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Electron Impact Ionization Cross-Section Data for Atoms, Atomic Ions, and Diatomic Molecules: I. Experimental Data

L. J. KIEFFER,* GORDON H. DUNN*

Joint Institute for Laboratory Astrophysics,† *Boulder, Colorado*

This review includes a compilation and critical evaluation of absolute cross sections for ionization of atoms and diatomic molecules by electron impact. Experimental techniques used for ionization are surveyed. Selected relative cross sections for production of multiply charged ions and a brief discussion of relative cross-section data near threshold are presented. Absolute limits are not set on the size of probable systematic errors in the various experiments.

I. INTRODUCTION

Ionization of atoms and molecules by electron impact is a subject of great practical interest for predicting the properties of nonequilibrium plasmas. This interest is represented in diverse fields of research such as stellar atmospheres, low- and high-temperature laboratory plasmas, atmospheric physics, and mass spectrometry. The experimental data are also of interest for comparison with theoretical predictions. The validity of various necessary approximations in the theories can thus be tested.

This review is an attempt to assemble and to evaluate the experimental cross-section data for electron-impact ionization of atoms, atomic ions, and diatomic molecules. More complicated molecules are not considered here. A subsequent review will include a summary of the theoretical methods and results and a comparison of these results with the experimental data. (This review and evaluation of the theoretical techniques for calculating electron-impact ionization cross sections is being prepared by Alan Burgess. This review is being supported by the University of Colorado under contract with the National Bureau of Standards through the National Standard Reference Data Program.)

The relevant data fall into two main classes: (1) "Gross" or "total" ionization cross sections, i.e., the cross sections for producing a single positive charge of any atomic or molecular species regardless of the mass or multiplicity of charge on the ions produced. These measurements are important for practical reasons as well as being important in evaluating cross sections for individual processes as discussed in later sections. (2) Cross sections for individual ionization processes, including dissociative ionization, ionization to a particular final state of an ion, and multiple ionization.

A general discussion of the various experimental techniques used to obtain the data is given in Sec. II. Table I in this section lists the criteria by which the data have been selected. Section III contains the cross-section data together with a discussion comparing the individual experiments.

Table II is a classification of the experiments according to the criteria in Table I. Section IV contains a brief discussion of some of the high-resolution, relative cross-section data and some interpretations thereof.

II. EXPERIMENTAL TECHNIQUES FOR DETERMINATION OF IONIZATION CROSS SECTIONS

A measurement of an ionization cross section usually involves the determination of the quantities in the relation

$$I_i(E)/I_e(E)=\rho L\sum_n n\sigma_n(E)=\rho L\sigma_T(E). \qquad (1)$$

Here $I_i(E)$ is the ion current generated by single electron impact, $I_e(E)$ is the current of bombarding electrons of energy E, ρ is the number density of the target gas, L is the collision path length over which the measured ion current is collected, and $\sigma_n(E)$ is the

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* Staff members, Laboratory Astrophysics Division, National Bureau of Standards.

† Of the National Bureau of Standards and the University of Colorado.

Table I. Necessary conditions in order to obtain accurate ionization cross sections.

Measured quantity	Necessary conditions
I_i	1. Collection of a known fraction of the ions. 2. No secondary electron current from ions hitting the collector. 3. No ions reflected from the collector. 4. No spurious ion or electron current. 5. Separation into final state components.
I_e	1. Total collection of electron current producing the ions. 2. No secondary electron current from electrons hitting the collector. 3. No reflection of electrons from the collector. 4. No collection of electrons ejected in the ionizing collision. 5. No collection of secondary electrons ejected from electron beam defining apertures.
ρ	1. Accurate number density standard for experiments done in static gas samples. 2. Temperatures of pressure gauge and ionization region known. 3. Accurate vapor pressure when a gas from a volatile liquid or solid is used. 4. Velocity of target known in beam experiments. 5. Accurate technique for measuring total target beam flux. 6. Measurement of inhomogeneities in target and electron beams.
L	1. Path length known for electron orbits when a confining magnetic field is used. A. Transverse velocity components due to electric or magnetic field effects. B. Transverse velocity components due to background gas scattering. 2. Path length known for electron orbits when no confining magnetic field is used. A. Transverse velocity components due to electron optical effects or space charge spreading. B. Transverse velocity components due to gas scattering.

cross section for producing an ion of nth degree of ionization in the collision. The summation is over the charge states which contribute to the collected current of ions. When all charge states are included, the summation is denoted by $\sigma_T(E)$, the total or gross cross section.

In spite of the conceptual simplicity of such an experiment and in spite of the large number of experiments done, the practical problems involved in obtaining accurate determinations of *all* the above quantities are severe.

Table I lists the most important conditions necessary for obtaining accurate measurements of the quantities needed to calculate $\sigma_n(E)$ from Eq. (1). These conditions are tabulated for use in discussing specific experiments, although, of course, one cannot include in such a general listing all the subtle difficulties which may be inherent in an individual experiment. In a similar way the magnitude of the various systematic errors is difficult to assess quantitatively. It is obviously incumbent upon all experimentors using Eq. (1) and its variations to *demonstrate* the functional dependences there and to *show* that systematic errors implied from Table I are absent or to estimate *realistically* their magnitude.

There are many types of apparatus for ionization studies, but most of them can be classified as one of the following:

A. Total ionization apparatus,
B. Total ionization tube with q/M discrimination,
C. Mass spectrometer,
D. Crossed-beam apparatus.

The problem of accurately defining electron energy is discussed in a separate paragraph as is the application of these methods to measuring ionization cross sections of molecules.

A. Total Ionization Apparatus

Early investigators (Ref. 1) of ionization tried many forms of apparatus, but it now appears that the most satisfactory type is that introduced by Jones (2) and used for the classic measurements of Smith (3) and Tate and Smith (4). The technique has recently been used by others (Refs. 5–8).

A schematic illustration of Tate and Smith's tube is shown in Fig. 1. Electrons from the differentially pumped filament F are accelerated through apertures S_1, S_2, and S_3 by an electric field maintained by a constant potential difference. A variable potential difference between S_3 and S_4 is used to give the electrons their final energy, and a longitudinal magnetic field B serves to confine the electrons in a beam. They are collected by the trap T, and their current is monitored with appropriate instruments. In determing $I_e(E)$, it is necessary to ascertain that reflected and secondary electrons in T do not escape, that electrons formed from ionizing the gas are small in number compared to the primary electron current, that photoelectrons do not constitute an appreciable fraction of the current, and that the number of secondary electrons formed on aperture edges is inappreciable. An electric field between P_3 and P_4 can ensure adequate trapping, and operation at low enough pressures can eliminate the problem of volume electrons and photoelectrons. The importance of secondary electrons which come from slit edges is best evaluated by examining the currents to and from all electrodes in the absence of a gas, and by performing

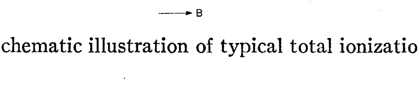

Fig. 1. Schematic illustration of typical total ionization tube.

a differential retarding analysis on the collected electrons to demonstrate the absence of a lower energy component.

Ions formed are accelerated by a uniform electric field between P_2 and P_1 and G. With a sufficiently strong field, the current measured to P_1 should be the ion current formed over a path length L. Secondary electrons ejected from P_1 by the ions or by photons do not escape because of the magnetic field. The determination of $I_i(E)$ must account for ions formed in the trap region or in the region prior to the space between P_2 and P_1 and G. Ions formed in these places by electrons of energy different from E may be accelerated into the collision region and collected on P_1. It is also necessary to demonstrate that the ion current to P_1 is independent of the applied ion collection field. This independence is necessary for complete collection of all ions, including ions formed with kinetic energy from dissociative ionization of molecules. At low electron energies—on the rising side of the cross-section curve—the ion drawout field may affect the collected ion current due to the spreading of the electron energy distribution by the electric field.

The path length L is nominally just the length l of p_1. However, because the electrons have a helical path in the magnetic field and a trochoidal drift in the crossed electric and magnetic fields, L is greater than l. The increase in length due to crossed field drift (Ref. 8) is a small fraction of a percent under typical conditions and may usually be neglected. If one assumes that the diameter of helices described by the electron paths is limited by an aperture of diameter d, then the maximum path length is given by

$$L=l[1-(v_\perp^2/v^2)]^{-\frac{1}{2}}, \tag{2}$$

where $v_\perp$ is the transverse electron velocity (limited by d) and v is the total velocity. [Massey and Burhop (9) give an approximate expression for this formula.]

For the condition $v_\perp=v$, L becomes infinite. For a fixed helix diameter d, there is a minimum energy for which this equation has meaning. Electrons with energies smaller than this minimum value clearly have helical paths with diameters smaller than d. However, this should be an absolute upper limit, assuming that there is no trochoidal drift. Asundi (10) noted that the transverse velocity components imparted to the electrons by the lens system of apertures may more reasonably fix the helix diameter. He made a simple estimate based upon electrostatic lenses, ignoring the magnetic field, and found $(v_\perp/v)^2\simeq 0.001$ for geometries such as Tate and Smith used. Craggs *et al.* (11) pointed out that another possible cause of transverse velocity components is gas scattering of the electrons. Rapp and Golden (7a) concluded that transverse velocities introduced by lens effects are even smaller than estimated by Asundi, primarily because of the confining effect of the magnetic field. They estimated the effect of gas scattering in H_2 near ionization threshold and found that $L\simeq 1.0014l$ with an H_2 pressure of about 5×10^{-5} Torr. The effect on cross section measurements due to transverse velocities imparted by lenses or gas scattering should be independent of magnetic field (as long as the crossed-field drift velocity is small compared to the longitudinal velocity). The presence of an effect from these sources should be detectable by noting systematic changes of the apparent cross section when lens-operating conditions or gas pressure are changed.

Assuming an ideal gas, the target density ρ can be computed from

$$\rho=(3.535\times10^{16})P_c(273/T_c),$$

where P_c and T_c are the pressure in mm Hg and temperature in °K, respectively, in the collision chamber and 3.535×10^{16} is the number of particles per cc at 1 mm pressure at 273 °K. If the gauge at temperature T_G used to determine P_c is connected to the chamber with tubing with a diameter small compared to the mean free path of the gas particles, then (Ref. 12) at equilibrium, $P_c/P_G=(T_c/T_G)^{\frac{1}{2}}$; and the equation for the density becomes

$$\rho=(3.535\times10^{16})\ 273\ P_G\ (T_cT_G)^{-\frac{1}{2}}. \tag{3}$$

It is not apparent whether all authors have properly accounted for temperature differences (see Table II, Sec. III), although the corrections can typically amount to 10%. Rapp and Golden pointed out that when different temperature and density regions are between the gauge and ionization chamber, the simple one-half power thermal transpiration law may not apply. Deviations from the ideal $(T)^{\frac{1}{2}}$ relation have been considered by other authors (13).

