Ionization and Metastable Excitation in Low-Energy Collisions of Ground State Argon Atoms*

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NGR-06-004-006

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ABSTRACT

A low-energy beam of argon atoms, formed by non-resonant charge transfer of Ar^+ in H_2, has been used to explore the near-threshold behavior for ionizing and exciting collisions between argon atoms. For excess center-of-mass energies below 12 eV, the ionization data are consistent with the empirical relationship $\sigma_- \approx 1.8 \times 10^{-21} (E-15.8)^{1.3}$, where E is the center of mass energy in electron-volts. Target gas mixtures of argon and acetylene were used in an effort to observe metastable atoms formed in atom-atom collisions by Penning ionization. In this case, beam energies were restricted to values less than 30 eV to avoid direct ionization of the acetylene (Penning) gas by the ground-state atom beam. At 14.5 eV c.m. energy, the cross section for metastable production is shown to be $(3.6 \pm 2.4) \times 10^{-20}$ cm^2, but this value is dependent upon assumed values of the Penning cross section for $Ar^* + C_2H_2$ collisions.

INTRODUCTION

In 1957, Petschek and Byron[1] proposed that the initial ionization of shock-heated argon proceeds via a two-step process. The first step is considered to be the excitation of argon by atom-atom collisions, $Ar + Ar \rightarrow Ar + Ar^*$. The second step is presumably the collision between an excited atom and another atom, $Ar^* + Ar \rightarrow Ar + Ar^+ + e^-$, which produces the first electrons in the bulk ionization process.

An activation energy for the excitation step has been reported by several investigators to bracket the first four excited states of the argon atom.[2-4] These excited states arise from the $3p^5 4s$ electron configuration.[5] Two of the states, those at 11.55 and 11.72 eV, are metastable and the others, at 11.62 and 11.83 eV, are not.

Since it was not known to what extent the excitation of metastable levels is responsible for the rate-controlling step to an excited state, atomic beam measurements of the cross section for metastable formation, σ_m, have been attempted. Also, measurements have been made of the total cross section for ionization, σ_-, during collisions between ground-state argon atoms for energies very near the ionization threshold. This latter cross section gives information about the energy dependence of the cross section for the second step in the initial ionization process, σ_2, since these two cross sections, σ_- and σ_2, are expected to have essentially the same threshold behavior[6] when compared in terms of the excess energy E_e available in the center-of-mass system: $E_e = \frac{1}{2} E_{lab} - E^*$, where E^* denotes the ionization potential or the excitation energy.

IONIZATION MEASUREMENTS

The total cross section for negative charge formation, σ_-, was measured in a manner previously described.[7-9] Measurements of σ_- for argon-argon collisions have been reported for excess c.m. energies above 10 eV using both argon and nitrogen as charge-transfer

gases.[10,11] However, in the present work, hydrogen was used in the charge-transfer cell by which argon ions, formed by electron impact and accelerated electrostatically, were neutralized to form an atomic beam.[12] Use of hydrogen as the charge-transfer gas eliminates any excitation in the neutral beam during neutralization for all beam energies below 230 eV.

In the present work, σ_- was measured for excess c.m. energies between 1.5 eV and 500 eV, by neutralizing an ion beam having a full width at half-maximum intensity of less than 1 eV (i.e., less than 0.5 eV in the c.m. system). It was desirable to isolate the target gas from the neutralization region to eliminate any $Ar^+ + Ar$ charge-transferring collisions, and the accompanying metastable formation.[13] Thus, a separate target chamber was used which allowed the neutral beam to pass into it via a differentially-pumped aperture. The pressure in this chamber, about 2×10^{-4} Torr, was monitored continuously with an MKS Instruments Baratron capacitance manometer.

In the target chamber the beam passed through a parallel-plate ionization detector.[8] Any negative charge formed along a guarded collector length of 10 cm was measured on a Cary model 401 vibrating reed electrometer. A 0.15 mil tungsten wire grid was used to suppress secondary electrons from the back plate of the detection assembly. The potential of the grid with respect to the collector was maintained at -300 volts, while with respect to the back plate it was kept at -90 volts. Measured corrections to the data were made for beam loss at the exit of the charge-transfer cell and at the entrance to the target chamber, as well as for incomplete collection of slow ions in the charge-transfer cell and incomplete collection of negative charge in the target chamber.

