

RESEARCH ON SLOW ELECTRON
COLLISION PROCESSES IN GASES

MASTER

Final Report

George C. Baldwin

Rensselaer Polytechnic Institute
Troy, New York

September 15, 1970 - December 31, 1972*

54 6,6000

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION
UNDER CONTRACT NOS. AT(30-1)4144 AND AT(11-1)3008

*Early phases of the work described in this report were performed prior to this period with financial support of the U. S. Office of Naval Research, and the final phases of the work were continued with the support of the Petroleum Research Fund of the American Chemical Society.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Research on low-energy electron collisions in gases by the time-of-flight velocity selection technique included, as a preliminary to total cross section measurements, investigations of the statistical and systematic errors inherent in the technique. In particular, thermal transpiration and instrumental fluctuation errors in manometry were investigated, and the results embodied in computer programs for data reduction. The instrumental system was improved to permit extended periods of data accumulation without manual attention. Total cross section measurements in helium, made prior to, and in molecular nitrogen, made after the supporting work was completed, are reported. The total cross section of helium is found to be higher than reported in previous beam determinations. That of nitrogen is found to be structureless at low energies.

CONTENTS

Introduction	1
Summary of Work Performed	1
Technical Report	
Experimental Method	4
Data Reduction Programs	4
Total Cross Section of Helium	6
Total Cross Section of Molecular Nitrogen	7
Evaluation of the Experimental Method	8
Publications	10
Personnel	11
References	13
Appendices	
Nitrogen Total Cross Section for Electrons below 2 eV	
Thermal Transpiration Error in Absolute Pressure Measurement with Capacitance Manometers	
A Single-Electron Time-of-Flight Stepped-Pressure Spectrometer for Total-Cross-Section Measurement at Low Electron Energies	
Statistical Error in Molecular Cross Section Measurements	
Electron Scattering off Atoms for Excitations to Valence and Rydberg States	
Dependence of Extrema in the Generalized Oscillator Strengths on Momentum Transfer and Effective Nuclear Charge for Atomic Transitions	

*Reprints & Reprints
Reviewed*

Introduction

The primary objective of this research is measurement of absolute total collision cross sections of atoms and molecules for electrons of energy below 2 eV, by means of a single-electron time-of-flight velocity spectrometer developed by the principal investigator in earlier research (1).

In order to accomplish the primary objective it was necessary first to perform related research on absolute manometry, to investigate processes involved in the generation and transmission of electrons through the spectrometer; to perform a theoretical analysis of the effects of statistical errors inherent in the technique; to develop an optimum procedure for measurement of cross sections; to perfect programs for data reduction by computer; and to develop special apparatus which enabled data to be accumulated over extended times without manual attention.

During the time covered by the subject contract, total cross sections were determined for helium. Transmission measurements were also made for molecular nitrogen, hydrogen and oxygen. It was not possible to complete these measurements in the third contract period, however, because of reduction in the level of effort. The nitrogen data has been subsequently analyzed with support from another source (2). It will be necessary to make additional measurements in the other gases before cross sections can be found, since the runs made did not include information subsequently found to be necessary.

Summary of Work Performed Under this Contract

Total cross sections were measured for helium in the energy range 0.4 - 2.0 eV (3,4) and for molecular nitrogen in the range 0.3 - 1.8 eV. The latter, not completed by the expiration date of the contract, were subsequently continued to completion with support of the Petroleum Research Fund of the American Chemical Society; publication of that work is expected shortly (5). The helium measurements were reported at the International Conference on the Physics of Electronic and Atomic Collisions in Amsterdam, July, 1971 and at the International Conference on Electron Spectroscopy at Asilomar in September, 1971.