Gauge pressure P_G is typically obtained by using a McLeod gauge, an absolute device which has been assumed to be accurate to a conservative 2 or 3%. Quite recently, Ishii and Nakayama (14) found that McLeod gauge readings strongly depended on temperature. This effect has since been observed by others (15), and within the accuracy of the techniques used, it has been found that the effect seems to agree with the prediction of Gaede (16). He suggested that the mercury stream from the gauge to the cold trap should act like a diffusion pump. Apparent errors at room temperatures have been found ranging from 1 or 2% for H_2 to 20 to 40% for xenon. Cooling the McLeod gauge cutoff (Refs. 14, 15) or refrigerating the whole gauge are techniques which have been used to diminish this systematic effect. Further definitive tests are certainly desirable, and better theoretical understanding is needed of all possible mechanisms which could cause the McLeod gauge to behave in such a manner. A dynamic technique for measuring pressure has been used in ionization measurements by Rapp and Golden

(7a). This technique requires effusive flow through a leak between a volume with a high pressure and the ionization chamber and out of the ionization chamber through another aperture leading to pumps. The technique has not been used nor tested enough to demonstrate whether it is free of systematic effects which may be as large as those encountered in using the McLeod gauge. At present ionization gauges are secondary standards and depend ultimately upon a primary standard such as the McLeod gauge. It appears that measurement of system pressure gives rise to one of the largest uncertainties in the determination of total ionization cross sections by this method.

Total ionization measurements have been recently made in a Lozier tube (Refs. 6, 11) and in a cylindrical tube which has grids (Ref. 17) instead of vanes as does the Lozier tube. These measurements depend upon Tate and Smith's (3, 4) measurements for calibration, and there are too few data to evaluate completely the method for absolute measurements. Except for the different problems of ion collection with these tubes, the same problems exist as for the parallel-plate method described above.

B. Total Ionization Tube with q/M Discrimination

The method discussed in Sec. IIA does not separate ionization components of different charge q and mass M that contribute to the summation in Eq. (1). To accomplish this, q/M analysis of the ions must be introduced. This was done by Bleakney (18) and by Tate and Smith (19), who made a narrow slit longitudinally in P_1, and who used a ribbon beam of electrons wider than the slit. Ions passing through the slit entered a q/M analyzer, were collected, and their current measured. By scanning the analyzer fields ion currents due to different q/M components could be measured. A simultaneous measurement of $\sigma_T(E)$ as described in Sec. IIA above could be made, and Eq. (1) could be solved for $\sigma_n(E)$. The same problems that were discussed above in Sec. IIA pertain to this device. In addition, q/M analysis has inherent problems which are discussed in the next paragraph.

C. Mass Spectrometer

The term mass spectrometer is used here generically to include any device which separates ions of different q/M. Standard techniques with these instruments and apparatus descriptions are widely discussed in the literature (Ref. 20). Because of the difficulty in ascertaining their collection efficiency, their primary value in ionization cross-section studies has been in determining *relative* cross sections as a function of electron energy, i.e., $C\sigma_n(E)$, where it is hoped and is usually assumed that C is constant. If C is a constant for each ionic species, the ratios $\sigma_{n_1}(E)/\sigma_{n_2}(E)$ can be determined. The mass spectrometer has been used very extensively in recent years to examine detailed variations of $\sigma_n(E)$ with E.

For measurements of this type to be deemed reliable, the experimentor must show that C is constant, i.e., that the ion collection efficiency is independent of q/M and of the electron energy E. He must show that ion source operating conditions—magnetic field, pressure, electron current—do not change the shape of the observed relative cross section.

Most ion sources contain various combinations (which stay relatively fixed during a q/M scan) of electric and magnetic fields for the purpose of ion extraction and focusing into the mass analyzer. Ions of different q/M will not necessarily behave in the same way in these fields, and the instruments will discriminate in detection of them. Discrimination may also occur at the detector if sufficient care is not taken to eliminate effects from secondary electron emission and from ion reflection, since these effects depend strongly on ion species and energy. An extreme example of this is encountered when an electron multiplier is used as detector, since the multiplier response depends (Ref. 21) quite strongly on q/M.

When a focusing mass spectrometer of the usual sector magnetic field variety is used, the collection efficiency of the instrument may change with electron energy if the electron beam changes size, shape, or position with energy. These changes can occur if all fields involved with the electron gun, including fields due to space charge, are not carefully scaled with the final accelerating field.

D. Crossed-Beam Apparatus

Many atomic species are not stable at normal temperatures, and techniques must be used which will produce the species in adequate abundance and in an environment where its ionization can be studied. This is the case, for example, with atomic hydrogen, oxygen, and nitrogen and with alkali metals, ions, and metastable atoms and molecules. The study of ionization of sodium in crossed beams of atoms and electrons was undertaken by Funk (22), and relative ionization cross sections of some alkali metals as a function of energy were measured by Tate and Smith (19) using an apparatus held at a high temperature to allow vaporization of the metal such as discussed in B. The most significant technique for study of such species is, however, the modulated crossed-beam technique which was apparently first used for ionization studies by Boyd and Green (23) and by Fite and Brackmann (24).

The application of this technique has resulted in apparatus which varies significantly in detail and in problems encountered, so a discussion of particular problems is deferred to a discussion of individual experiments.

The general technique can be understood in terms of the block diagram in Fig. 2. A beam of target particles is crossed with a beam of electrons in high vacuum, and ions resulting from the collision are detected. Usually particles of either one beam or the other collide with the background gas to produce unwanted ions of the type which one desires to detect. The number of ions from this source is often much greater than that from the intended target–electron collision; thus long sampling times are required to keep the statistical fluctuations in the background from being large compared to the signal. These long times, however, impose impractical stability limitations upon such variables as background pressure, beam magnitude, amplifier gains, etc. These limitations are overcome by chopping one or both of the beams and observing the resultant modulated ion signal in the proper phase with the modulated primary beam. [It is usual to modulate the beam that is least likely to give rise to a background ion current in the collector. Dolder *et al.* (25) in measuring ionization of ions chopped both beams with varying phases.] Required sampling times to achieve a given signal to statistical noise ratio are still comparable to the times needed in nonchopped cases, but extreme stability of parameters mentioned must now be maintained only over the chopping period.

Some changes in Eq. (1) are necessary, since the beams may not be homogeneous in space and since the target beam may have an appreciable velocity compared to that of the electrons. The equation becomes (Ref. 25):

$$I_i/I_e=\sigma(E)R[(v_e^2+v_t^2)^{\frac{1}{2}}/v_tv_e]F, \qquad (4)$$

where v_e and v_t are velocities of the electrons and target particles, respectively (assumed to be perpendicular), R is the number of target particles per second arriving at the target detector, E is the relative energy of target and electron which is or order $E_e+(M_e/M_i)E_t$, and $\sigma(E)$ may be either $\sigma_T(E)$ or $\sigma_n(E)$ as defined in Eq. (1). The factor F is a measure of the overlap of the two beams; and if the beams are individually parallel (i.e., do not diverge or converge) over the length of the interaction region, F may be calculated from

$$F=\int j_e(z)j_t(z)dz\left[\int j_t(z)dz\int j_e(z)dz\right]^{-1}. \qquad (5)$$

Here $j_e(z)$ and $j_t(z)$ are the spatial distributions of the electron and target beams, respectively, which are usually measured by scanning each beam with a fine slit movable in the dimension z (Refs. 25–27). The integrations are practically over the real extents of the beams. Since it is difficult to estimate systematic errors in F, it is necessary to demonstrate experimentally the independence of $\sigma(E)$ on F.

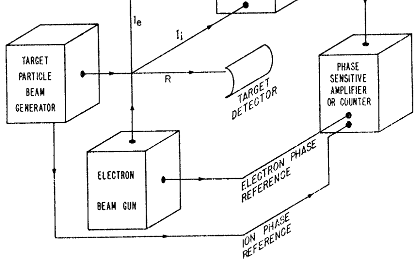

FIG. 2. Block diagram of a typical crossed-beam apparatus for measuring ionization cross sections by electron impact.

When the target particles are neutral and in the ground state, R is difficult to measure. Some experimentors (Refs. 24, 28–31) normalize the signal from a beam of atoms to measurements on a beam of the stable parent diatomic molecules which in turn have been measured with techniques described above, e.g., ionization of H atoms is compared with ionization of H_2. In this way, if mass flow from the source is kept constant, the cross sections can be normalized to the measured molecular cross sections without knowing R absolutely. Experiments on alkali metals (Refs. 32, 33) make use of the surface ionization detector to measure R. For its absolute calibration, however, this detector depends upon the assumption (Ref. 34) that the reflection coefficient of incident atoms and of the resultant ions is zero and that the number of ions evaporated from the surface, for those beam atoms that are absorbed, is the same as the number evaporated under steady-state conditions. There do not seem to be any measurements at very low energies, but experiments on ions at higher energies (Ref. 35) show reflection coefficients 10–30% and rising with decreasing energy. The recent experiment of Schroen (36) indicates that the reflection coefficient for potassium atoms on pure tungsten and platinum surfaces is probably zero. The assumption is also made that the ionization efficiency for all alkali atoms on oxidized tungsten is 100%. Absolute calibration in such experiments thus seems open to some question. R. H. McFarland [Abstracts of Papers presented at *IV International Conference on the Physics of Electronic and Atomic Collisions* (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 416] has used a known amount of alkali beam material and monitored the beam over many hours until the known oven load was completely depleted. With a knowledge of geometry R could be calculated. This method gave cross sections slightly higher than are obtained by using a surface ionization detector. Calorimetry was used by Peterson (26) to measure R for a fast nitrogen atom beam formed by charge exchange of N^+. The absolute calibration of this technique depends upon the assumption that the accomodation coefficients of fast N^+ and N on a surface are the same. Here again there does not seem to be any direct experimental evidence that this assumption is justified.

Collection and detection of ions formed in these experiments are done in a variety of ways which are not all described here. When q/M analysis is employed the usual assumption is that negligible momentum is transferred by the electron to the atom in the collision. This assumption is easily justified when the target beam is energetic. When the target is a thermal beam, however, the momentum transferred (at ionization threshold all the electron momentum is transferred to the atom) can be a significant part of the total momentum. This implies that sizable deviations of resultant ion trajectories may take place. The assumption of negligible momentum transfer would thus appear questionable—contrary to rather convincing indirect evidence of Fite and Brackmann (24) that the assumption is good. It is important that collection and detection efficiency be carefully analyzed and described by authors using crossed-beam techniques, since obscure effects such as momentum transfer, space charge deflection of the primary beam, and unknown or variable dispersion of the analyzer may give rise to systematic errors.

