Parametrization of Electron Impact Ionization Cross Sections for CO, CO$_2$, CH$_4$, NH$_3$, and SO$_2$

Santosh K. Srivastava
Hùng P. Nguyên

April 1, 1987

Prepared for
Air Force Office of Scientific Research
and
National Aeronautics and Space Administration
by
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California
Parametrization of Electron Impact Ionization Cross Sections for CO, CO$_2$, CH$_4$, NH$_3$, and SO$_2$

Santosh K. Srivastava
Hùng P. Nguyễn

April 1, 1987

Prepared for
Air Force Office of Scientific Research
and
National Aeronautics and Space Administration
by
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California
The research described in this publication was carried out by the Jet Propulsion Laboratory, California Institute of Technology, and was sponsored by the Air Force Office of Scientific Research and the National Aeronautics and Space Administration.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not constitute or imply its endorsement by the United States Government or the Jet Propulsion Laboratory, California Institute of Technology.
ABSTRACT

The electron impact ionization and dissociative ionization cross section data of CO, CO₂, CH₄, NH₃, and SO₂, measured in our laboratory, have been parametrized utilizing an empirical formula based on the Born approximation. For this purpose a $\chi^2$ minimization technique was employed which provided an excellent fit to the experimental data.
TABLE OF CONTENTS

I. Introduction 1

II. Procedure for Parametrization 5

III. Results and Discussion 14

IV. Acknowledgement 15

V. References 16

Appendix I: Experimental Apparatus and Method 46

Appendix II: Program Listing for HP9836C Computer 50
Figures

1. Flow diagram 12

2. Subprocedure CURFIT 13

3. Dissociative ionization and attachment spectrometer 20

4. Total electron impact ionization cross section for CO. 21

5. Electron impact ionization cross section for the production of CO\(^+\) from CO. 22

6. Electron impact ionization cross section for the production of C\(^+\) from CO. 23

7. Electron impact ionization cross section for the production of O\(^+\) from CO. 24

8. Total electron impact ionization cross section for CO\(_2\). 25

9. Electron impact ionization cross section for the production of CO\(_2^+\) from CO\(_2\). 26

10. Electron impact ionization cross section for the production of CO\(^+\) from CO\(_2\). 27

11. Electron impact ionization cross section for the production of C\(^+\) from CO\(_2\). 28

12. Electron impact ionization cross section for the production of O\(^+\) from CO\(_2\). 29
13. Total electron impact ionization cross section for $CH_4$.  

14. Electron impact ionization cross section for the production of $CH^+_4$ from $CH_4$.  

15. Electron impact ionization cross section for the production of $CH^+_3$ from $CH_4$.  

16. Electron impact ionization cross section for the production of $CH^+_2$ from $CH_4$.  

17. Electron impact ionization cross section for the production of $CH^+$ from $CH_4$.  

18. Electron impact ionization cross section for the production of $C^+$ from $CH_4$.  

19. Total electron impact ionization cross section for $NH_3$.  

20. Electron impact ionization cross section for the production of $NH^+_3$ from $NH_3$.  

21. Electron impact ionization cross section for the production of $NH^+_2$ from $NH_3$.  

22. Electron impact ionization cross section for the production of $NH^+$ from $NH_3$.  

23. Electron impact ionization cross section for the production of $N^+$ from $NH_3$.  

24. Total electron impact ionization cross section for $SO_2$.  

vii
25. Electron impact ionization cross section for the production of $SO_2^+$ from $SO_2$.  


27. Electron impact ionization cross section for the production of $S^+$ from $SO_2$.  


Table  

I. The parameters $A$ and $a_i$'s of (8) for the fitted cross sections.
I. INTRODUCTION

Cross sections for the production of positive ions by electron impact on molecules find application in a wide variety of plasmas. The collision process may be represented by the following relations:

$$e^- + MN \xrightarrow{\sigma} MN^+ + 2e^- \quad (1)$$

$$\xrightarrow{\sigma} M^+ + N + 2e^- \quad (2a)$$

$$\xrightarrow{\sigma} M + N^+ + 2e^- \quad (2b)$$

$$\xrightarrow{\sigma} M^+ + N^+ + 3e^- \quad (3)$$

$$\xrightarrow{\sigma} Species \ of \ higher \ stages \ of \ ionization, \quad (4)$$

where $\sigma$ is the cross section, $MN$ is a diatomic molecule with $M$ and $N$ as component atoms and the "+" sign indicates a positive ion. Although equations (1) through (4) have been written for a diatomic molecule, similar relations hold for polyatomic molecules.

There are various definitions of the cross section, $\sigma$. They are given below:

a) **Partial cross section, $\sigma_p$** : It represents the individual process given by equations (1) through (4).

b) **Total cross section, $\sigma(T)$** : The total cross section is defined according
to the method used for its determination:

i) If the particle counting method is employed for obtaining the total number of ions (singly as well as multiply ionized) produced as a result of electron impact then it is known as total counting ionization cross section, \( \sigma_e(T) \), and is given by:

\[
\sigma_e(T) = \sum_p \sigma_p + \sum_i \sigma_p^i,
\]

where \( \sigma_p \) is the partial ionization process described by eqs. (1) through (3) and \( \sigma_p^i \) is the partial cross section for the \( i^{th} \) stage of ionization.

ii) If the cross section data are generated by measuring the total ion current then the total ionization cross section, \( \sigma_I(T) \), is as follows:

\[
\sigma_I(T) = \sum_p \sigma_p + \sum_i Z_i \sigma_p^i,
\]

where \( Z_i \) is the stage of ionization.

Cross sections for ionization have been measured since the 1930's. The various methods employed, in the past, for this purpose have been described in detail in several review articles previously published in the literature. Theoretical calculations for these cross sections are difficult due to many channels in the continuum contributing to the ionization process. Recently, however, the status of the theory of ionization of atoms and ions has been reviewed by Younger. A similar survey for molecules has also been made.
by Rudge.6.

The first approach to the calculation of ionization cross sections was based on the classical theory and was presented by Thomson7 in 1912. His expression for the ionization is as follows:

\[ \sigma_p = 4\xi \left(\frac{I_H}{I}\right)^2 X^{-\frac{1}{2}}(1 - X^{-1})\pi a_0^2 \]  

(7)

where \( \xi \) is the number of electrons in the target with binding energy \( I \), \( X \approx EI^{-1} \) is the reduced ionization energy and \( I_H \) is the ionization energy of the hydrogen atom.


Quantum mechanical calculations by Bethe23, however, showed that the simple asymptotic behavior of \( \sigma_p \) (eq.7) is incorrect and it should vary as \( \frac{\ln(E)}{E} \) at high electron impact energies. Based on Bethe's theory, Bell et al.22 proposed an empirical formula for atoms and ions to fit the experimental data at all energies of the colliding electron. It is as follows:
\[
\sigma_p(E) = \frac{1}{IE} \left[ A \ln \left( \frac{E}{I} \right) + \sum_{i=1}^{N} a_i \left( 1 - \frac{I}{E} \right)^i \right]
\]  

(8)

where \( A \) and \( a_i \) are fitting coefficients and all other quantities have been defined previously. The above formula takes care of the behavior of \( \sigma_p(E) \) at high electron impact energies. The coefficient \( A \) can be calculated by fitting to the Bethe relation at high energies:

\[
\sigma_p(E) = \frac{1}{IE} [A \ln(E) + B].
\]  

(9)

It can also be obtained from the following relation:

\[
A = \frac{1}{\pi \alpha} \int_{I}^{\infty} \frac{\sigma_{ph}}{E} dE
\]  

(10)

where \( \sigma_{ph} \) is the photon-ionization cross sections for CO, CO\(_2\), CH\(_4\), NH\(_3\), and SO\(_2\). For the sake of convenience of the modelers to utilize our data, we have parametrized them using equations (8) and (9). Experimental apparatus and procedures for obtaining these data are described in appendix I. Section II describes the fitting procedure, and in section III, results are presented and discussed.
II. PROCEDURE FOR PARAMETRIZATION

a) Methods

Cross sections for electron impact ionization of CO, CO$_2$, CH$_4$, NH$_3$, and SO$_2$ were previously measured in our laboratory. Equation (8) was then fitted to these cross sections by a $\chi^2$ minimization technique. The details are described below. For in-depth discussion of the methodology, refer to Bevington$^{24}$.