Research was conducted on the thermal transpiration effect (6). In capacitance manometry, employed in this research, this effect can contribute an error of as much as 2.6% in the determination of molecular concentration and, therefore, of the collision cross section, in gases at low absolute pressure unless appropriate corrections can be determined experimentally. The magnitude of the effect was determined as a function of pressure for helium and nitrogen, and coefficients were determined for an empirical equation which permits true pressure to be calculated from the indicated pressure readings. This work was published in the January/February 1973 issue of the Journal of Vacuum Science and Technology and reported orally at a symposium of the American Vacuum Society in October, 1972 at Chicago.

Research was conducted on the statistical errors in the use of particle counting techniques for the measurement of absolute collision cross sections in gases (7). It was shown that statistical fluctuations lead not only to random, but also to systematic error in the deduction of the cross section. Algorithms were deduced from which appropriate corrections can be made to experimental data, provided that information concerning fluctuations of the specimen gas concentration is available. A report of this work was presented at the Gaseous Electronics Conference in London, Ontario in October, 1972, and published in the Review of Scientific Instruments, July, 1973.

An experimental procedure was developed, based upon the statistical analysis described above, for which maximum precision in the determination of cross section can be realized with a given total time of measurement. Sources of error in the method were identified and evaluated (4,7).

An automated system for gas flow control, timing of data collection periods, and periodic sampling of the manometer was developed and incorporated in the spectrometer system (5). Provision was also made for mass analysis of gas samples emerging from the spectrometer, in order to assure acceptable purity. This system was described at the April, 1971 Washington meeting of the American Physical Society, at the International Conference on Electron Spectroscopy at Asilomar in September, 1971, and published in the proceedings of the latter.

Computational programs were written for data reduction, based on algorithms developed in the statistical error analysis. Completion of this work after the end of the contract period was assured with support from the American Chemical Society Petroleum Research Fund. Written for an IBM-1130 computer which is available in this laboratory, these programs provide for transfer of raw data from paper tapes to a magnetic disk file indexed for retrieval of data; for the introduction of calibrations, background corrections, thermal transpiration corrections, and corrections for pressure fluctuations; for plotting of raw and/or reduced data; for calculation of cross sections and rms errors; for combination, with resolution-averaging, of cross sections determined in several runs; and for plotting these averaged cross sections.

In a thesis investigation for the M.S. degree carried out by Peter Morley (8), electron time-of-flight spectra transmitted by the open-beam spectrometer system under a wide range of operating parameters were studied in an attempt to understand the present 0.25 eV energy limit of the apparatus, which, when the spectrometer was first built, extended down to 0.1 eV. This problem was traced to deterioration of the magnetic shielding within the envelope of the spectrometer. Our budget has not permitted re-annealing or replacement of the shields. In this project, an electron source of improved design was also constructed, in which the photoemissive surface is a thin film of gold, vacuum-deposited onto a fused quartz substrate. The latter is in the form of a small sphere at the end of a quartz light-pipe. Illumination of the gold from within the integrating sphere is intended to generate a higher total intensity and a relatively greater proportion of slow electrons in the emission spectrum, while at the same time reducing background due to light reflected onto other components of the spectrometer.

This contract also provided partial support of Professor Kenneth Miller's theoretical investigations of electron-atom scattering at slightly higher energies (9,10). Miller has studied the differential cross sections for atomic transitions of

the types $2p)ns)$ and $2p)np)$ within the first Born approximation. It was found that the generalized oscillator strength can be a useful property for identification of Rydberg series. Professor Miller was also supported on this work by the Petroleum Research Fund of the American Chemical Society (11).

Experimental Method

This research was performed with a single-electron time-of-flight velocity spectrometer (12).

The total cross section is inferred from comparison of electron time-of-flight distributions measured at a sequence of pressures of a specimen gas (7). The electrons are generated and detected singly. The gas under study fills the entire flight path (46.5 cm) from source to detector. Its concentration is determined from pressure measurements with an electronically-sampled capacitance manometer; pressure is in the range from 0.1 to 10 millitorr, and the temperature is assumed to be that of the thermally-insulated enclosure.