E. Determination and Definition of Electron Energy, *E*

Due to potential drop across the filament, contact potential differences between electrodes, and surface potential differences of the electrodes, the electron energy E may be quite different from the nominal voltage difference applied between the cathode and collision region. The difference between the actual electron energy and the "nominal energy" may amount to a volt or more. This may not be important at high energies where the cross section varies relatively slowly, but may make a large difference in the apparent cross section at low energies where the cross section rises steeply. Absolute calibration of energy is normally done by introducing a gas sample for which the ionization energy is known spectroscopically. The appearance of singly charged ions of this gas is observed, and "the straight line portion" of the ionization efficiency curve is extrapolated to the abscissa. The intercept is taken as the spectroscopic ionization energy, and the energy scale is shifted to agree. Asundi and Kurepa (37) have shown that when the electron beam has a thermal energy distribution the intercept is shifted by $2kT$ toward lower energies from the actual critical potential. Energy distributions distorted by nonuniform surface potentials, by electric fields in the interaction region, etc., gives rise to different shifts. The extrapolation procedure above is valid only for comparing differences in appearance potential, i.e., it does not set the absolute scale of energy unless the shift in the intercept is taken into account. If the calibration gas and sample gas are introduced into the chamber separately, it is possible that surface potentials will change enough from one gas to the other to render this procedure useless. It is thus desirable where possible to mix sample and calibration gases for comparison. Even in this case, there may be a shift in the energy scale because of altered surface potentials caused by ions from the gas with the lower ionization potential. Straight line extrapolation may not always be justified if the ion has low-lying excited states or if there are autoionizing levels in the vicinity of threshold. If the shape of the electron energy distribution is grossly distorted, these simple techniques cannot be used. The cross section should be unfolded using knowledge of the electron energy distribution.

The observed ion signal for any setting of the nominal electron energy is proportional to the integral over energy of the product of the cross section and the electron energy distribution. Fine details occurring in an energy range comparable to or less than the width of the electron energy distribution may thus be obscured or distorted, and it is important in order to observe these details to have the energy distribution be as narrow as possible.

Nottingham (38) used magnetic selection of electron energies to study ionization of mercury, but little more was done with the technique. Perhaps the next advance in energy selection was the introduction of the ingenious retarding potential difference (RPD) technique by Fox *et al.* (39) in 1951. Other techniques used effectively for ionization work in recent years include energy analysis with uniform electric fields (Ref. 40) and cylindrical fields varying as the inverse distance from the center (Ref. 41). Morrison (42) has recently used energy analysis from a 127° analyzer and a sophisticated unfolding technique to resolve details in the cross section.

Morrison (43) has used another technique to observe details in ionization cross sections. This involves a small amplitude modulation of the electron accelerating voltage. The ion current will be modulated at frequencies which are harmonics of the electron modulation frequency, and the amplitude of the Mth harmonic in the ion current is proportional to the Mth derivative of the ionization cross section.

These methods, normally used in conjunction with mass spectrometers, are subject to many serious instrumental errors, and great care must be exercised in applying the technique and interpreting the results. The disparity in results obtained using these techniques is discussed later. For example, it is found (Ref. 44) that results using the RPD method vary with the magnetic field collimating the electrons and sometimes vary (Ref. 45) with the applied electric field extracting the ions. Extraneous results have been demonstrated (Ref. 46) with the 127° analyzer when ions are apparently formed by bombardment of gas adsorbed on the ion-source walls. Because of interactions with the lattice, these ions are formed with an energy dependence different than that for free molecules. Marmet (47) has recently analyzed some of the systematic errors which can be present with the devices noted here. He also emphasized that an appreciable spread in effective interaction energy is introduced from the target gas energy—especially for light gases. This latter effect is not negligible when a claim of 0.050-V resolution and better is made.

F. Ionization of Diatomic Molecules

Little reference has been made thus far to the specific problems encountered in measuring ionization cross sections of molecules. The distinguishing feature in molecular ionization is that some fraction of ionizing collisions result in atomic ions with kinetic energies in the range 1–15 eV, i.e., dissociative ionization occurs. In addition, the velocities of the ions may not be isotropically oriented in space, but will instead have some definite distribution of directions relative to the impacting electron beam (Refs. 48, 49).

Presence of these ions necessitates the use of higher collection fields in total ionization apparatus as discussed in Sec. IIA but does not introduce any other apparent difficulties in measuring $\sigma_T(E)$. However, these energetic particles are represented by one or more of the summation terms in Eq. (1), and severe difficulties are encountered in trying to arrive at individual terms. It appears that no ion sources for mass spectrometers have been devised which do not strongly discriminate against these energetic particles as compared to the thermal molecular ions formed, and reliable ratios of the individual cross sections have not been obtained with such devices.

Apparatus such as the one shown in Fig. 1 can be used to obtain approximate absolute values (Refs. 7b, 7c, 50) for the energetic ion cross sections. The voltage on P_1, G is made positive by an amount ΔV above the mean potential along which the electrons travel. Those ions with kinetic energies greater than ΔV reach P_1, and their current is measured. By applying a correction for the solid angle subtended by P_1, the cross section can be deduced. When making this correction one should also take into account the angular distribution of velocities of the dissociating particles as a function of electron energy. Unfortunately, this distribution is known only for hydrogen (Ref. 49), so an isotropic distribution has been assumed (Ref. 7b, 7c, 50). Reflection of ions from P_1 is not accounted for and may introduce some error.

Cook and Peterson (51) have applied a fast beam technique to look at ionizing processes in N_2 which include dissociative ionization, but comparison of some of their results with what appear to be reliable total ionization data (Refs. 4, 7a) leads one to conclude that further development of this difficult technique is needed.

A further complication arises in molecular ionization when one tries to separate the summation components in Eq. (1). This is due to the fact that a twice ionized, homonuclear, diatomic molecule has the same q/M as the atomic ion resulting from dissociative ionization. Isotopic substitution so that the molecule is no longer exactly homonuclear has been used by Morrison (52) to observe multiple ionization in some homonuclear molecules.

G. Fluorescence Measurements

Those who must know ionization cross sections for understanding plasma phenomena and those who want to test theoretical predictions of ionization need to know the final states of the ions observed in experiments purporting to measure ionization cross sections. It is apparent that the methods mentioned in the preceding paragraphs do little to determine final states of ions.

One technique which can be applied in a limited number of cases is to measure the light emitted from excited ions formed by electrons of known energy. The problems of measuring the quantities appearing in the obvious variation of Eq. (1) are present as in the methods above. In addition the method has the difficult problem of absolute radiometry. This fluorescence technique has been used to observe ionization to the $n=4$ level (Ref. 53) of He^+ and to the $v=0$ level (Ref. 54–56) of the $B\ ^2\Sigma_u^+$ state of N_2^+.

III. EXPERIMENTAL RESULTS

A. Introduction

The first step in selection of the data was a survey of the literature which purported to contain experimental electron impact ionization cross-section data (Ref. 57).

The question of what are valid sources, published or unpublished, is, of course, a matter of opinion. In general we have selected data from recognized journals. In one case data have been included from an unpublished thesis. In several cases information has been included from the published proceedings of conferences which were not reviewed. Original data has been obtained from the authors which in some cases was not presented in publications. In all cases the actual source of the data as distinct from the general reference is identified. The method of obtaining data from figures is discussed below.

Regardless of the source, all of the experiments for which data are presented in this section were compared with criteria given in Table I to determine whether they may have been subject to the systematic errors discussed in Sec. II. To make this comparison we used the published material available and correspondence or personal contact with the authors when possible.

All of the experiments for which data are presented were subject to many of the systematic errors discussed in Sec. II (see Table II). Experiments for which data

TABLE II. Classification of experiments and their probable systematic errors. Only experiments for which results are presented in Secs. IIIB (1), IIIB (2), and IIIB (3) are listed here. The experiment of Fite (66) is not included because not enough information was available to compare it with the criteria given in Table I. The experiment is discussed in Sec. IIIB (3). The column headings and numbers in the columns refer to the criteria of Table I. "The Type" of data is either absolute *A* or relative *R*. All of the relative results were normalized, and the footnotes describe the method used by the authors to do so.

Author (year)	Species	Type of apparatus	Type of data	I_i	I_e	ρ	L
1. T. J. Jones (2) *1927*	Hg	Parallel plate total ion collection	*A*	4[a], 5	4, 5	2[b], 3[c]	1 A, 1B
2. W. Bleakney (59) *1930*	Hg	Parallel plate, total ion collection with mass spectrometer	*A*[d]	4[e]	2, 3, 5		1 A
3. P. T. Smith (3) *1930*	He, Ne, Ar	Parallel plate total ion collection	*A*	5		1	1 A, 1 B
4. P. T. Smith (60) *1931*	Hg	Parallel plate total ion collection	*A*	5	4, 5	3[f]	1 A, 1B
5. J. T. Tate, P. T. Smith (4) *1932*	H_2, N_2, O_2, NO, CO	Parallel plate total ion collection	*A*	3, 1, 5	4	1	1 A, 1 B
6. J. W. Liska (61) *1934*	He, Hg	Parallel plate geometry, small solid angle for collection of ions	*R*[g]	1, 5	1, 2, 3, 4, 5		1 A, 1 B
7. H. Harrison (62) *1956*	He, Hg, H_2	Parallel plate total collection and rf mass spectrometer	*A*[h]	1[i,j], 3, 4[k]		1[l], 2	1 A, 1 B
8. W. L. Fite, R. T. Brackmann (24) *1958*	H	Crossed beam with mass spectrometer	*R*[m]	1[n]			2 A
9. W. L. Fite, R. T. Brackmann (28)[o] *1959*	O	Crossed beam with mass spectrometer and total ion collector	*R*[p]	1[q]	3	6	2 B
10. B. A. Tozer, J. D. Craggs (65) *1960*	Ar, Kr, Xe	Lozier tube with cylindrical drawout field	*R*[r]	1, 3, 5	1, 2, 3, 4, 5	1, 2	1 A, 1 B
11. A. Boksenberg (31) *1961*	H, O	Mass spectrometer (H): mass spectrometer with total ion collector (O)	*R*[s]	1[t]	3, 5	6	1 A[u]
12. K. T. Dolder, M. F. A. Harrison, P. C. Thonemann (25) *1961*	He^+	Crossed beam with mass spectrometer and total ion collection	*A*	1, 3, 4			2 A
13. E. W. Rothe, L. L. Marino, R. H. Neynaber, S. M. Trujillo (29) *1962*	H, O	Crossed beam with total ion collection	*R*[v]	1[w], 3, 5	1, 2, 3, 5	6	2 A
14. G. J. Schulz (17) *1962*	O_2	Total ion collection with cylindrical drawout field	*A*	1, 3, 5	1, 2, 3, 4, 5	2	1 A, 1 B
15. A. C. H. Smith, E. Caplinger, R. H. Neynaber, E. W. Rothe, S. M. Trujillo (30) *1962*	N	Crossed beam with total ion collection	*R*[x]	3, 4[y], 5		4[z], 6	1 A, 1 B
16. R. K. Asundi, M. V. Kurepa (5) *1963*	He, Ne, Ar, Kr, Xe	Parallel plate total ion collection[aa]	*A*[aa]	5	4, 5	1, 2	1 A, 1 B
17 R. K. Asundi, J. D. Craggs, M. V. Kurepa (6) *1963*	CO, O_2	Parallel plate total ion collection	*A*	3, 4[bb], 5	2, 3, 4, 5	1, 2	1 A, 1 B
18. K. T. Dolder, M. F. A. Harrison, P. C. Thonemann (63) *1963*	Ne^+	Crossed beam with mass spectrometer and total ion collection	*A*	1, 3			2 A
19. M. F. A. Harrison, K. T. Dolder, P. C. Thonemann (64) *1963*	N^+	Crossed beam with mass spectrometer and total ion collection	*A*	1, 3, 4			2 A

TABLE II. (*Continued*)

20. J. R. Peterson (26) *1963*	N	Fast crossed beam with mass spectrometer and total ion collection	*A*	1, 3, 4	1, 2, 3, 5	5[cc]	1 A
21. D. Rapp, P. Englander-Golden (7a) *1965*	He, Ne, Ar, Kr, Xe, H_2, D_2, N_2, O_2, CO, NO	Parallel plate total ion collection	*A*	5, 3	5	1	1 A, 1 B
22. R. H. McFarland, J. D. Kinney (33) *1965*	Li, Na, K, Rb, Cs	Crossed-beam total ion collection	*A*	3, 5	1[dd]	5[ee], 6	2 A
23. B. L. Schram, F. J. de Heer, M. J. van der Wiel, J. Kistemaker (8) *1965*	He, Ne, Ar, Kr, Xe, H_2, D_2, N_2, O_2	Parallel plate total ion collection	*A*	3, 5	5	2	
24. J. W. Hooper, W. C. Lineberger, E. W. McDaniel, F. M. Bacon (27) *1966*	Li^+, Na^+, K^+	Crossed-beam total ion collection	*A*	1, 3			2 A

---

[a] Ions formed in the electron collector may have gotten back to the ion collector.