For this purpose, we define a parameter $\chi^2$ in the following way:

$$\chi^2 = \frac{1}{N - M} \sum_{i=1}^{N} \frac{1}{\sigma_i^2} [f_i(x_i) - f_t(x_i)]^2,$$

(11)

where $M$ is the number of parameters, $N$ the number of data points, $\frac{1}{\sigma_i^2}$ the weight for each data point, $f_i(x_i)$ the experimental data at $x_i$, and $f_t(x_i)$ is the theoretical value at $x_i$, calculated from eq.(8). Since $x_i$'s (experimental data) do not change in the fitting procedure, $f_t(x)$ is a function of $a_i$'s alone, i.e., $f_t(x) \equiv f_t(a_1, a_2, \ldots, a_M)$. Consequently, $\chi^2$ is also a function of the parameters $a_i$'s alone,

$$\chi^2 \equiv \chi^2(a_1, a_2, \ldots, a_M).$$
Thus we can obtain a minimal value for \( \chi^2 \), at least a locally minimal value, by manipulating \( a_i \)'s on the \( a_i \)-space. There are many ways to minimize \( \chi^2 \), two of which are used in this report. They are the gradient search and the linearization of the fitting function. These methods are described in detail below:

i) \textit{Gradient search}

In the gradient search, the negative gradient of \( \chi^2 \)

\[
-\nabla \chi_o^2 = \sum_{i}^{M} \delta a_i \hat{a}_i, \tag{12}
\]

is calculated at some point \((a_1^*, a_2^*, \ldots, a_M^*)\). The parameters \( a_i \)'s are then incremented simultaneously by \( \delta a_i \), that is in the direction of the negative gradient \(-\nabla \chi_o^2\). \( \hat{a}_i \), in this case, is the unit orthogonal vector in the direction of \( a_i \) in the \( a_i \)-space, \( \delta a_i \) is the \( a_i \)-component of the gradient \(-\nabla \chi_o^2\).

Expanding \( \chi^2 \), using Taylor's series expansion, as a function of parameters \( a_i \)'s, we have

\[
\chi^2 = \chi_o^2 + \sum_{j=1}^{M} \left[ \frac{\partial \chi^2}{\partial a_j} \delta a_j \right]. \tag{13}
\]

The optimum values for parameter increments, \( \delta a_j \)'s, are those for which \( \chi^2 \) is a minimum, that is when
\[
\frac{\partial x^2}{\partial a_k} = \frac{\partial x^2}{\partial a_k} + \sum_{j=1}^{M} \left[ \frac{\partial^2 x^2}{\partial a_j \partial a_k} \delta a_j \right] = 0, \quad k = 1 \ldots M \quad (14)
\]

We have, from eq.(14), a set of \( M \) simultaneous linear equations in \( \delta a_j \)'s. To solve for \( \delta a_j \)'s, we first express these equations in matrix form. Letting

\[
\beta = \left( \begin{array}{c} \frac{\partial x^2}{\partial a_1} \\ \vdots \\ \frac{\partial x^2}{\partial a_M} \end{array} \right),
\]

\[
\delta a = \left( \begin{array}{c} \delta a_1 \\ \vdots \\ \delta a_M \end{array} \right), \quad (15)
\]

\[
\alpha = \left( \begin{array}{ccc} \frac{\partial^2 x^2}{\partial a_1 \partial a_1} & \cdots & \frac{\partial^2 x^2}{\partial a_M \partial a_1} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 x^2}{\partial a_1 \partial a_M} & \cdots & \frac{\partial^2 x^2}{\partial a_M \partial a_M} \end{array} \right);
\]

and substituting eq.(15) into eq.(14), we have

\[
\beta = \delta a \cdot \alpha. \quad (16)
\]

Multiplying both sides of eq.(16) by \( \alpha^{-1} \) we have a matrix of the parameter increments \( \delta a \):

\[
\delta a = \beta \cdot \alpha^{-1}. \quad (17)
\]
ii) Linearization of the fitting function.

Instead of expanding $\chi^2$ as in the gradient search method, we expand $f_t(z)$ as a function of parameters $a_i$'s,

$$f_t(z) = f_0(z) + \sum_{j=1}^{M} \left[ \frac{\partial f_0(z)}{\partial a_j} \delta a_j \right].$$ (18)

Together with eq.(11), $\chi^2$ can then be expressed as,

$$\chi^2 = \frac{1}{N-M} \sum_i^N \frac{1}{\sigma_i^2} [f_e(x_i) - f_t(x_i)]^2$$

$$= \frac{1}{N-M} \sum_i^N \frac{1}{\sigma_i^2} \left\{ f_e(x_i) - f_0(x_i) - \sum_{j=1}^{M} \left[ \frac{\partial f_0(z)}{\partial a_j} \delta a_j \right] \right\}^2.$$ (19)

Minimizing $\chi^2$ with respect to $\delta a_k$, we have

$$\frac{\partial \chi^2}{\partial (\delta a_k)} = -\frac{2}{N-M} \sum_i^N \frac{1}{\sigma_i^2} \left\{ f_e(x_i) - f_0(x_i) - \sum_{j=1}^{M} \left[ \frac{\partial f_0(z)}{\partial a_j} \delta a_j \right] \right\} \frac{\partial f_0(x_i)}{\partial a_k}$$

$$= 0, \quad k = 1 \ldots M$$ (20)

As before, we have $\beta = \delta a \cdot \alpha$, in matrix form, or in a more explicit form,

$$\beta_k = \sum_i^N \frac{1}{\sigma_i^2} [f_e(x_i) - f_0(x_i)] \frac{\partial f_0(x_i)}{\partial a_k}$$

$$= \frac{\partial}{\partial a_k} (\chi^2)$$ (21)
and

\[ \alpha_{jk} \approx \sum_{i=1}^{N} \left[ \frac{1}{\sigma_i^2} \frac{\partial f_0(x_i)}{\partial a_j} \frac{\partial f_0(x_i)}{\partial a_k} \right] \]

\[ j, k = 1..M. \]  

(22)

b) Advantages and disadvantages of the above two methods

Theoretically, the gradient search will take the search to the minimal point of \( \chi^2 \). However, from a computational point of view, it presents some difficulties. Computing the gradient of \( \chi^2 \) requires the computer to go through many calculations. Thus at a near-minimal point, where the increments \( \delta a_j \)'s are considerably small, the gradient search has to be utilized many times and thus renders the method inefficient. The linearization of the fitting function, on the other hand, gives good results near the minimum point. However, by the nature of the Taylor's expansion, this method is unreliable when \( \chi_0^2 \) is too far away from the minimum point.

c) Gradient-Expansion search method

It is obvious then that these two methods are complementary. As discussed in the last section, the gradient search is effective when \( \chi^2 \) is at a point far away from the minimum point, and the linearization method is effective nearby. The best features of these two methods can be incorporated into one by increasing the diagonal terms of matrix \( \alpha \) by a factor of \( \lambda \), so that:

\[ \beta = \delta a \cdot \alpha, \]  

(23)
where
\[ \alpha_{jk} = \begin{cases} \alpha_{jk}(1 + \lambda), & \text{if } j = k, \\ \alpha_{jk}, & \text{if } j \neq k. \end{cases} \]  

(24)

If \( \lambda \) is small, the above equation is similar to that obtained from the linearization method. If \( \lambda \) is large, the diagonal terms dominate the matrix, thus we have
\[ \beta_i \approx \lambda \cdot \delta a_i \cdot a_{ii} \]  

(25)

which yields similar solutions to those obtained from the gradient search method.

d) Algorithm

The above search method can be summarized as follows:

1) Set \( \lambda = 0.0001 \); Compute \( \chi^2(a) \),

2) Compute \( \delta a \) and \( \chi^2(a + \delta a) \),

3) If \( \chi^2(a + \delta a) > \chi^2(a) \), increase \( \lambda \) by a factor of 10 and repeat step 2,

4) If \( \chi^2(a + \delta a) < \chi^2(a) \), decrease \( \lambda \) by a factor of 10 and return to repeat step 2, substituting \( a + \delta a \) for \( a \),

where \( a = (a_1, a_2, \ldots, a_M) \), and \( \delta a = (\delta a_1, \delta a_2, \ldots, \delta a_M) \)

The above steps can be terminated when the difference of \( \chi^2(a + \delta a) \) and \( \chi^2(a) \) is smaller than some predetermined constant; 0.0001 was used in this report.
The programs, using the methods discussed above, were written in Pascal language and were executed on the HP9836C and Apple IIe computers and implemented by Caltech’s CS10 graphics library. The program for HP9836C is listed in appendix II. Flow diagrams from these programs are given in Figures 1 and 2.
\[ \lambda = 0.0001 \]

\[ n_{\text{free}} = N - M \]

Calculate weight, \( \frac{1}{\sigma^2} \)

Calculate chisqr2

If \( n_{\text{free}} > 0 \):

No

chisqr2 = 0

Yes

\[ x_1 = \text{chisqr2} \]

CURFIT subprocedure

If \( x_1 - \text{chisqr2} < 0.0001 \):

No

Yes

END

Figure 1. Flow diagram
START

Calculate $\beta$ and $\alpha$ matrices

$\text{chisqr1} = \text{chisqr2}$

\[ A_{jk} = \frac{\beta_{jk}}{\sqrt{\alpha_{jj} \alpha_{kk}}} \]

\[ A_{jj} = 1 + A_{jj} \]