Since a wide range of energies is measured simultaneously, this method gives the energy dependence of the cross section directly. However, its accuracy depends on insensitivity of the electron source to ambient pressure of the specimen gas, on the accuracy of the manometer, and on the stability of the apparatus over long periods required for the accumulation of statistically significant data.

Detailed descriptions of this method and of the present instrument have been published. Sources and limits of error are included in these references.

Data Reduction Programs

Computer programs have been written for use in processing data obtained in this research, according to a scheme given in the publications listed below.

Each run consists of a sequence of two or more blocks of 512 channels of data. The first 256 channels contain distributions of electron counts registered in each time-of-flight channel; these

contain both the so-called "prompt electrons" which monitor the exposure and the "transmitted electrons" which have passed through the system from source to detector. The second 256 channels contain the distribution of pressure samplings of the manometer registering gas pressure in the spectrometer.

This information is punched out after each block has been recorded, while the gas flow rate is being readjusted for the next block, onto paper tape. To each paper tape record of a run is added a "signature tape," which contains calibration and other information identifying the particular run and its parameters.

Computer program INDXA controls transfer of data from the tape onto a magnetic storage disk. The data on the signature tape followed by the various blocks of TOF/P data are printed out as they are transferred from tape to disk. Each run is assigned a serial number and an entry is made in an index file. At the conclusion of the data transfer, the contents of the directory file are printed out, and the number of remaining file spaces in the disk data file is indicated for use in planning future runs.

Computer program PLOTA permits plotting of raw counter data (pressure readings optional) on semilogarithmic scales.

Computer program ETOF1, followed by ETOF2, reduce the data and determine cross sections for runs selected by punched card from the data file. Punched card input is also necessary to specify the region of the TOF data in which prompt, transmitted and background counts are located.

ETOF1 performs block-by-block calculations, first finding the average gas pressure from the pressure-sampling distribution data together with calibration information on the signature tape, and calculates the mean square pressure fluctuation. The average pressure indication is corrected for thermal transpiration error. Electron counts are corrected for background. The prompt group is summed to provide a measure of exposure, and all block counts are normalized to the average of the prompt electron counts in the respective blocks. These results are printed out for manual inspection; any blocks of data which appear to be imperfect can be re-

jected at this point. ETOF2 is then called and channel-by-channel analysis carried out. For this, the count-weighted average pressure in the run is determined for each channel, and from this, according to the prescription given by the statistical analysis (7) the most probable value of the cross section for that energy channel is found. If the channel counts total less than 100, adjacent channels are combined until this requirement is met. The average energy corresponding to each time-of-flight channel (or group of channels) is calculated. The results are printed as a table of energy, number of counts registered, average pressure at which counts were observed, total cross section, and rms cross section uncertainty.

Total Cross Section of Helium

Figure 1 displays measured values of total cross section for helium, with rms uncertainties due to counting statistics (but not the additional uncertainty due to pressure variation (7) which was not evaluated during the helium runs) indicated by vertical bars. These uncertainties become large at high and low energies, limiting the energy range, because of reduced electron counting rate. At mid-range, near 1 eV, the precision is much higher. It is believed, from subsequent experience, that the additional uncertainty contributed by pressure variation amounts to at most 2% of the total cross section. There is no structure in the total cross section above 0.4 eV.

For comparison, early measurements of Ramsauer and Kollath and more recent measurements of Golden are shown (13). The agreement is not good, either in absolute value or in energy dependence, with the Ramsauer data; the energy dependence is similar to that of Golden's data but the absolute value is considerably higher.

The momentum transfer cross section reported by Crompton et al (14) is also presented. This agrees more closely with the present total cross section results.