[b] Efficiency data presented was for an ionization chamber temperature of 70°C.

[c] Vapor pressure at 0°C from A. Smith and A. W. C. Menzies [Ann. Phys. (Paris) **33,** 979 (1910)] now considered incorrect.

[d] Relative numbers of multiply charged ions also given.

[e] Ions formed in the electron collector may have gotten back to the ion collector.

[f] No mention of vapor pressure data used.

[g] Relative values normalized to P. T. Smith's (3, 60) at maximum of cross section for Hg and at 2500 V for He.

[h] Relative numbers of multiply charged ions were also measured using rf mass spectrometer.

[i] A grid was in front of the ion collector. No discussion was given to indicate a correction was made for its finite transmission. The potential difference between the parallel plates was only 9 V. This is insufficient to collect all the energetic protons from dissociative ionization of H_2.

[j] It was assumed that the rf mass spectrometer had the same collection efficiency for all multiply charged ions.

[k] Ions formed in the electron collector may have gotten back to the ion collector.

[l] A calibrated ion gauge was used to make pressure measurements.

[m] Cross sections normalized to Tate and Smith's (4) total ionization cross sections for H_2. The procedure used neglected ion current from dissociatively ionized H_2 molecules.

[n] Possible sideways momentum imparted to ions by electron impact.

[o] See ASTIA Document No. AD 208599 for more details about this experiment.

[p] Relative cross sections normalized to Tate and Smith's (4) total ionization cross sections for O_2.

[q] Technique for collecting all ions does not appear to yield saturation under any conditions. See Boyd and Green (23).

[r] Relative cross sections normalized to Smith's (3) cross section for argon at 80 eV.

[s] Atomic hydrogen cross sections normalized to Born approximation calculation at 300 V. Atomic oxygen cross sections normalized using Tate and Smith's (4) total ionization cross sections for molecular oxygen.

[t] No data were presented to show saturation of ion current for oxygen.

[u] Path length corrections were made using Tate and Smith's (4) total ion cross sections and a weighted sum of mass analyzed currents.

[v] Relative cross sections normalized to Tate and Smith's (4) total ionization cross sections.

[w] Inadequate evidence for saturation of ion current was presented.

[x] Relative cross sections normalized to Tate and Smith's (4) total ionization cross sections for molecular nitrogen.

[y] Neutral beam may have had metastable species in it.

[z] Particle velocities in neutral beam may have been different for discharge on and off conditions.

[aa] Data were also taken with a Lozier tube apparatus, but these data have not been given in the figures.

[bb] Ions formed in the electron collector may have gotten back to the ion collector.

[cc] Calorimetric beam detector efficiencies are uncertain.

[dd] No details of electron gun and collector were given.

[ee] Hot wire beam detector efficiencies are uncertain (see discussion Sec. II).

are not presented were rejected for one of the following reasons:

(1) The experimental technique used had been demonstrated to be unreliable.

(2) Systematic effects were observed by the authors while taking the data, for which no correction was applied, or it appeared that in our judgment the correction was not properly made. The data are presented whenever there is reasonable doubt about rejection.

(3) The data are only of historical interest and have been superseded.

Some mass spectrometer data on the relative abundance of multiply charged atomic ions and on ionization threshold behavior are presented in Sec. IIIB(5) and IV, respectively.

Table II lists the authors whose data are presented in Sec. IIIB(1), B(2), and B(3). The table also classifies the experiments and lists the "likely" systematic errors implied when the conditions given in Table I were not satisfied. Systematic errors are listed as "likely" if the experimental technique used was subject to an error implied in Table I and if: (1) the author did not discuss it; (2) the author gave inadequate evidence for the absence of the error; or (3) the author indicated its presence but did not adequately correct for it. The latter cases are discussed in the Comments in Table II. The numbers listed in Table II under columns I_i, I_e, ρ, and L refer to the designations in Table I.

There is some evidence that some data should be preferred over others, but in no case was the evidence unequivocal. These cases are discussed specifically.

All of the absolute or normalized data points presented are either taken directly from tables given by the authors or read from their graphs. In no case is interpolated data given. The data of Sheridan, Oldenberg, and Carleton (55) on the ionization of N_2 to an excited state of N_2^+ and the data of Stanton and Monahan on the relative yield of He^+ to He^{2+} were originally presented as line drawings in a graph. These results are presented here in the same form. For data which were only available graphically, enlarged photographs were made, and the cross section and electron energy values for each data point were determined by measuring the positions of the points relative to the scale given on the graph. Although this technique might seem questionable, it appears to be quite accurate. One set of data compiled in this manner was compared with a set of tables supplied later by the author; all cross section and energy values agreed to within 1% or better. Any tabular data supplied by the authors which were not included in their published paper or circulated report are noted.

Most of the absolute and normalized data are "total" cross sections σ_T, as defined by Eq. (1). In some cases, where mass spectrometer analysis of the ions was done, the cross sections given are for the production of ion species of specific charge/mass ratio. Such cases are specifically noted. In all cases use of the term "total cross section" implies that no charge, or mass analysis, was made.

The relative cross sections for the production of multiply charged atomic ions from atoms [Sec. IIIB(5)] are expressed as σ_{n+}/σ_T. All data points on the figures in Sec. IIIB(5) indicate a measurement of either i_{n+} or σ_{n+}, where

$$i_{n+} \propto n\sigma_{n+}. \tag{6}$$

All of these data are relative, and in some cases a measurement of i_{n+} or σ_{n+} was not made for each ion species at every electron energy. In order to evaluate σ_{n+}/σ_T at such electron energies, it was assumed that

$$\sigma_{n+}/\sigma_T = n^{-1}[i_{n+}/(i_{1+}+i_{2+}+i_{3+}\ldots)], \tag{7}$$

in which some of the ion currents in the denominator of the right-hand side of the equation may have been interpolated from the graph or table presented by the author. As stated above, the relative ion currents [or cross sections, since they are simply related by Eq. (6)] in the numerator of Eq. (7) are data points given in the graph or table presented by the author and are not interpolated.

The electron energy scale for each of the cross sections should be called "nominal" in the sense that the origin is uncertain. No attempt was made to correct the energy scale given by the author, and in no case, did the authors present an energy profile of the electron beam and unfold the cross section. Because of this and because of the uncertainty of the threshold behavior of ionization cross sections, it is likely that the absolute energy scale may differ from the "nominal" by ±1.0 eV.

Much of the older data in the literature were given as efficiency versus electron energy. Ionization efficiency is defined as the number of unit positive charges produced in a 1-cm path at 1-mm pressure and 0 °C per electron. To convert ionization efficiency to cross section, the number of molecules/cm^3 at 1 mm of pressure and 0°C was taken to be 3.53490×10^{16}. This number was derived by using the following constants (Ref. 58): volume of a g-mole, 22420.7 cm^3; 1 atm, 76.0000 cm Hg; Avogadro's number, 6.02338×10^{23} molecules/g-mole. To convert ionization efficiency to cross section in πa_0^2 units (assuming single impact), efficiency was multiplied by 0.321573. To convert cross sections in 10^{-16} cm^2 units to πa_0^2 units, cross sections in 10^{-16} cm^2 units were multiplied by 1.13673.

In spite of the fact that the total cross-section data appear to be more accurately known (based on comparison of independent absolute experiments), one might question their usefulness, since one would really like to know the charge, mass, and state of the various ions created by electron impact. There are three reasons why we consider these cross sections to be important.

First, total cross sections are very intimately connected with the measurement of number density of atomic scatterers at low pressure ($<10^{-3}$ Torr). The uncertainty of number density in gases at low pressure is probably responsible for the largest systematic errors in most of the total ionization cross-section measurements. In other words, if the atomic and molecular total ionization cross sections were known, one could, in principle, construct an absolute ion gauge.

Second, these cross sections are in general more accurately known than those for creating a specific ion species, since their determination only requires a measurement of the total ion current. Because the total ionization cross section is a weighted sum of all cross sections for producing ions, it provides, if accurately known, an upper limit on this sum.

Finally, in many experiments the total absolute cross sections for stable species are used to normalize the relative cross sections for unstable species such as H, N, and O. From one point of view the total cross sections can be regarded as most fundamental, since most of our knowledge of the absolute cross sections for creating ions of specific charge and mass rest on these measurements.