The results of the σ_- measurements are shown in Fig. 1. No corrections have been applied to account for beam energy spread. The vertical error bars at low energies are indicative of the uncertainty present in the measurement resulting from uncertainties in the background and the measured correction to the data for secondary electrons due to the grid.[8] In addition to the error bars shown, a systematic uncertainty of $\pm 30\%$ is assigned to the

absolute cross section measurements. The straight line drawn through the data below 12 eV excess c.m. energy suggests a threshold power law:

$$\sigma_- \approx 1.8 \times 10^{-21} (E_{c.m} - 15.8)^{1.3} \ (cm^2) \qquad (1)$$

The structure present between 50 and 150 eV found in earlier work[10,11] is seen to persist for a H_2-neutralized beam. Therefore, this structure in the total ionization cross section must be a result of interaction between two ground state argon atoms. This was first concluded in earlier work with a nitrogen charge-transfer gas.[11] A corresponding variation in the cross section for extreme-ultraviolet photon production has also been observed for excess c.m. energies above 15 eV.[14]

METASTABLE EXCITATION MEASUREMENTS

As in the ionization measurement, a fast beam of neutral, ground-state argon atoms was obtained by charge transfer in hydrogen. In the target chamber was placed a mixture of argon and acetylene. Any argon metastables formed have sufficient energy of excitation to Penning-ionize acetylene. (Acetylene has an ionization potential of 11.4 eV.) In this way, metastable formation from Ar-Ar collisions was detected by measuring the negative charge produced in the mixture between the ionization plates. Since it was necessary that no other process be present leading to significant negative charge production, restrictions were placed on the maximum energy at which the process was studied. The lower energy limit is threshold for the excitation process:

$$Ar + Ar \rightarrow Ar^* + Ar, \qquad (2)$$

at 23.1 eV laboratory energy. The upper limit of the energy "window" is the threshold for the direct ionization of acetylene:

$$Ar + C_2H_2 \rightarrow Ar + C_2H_2^+ + e^- \qquad (3)$$

at 29.0 eV.

The Penning ionization current for any particular target mixture is in a certain proportion to the cross section for excitation of

metastable argon, if this current has been normalized to unit argon pressure and unit incident beam intensity. In Fig. 2 the normalized current is plotted as a function of increasing target pressure. In this figure, a one-to-one correspondence is assumed between each excitation event and a Penning ionization event, i.e., the Penning detection efficiency is taken to be unity. The ordinate is therefore termed the apparent excitation cross section. The argon pressure in the target was kept at about 2×10^{-4} Torr throughout the measurements at 24.4 eV and 27.4 eV laboratory energy. However, the acetylene concentration was increased until the total pressure in the target was 1×10^{-3} Torr. Severe beam attenuation sets in above a total pressure of $\sim 6 \times 10^{-2}$ Torr. The target mixture for optimum detection efficiency was about 4×10^{-4} Torr of acetylene with 2×10^{-4} Torr of argon. With the use of this mixture, the data shown in Fig. 3 were obtained. Here, the apparent cross section is plotted as a function of center-of-mass energy between colliding argon atoms. In both Fig. 2 and Fig. 3, the error bars were determined by consideration of uncertainties in the ionization current and the background current. Occasionally, because of random fluctuations, the background current was larger than the ionization current, giving a negative apparent cross section. These negative values have statistical meaning only. In Fig. 3, measurements were extended beyond the upper limit of the energy window and corrections for Ar - C_2H_2 direct ionization had to be made, resulting in greater uncertainty for these points.

By making the assumption that excited atoms have small angles of deflection from the beam axis (a valid assumption near threshold), a simple calculation can be made of the number of excited atoms detected (See Appendix). For an acetylene pressure of 4×10^{-4} Torr, a collection length of 10 cm, and a Penning ionization cross section of 54Å^2 (a value obtained from extrapolated measurements of deactivation cross sections for $Ar^* + C_2H_2$),[15] it was found that about 50% of those metastables formed are detected. Thus, the apparent cross section plotted in Fig. 3 may be multiplied by a factor of 2 to

obtain an estimate of the actual cross section for metastable formation in Ar-Ar collisions, σ_m. At 14.5 eV center-of-mass energy, $\sigma_m = (3.6 \pm 2.4) \times 10^{-20}$ cm^2. We emphasize that this value depends directly on the calculated detection efficiency and hence upon the value used for the Penning ionization cross section.