At low energies in helium, only elastic scattering contributes to the total cross section Q_0 . If the differential cross section for elastic scattering is represented by $Q_0 I(\theta)$, the proba-

bility that an electron be elastically scattered into the solid angle element $\sin \theta \, d\theta \, d\phi$ is $Q_0 \, I(\theta) \sin \theta \, d\theta \, d\phi$. The total and the momentum transfer cross sections are related by

$$Q_m = Q_0 \int_0^\pi \int_0^{2\pi} I(\theta) (1 - \cos \theta) \sin \theta \, d\theta \, d\phi$$

The relative difference in numerical values of these two cross sections, is then

$$\frac{Q_m - Q_0}{Q_0} = -\frac{1}{4} \int_0^\pi I(x/2) \sin x \, dx .$$

If the scattering is isotropic, or, more generally, if

$$I(\theta) = I(\pi - \theta) ,$$

the two integral cross sections are numerically equal, as observed here.

At these energies, only the $\ell = 0$ partial wave is expected to contribute to the elastic scattering in helium and there is no inelastic scattering indicated by these measurements. The agreement with the results of Crompton rather than with the other beam experiments therefore suggests that the latter contain systematic errors. Golden (15) has suggested that there are reasons to attribute the structure in the Ramsauer results to systematic error. We are inclined to believe that Golden's (15) results may also contain systematic error — probably of manometry, since he employed an ionization gauge calibrated by a capacitance manometer — in both of which thermal transpiration effects are appreciable -- together with a McLeod gauge -- which has a streaming error. It is also possible that Ramsauer's magnetic deflection technique can underestimate low energy scattering by failing to remove scattered electrons completely; these can reflect repeatedly at the surfaces of the scattering chamber until they diffuse through the exit slit. Because of the general agreement in the energy trends, we suspect the disagreement in absolute value to be one of manometry.

Total Cross Section of Molecular Nitrogen

A draft of a paper is appended to this report which describes measurements of total cross sections in molecular nitrogen. This

work was begun during the contract period but completed afterward with support from the Petroleum Research Fund of the American Chemical Society. This paper is being slightly revised in accordance with suggestions from an editorial referee prior to publication in The Physical Review. (Delay in completing this work is the reason for the delay in submission of this report.)

As in the case of helium, the results for nitrogen are in agreement with other work (16) but not with measurements of Golden (17). In particular, there is no evidence for vibrational fine structure below 1.6 eV (13).

Evaluation of the Experimental Method

Agreement of results obtained in this research with other evidence demonstrates that the time-of-flight system which has been developed and tested is now capable of making significant contributions to atomic and molecular physics. The rather low statistical accuracy of the measurements made so far can be considerably improved, and the productivity can be substantially increased. Routine measurements of total cross sections in the energy range from 2.0 eV down to 0.25 eV is possible with the present equipment; that range can be extended to lower energy by straightforward, simple improvements. The productivity of this research is limited only by the availability of manpower and computing facilities for taking and interpreting data. The limitation on statistical precision of the measurements is simply one of exposure time or counting rate, which can be improved. The limitation on resolution is the availability of manpower and equipment for replacing obsolescent components. No further major developments of apparatus or technique are required.

Significant research in this field could be performed by two equivalent full-time faculty and four or more graduate students, after some of the equipment has been updated and direct, priority access to an appropriate computer facility obtained.

Thus, it is possible to achieve a desirable goal of research in this field of over fifty years standing. Low energy cross sections still remain one of the most difficult of current experi-

mental problems, however (18). The time-of-flight technique offers the best hope of achieving this goal. The magnitude of the effort required to establish the technique was, unfortunately, greatly underestimated. Many problems which beset other techniques are also troublesome in this (e.g., manometry), and others peculiar to this method have become apparent. This is particularly true of measurements of absolute, rather than merely of relative cross sections.

The advantages of time-of-flight have been recognized by other investigators, who are beginning to apply it to electron collision research (19). However, this program is unique, so far as we know, in that it has emphasized absolute, rather than relative cross section measurement.

For absolute cross section measurement by time-of-flight (4,12), magnetic fields must be strictly excluded and electric collecting fields included so that all scattered electrons are removed from the apparatus. On the other hand, it is permissible to increase the counting rate greatly by confining the electrons with a coaxial magnetic field if one is interested only in non-absolute spectrometry. Use of differentially pumped thermionic sources with grid control is permissible in non-absolute electron spectrometry. Absolute cross section measurement, on the other hand, requires uniform temperature and pressure over the entire electron path within the spectrometer; these conditions are compatible only with photoelectric generation of electron pulses (12).