B. Cross-Section Data

(*1*) *Absolute and Normalized Cross Sections for Ionization of Atoms*

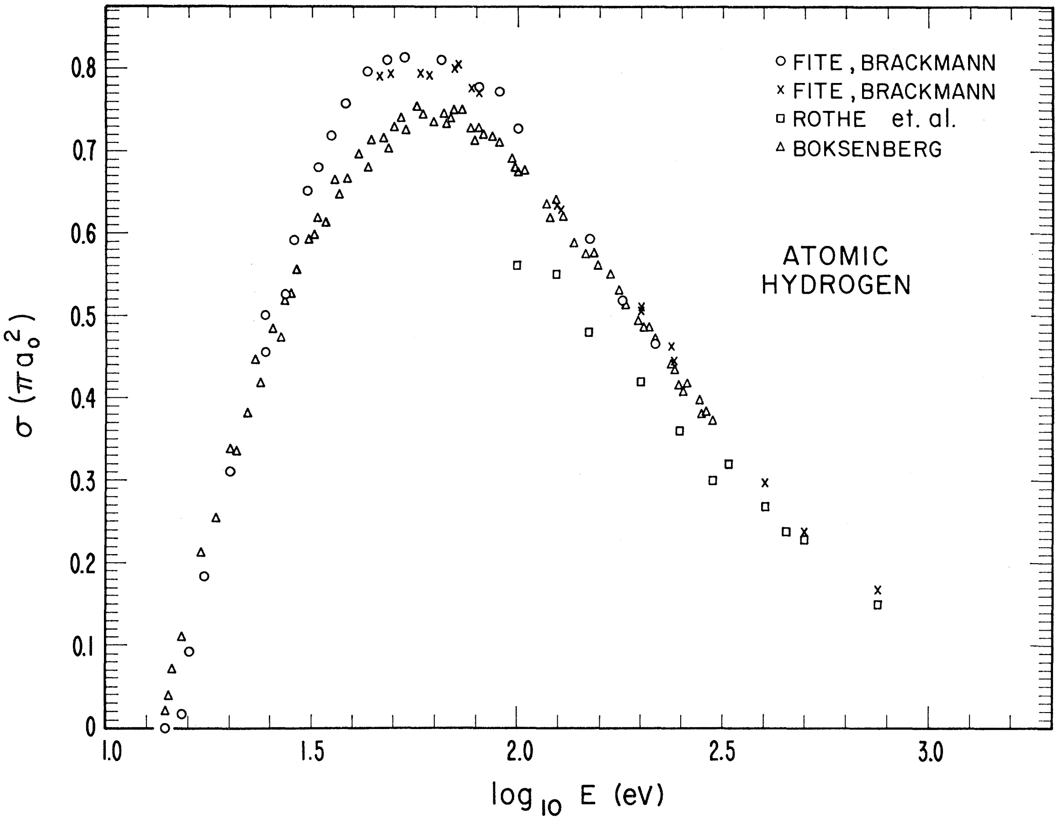

FIG. 3. Normalized cross sections for ionization of atomic hydrogen. ○—Fite, Brackmann are the data referred to by the authors as "relative"; they were normalized to Born approximation calculations at 500 eV. ×—Fite, Brackmann are the data referred to by the authors as "absolute"; they were normalized using the total absolute cross sections measured by Tate and Smith (4) for molecular hydrogen. References: Fite (24); Rothe (29); Boksenberg (31).

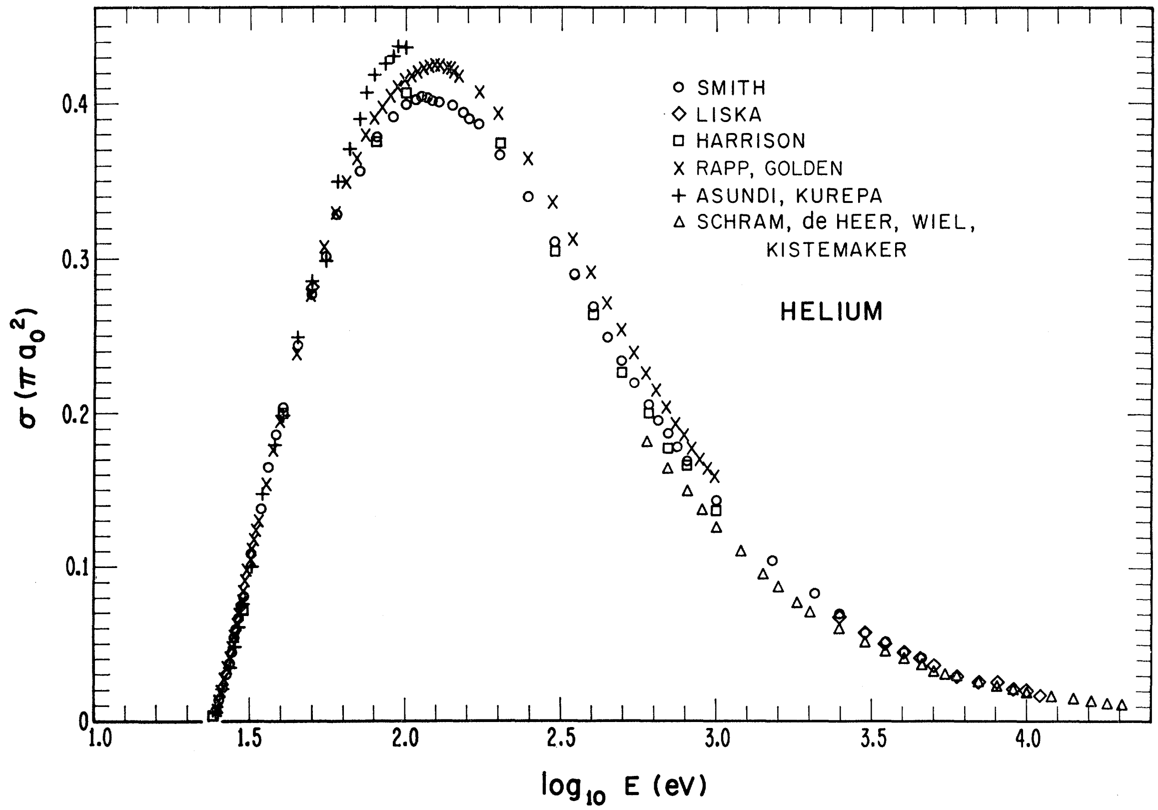

FIG. 4. Total cross sections for the ionization of atomic helium. References: Smith (3); Liska (61); Harrison (62); Rapp (7a); Asundi (5); Schram (8).

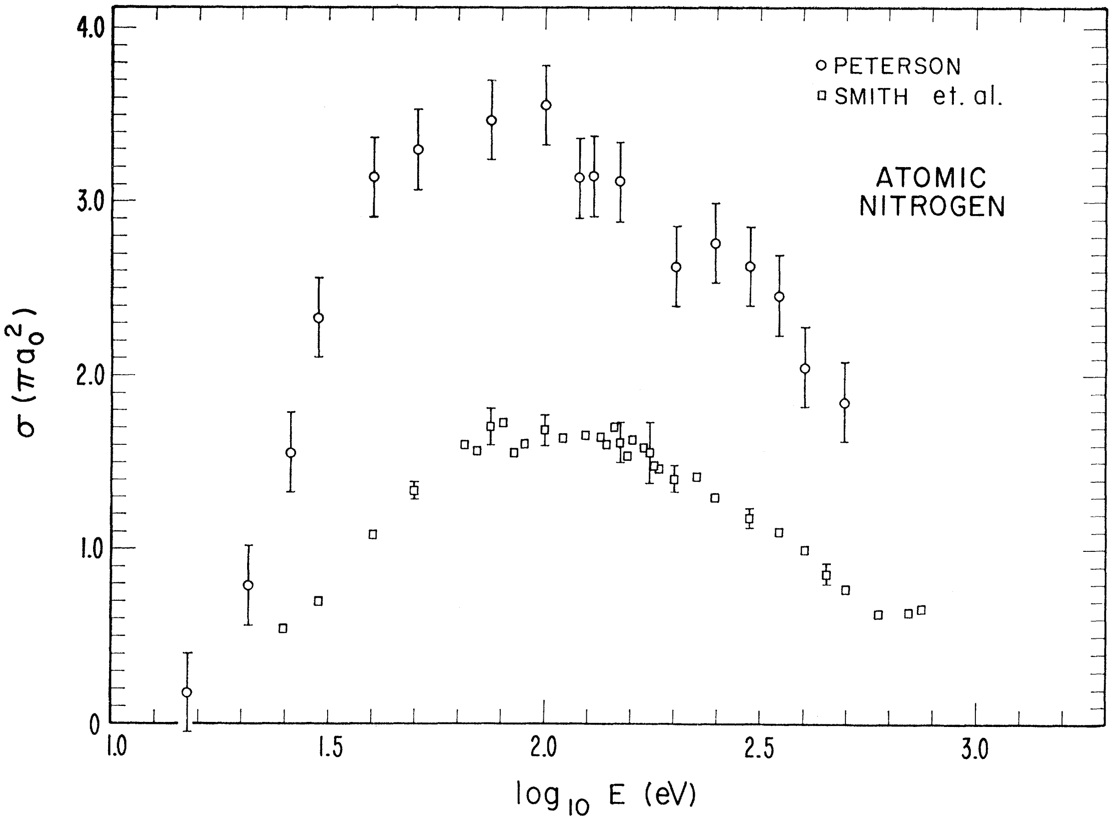

Fig. 5. Cross sections for ionization of atomic nitrogen. The data of Smith (30) are total cross sections. The data of Peterson (26) because of mass analysis are cross sections for the production of N^+ from N.

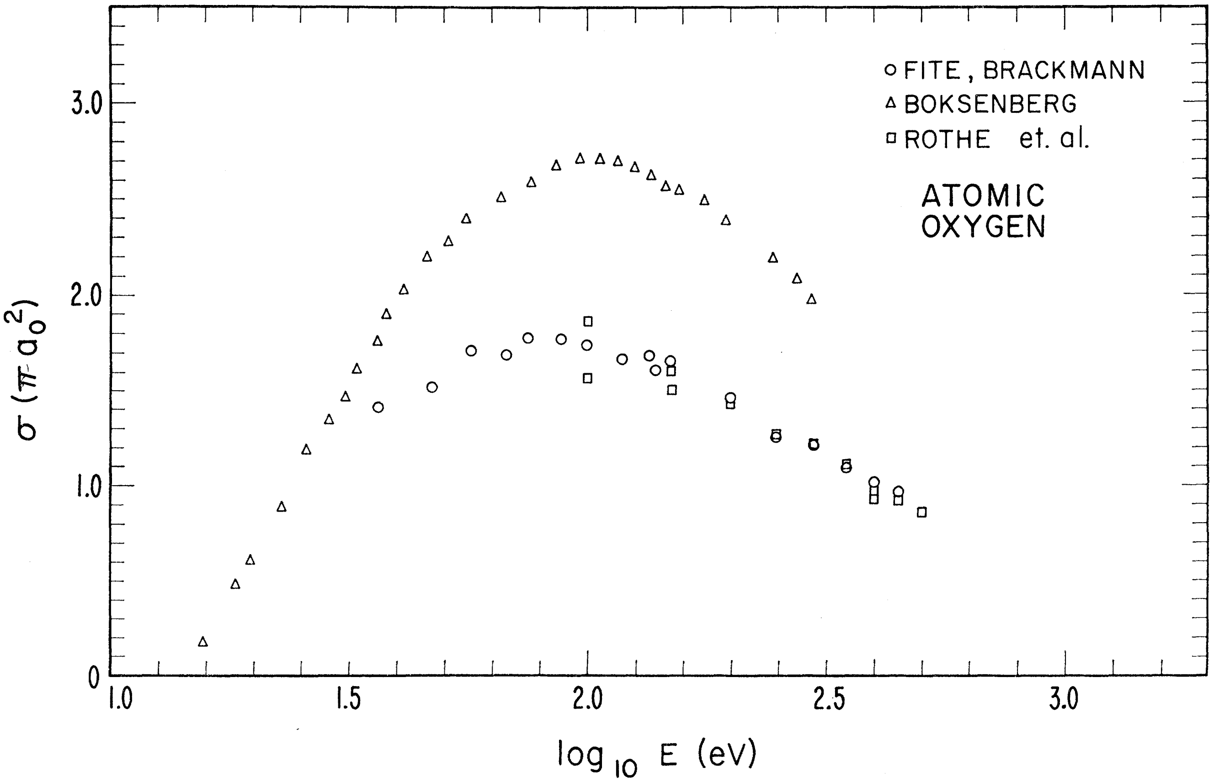

Fig. 6. Cross sections for ionization of atomic oxygen. The data of Rothe (29) are total cross sections. The data of Fite (28) and that of Boksenberg (31) because of mass analysis are cross sections for the production of O^+ from O.