Invert $A$

$B = \text{array of parameters}$

\[ B = B + \frac{\beta_i A_{ik}}{\sqrt{\alpha_{jj} \alpha_{kk}}} \]

Calculate $\text{chisqr2}$

$\lambda = \lambda \cdot 10$

Yes

$\text{Chisqr2} > \text{Chisqr1}$

No

array of parameters = $B$

$\sigma$ of $j^{th}$ parameter = $\sqrt{\frac{A_{jj}}{\alpha_{kk}}}$

$\lambda = \lambda/10$

END

Figure 2. Subprocedure CURFIT
III. RESULTS AND DISCUSSION

Utilizing eq.(8) and the fitting procedure described in section II, the values of coefficients $A$ and $a_i$'s were determined. They are presented in Table I. Fitted data are also shown in graphical forms in figures 2 through 26. Except for $SO_2$, the experimental measurements were up to 510 eV electron impact energy. The data uncertainty was about 15%. The error bars are shown in all figures. In the cases of $CO$, $CO_2$, $CH_4$, and $NH_3$, eq.(8) has provided an excellent fit to the experimental data. However, the data for $SO_2$ are only up to 200 eV and the fits are not very satisfactory.
IV. ACKNOWLEDGEMENT

We would like to thank the SURF program at Caltech for providing a financial grant to one of us (HPN). We would also like to thank Mr. C. Thoms and Dr. E. Krishnakumar for their help and discussion during the course of this work. The research described in this report was carried out at the Jet Propulsion Laboratory, California Institute of Technology, and was sponsored by SURF, AFOSR, and the National Aeronautics and Space Administration.
V. REFERENCES


23. H. Bethe, Ann. Physik 5, 325 (1930); also Z. Physik 76, 293 (1932).


TABLE I

The parameters $A$ and $a_i$'s of (8) for the fitted cross sections. These parameters are in the units of $10^{-14}eV^2\cdot cm^2$.

<table>
<thead>
<tr>
<th>Mol. Prod.</th>
<th>$A$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_5$</th>
<th>$a_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>65.459</td>
<td>65.00</td>
<td>-22.427</td>
<td>-26.250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.433</td>
<td>-1.262</td>
<td>-2.514</td>
<td>6.436</td>
<td>-3.055</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>77.266</td>
<td>-75.035</td>
<td>-46.899</td>
<td>27.582</td>
<td>-41.401</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$^+$</td>
<td>49.342</td>
<td>-46.397</td>
<td>-39.366</td>
<td>45.765</td>
<td>-51.574</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>6.781</td>
<td>6.653</td>
<td>5.229</td>
<td>7.254</td>
<td>-11.443</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>2.384</td>
<td>-2.368</td>
<td>0.984</td>
<td>-10.776</td>
<td>29.389</td>
<td>-18.058</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>52.961</td>
<td>-51.003</td>
<td>-35.790</td>
<td>24.074</td>
<td>-31.205</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>25.660</td>
<td>24.545</td>
<td>-9.057</td>
<td>-1.971</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3^+$</td>
<td>-32.326</td>
<td>32.268</td>
<td>-9.057</td>
<td>-1.971</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>30.133</td>
<td>-27.286</td>
<td>-43.680</td>
<td>169.936</td>
<td>-276.50</td>
<td>140.548</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>60.704</td>
<td>-54.546</td>
<td>-82.229</td>
<td>287.768</td>
<td>-447.52</td>
<td>225.250</td>
<td></td>
</tr>
<tr>
<td>NH$_2^+$</td>
<td>57.455</td>
<td>-58.280</td>
<td>-1.297</td>
<td>-31.188</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$^+$</td>
<td>2.359</td>
<td>-1.796</td>
<td>-10.851</td>
<td>68.642</td>
<td>-186.8</td>
<td>233.891</td>
<td>-104.63</td>
</tr>
<tr>
<td>Total</td>
<td>60.008</td>
<td>-59.746</td>
<td>-15.417</td>
<td>88.234</td>
<td>113.977</td>
<td>-71.625</td>
<td></td>
</tr>
<tr>
<td>SO$_2$</td>
<td>66.607</td>
<td>-63.735</td>
<td>-75.659</td>
<td>331.36</td>
<td>-674.18</td>
<td>472.058</td>
<td>-91.948</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>29.372</td>
<td>-24.266</td>
<td>-57.076</td>
<td>196.126</td>
<td>-329.76</td>
<td>173.684</td>
<td></td>
</tr>
<tr>
<td>O$^+$</td>
<td>2.010</td>
<td>-1.707</td>
<td>-2.537</td>
<td>9.661</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>80.341</td>
<td>-77.366</td>
<td>5.886</td>
<td>-311.92</td>
<td>1414.13</td>
<td>-2309.7</td>
<td>1252.17</td>
</tr>
</tbody>
</table>
Figure 3. Dissociative ionization and attachment spectrometer (dimensions not to scale)
Figure 4. Total electron impact ionization cross section for CO.
Figure 5. Electron impact ionization cross section for the production of CO$^+$ from CO.
Figure 6. Electron impact ionization cross section for the production of C\(^+\) from CO
Figure 8. Total electron impact ionization cross section for CO$_2$. 
Figure 9. Electron impact ionization cross section for the production of $\text{CO}_2^+$ from $\text{CO}_2$.
Figure 10. Electron impact ionization cross section for the production of CO$^+$ from CO$_2$
Figure 11. Electron impact ionization cross section for the production of C+ from CO₂
Figure 12. Electron impact ionization cross section for the production of $\text{O}^+$ from $\text{CO}_2$
Figure 13. Total electron impact ionization cross section for CH$_4$. 
Figure 14. Electron impact ionization cross section for the production of CH$_4^+$ from CH$_4$. 

$CH_4^+ (CH_4)$

Electron Impact Energy, eV
Figure 15. Electron impact ionization cross section for the production of CH$_3^+$ from CH$_4$. 

\( \sigma_p (10^{-16} \text{ cm}^2) \) vs. ELECTRON IMPACT ENERGY, eV
Figure 16. Electron impact ionization cross section for the production of CH$_2^+$ from CH$_4$
Figure 17. Electron impact ionization cross section for the production of CH$^+$ from CH$_4$. 
Figure 18. Electron impact ionization cross section for the production of C$^+$ from CH$_4$. 
Figure 19. Total electron impact ionization cross section for NH$_3$. 
Figure 21. Electron impact ionization cross section for the production of $\text{NH}_2^+$ from $\text{NH}_3$. 

$\text{NH}_2^+ (\text{NH}_3)$
Figure 22. Electron impact ionization cross section for the production of NH$^+$ from NH$_3$. 

\[ \sigma_{\text{p}} \left( 10^{-17} \text{ cm}^2 \right) \]

\[ \text{ELECTRON IMPACT ENERGY, eV} \]

\[ \text{NH}^+ (\text{NH}_3) \]
Figure 23. Electron impact ionization cross section for the production of N\(^+\) from NH\(_3\)
Figure 24. Total electron impact ionization cross section for SO₂
Figure 25. Electron impact ionization cross section for the production of $\text{SO}_2^+$ from $\text{SO}_2$. 

$\text{SO}_2^+$ ($\text{SO}_2$)
Figure 26. Electron impact ionization cross section for the production of SO\(^+\) from SO\(_2\)
Figure 27. Electron impact ionization cross section for the production of $S^+$ from $SO_2$. 

$S^+(SO_2)$ 

$E_{\text{electron}}$ (eV) 

$E_{\text{impact energy}}$, eV 

$\rho_2^{\omega\ell_{-1}}$ 

$\phi_2^{\ell_{-1}}$ 

$\phi_2^{\ell_{-1}}$
Figure 28. Electron impact ionization cross section for the production of O$^+$ from SO$_2$. 
APPENDIX I
EXPERIMENTAL APPARATUS AND METHOD

A schematic diagram of the apparatus is shown in Fig.3. It utilizes a crossed electron beam—molecular/atomic beam collision geometry. In the case of gases, the beam of atoms or molecules is produced by flowing the gas through a capillary array. Alternatively, in the case of species which are solids or liquids at room temperature, an electron bombarded oven or a resistance heated oven is utilized to produce the target beam. The beam of electrons is generated by heating a pure tungsten filament. The electrons are first extracted from the filament and are then accelerated or decelerated by three cylindrical lenses. This beam is collimated by the help of an axial B field which is produced by a solenoid within which the electron gun and a Faraday cup are housed. The solenoid produces the B field of the order 200 G.

The present beam of electrons is energy unselected. An energy profile of this beam was obtained by utilizing the retarding potential on the Faraday cup. It is found that the full width at half maximum (FWHM) is approximately 300 meV. The energy of the electrons is varied by changing the bias on the filament with respect to the last electrode of the electron gun. This electrode is kept at ground (earth) potential. It was found that the beam current, as measured by the Faraday cup, remained constant as the energy
of the beam was changed from 0.5 to about 10 eV which is the range of the present interest. Although the energy of the electron beam can be obtained by recording the filament bias voltage, the contact potentials at various surfaces tend to change it from its actual value. In the present work, the energy of the beam was calibrated by utilizing the accurately known values of ionization potentials of the rare gases.