From shock tube measurements, McLaren and Hobson[4] estimated a slope for the linear threshold excitation law which they assumed. This slope indicated an excitation cross section for argon collisions at 14.5 eV c.m. energy of $(7.8 \pm 0.8) \times 10^{-20}$ cm^2. Earlier work by other investigators[2,3] had implied excitation cross sections as large as 2×10^{-18} cm^2. It is probable, however, that excitation to metastable states is not the only mechanism in the first step of the bulk ionization process. Excitation to levels which decay by resonance radiation and subsequent radiation trapping is still a likely source of the excited-state population. Beam measurements of excitation to these radiating levels are described in a separate paper.[14]

ACKNOWLEDGMENTS

One of us (P.O.H.) gratefully acknowledges a graduate fellowship from the Boettcher Foundation. We are indebted to C. F. Hansen and N. G. Utterback for helpful discussions and comments.

References

1. H. E. Petschek and S. Byron, Ann. Phys. (N.Y.) 1, 270 (1957).
2. K. E. Harwell and R. G. Jahn, Phys. Fluids 7, 214 (1964).
3. A. J. Kelly, J. Chem. Phys. 45, 1723 (1966).
4. T. I. McLaren and R. M. Hobson, Phys. Fluids 11, 2162 (1968).
5. C. Moore, Atomic Energy Levels, Vol I, National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D.C. (1949).
6. C. F. Hansen, Sixth International Symposium on Rarefied Gas Dynamics, July 23-26, 1968, Massachusetts Institute of Technology, Cambridge, Massachusetts.
7. N. G. Utterback and G. H. Miller, Rev. Sci. Inst. 32, 1101 (1961).
8. N. G. Utterback and G. H. Miller, Phys. Rev. 124, 1477 (1961).
9. R. C. Amme and P. O. Haugsjaa, Phys. Rev. 177, 230 (1969).
10. H. C. Hayden and R. C. Amme, Phys. Rev. 141, 30 (1966).
11. R. C. Amme and H. C. Hayden, J. Chem. Phys. 44, 2828 (1966).
12. R. C. Amme and J. F. McIlwain, J. Chem. Phys. 45, 1224 (1966).
13. P. O. Haugsjaa, R. C. Amme and N. G. Utterback, Phys. Rev. Letters 22, 322 (1969).
14. P. O. Haugsjaa and R. C. Amme, Phys. Rev. Letters 23, Sept.22, 1969.
15. M. Hollstein, D. C. Lorents, J. R. Peterson, and R. A. Young, Research on Metastable Species in Atomic and Molecular Beams Produced by Charge Transfer, Stanford Research Institute Semi-Annual Report, 29 Dec. (1967), Menlo Park, California.

APPENDIX

For impact energies near threshold, it may be assumed that, after excitation, the argon metastable will move forward in the laboratory system. Thus, one may consider the flux of metastable atoms, M, as interacting with the acetylene target of density n_H over the same interval, $d\ell$, as the argon beam interacts with the argon target of density n_A. We may write

$$dM = \sigma_m n_A B\, d\ell - \sigma_P n_H M d\ell \quad ,$$

where σ_m and σ_P are respectively the cross sections for metastable formation and destruction (assumed to be the Penning ionization cross section). If B is nearly constant over the detection length ℓ, the solution to this first order linear differential equation is

$$M = (\sigma_m n_A B/\sigma_P n_H)[1 - \exp(-\sigma_P n_H \ell)] \quad .$$

For energies within the "window", the only possible source of ionization current I is the Penning process. Thus, $dI = \sigma_P n_H M d\ell$, or,

$$dI = \sigma_m n_A B [1 - \exp(-\sigma_P n_H \ell)] d\ell \quad .$$

Integration over the collection length and substitution for n_H and n_A, the number densities corresponding to the target gas partial pressures utilized, gives I as a function of the Penning cross section. Extrapolation of the deactivation cross sections for $Ar^* + C_2H_2$ presented in Ref. 15 to 6 eV gives a value $\sigma_P \approx 54 \text{Å}^2$. For the measured cross section, $\sigma \equiv I/[(10 \text{ cm}) B n_A]$, one then finds $\sigma \approx 0.50\, \sigma_m$, or