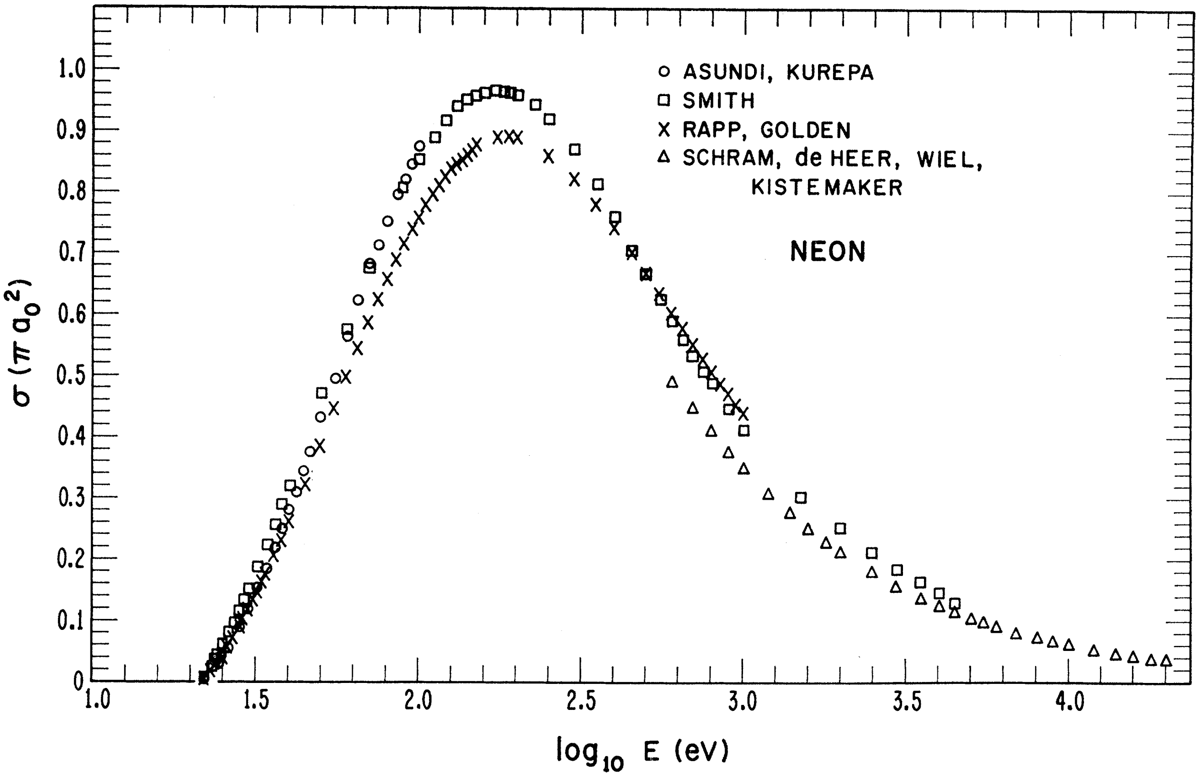

FIG. 7. Total cross sections for the ionization of atomic neon. References: Asundi (5); Smith (3); Rapp (7a); Schram (8).

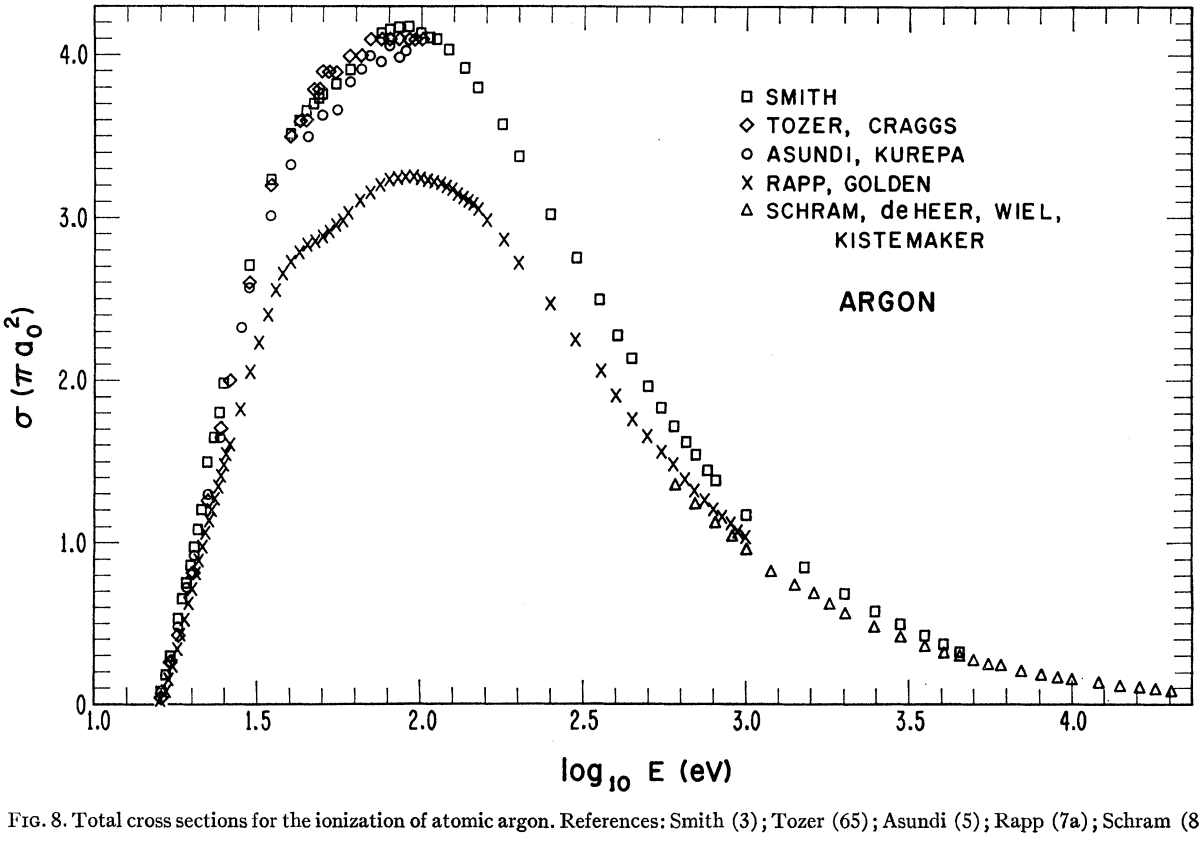

FIG. 8. Total cross sections for the ionization of atomic argon. References: Smith (3); Tozer (65); Asundi (5); Rapp (7a); Schram (8).

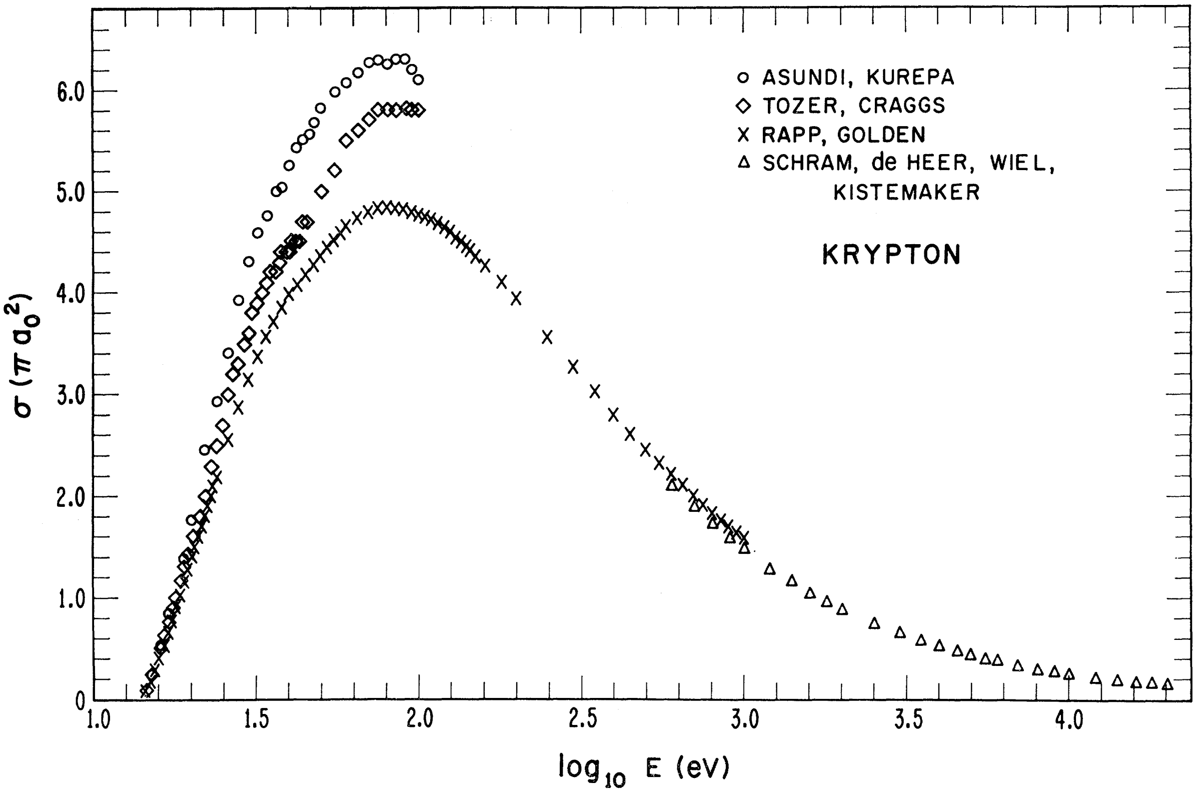

Fig. 9. Total cross sections for the ionization of atomic krypton. References: Asundi (5); Tozer (65); Rapp (7a); Schram (8).