A unique feature of the present research is its detailed evaluation of sources of error (7); it is believed that no previous program for absolute total cross section measurements by beam techniques has included so thorough an analysis of the magnitudes and sources of both random and systematic error.

A disadvantage of the method used in this research is low electron counting rate, limited by the low repetition rate of the pulsed light source. Since no mode-locked or high repetition-rate laser source, capable of exciting photoemission from a suffi-

ciently inert (work function 5 eV) surface has been available, it was necessary to use a spark gap, which required considerable development to insure reproducible performance and long life.

Long turn-around time between data accumulation (paper tape) and its subsequent reduction (on a computer which belongs to another, high-priority research program) has also seriously curtailed productivity. An on-line computer, providing for control of experimental parameters as well as for prompt data reduction, would greatly increase the productivity of the present spectrometer installation. Proposals to this end have been unsuccessful, however.

A particularly frustrating problem is the fact that much of the electronic equipment is obsolescent; frequent servicing is the rule. Locally-made electronic components employ integrated circuits wherever possible to increase their reliability.

Finally, the manpower which could be applied to this research has not been adequate to the task. At no time has the budget permitted applying two full-time men to the research, and only limited access to the student resources of the Institute has been possible.

These difficulties all result from a total budget too low to permit efficient effort. Lack of adequate equipment and manpower has forced compromises; e.g., postponement of significant developments, servicing and modification of old equipment which should have been replaced; diverting manpower from research to maintenance.

Publications

The following publications relate to work supported in part by this contract:

"Time-of-Flight Measurements of the Total Electron-Helium Atom Cross Section," G. C. Baldwin, Proc. VIIth Int. Conf. on the Physics of Elec. and At. Coll., 94, North-Holland Pub. Co., Amsterdam, 1971.

"A Single-Electron Time-of-Flight Stepped-Pressure Spectrometer for Total Cross Section Measurements at Low Electron Energies," G. C. Baldwin, M. R. Gaerttner and W. A. Bryant, chapter in Electron-Spectroscopy, ed. by D. A. Shirley, pp. 159-175, North-Holland Pub. Co., Amsterdam, 1971.

"Electron Time-of-Flight Instrumentation," W. A. Bryant and G. C. Baldwin, Bull. Amer. Phys. Soc. 16, 586, 1971; "Specimen Gas Supply for TOF Electron Spectrometry," M. R. Gaerttner, G. C. Baldwin and W. A. Bryant, *ibid*; "Determination of Cross Section from Single Electron Transmission," G. C. Baldwin and W. A. Bryant, *ibid*.

"Thermal Transpiration Error in Absolute Pressure Measurements with Capacitance Manometers," G. C. Baldwin and M. R. Gaerttner, Jour. Vac. Sci. and Technol. 10, 215-217, 1973.

"Statistical Error in Molecular Cross Section Measurement," G. C. Baldwin and K. J. Miller, Rev. Sci. Instr. 44, 860-867, 1973.

"Electron Scattering of Atoms for Excitation to Valence and Rydberg States," K. J. Miller, Int. Jour. Quant. Chem 5, 71 (1971).

"Dependence of Extrema in the Generalized Oscillator Strengths on Momentum Transfer and Effective Nuclear Charge for Atomic Transitions," K. J. Miller, to be published in Jour. Chem. Phys., October, 1973.

"Nitrogen Total Cross Section for Electrons below 2 eV," G. C. Baldwin, submitted to Phys. Rev. in June, 1973, and currently being revised in accordance with referee's comments.

An unpublished thesis, in partial fulfillment of requirements for the ME degree, entitled "Time-of-Flight Electron Spectrum Measurements," was submitted in August 1972 by Peter J. Morley.

Personnel

Professor George C. Baldwin, Division of Nuclear Engineering and Science, is the principal investigator.