The positive ions produced by collision of electrons with the target molecules are extracted out of the B field by two parallel molybdenum wire meshes between which a voltage is applied. This voltage produces a homogeneous electric field with a gradient of 3 to 10 V/cm at the target. The direction of the field is normal to both electron beam and molecular beam. One grid is biased negative with respect to the ground and the other positive. The molecular beam is kept at ground potential. It was found that this arrangement did not disturb the electron beam. The efficiency of extraction of ions was measured by changing the extracting electric field from 0 up to 10 V/cm. It was found that by increasing the electric field strength, the detected ion intensity increased rapidly in the beginning. However, at about 3 eV and above the ion intensity became almost constant as a function of the field strength. This indicated that the measured ion current did not depend on the initial energy and angular distribution of the ions. All our measurements were performed in this region of extracting voltage. The extracted ions are accelerated from 0 to about 200 V/cm and focused at the entrance aperture of a quadrupole mass spectrometer by an ion lens (Fig.1). This mass spectrometer has a resolution of approximately 1 amu. The mass analyzed ions are accelerated by a 3.2 kV potential and are detected by a spiraltron
multiplier. Each ion is counted as an event by a multichannel scaler.

A vacuum of about $10^{-8}$ Torr was obtained when the gas forming the molecular beam was not flowed into the vacuum chamber. However, the pressure rose to about $10^{-7}$ Torr when the molecular beam was on.

In order to obtain the absolute values of the cross sections, the relative flow technique developed in our laboratory for collision cross section measurement was utilized. The method employs a measurement of the ratio of the intensity of the positive ions of the unknown species (for example, $O^+/SO_2$, $S^+/SO_2$, $SO^+/SO_2$, $SO_3^+/SO_2$) to that of a known species (for example, $He^+/He$, $Ne^+/Ne$, $Ar^+/Ar$, or $Kr^+/Kr$). At the same time, the flow rates and pressure behind the capillary array are measured. First, the gas $AB$ whose ionization cross section has to be measured is flowed through the capillary array and a beam is formed. The positive ion intensity $I(B^+)$ is then measured. Subsequently, the gas $AB$ is turned off and Ar is flowed through the capillary array. The positive ion current $I(Ar^+)$ is again recorded. Providing that the measurement is performed under the conditions of molecular flow through the capillary array, the following relation is used to obtain the cross section:

$$\sigma \left( \frac{B^+}{AB} \right) = \sigma \left( \frac{Ar^+}{Ar} \right) \cdot \frac{I(B^+)}{I(Ar^+)} \cdot \left[ \frac{m(Ar)}{m(AB)} \right]^{1/2} \cdot \left( \frac{N(Ar)}{N(AB)} \right) \cdot K,$$

(26)

where $m(AB)$ and $m(Ar)$ are molecular weight of respective gases, $N(Ar)$ and $N(AB)$ are the flow rates of the two gases through the capillary array, and $K$ is a calibration constant which determines the transmission efficiency of the
ion optics, quadrupole mass spectrometer, and charged particle detector for $B^+$ and $Ar^+$.

The calibration constant $K$ for the various masses was experimentally obtained. We chose gases whose ionization cross sections are well known. These are $(H^+/H_2)^{26}$, $(He^+/He)^{27}$, $(O^+,O_2)^{26}$, $(Ne^+/Ne)^{27}$, $(Ar^+/Ar)^{27}$, and $(Kr^+/Kr)^{27}$. Since all the quantities in Eq.(23) are either known or can be obtained experimentally for the two gases out of the ones mentioned above except $K$, the values of $K$ for various mass numbers ranging from $H$ to $Kr$ can be calculated. We followed this method for calibrating our instrument. The relative efficiency $K$ as a function of the mass number is a bell shaped curve. It is increasing with the mass number up to about mass number 45, then it is decreasing at higher mass numbers. Our results are in agreement with Ehlert's measurements. More detail about the relative efficiency measurement can be found in Orient and Srivastava's paper.

The contribution of the background scattering (both direct beam contribution and scattering by the background gas) to the scattering from the target gas beam is measured by providing an alternate leak to the vacuum chambers. The flow to the chamber is switched from the capillary array to the alternate gas inlet and the proper background pressure for the desired gas is established. The mass selected beam intensity is then measured as a function of the electron beam energy. It is found that the maximum value of the background scattering is about 5%.
APPENDIX II

Program Listing for HP9836C Computer
program surf1 (input, output);
import mylib;
{ graphic library C.I.T. }
const
top = 350; pi = 3.14159268; maxdata = 200;
bottom = 20; maxpar = 30; termx = 9999;
left = 20; long = 480; maxfunc = 100;
right = 500; height = 330; maxstack = 20;
type
chars = '#'..'z';
charset = set of chars;
elem_type = (cons, coef, oper, vars, ends); { type of function elements }
oper_type = (oadd, osub, omul, odiv, opwr, oexp, olog, ocos, osin, oatn,
otan, ocsn, osnh, otnh); { defined basic operators }
func_rec = record
  case datum : elem_type of
    vars : (valr : real);
    coef, cons : (vali : integer);
    oper : (valo : oper_type);
end;
func_arr = array [0..maxfunc] of func_rec; { function array }
stack_arr = array [1..maxstack] of real;
vhype = (vertical, horizontal); { uncertainty type }
mode_type = (instr, none, stat);
theograf = array [left..right] of real; { array of graph }
coeff_rec = record
  a, siga, dela : real;
end;
coeff_type = array [1..maxpar] of coeff_rec; { array of coefficients }
cons_type = array [1..maxpar] of real; { array of function constants }
data_rec = record
  x, y, sigy : real;
end;
exydata = array [1..maxdata] of data_rec; { array of data }
filedata = file of data_rec;
filefuncrec = record
  sort, sub : integer;
end;
filefunc = file of filefuncrec;
mattype = array [1..maxpar, 1..maxpar] of real;
onedda = array [1..maxdata] of real;
var
dmaxy, dminy, maxx, maxy, minx, miny : real;
lamda, x2, x1, corrx, corry, cutoff : real;
funca : func_arr;
datg, dat : theograf;
coeff : coeff_type;
name : string[12];
filea : filedata;
fileb : filefunc;
cfterms, connum, npts, nfree, color : integer;
cona : cons_type;
function ff (fop : oper_type; xi, xi_1 : real): real; 
begin 
  case fop of 
  osub : ff := xi_1 - xi; 
  oadd : ff := xi_1 + xi; 
  omul : ff := xi_1 * xi; 
  odiv : ff := xi_1 / xi; 
  opwr : ff := exp(xi*ln(xi_1)); 
  oexp : if abs(xi) < 700 then ff := exp(xi) else if xi > 0 then ff := 1e300 else ff := 1e-300; 
  olog : if xi > 1e-300 then ff := ln(xi) else ff := -1e300; 
  ocos : ff := cos(xi); 
  osin : ff := sin(xi); 
  oatan : ff := arctan(xi); 
  otan : ff := sin(xi)/cos(xi); 
  osnh : if abs(xi) < 700 then ff := 0.5*(exp(xi) - exp(-xi)) else if xi > 0 then ff := 1e300 else ff := -1e300; 
  ocsh : if abs(xi) < 700 then ff := 0.5*(exp(xi) + exp(-xi)) else ff := 1e300; 
  otanh : if abs(xi) > 700 then ff := (exp(xi) - exp(-xi))/(exp(xi) + exp(-xi)) else if xi > 0 then ff := 1 else ff := -1;
end;
end;

function f (ffunca : func_arr; fx, fcutoff : real; fcoeff : coeff_type; fcona : cons_type): real; 
begin 
  var i, st : integer; fstck : stck_arr; 
  begin 
    st := 0; 
    i := 1; 
    if fx <= fcutoff then f := 0 else begin 
      begin 
        while ffunca[i].datum <> ends do begin 
          if ffunca[i].datum <> oper then st := st + 1; 
          begin 
            case datum of 
              vars : fstck[st] := fx; 
              cons : fstck[st] := fcona[valu]; 
              coef : fstck[st] := fcoeff[valu].a; 
              oper : case valo of 
                oadd, osub, odiv, omul, opwr : begin 
                  fstck[st-1] := ff(valo, fstck[st], fstck[st-1]); 
                end; 
            end; 
          end; 
        end; 
      end; 
    end; 
  end; 
end;
st := st -1;
end;
oexp,alog,ocos,osin,oatn,otan,ocsh,osnh,otnh :
fstck[st] := ff(valo,fstck[st],fstck[st]);
end;
i := i + 1;
\{ increment stack count \}
f := fstck[1];
\{ f is first element of stack \}
end;

