)?
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     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
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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 6433
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
```

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1105 15623 1031          JA DELPT          /RETURN WITH VALUE IN FAC
     15624 5574
1106                /PRINT PAGE HEADING AND LABEL THE Y AXES
1107 15625 1031 AXLABL, 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 1071          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 NOSPAC       /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
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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 6467
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
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16013 7455
16014 1121         JSA FCON       /CONVERT IT
16015 6760
16016 4001         TRAP4 PSTRA    /PUT IT IN THE BUFFER
16017 1472
16020 0400         FLDA (.1
16021 7543
16022 5252         FADDM MIN      /BOP FOR THE NEXT LABEL
16023 1031         JA PRNTDV      /RETURN
16024 6004
             /PLOT THE Y AXIS DIVISIONS
16025 1031 PUYDV,  JA .
16026 6025
16027 0301         FLDA NUMYDV
16030 0003         FNEG
16031 0022         ATX 2          /SET THE COUNT
16032 0255         FLDA YFACTR
16033 1257         FADD KTRANS    /FORM THE INITIAL DISPLACEMENT
16034 6202         FSTA B2        /STORE FOR FUTURE INCREMENTATION
16035 0202         FLDA B2        /GET THE DISPLACEMENT
16036 1121         JSA PTPUT      /SET THE CORRECT POINT IN THE PLOTTER
16037 6063
16040 0255         FLDA YFACTR    /BUFFER
16041 5202         FADDM B2       /BOP THE DISPLACEMENT
16042 2121         JXN .-5,2+     /LOOP TILL ALL DIVISIONS ARE DONE
16043 6035
16044 1031         JA PUYDV       /RETURN
16045 6025
             /PLOT AN X AXIS DIVISION
16046 1031 PUXDV,  JA .
16047 6046
16050 0002         FCLA
16051 1257         FADD KTRANS
16052 6267         FSTA START     /SET THE STARTING POINT
16053 0400         FLDA (10.
16054 7524
16055 1257         FADD KTRANS
16056 6270         FSTA ENDBIT    /SET THE ENDING POINT
16057 1121         JSA LINPUT     /PUT THE LINE INTO THE BUFFER
16060 6133
16061 1031         JA PUXDV       /RETURN
16062 6046
             /SET A BIT TO PUT A POINT ON THE LP
             /ENTER WITH THE DISPLACEMENT IN FAC
16063 1031 PTPUT,  JA .
16064 6063
16065 1121         JSA ROUND      /ROUND THE DISPLACEMENT
16066 6313
16067 1121         JSA LIMCK      /CHECK THAT IT DOESNT EXCEED THE GRAPH
16070 6330
16071 6264         FSTA PTLOC     /LIMITS. STORE IT HERE
16072 0400         FLDA (8.
16073 7505
16074 6210         FSTA B10       /DIVISOR FOR MODULUS FUNCTION
16075 0264         FLDA PTLOC     /GET OUR DISPLACEMENT
16076 3210         FDIV B10       /DIVIDE BY 8 TO GET THE CORRECT
16077 6265         FSTA WRDLOC    /WORD LOCATION IN THE BUFFER
16100 0264         FLDA PTLOC
16101 1121         JSA AMOD       /USE THE REMAINDER TO SET THE
16102 6530
16103 6266         FSTA BITLOC    /CORRECT BIT
16104 0265         FLDA WRDLOC
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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      /THERE. 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 (8.
     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
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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. PREFORM 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 INCULSIVE 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
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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 LPTERR, 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         STARTF          /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
     16437 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
ACV     11062
ACQUI   14517
ACQUIR  10310
ACQ1    11123
ACQ2    11126
ACQ3    11145
AGAIN   15333
AMOD    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
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CHNA   10735
CHNFLG 10051
CHN1   10357
CKFLG  10771
CLAR   00001
CMNDER 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
DOMADV 13540
DTALOA 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
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ERRNUM 10067
EXIT   10727
FCON   16760
FILERR 10461
FILSAV 10426
FIX    12660
FLOAT  16472
FPC    10031
FPPG   11006
FPPG0  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
GTPARM 11420
GTTY   11400
HEADA  10460
HEADR  03000
HIINT  12724
HILOC  12710
HWPTR  10076
IEHED  12026
IELOC  03400
IEPRIN 14271
IEPRNT 10465
IFP1   14275
INCEPT 03110
INLOP  15313
INPL   11307
INTFAC 12732
INTOEN 13577
INTVL  12666
INVTRP 14123
IROW   12740
ISTBLK 10047
IUNIT  10046
JCOL   12743
KTRANS 13015
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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
LPTERR 16311
LPTRC  11000
LSAVE  11312
LSQHED 12133
LSTSQ  14354
LSTSQ1 14456
LWORD  16233
LWPTR  10077
MAJADV 13406
MASHED 12200
MASLOC 03030
MASPRT 10475
MASS   13130
MASSER 13160
MAXIM  13122
MCCPMS 17515
MCDIGC 17140
MCGETD 17313
MCLBLK 17423
MCPDOT 17505
MCPEXP 17441
MCPRTD 17527
MCPUTC 17354
MCRTP0 77000
MCRTP1 77030
MCRTP2 77033
MCRTP3 77036
MCRTP4 77041
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MCRTP5 77044
MCRTP6 77047
MCRTP7 77052
MCRTP8 77055
MC0TAB 17405
MC1TAB 17545
MC2TAB 17603
MC260  17730
MC3TAB 17641
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
NOPANG 03013
NORM   13340
NOPMUL 03010
NORM1  13446
NORM2  13461
NORPRM 10505
NOSPAC 13020
NRANG  14735
NSAM   11301
NSCANS 10074
NSHIFT 11310
NSTEPS 10073
NTIMES 11311
NULNTH 13001
NUMA   11607
NUML   11610
NUMPLT 12735
NUMYDV 13103
OMR    10034
OPTMA  10734
OPTMIZ 10600
OPTM1  10602
OR     11626
ORPTR  11641
OTRL   11306
OUTLOP 15267
PBUFA  10057
PBUFL  11341
PBUFRA 11340
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PCNT    11460
PCONST  13117
PCRLF   11537
PDP     00002
PLPTR   11440
PLT     00007
PLTFLG  13026
PRNT    00006
PRNTAB  10627
PRNTDV  16004
PSTR    11464
PSTRA   11472
PSTRA1  11477
PSTRGO  11526
PSTR1   11502
PTABL   14746
PTABL1  15006
PTABL2  14774
PTLOC   13034
PTPUT   16063
PTTY    11313
PUBLK   16467
PUCNTA  10956
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   13744
RANGER  13307
RATIO   12702
READ    10040
READTA  10641
REOT    00004
RESET   00005
RFMP    00011
RETURN  10042
RFFED   00003
RLTER   00002
RNDCHR  16325
RNGE    12671
ROUND   16313
SAML    11302
SAMPL   11200
SAMPLE  14532
SAMPL1  11217
SAMPL2  11264
SAM11   00111
SCANER  13336
SCANL   11165
SCANS   13313
SEARCH  13610
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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
TABHED 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
ULIMIT 13072
UNIT   10043
UPOINT 13061
UWORD  16263
WARPLT 15072
WRDLOC 13037
WRITE  10041
WRPLT  10677
WTLOC  03250
XFACTR 13004
XIT    10065
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XLNTH  13075
XVALUE 13012
YFACTR 13007
YLNTH  13100
ZROBUF 16372
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