Professor Kenneth J. Miller, Department of Chemistry, provided theoretical support during the contract period.

Dr. Martin R. Gaerttner was employed as a postdoctoral associate during the period January 1, 1971 through August 31, 1971. Dr. Gaerttner, in spite of his unusually brief stay, contributed significantly to the program, but was obliged to terminate earlier than expected because of reduced support. His departure was a distinct loss.

Mr. Willard A. Bryant, Research Associate, was associated on a part-time basis on this program from its inception until the summer of 1971, after which it was no longer possible to afford his services. Mr. Bryant developed much of the electronic equipment in use in the present system, and the initial versions of data reduction programs.

George T. Baldwin was engaged as an unpaid assistant for completion of the data reduction computer programs during the summer of 1972. Revision of algorithms for cross section determination had made it necessary to revise completely the earlier data reduction programs developed by Mr. Bryant. This work was sufficiently complete by September, when Baldwin left to return to another college, that the remaining steps could be completed by the principal investigator.

Peter J. Morley, graduate student, also unpaid, was associated with the program during the period September, 1971 through June, 1972 for a master's thesis project.

The assistance of other members of the Division of Nuclear Engineering and Science and in particular of the staff of the LINAC project is greatly appreciated; we are particularly appreciative of their assistance in the use of the LINAC computer system.

References

1. "Time-of-Flight Electron-Spectrometry," Contract N00014-67-A-0117-0003 issued by the U. S. Office of Naval Research.
2. Petroleum Research Fund, Grant No. 6448 AC 5,6.
3. G. C. Baldwin, Proc. VIIth Int. Conf. on Phys. of Electronic and Atomic Coll., Amsterdam, N.V., 94, 1972.
4. G. C. Baldwin, W. A. Bryant and M. R. Gaerttner, in Electron Spectroscopy, ed. by D. Shirley, pp. 159-175, North-Holland Pub. Co., Amsterdam, 1972.
5. "Nitrogen Total Cross Section for Electrons below 2 eV," G. C. Baldwin, submitted to the Physical Review.
6. G. C. Baldwin and M. R. Gaerttner, Jour. Vac. Sci. and Tech. 10, 215-217, 1973.
7. G. C. Baldwin and K. J. Miller, Rev. Sci. Instrs. 44, 860-867, 1973.
8. P. D. Morley, RPI Master's Thesis, August, 1972.
9. K. J. Miller, Int. Jour. Quant. Chem. 5, 71, 1971.
10. K. J. Miller, J. Chem. Phys., to be published October 1973.
11. Petroleum Research Fund, Grant No. 5642AC5.
12. G. C. Baldwin and S. I. Friedman, Rev. Sci. Instrs. 38, 519-531, 1967.
13. See the compilation in L. J. Kieffer, "Low Energy Electron-Collision Cross Section Data: Part III," Atomic Data 2, 311 1971.
14. R. W. Crompton, M. T. Elford and A. G. Robertson, Austr. Jour. Phys. 23, 667, 1970.
15. D. E. Golden and H. W. Bandel, Phys. Rev. 138, A14, 1965.
16. A. G. Englehardt, A. V. Phelps and C. G. Risk, Phys. Rev. 135, A1566, 1964.
17. D. E. Golden, Phys. Rev. Letters 17, 847, 1966.
18. B. Bederson and L. J. Kieffer, Rev. Mod. Phys. 43, 601, 1971.
19. R. Stein, private communication; J. E. Land and W. Raith, Atomic Physics, 3, 553, ed. by S. J. Smith, Plenum Pub. Co., New York, 1973.