{---------------------------------------------}

procedure maxmindata(mindat: expdata);
\{ find maximum and minimum \}
var i: integer;
\{ of both x and y of data \}
begin
maxx := mindat[1].x;
\{ initial max. min. \}
maxy := mindat[1].y + mindat[1].sigy;
minx := mindat[1].x;
miny := mindat[1].y - mindat[1].sigy;
for i := 1 to npts do
\{ search for max. min. \}
with mindat[i] do
begin
if x > maxx then maxx := x;
if x < minx then minx := x;
if y + sigy > maxy then maxy := y + sigy;
if y - sigy < miny then miny := y - sigy;
end;
dmaxy := maxy;
\{ save dmaxy, dminy for graph \}
dminy := miny;
corrx := long/(maxx - minx);
\{correction factors for screen\}
corry := height/(maxy - miny);
end;

{---------------------------------------------}

procedure maxmin;
\{ calculate max and min for \}
var i: integer;
\{ both the graph \}
\{ and input data \}
begin
maxy := dmaxy;
miny := dminy;
for i := left to right do
\{ recalculate y correction \}
begin
if dat[i] > maxy then maxy := dat[i];
if dat[i] < miny then miny := dat[i];
end;
corry := height/(maxy - miny);
end;
function theodata(tfunca : func_arr; tcoeff : coeff_type;
    tcona : cons_type) : theograf; { calculate values for graph }
var i : integer; tcorx : real;
begintcorx := long/(maxx - minx);
for i := left to right do { for every pixel points }
    theodata[i] := f(tfunca, minx + (i-left)/tcorx, cutoff, tcoeff, tcona);
end;

function theonorm(tdat : theograf) : theograf; { normalize values for graph }
var i : integer;
beginforsi := left to right do theonorm[i] := (tdat[i] - miny)*corry + bottom;
end;

function expnorm(eindat : expdata) : expdata; { normalize data for graphics }
var i : integer;
beginforsi := 1 to npts dobegin
    expnorm[i].x := (eindat[i].x - minx)*corrx + left;
    expnorm[i].y := (eindat[i].y - miny)*corry + bottom;
    expnorm[i].sigy := eindat[i].sigy*corry;
end;
end;

procedure drawtheo(ddatg : theograf); { draw the graph function }
var i : integer;
beginn_move(left, round(ddatg[left])); { first point }
for i := left to right do
    m_draw(i, round(ddatg[i]));
end;

procedure drawexp(dindatg : expdata; dnpts : integer); { draw data points }
var i, dx, dy, dsigy : integer;
beginn := 1 to dnpts do

begin
  dx := round(dindatg[i].x);  { rounding normalized values } 
dy := round(dindatg[i].y); 
dsigy := round(dindatg[i].sigy); 
m_drawrect(dx-1, dy-1, dx+1, dy+1);  { draw small box for point } 
m_move(dx-1, dy+dsigy); 
m_draw(dx+1, dy+dsigy); 
m_move(dx, dy+dsigy); 
m_draw(dx, dy-dsigy); 
m_draw(dx-1, dy-dsigy); 
m_draw(dx+1, dy-dsigy); 
end;
end;

{-----------------------------------------------}

procedure readdata(var rindat : expdata;var rnpts : integer;strt:integer);
var i : integer;  { user input data }
begin
  write('Condition of sigma-y: 1-Statistical 2-No sigma-y 3-Instrumental '); 
  readln(i);
  rnpts := strt;  { strt = 0 for new data }
repeat
  rnpts := rnpts+1;
  case i of
    1,2 : begin
      rindat[rnpts].sigy := 0;
      if i = 1 then mode := stat else mode := none;
      write('(',rnpts:1,') x, y? (x = 9999 to end) '); 
      readln(rindat[rnpts].x, rindat[rnpts].y);
    end;
    3 : begin
      mode := instr;
      write('(',rnpts:1,') x, y, sigma-y? (x = 9999 to end) '); 
      readln(rindat[rnpts].x, rindat[rnpts].y, rindat[rnpts].sigy);
    end;
    otherwise;
  end;
until (rindat[rnpts].x = termx) or (rnpts = maxdata) or (i<1) or (i>3);
if rindat[rnpts].x = termx then rnpts := rnpts-1;{ do not store 9999 }
end;

{-----------------------------------------------}

procedure savefile(sindat : expdata;snpts : integer);
var i : integer;  { save input data }
begin
  write('name of file '); 
  readln(name);
end;

-- 55 --
```plaintext
rewrite(filea, name);
for i := 1 to snpts do
  begin
    filea' := sindat[i];
    put(filea);
  end;
close(filea, 'save');
end;

{----------------------------------------------------------------------}

procedure readfile(var rindat : expdata; var rnpts : integer; strt : integer);
var i : integer;
begin
  write('read from ');
  readln(name);
  reset(filea, name);
  rnpts := strt;
  while not eof(filea) do
    begin
      rnpts := rnpts + 1;
      rindat[rnpts] := filea';
      get(filea);
    end;
close(filea);
  write('Is sigma-y 1-Statistical 2-None 3-Instrumental ');
  readln(i);
  case i of
    1 : mode := stat;
    2 : mode := none;
    3 : mode := instr;
  otherwise;
  end;
end;

{----------------------------------------------------------------------}

function weight(windat: expdata; i: integer): real;{ calculate weights for } begin
  with windat[i] do
    case mode of
      stat : if y <> 0 then weight := 1/abs(y)
        else weight := 1;
      none : weight := 1;
      instr: if sigy <> 0 then weight := 1/sqr(sigy) else weight := 1e10;
    end;
end;

{----------------------------------------------------------------------}

function chisqr(cindat : expdata; cfunc : func_arr; ccoeff: coeff_type): real; var cx2 : real;{ calculate chi square } begin
  { each data points
    with cindat do
      case mode of
        stat : if cfunc <> 0 then weight := 1/abs(cfunc)
          else weight := 1;
        none : weight := 1;
        instr: if ccoeff <> 0 then weight := 1/sqr(ccoeff) else weight := 1e10;
      end;
end;
```
begin
    cx2 := 0;
    if nfree <= 0 then chisqr := 0 else
    begin
        for i := 1 to npts do cx2 := cx2 + weight(cindat[i])*sqr(abs(cindat[i].y - f(cfunc,cindat[i].x,cutoff,ccoeff,cona)));
        chisqr := cx2/nfree;  \{ reduced chi squared \}
    end;
end;

{-------------------------------------------------------------------------------------------------------------}

function deriv(dindat : expdata;i : integer):oneddata;
var j : integer; \{ calculate derivatives \}
    coj,yfit,dumder : real; \{ with respect to all coeff. \}
begin
    for j := 1 to cfterms do
    begin
        coj := coeff[j].a;
        coeff[j].a := coj + coeff[j].dela;
        yfit := f(funca,dindat[i].x,cutoff,ccoeff,cona);
        coeff[j].a := coj - coeff[j].dela;
        dumder := (yfit-f(funca,dindat[i].x,cutoff,ccoeff,cona))/(2*coeff[j].dela);
        if dumder <> 0 then deriv[j] := dumder else deriv[j] := 1e-10;
        coeff[j].a := coj;
    end;
end;

{-------------------------------------------------------------------------------------------------------------}

procedure swap(var s1,s2 : real); \{ swap two numbers s1 and s2 \}
var dummy : real;
begin
    dummy := s1;
    s1 := s2;
    s2 := dummy;
end;

{-------------------------------------------------------------------------------------------------------------}

procedure matinv(var marray : mattype;var merr : boolean);
var i,j,k,l : integer; \{ invert matrice, calc. det. \}
    arrmax,dummy : real; ik,jk : array [1..maxpar] of integer;
begin
    merr := false;
    for k := 1 to cfterms do
    begin
        arrmax := 0;
        for i := k to cfterms do \{ find largest element \}
        begin
            ik := i;
            jk := k;
            arrmax := max(arrmax,iarrmax[ik,jk]);
        end;
        for i := 1 to cfterms do iarrmax[i,k] := 0;
        for i := k to cfterms do
        begin
            iarrmax[i,k] := arrmax;
            for j := i to cfterms do
            begin
                if iarrmax[i,k] > arrmax then
                    ik := i;
                    jk := k;
                arrmax := arrmax - iarrmax[i,k];
                iarrmax[i,k] := arrmax;
            end;
        end;
    end;
end;
for j := k to cfterms do
    if abs(arrmax) <= abs(marray[i,j]) then
        begin
            arrmax := marray[i,j];
            ik[k] := i;
            jk[k] := j;
        end;
    if arrmax = 0 then merr := true else begin
        i := ik[k];
        if i>k then
            for j := 1 to cfterms do swap(marray[k,j],marray[i,j]);
        j := jk[k];
        if j>k then
            for i := 1 to cfterms do swap(marray[i,k],marray[i,j]);
    end;
if not merr then begin
    for i := 1 to cfterms do
        if i<>k then marray[i,k] := -marray[i,k]/arrmax;
    for i := 1 to cfterms do
        for j := 1 to cfterms do
            if (i<>k) and (j<>k) then
                marray[i,j] := marray[i,j] + marray[i,k]*marray[k,j];
        for j := 1 to cfterms do
            if j<>k then marray[k,j] := marray[k,j]/arrmax;
    marray[k,k] := 1/arrmax;
end;
if not merr then begin
    for l := 1 to cfterms do
        begin
            k := cfterms - l + 1;
            j := ik[k];
            if j>k then
                for i := 1 to cfterms do swap(marray[i,k],marray[i,j]);
            i := jk[k];
            if i>k then
                for j := 1 to cfterms do swap(marray[k,j],marray[i,j]);
        end;
end;
---------------------------------------------------------------------