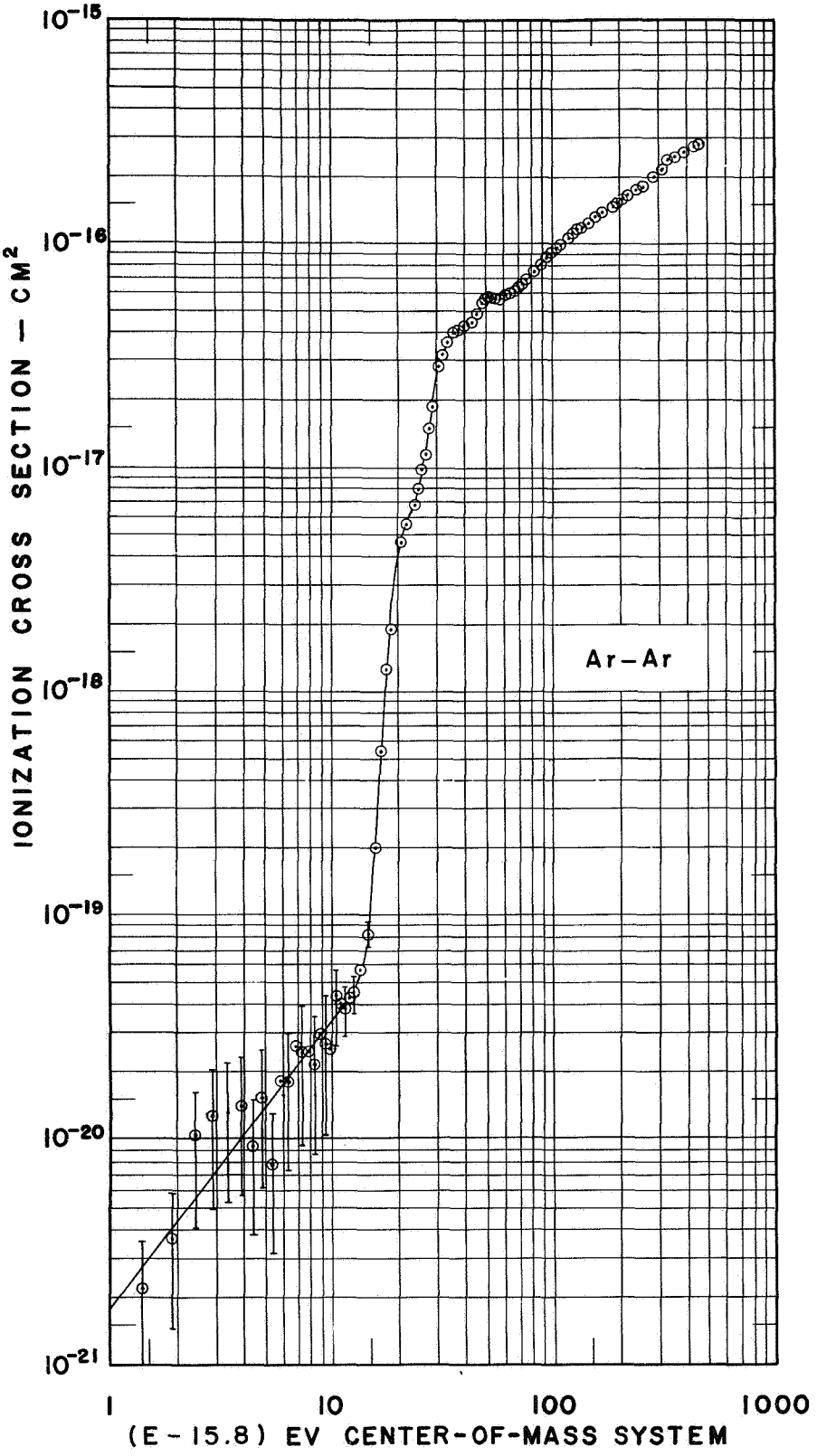
$$\sigma_m \approx 2\sigma \quad .$$

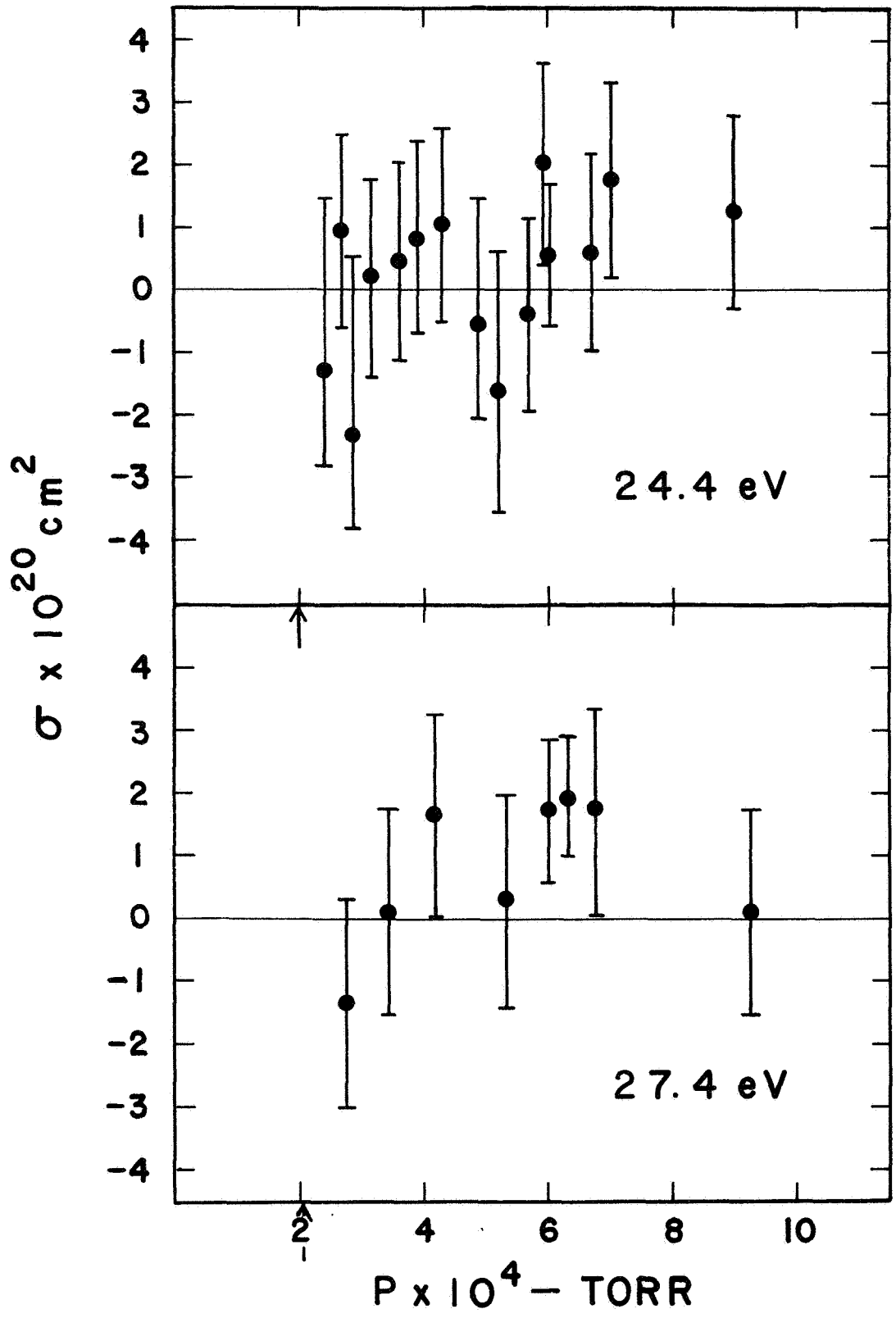
Figure Captions

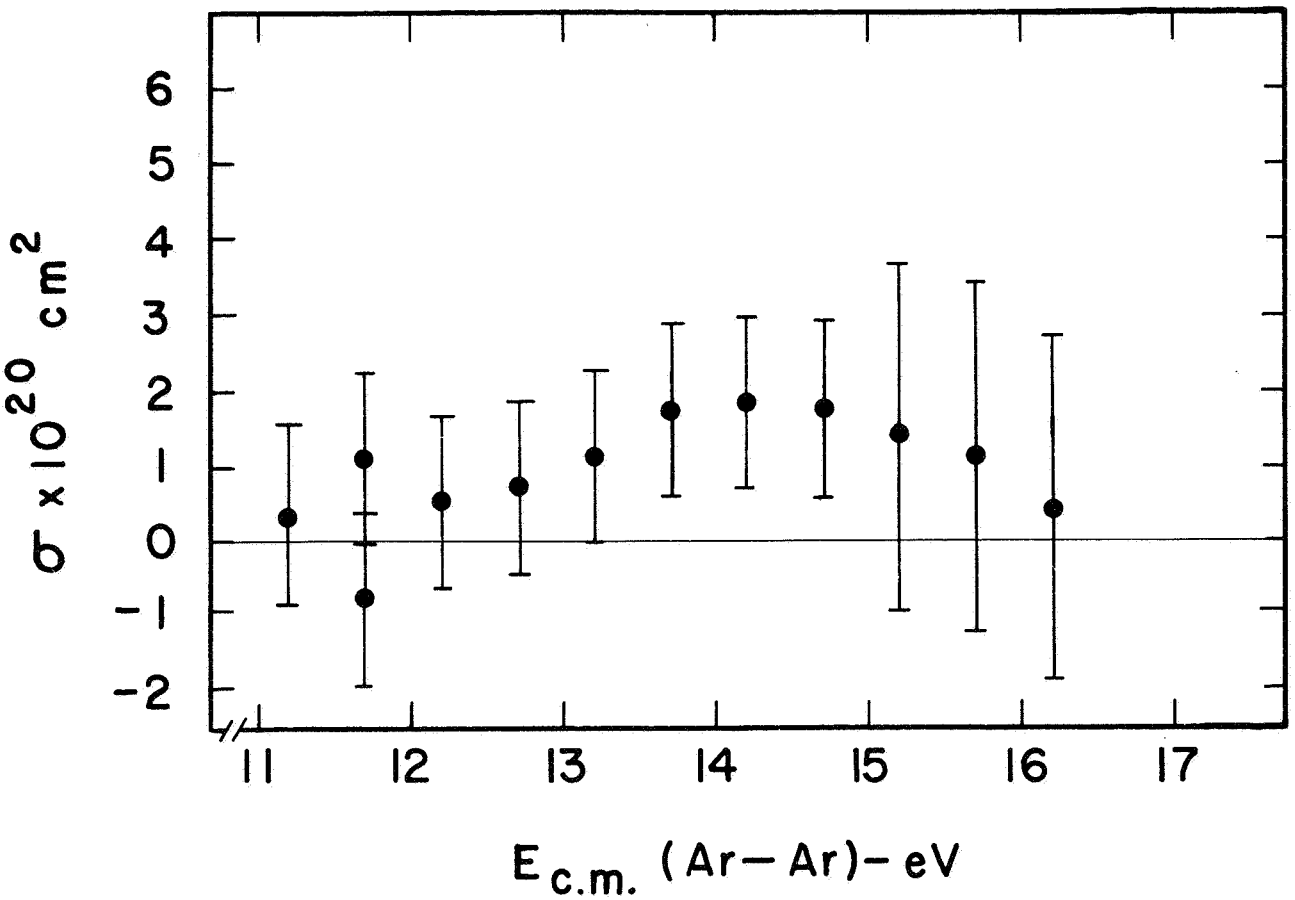
Fig. 1. Total ionization cross section for argon-argon collisions with H_2 employed as beam-neutralizing gas.

Fig. 2. Apparent cross section for argon metastable-atom production from Ar + Ar collisions as a function of total target-gas pressure. The argon pressure was maintained at 0.2 mTorr and the acetylene gas pressure was varied. Results are shown for two different laboratory beam energies.

Fig. 3. Apparent cross section for argon metastable production vs. center-of-mass energy. Error bars include uncertainties in background current and in electrometer measurements. The actual cross section is estimated to be 2σ, but depends directly upon the Penning cross section for $Ar^* + C_2H_2$.


IONIZATION CROSS SECTION — CM²
10⁻¹⁵
10⁻¹⁶
10⁻¹⁷
10⁻¹⁸
10⁻¹⁹
10⁻²⁰
10⁻²¹
Ar–Ar
1
10
100
1000
(E – 15.8) EV CENTER-OF-MASS SYSTEM


4
3
2
1
0
-1
-2
-3
-4
24.4 eV
27.4 eV
σ x 10^20 cm^2
2
4
6
8
10
P x 10^4 — TORR


6
5
4
3
2
1
0
-1
-2
σ x 10^20 cm^2
11
12
13
14
15
16
17
E c.m. (Ar–Ar)– eV