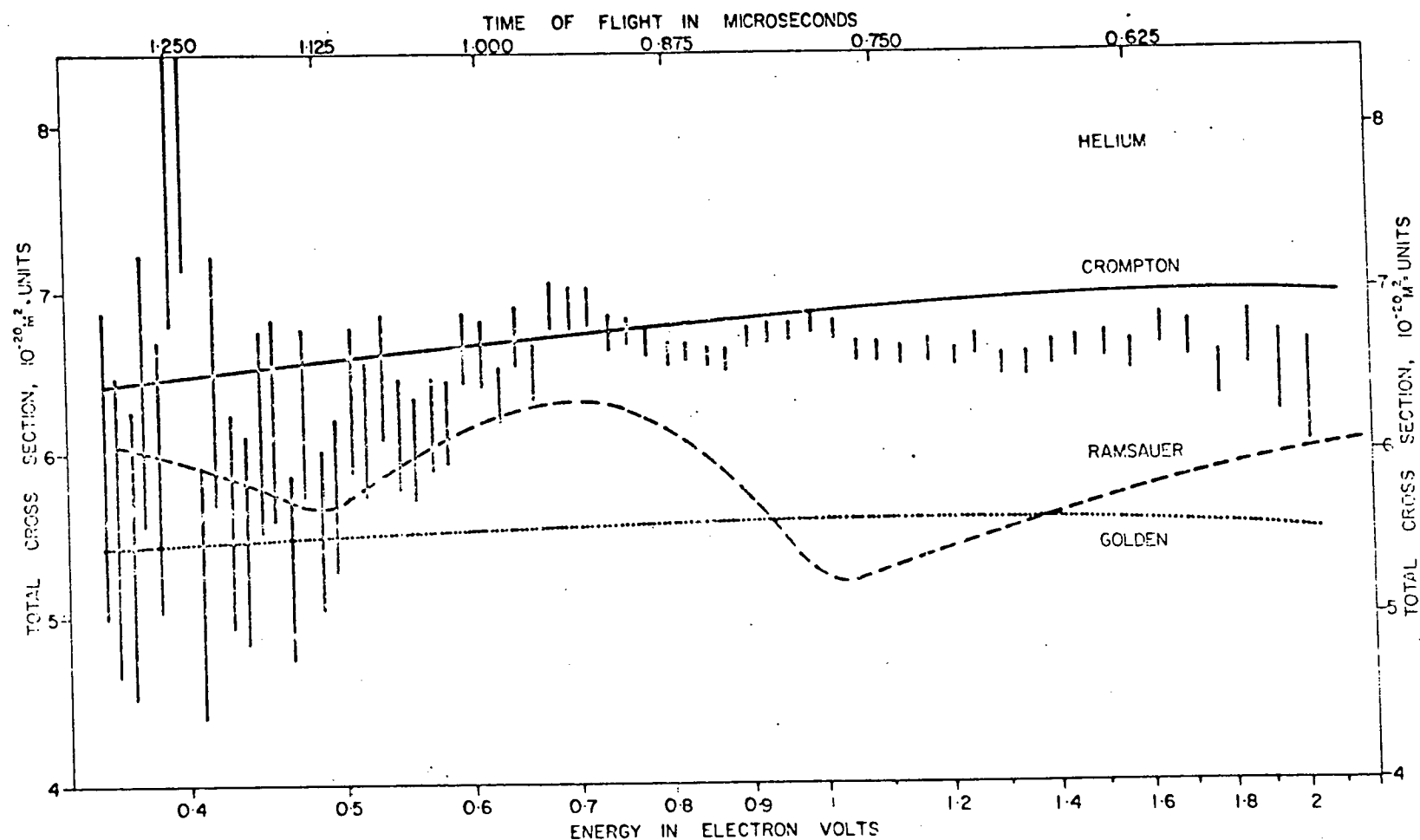


Figure 1 Total cross section of helium deduced from a 14-block, 36-hour transmission run. Vertical bars indicate statistical errors in each time-of-flight channel; at low energies the relatively small count leads to large uncertainty. A thermal transpiration correction of +2.6% should be applied to the measured cross sections. The curve labeled "Crompton" is the momentum cross section from reference 14; "Golden," the total cross section by beam measurement of reference 15; "Ramsauer," the 1927 beam measurement of Ramsauer and Kollath.