procedure curfit(cindat : exndata;var coeff : coeff_type;
    var cx2 : real;cwt : oneddata); { calculate grad. & new coeff.}
var xsql : real;
cderiv : oneddata;
b : coeff_type;
carray, alpha : mattype;
i,j,k,l : integer;
beta : array[1..maxpar] of real;
cerr : boolean;
begin
for j := 1 to cfterms do
begin
beta[j] := 0;
for k := 1 to j do alpha[j,k] := 0;
end;
for i := 1 to npts do
begin
cderiv := deriv(cindat,i);
for j := 1 to cfterms do
begin
beta[l] := beta[l] + cwt[i]*
(cindat[i].y-f(funca,cindat[i].x,cutoff,ccoef,cona))*cderiv[l];
for k := 1 to j do
alpha[j,k] := alpha[j,k] + cwt[i]*cderiv[j]*cderiv[k];
end;
end;
for j := 1 to cfterms do
  for k := 1 to j do alpha[j,k] := alpha[j,k];
xsql := cx2;
repeat
  for j := 1 to cfterms do
begin
    for k := 1 to cfterms do
begin
      caray[j,k] := alpha[j,k]/sqt(alpha[j,j]*alpha[k,k]);
      caray[j,j] := 1 + lamda;
    end;
  end;
matinv(caray,cerr);
if cerr then writeln('Non-unique system of equation found ');
b := ccoef;
for j := 1 to cfterms do
for k := 1 to cfterms do
b[j].a := b[j].a +
beta[k]*caray[j,k]/sqt(alpha[j,j]*alpha[k,k]);
cx2 := chisq(cindat,funca,b);
if cx2 > xsq1 then lamda := lamda*10;
until cx2 <= xsq1;
ccoef := b;
for j := 1 to cfterms do ccoef[j].siga := sqrt(caray[j,j]/alpha[j,j]);
lamda := lamda/10;
end;

procedure drawscale(dmin,dmax:real;dcon,dsc:integer;dvh:vhtype);
var dfac : real;
begin
  pwcor, pwmax, pwmin, pwdif, gmin, gmax, i, k : integer;

{
if dmax > dmin then
  { compare magnitudes of max. }
  begin
    { min. and calculate steps }
    if abs(dmax) < 1 then pwcor := -1 else pwcor := 0; { for scales }
    if dmax <> 0 then pwmax := trunc(ln(abs(dmax))/ln(10)) + pwcor
      else pwmax := -400;
    if dmin <> 0 then pwmin := trunc(ln(abs(dmin))/ln(10)) + pwcor
      else pwmin := -400;
    pwdiff := trunc(ln(dmax-dmin)/ln(10)) + pwcor;
    if pwmax > pwmin then dfac := exp((-1 + pwmax)*ln(10))
      else dfac := exp((-1 + pwmin)*ln(10))
    gmax := trunc(dmax/dfac);
    gmin := round(dmin/dfac + 0.5);
    for i := gmin to gmax do
      begin
        case dvh of
          vertical : begin
            { left and right verticals }
            k := round(corry*(i*dfac - dmin));
            m_move(dcon,k + bottom);
            if (i=0) and (dcon = left) then
              m_draw(right,k + bottom) else
            if i mod 10 = 0 then m_draw(dcon+3*dsc,k+bottom)
              else m_draw(dcon+dsc,k + bottom);
          end;
          horizontal:begin
            { top and bottom horizontals }
            k := round(corrx*(i*dfac - dmin));
            m_move(k + left,dcon);
            if (i=0) and (dcon = bottom) then
              m_draw(k + left,top) else
            if i mod 10 = 0 then m_draw(k + left,dcon+3*dsc)
              else m_draw(k + left,dcon+dsc);
          end;
        end;
      end;
    end;
  end;
end;

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

procedure drawframe;
begin
  { draw rectangle w/ scale }
  m_color(m_yellow);
  m_drawrect(left,bottom,right,top);
  { draw box }
  writeln('maxy = ',maxy,' miny = ',miny);
  { draw scales }
  drawscale(miny,maxy,left,5,vertical);
  drawscale(miny,maxy,right,-5,vertical);
  drawscale(minx,maxx,top,-5,horizontal);
  writeln('maxx = ',maxx,' minx = ',minx);
  drawscale(minx,maxx,bottom,5,horizontal);

CS10
February 14, 1987
- 60 -
m_color(m_red);
m_move(left,10);
m_displaytext('Data file: ');
m_displaytext(name);
end;

{------------------------------------------------------------------}

procedure draweverything(dindat : expdata;var ddat : theograf);
var dindatg : expdata; ddatg : theograf; { draw both data and function }
begin
maxmindata(dindat); { calculating... }
ddat := theodata(funca,coeff,cona);
maxmin;
dindatg := expnorm(dindat);
ddatg := theonorm(ddat);
m_clear; { and drawing }
drawframe;
m_color(color);
drawtheo(ddatg);
m_color(m_red);
drawexp(dindatg,npts);
end;

{------------------------------------------------------------------}

procedure wrtfunc(wfunca : func_arr); { write function in reverse }
var i : integer; { polish notation }
begin
writeln; write('f = ');
i := 1;
if wfunca[i].datum = ends then writeln('undefined');{ undefined functions }
while wfunca[i].datum <> ends do { changing into human }
begin
with wfunca[i] do
{ readable forms }
case datum of
  vars : write('x');
  coef : write('((C'.vali:1,')');
  cons : write('((A'.vali:1,')');
  oper : case valo of
    oadd : write('+');
    oexp : write('exp');
    osub : write('-');
    olog : write('log');
    odiv : write('/');
    ocos : write('cos');
    omul : write('*');
    osin : write('sin');
    opwr : write('^');
    otn : write('arctan');
    otn : write('tanh');
  end;
end;
procedure readfunc(var rfunc : func_arr;var rcftersms,rconnum : integer);  
var ch : char;  
i : integer;  
notaset : charset;  
begin  
page;  
rcftersms := 0;  
rconnum := 0;  
i := 0;  
rfunc[i].datum := ends;  
notaset := ['#','@','+','-','*','/',',','e','l',  
  's','c','a','t','C','S','T','x',',',';'];  
writeln('to enter a constant, type @ then the constant # and <RETURN>');  
writeln('to enter a coefficient, type # then the coeff.# and <RETURN>');  
writeln('other accepted notations : ');  
writeln('+, -, *, /, ^, e(xp), l(og), s(in), c(os), x(var), , (undo), ; (end');  
writeln('t(an), C(osh), S(inh), T(anh)');  
writeln; writeln('Useful equations for statistical study');  
writeln('Gaussian = (C1)(C2)(C3)/(2)(0.5)^/(0.5)x((C4)-(C3)/(2)^*exp*');  
writeln('Lorentz = (C1)(C2)(2)/(2)^*x(C3)-(2)^*x(C2)/(2)^*+/(2)^*');  
writeln('Resonance= (C1)(2)^*x(2)^*(C1)(2)^*-(2)^*x(C2)(2)^*+(0.5)^*/');  
writeln; writeln('enter function in REVERSE POLISH NOTATION');  
writeln; write('f = ');  
repeat  
  read(ch);  
  if not (ch in notaset) then  
    begin  
      write(' input error ');  
      wrtfunc(rfunc);  
    end  
  else  
    begin  
      i := i + 1;  
      rfunc[i+1].datum := ends;  
      with rfunc[i] do  
        case ch of  
          'X' : datum := vars;  
          '@' : begin  
            datum := cons;  
            write('?');  
            readin(vali);  
            if vali > rconnum then rconnum := vali;  
            wrtfunc(rfunc);  
          end;  
    end;
'#': begin

datum := coef;
write('?');
readln(vali);
if vali > rcfterms then rcfterms := vali;
wrtfunc(rfunc);
end;
'.': i := i - 2;
'+', '-', '*', '/', ', 'e', 'l', 's', 'c', 'a', 't', 'C', 'S', 'T';
: begin
datum := oper;
case ch of
  '+' : valo := oadd;
  '-' : valo := osub;
  '*' : valo := omul;
  '/' : valo := odiv;
  '^' : valo := opwr;
  't' : valo := otan;
  'S' : valo := osnh;
end;
end;
}: datum := ends;
end;
otherwise;
end;
until ch = ';';
end;