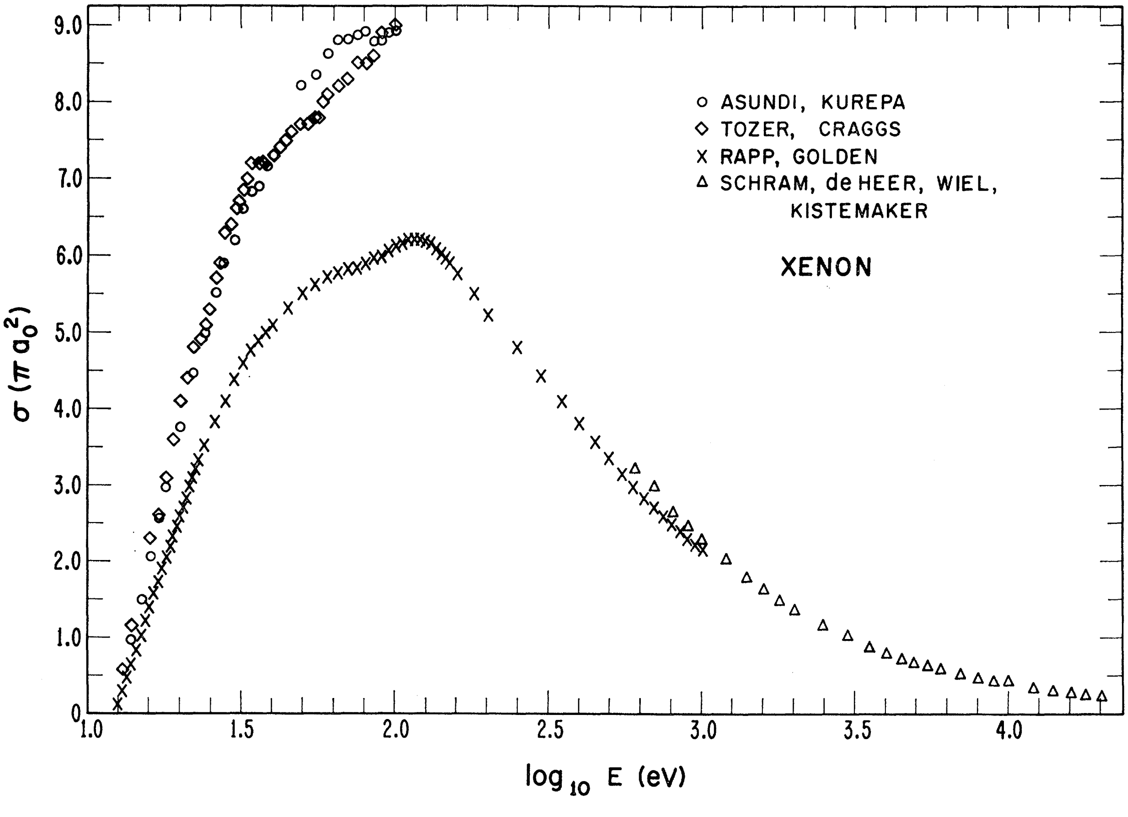

Fig. 10. Total cross sections for the ionization of atomic xenon. References: Asundi (5); Tozer (65); Rapp (7a); Schram (8).

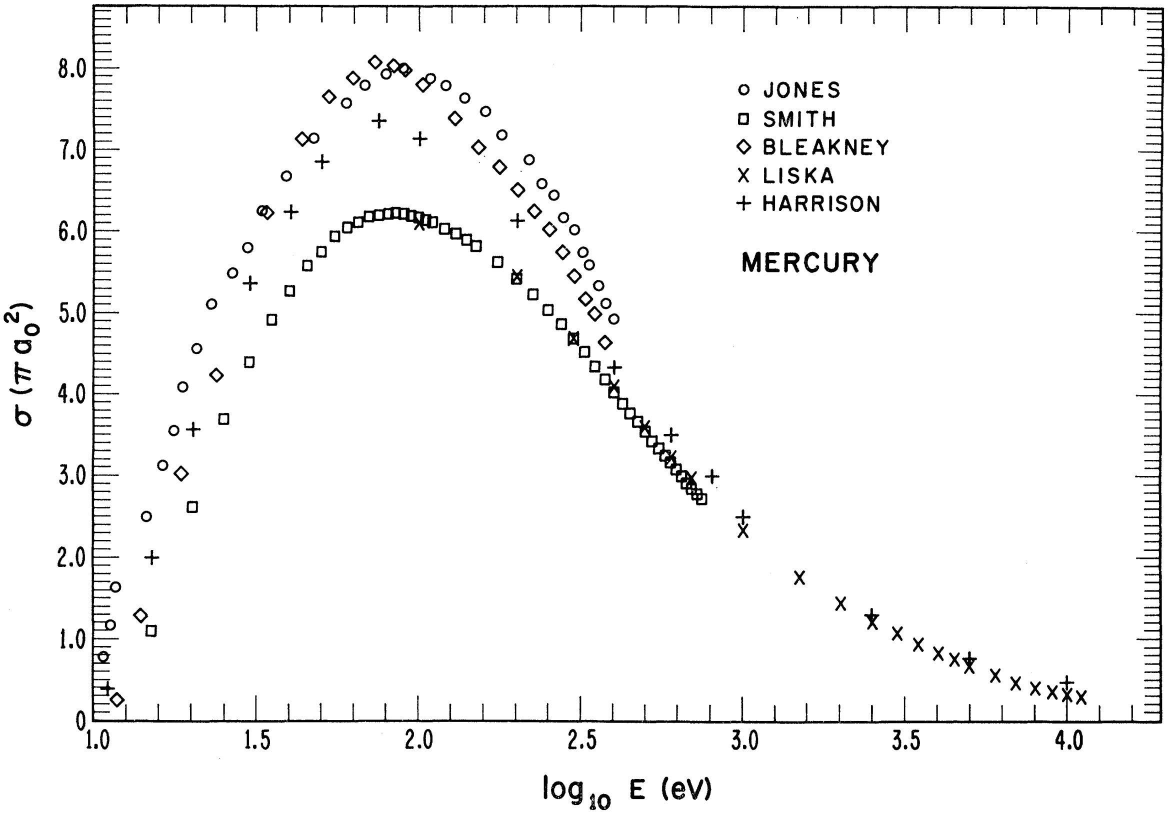

FIG. 11. Total cross sections for the ionization of atomic mercury. References: Jones (2); Smith (60); Bleakney (59); Liska (61); Harrison (62).

(2) *Absolute Cross Sections for Ionization of Diatomic Molecules*

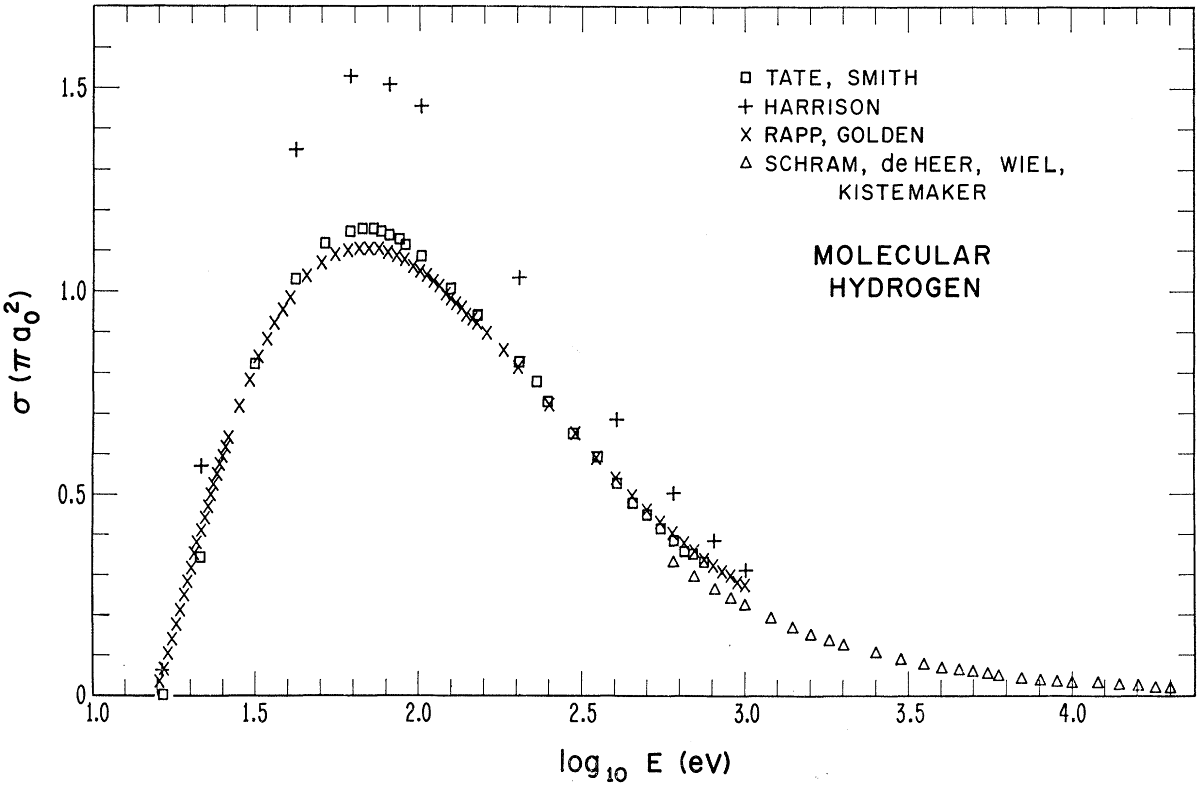

FIG. 12. Total cross sections for the ionization of molecular hydrogen. References: Tate (4); Harrison (62); Rapp (7a); Schram (8).

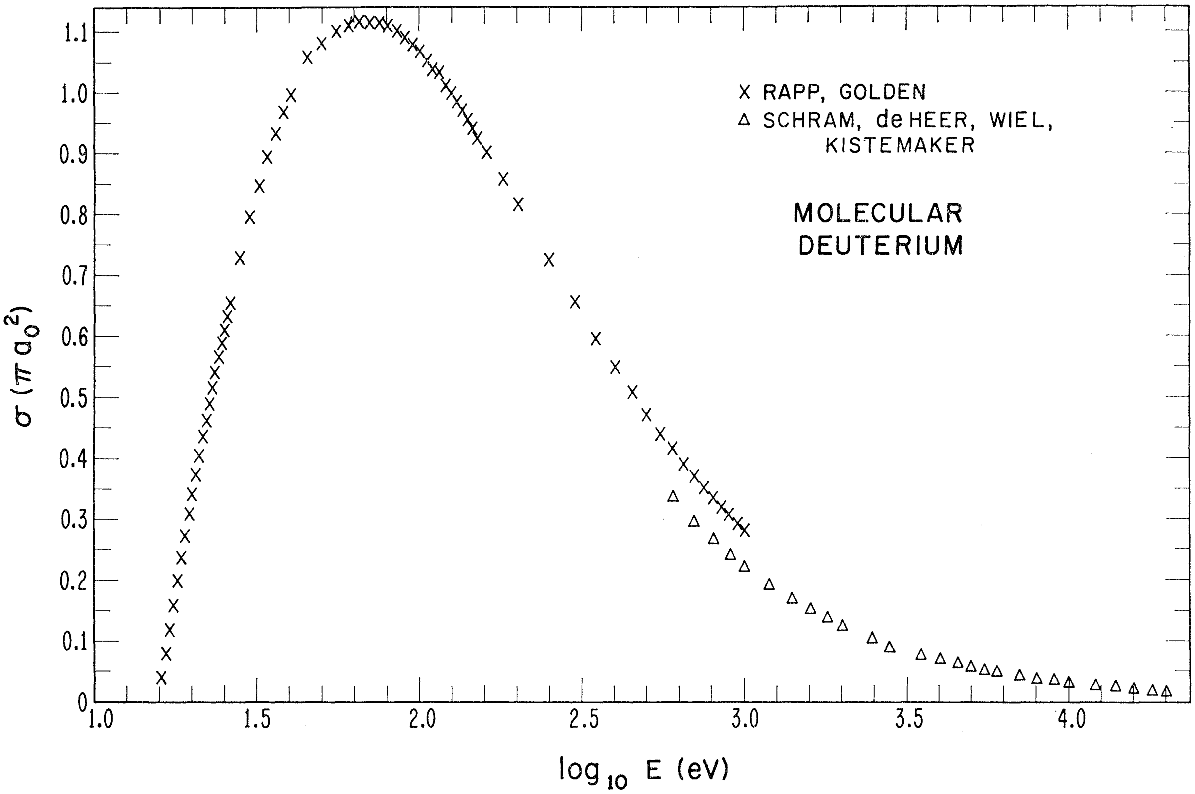

Fig. 13. Total cross sections for the ionization of molecular deuterium. References: Rapp (7a); Schram (8).