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

procedure currentfit(x2 : real);
{ display information of fit }
var i : integer;
begin
page;
write('Data file: ',name);
case mode of
  stat : writeln(' Sigma Y: Statistical');
  none : writeln(' No sigma y');
  instr : writeln(' Sigma Y: Instrumental');
end;
write('Function of graph is ');{ write function, its }
wrtfunc(funca);
{ constants and coefficients }
writeln;
for i := 1 to connum do
  writeln('A',i:1,' = ',cona[i]);
for i := 1 to cfterms do
  writeln('C',i:1,' = ',coeff[i].a,' Sigma C',i:1,' = ',coeff[i].siga);
writeln('Chi square = ',x2);
writeln('Minimum y = ',miny,' Maximum y = ',maxy);
writeln('Minimum x = ',minx,' Maximum x = ',maxx);
write('hit any key to return');
read(mch);
end;

{----------------------------------------------}

procedure fit(var x2 : real);
var m : integer; x1, chidif : real; wt : onedata;
begin
write('color? ');
readln(color);
write('cut off point? ');
readln(cutoff);
write('enter maximal absolute difference of successive chi square (0.0001) ');
readln(chidif);
write('display graph as function being fitted? ');
readln(mch);
lamda := 0.001;
nfree := npts - cfterms;
for m := 1 to cfterms do
begin
    write('C',m:1,'?', delta? ');
    readln(coeff[m].a, coeff[m].dela);
end;
for m := 1 to npts do wt[m] := weight(indat,m);
x2 := chisqr(indat,funca,coeff);
writeln('chi square = ',x2);
if mch = 'y' then draweverything(indat,dat);
repeat
    writeln('lamda = ',lamda,' ....fitting....');
x1 := x2;
    if nfree > 0 then curfit(indat,coeff,x2,wt);
    writeln; writeln; writeln;
    for m := 1 to cfterms do
        writeln('C',m:1,' = ',coeff[m].a,
            'Sigma C',m:1,' = ',coeff[m].siga);
    writeln('chi square = ',x2);
    if mch = 'y' then draweverything(indat,dat);
until abs(x1-x2) <= chidif;
writeln('fitting completed');
draweverything(indat,dat);
currentfit(x2);
end;

{----------------------------------------------}

procedure drawfunc;
var m : integer;

{ draw graph between x1 & x2 }

C10
February 14, 1987
begin
m_clear;
write('Enter minimum x and maximum x');
readln(minx,maxx);
{ normalizing... } 
dmaxy := -0.999e99;
dminy := 0.999e99;
write('New coefficients? ');
readln(mch);
if mch = 'y' then
begin
for m := 1 to cterms do
begin
write('C.m: ',' = ');
readln(coeffs[m].a);
end;
corrX := long/((maxx - minx));
dat := theodata(funca.coeff,cona);
maxmin;
datg := theonorm(dat);
write('Color of graph? ');
readln(color);
drawframe;
m_color(color);
drawtheo(datg);
end;
{ drawing... }

{-------------------}
procedure displaydata(dindat:expdata;dnpts: integer);
var i : integer;
begin
{ display current data file }
page;
writeln('Data file: ','name);
if dnpts > 0 then
for i := 1 to dnpts do
with dindat[i] do
begin
write('X(i:1,) = ','x','
write('Y(i:1,) = ','y','
writeln('SIGMA-Y(i:1,) = ','sigy);
if i mod 20 = 0 then
begin
{ end of screen }

begin
write('hit any key to continue ');
read(mch);
page;
end;

end;
write('hit any key to return');
read(mch);
end;
{ end of data }
procedure drawdata (din : expdata);
    var dindatg : expdata;
    begin
        maximindata (din);
        dindatg := expnorm (din);
        m_clear;
        drawframe;
        m_color (m_red);
        drawexp (dindatg, npts);
    end;

procedure deffunc (var dfunca : func_arr ; var dcf : dconnum : integer);
    var m : integer;
    begin
        repeat
            readfunc (dfunca, dcf, dconnum);
            writeln;
            write ('correct? ');
            readln (mch);
            dfunca [0] . datum := cons;
            dfunca [0] . vali := 0;
            if (dconnum > 0) and (mch = 'y') then
            for m := 1 to dconnum do
                begin
                    write ('A', m, '=', ');
                    readln (cona[m]);
                end;
        until mch = 'y';
    end;

procedure transfer (var tindat : expdata ; var tarray : oneddata ; dir, subrec : integer);
    var i : integer;
    begin
        for i := 1 to npts do
            case dir of
                1 : case subrec of
                    1 : tarray[i] := tindat[i] . x;
                    2 : tarray[i] := tindat[i] . y;
                    3 : tarray[i] := tindat[i] . sigy;
                    end;
                2 : case subrec of
                    }


1:  tindat[i].x := tarray[i];
2:  tindat[i].y := tarray[i];
3:  tindat[i].sigy := tarray[i];
end;
end;

{ --------------------------------------------------------- }

procedure modify(var mindat:expdata);
var i,tcom: integer;
uarray,varray: oneddata;
begin
repeat
writeln('1 --> (X -> Uarray)');
writeln('3 --> (Y -> Uarray)');
writeln('5 --> (SIGMA Y -> Uarray)');
writeln('7 --> (Uarray -> X)');
writeln('9 --> (Uarray -> Y)');
writeln('11 --> (Uarray -> SIGMA Y)');
writeln('13 --> (U = f(U))');
writeln('15 --> (U = f(V))');
writeln('other numbers --> end');
readln(tcom);
case tcom of
  1:  transfer(mindat,uarray,1,1);
  2:  transfer(mindat,uarray,1,2);
  3:  transfer(mindat,uarray,1,3);
  4:  transfer(mindat,uarray,2,1);
  5:  transfer(mindat,uarray,2,2);
  6:  transfer(mindat,uarray,2,3);
  7:  transfer(mindat,uarray,2,1);
  8:  transfer(mindat,uarray,2,2);
  9:  transfer(mindat,uarray,2,3);
 10:  transfer(mindat,uarray,2,2);
 11:  transfer(mindat,uarray,2,3);
 12:  transfer(mindat,uarray,2,3);
 13,14,15: begin
    deffunc(funca,cfterms,connum);
    for i := 1 to npts do
      case tcom of
        13:  uarray[i] := f(funca,uarray[i],-1e300,coeff,cona);
        14:  varray[i] := f(funca,varray[i],-1e300,coeff,cona);
        15:  uarray[i] := f(funca,varray[i],-1e300,coeff,cona);
      end;
    end;
  16:  displaydata(mindat,npts);
  otherwise;
end
{ make modifications to data }
{ as a whole group }
{ instructions }
{ transfering... }
{ transforming data }

---

CS10
February 14, 1987
end;
until (tcom < 1) or (tcom > 16):
end;

{---------------------------------------------------------------}

procedure update(var uindat : expdata;var unpts : integer);
var i,j,k: integer; newval : real; { make changes and add data }
begin
repeat
writeln('1-Remove data point 2-Add data 3-Change data 4-Display data ');
write('other numbers to exit ');
readln(i);
case i of
  1: repeat { removing a single data point}
    write('remove item #? (9999 to terminate) ');
    readln(j);
    if (j<unpts) and (j>0) then
    begin
      for k := j to unpts -1 do
        uindat[k] := uindat[k+1];
      unpts := unpts - 1;
    end
    else if j = unpts then unpts := unpts - 1;
    until j = termx;
  2: readdata(uindat,unpts,unpts); { add data points }
  3: repeat { change data }
    write('item #? (9999 to terminate) ');
    readln(j);
    if j <= unpts then
      with uindat[j] do
      begin
        write('X(',j:1,') = ',x,'  Y(',j:1,') = ',y,' SIGMA-Y(',j:1,') = ',sigy);
      end
    readln(newval);
    case k of
      1: x := newval;
      2: y := newval;
      3: sigy := newval;
      otherwise;
    end;
    until j = termx;
  4: displaydata(uindat,unpts); { display data }
otherwise;
end;
end;  
until (i<1) or (i>4);  
end;  

{--------------------------------------------------------------------------}

function diffdata(dindat : expdata; ddat : theograf):expdata;  
var i : integer;  { get difference plot }  
begin  
diffdata := dindat;  
for i := 1 to npts do  
diffdata[i].y := dindat[i].y - ddat[round((dindat[i].x-minx)*corrx + left)];  
end;  

{--------------------------------------------------------------------------}

procedure getfunc(var gfunc : func_arr; var gcfterm, gconnum : integer);  
var i : integer;  { read function in R.P.N. }  
funcname : string[12];  { from file }  
dumfunc : filefuncrec;  { initializations }  
begin  
page;  
write('Read function from file? ');  
readln(funcname);  
reset(fileb, funcname);  
gcfterm := 0;  
gconnum := 0;  
i := 0;  
gfunc[0].datum := cons;  
gfunc[0].vali := 0;  
repeat  
i := i + 1;  
gfunc[i+1].datum := ends;  
dumfunc := fileb";  
with gfunc[i] do  
with dumfunc do  
  case sort of  
  1 : datum := vars;  
  2 : begin  
    datum := cons;  
    vali := sub;  
    if vali > gconnum then gconnum := vali;  
    end;  
  3 : begin  
    datum := coef;  
    vali := sub;  
    if vali > gcfterm then gcfterm := vali;  
    end;  
  4 : begin  
    datum := oper;  

February 14, 1987
case sub of
  1: valo := oadd;
  2: valo := osub;
  3: valo := omul;
  4: valo := odiv;
  5: valo := opwr;
  6: valo := oexp;
  7: valo := olog;
  8: valo :=ocos;
  9: valo := osin;
 10: valo := oatan;
 11: valo := oatn;
 12: valo := ocsn;
 13: valo := osnh;
 14: valo := otnh;
end;
end;
otherwise;
end;
get(fileb);
until eof(fileb);
close(fileb);
wtfunc(gfunc); writeln;
if gconnum > 0 then
  begin
    for i := 1 to gconnum do
      begin
        write('A',i:1,' = ');
        readln(cona[i]);
      end;
  end;
{ get constants if appropriate}
{---------------------------------------------------------------}

procedure savefunc(sfunc : func_arr); { save function in R.P.N. }
var i : integer;
  funcname : string[12];
dumfunc : filefuncrec;
begin
  funcname := string[12];
dumfunc := filefuncrec;
  begin
    page;
    write('Save function to file? ');
    readln(funcname);
    rewrite(fileb,funcname);
    i := 1;
  repeat
    with sfunc[i] do
      begin
        case datum of
          vars : dumfunc.sort := 1;
          cons : begin
            dumfunc.sort := 2;
            dumfunc.sub := vali;
          end;
          coef : begin
            dumfunc.sort := 3;
            dumfunc.sub := vali;
          end;
          oper : begin
            dumfunc.sort := 4;
          end;
          end;
with dumfunc do
    case valo of
    oadd : sub := 1;       oexp : sub := 6;
    osub : sub := 2;       olog : sub := 7;
    omul : sub := 3;       ocos : sub := 8;
    odiv : sub := 4;       osin : sub := 9;
    opwr : sub := 5;       oatn : sub := 11;
    otan : sub := 10;      ocsn : sub := 12;
    osnh : sub := 13;      otnh : sub := 14;
    end;
end;
otherwise;
end;
fileb := dumfunc;
put(fileb);
i := i + 1;
until sfunc[i].datum = ends;
close(fileb,'save');
end;

{-----------------------------------------------------------------}

procedure extrapolate; { extrapolate known function }
var ex,ey : real;
begin
page;
wrriteln('To terminate, enter 9999 for x');
repeat
    write('x = ');    
    readln(ex);
    ey := f(funca,ex,cutoff,coeff,con);  
    writeln('x = ',ex,' f(x) = ',ey);
until ex = termx;
end;

{-----------------------------------------------------------------}

procedure wait_for_pen(var wpen : m_tablet_info;wcorx,wcory,wx,wy : real);
begin { wait til pen is depressed }
repeat  { and return coordinate }
    repeat
        m_readpen(wpen);
        until wpen.moving or wpen.dn;
    page;
    writeln(wpen.x*wcorx + wx,' ',wpen.y*wcory + wy);
    until wpen.dn;
end;

{-----------------------------------------------------------------}
procedure readgraf(var rindat : expdata; var rnpts : integer);
var mypen : m_tablet_info;  \{ read data from graph  \}
rmaxx, rmaxy, rminx, rminy, rcorx, rcory : real;  \{ on graphics tablet  \}
amaxx, amaxy, aminx, aminy, scorx, scory : real;
begin
  page;
m_move(10,360);  \{ place graph on graphics tablet \}
m_displaytext('move pen to the lower left corner of your graph and press');
  wait_for_pen(mypen,1,1,0,0);
rminx := mypen.x;
rminy := mypen.y;
  m_clear;
m_move(10,360);  \{ move pen to the upper right corner of your graph and press \}
  wait_for_pen(mypen,1,1,0,0);
rmaxx := mypen.x;
rmaxy := mypen.y;
write('enter actual minx, maxx, miny, maxy ');
readln(aminx, amaxx, aminy, amaxy);  \{ get actual values on graph \}
rcorx := (amaxx - aminx)/(rmaxx - rminx);  \{ normalizing... \}
rcory := (amaxy - aminy)/(rmaxy - rminy);
scorx := long/(rmaxx - rminx);
scory := height/(rmaxy - rminy);
m_clear;
m_move(10,360);
  m_displaytext('move to point to be collected and depress, box 1 to end');
rnpts := 0;
m_color(m_yellow);
m_drawrect(left,bottom,right,top);
m_color(m_red);
mch := 'n';  \{ flag to stop data entry \}
repeat
  rnpts := rnpts + 1;
  wait_for_pen(mypen,rcorx,rcory,
    -rminx*rcorx + aminx,-rminy*rcory + aminy);
  rindat[rnpts].x := (mypen.x-rminx)*rcorx + aminx;
rindat[rnpts].y := (mypen.y-rminy)*rcory + aminy;
rindat[rnpts].sigy := 0;
m_circle(round(scorx*(mypen.x-rminx)+left),
  round(scory*(mypen.y-rminy)+bottom),1);
  if ((mypen.x>0) and (mypen.x<22)) and
      ((mypen.y>393) and (mypen.y<417)) then begin
    write('data entry complete? ');
    readln(mch);
  end;
until (mch = 'y') or (rnpts = 100);
rnpts := rnpts - 1; { do not enter menu value }
end;

//---------------------------------------------------------

procedure menu;
var com : integer; difdat : expdata; { display menu and interact with user }
begin
writeln('1-Get a file 2-Save current file 3-Define a function');
writeln('4-Input data 5-Fit 6-Plot data');
writeln('7-Plot function 8-Display data 9-Modify data');
writeln('10-Update data 11-Difference Plot 12-Function & Data');
writeln('13-Get function 14-Save function 15-Extra-(Inter)-polate');
writeln('16-Chi square 17-Digitize graph 18-Combine files');
readln(com);
case com of
  1 : begin
    readfile(indat,npts,O); { get data file }
    nfree := npts - cfterms;
    end;
  2 : if npts > 0 then savefile(indat,npts); { save datafile }
  3 : deffunc(funca,cfterms,connum); { user input function }
  4 : begin
     name := 'not named';
     readdata(indat,npts,O); { user input data }
     nfree := npts - cfterms;
     end;
  5 : if npts > 0 then fit(x2); { fitting }
  6 : if npts > 1 then drawdata(indat); { plotting data }
  7 : drawfunc; { plotting function }
  8 : displaydata(indat,npts); { display data }
  9 : if npts > 0 then modify(indat); { modify group of data }
 10: if npts > 0 then update(indat,npts); { update one data point }
 11: begin { difference plot }
    writeln('enter c for difference plot IFF data was fitted');
    readln(mch);
    if mch = 'c' then begin
      difdat := diffdata(indat,dat);
      maxmindata(difdat);
      if npts > 1 then drawdata(difdat);
      currentfit(x2);
      end;
    end;
  12: begin { plot both data and graph }
    writeln('enter c for plot IFF data was fitted');
    readln(mch);
    x2 := chisqr(indat,funca,coeff);

if mch = 'c' then begin draweverything(indat,dat);
currentfit(x2); end;

13: getfunc(funca,cfterms,connum); { read function from file }
14: if funca[1].datum <> ends then savefunc(funca); { save defined function }
15: extrapolate; { extrapolating from known fcn }
16: begin { given a function and a set }
draweverything(indat,dat); { of data point, plot and }
x2 := chisqr(indat,funca,coeff); { determine chi square }
currentfit(x2);
end;
17: readgraf(indat,npts); { read from graph on tablet }
18: if npts > 0 then readfile(indat,npts,npts); { Combine two files }
19: exitprog := true; { exiting program }
otherwise;
end;
end;

procedure currentinfo; { display status of data etc. }
var i : integer;
begin
page;
write('Current data file is ,name);
{ name of data and function }
case mode of
stat : writeln(' Sigma Y : Statistical');
none : writeln(' No sigma y');
instr: writeln(' Sigma Y : Instrumental');
end;
write('Current function is ,wrtfunc(funca);
write;
if connum > 0 then for i := 1 to connum do { constants }
write('A',i:1,' = ',cona[i]);
write;
end;

begin
page; { initialization }
funca[1].datum := ends;
name := 'none';
exitprog := false;
cfterms := 2;
mode := none;
m_init_graphics;
repeat
{ begin interaction with user }
end;
currentinfo;
menu;
until exitprog;
end.