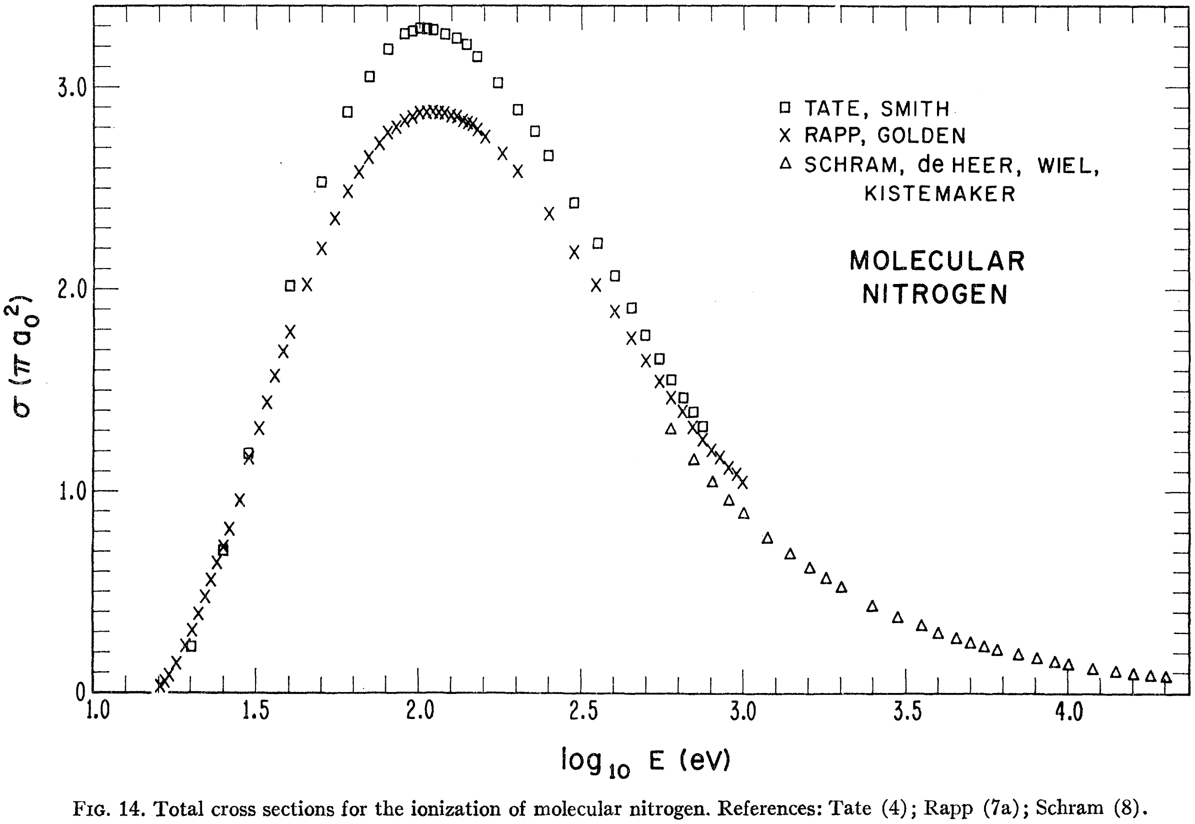

Fig. 14. Total cross sections for the ionization of molecular nitrogen. References: Tate (4); Rapp (7a); Schram (8).

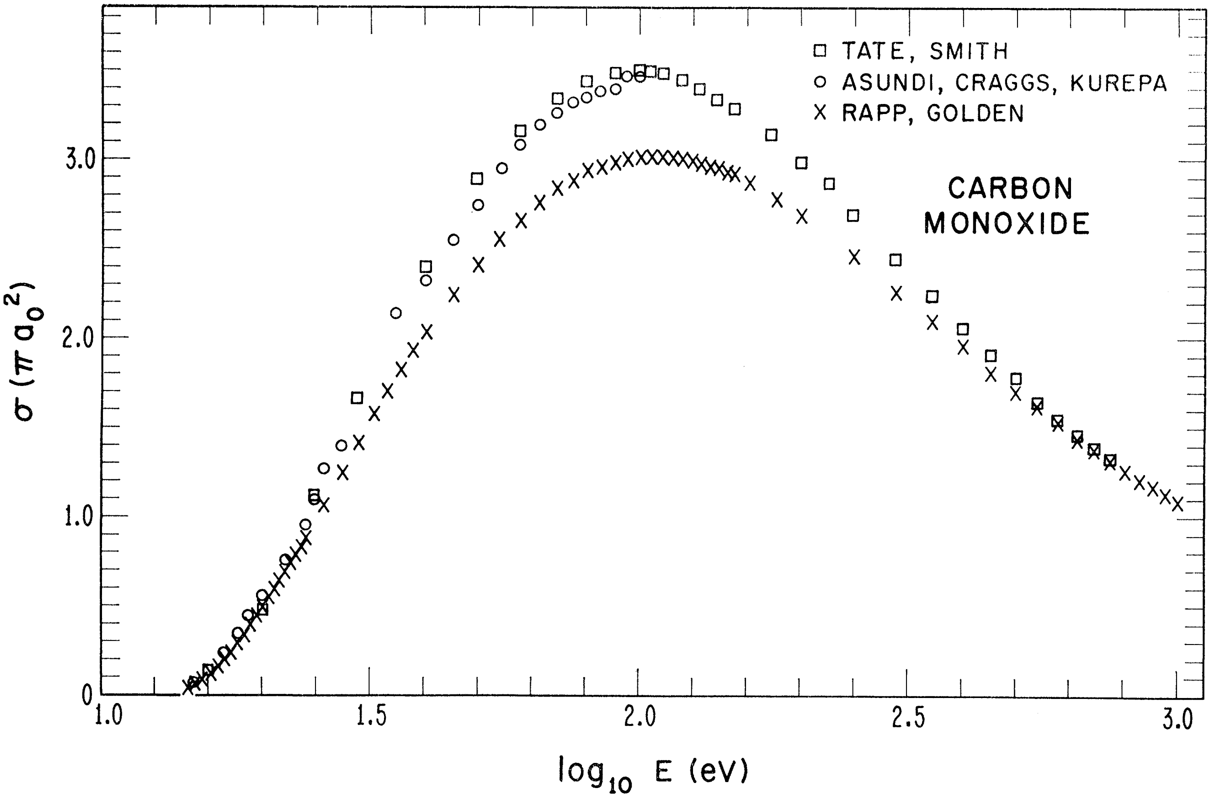

FIG. 15. Total cross sections for the ionization of carbon monoxide. References: Tate (4); Asundi (6); Rapp (7a).

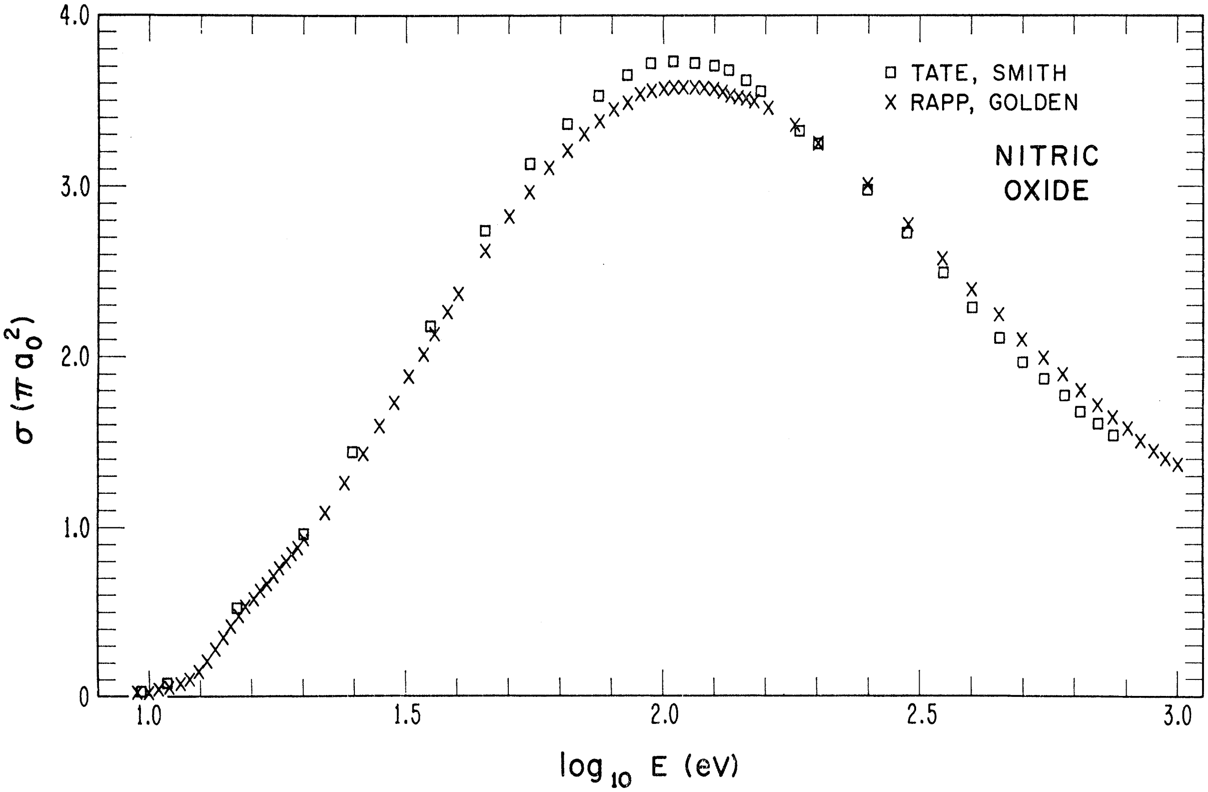

FIG. 16. Total cross sections for the ionization of nitric oxide. References: Tate (4); Rapp (7a).

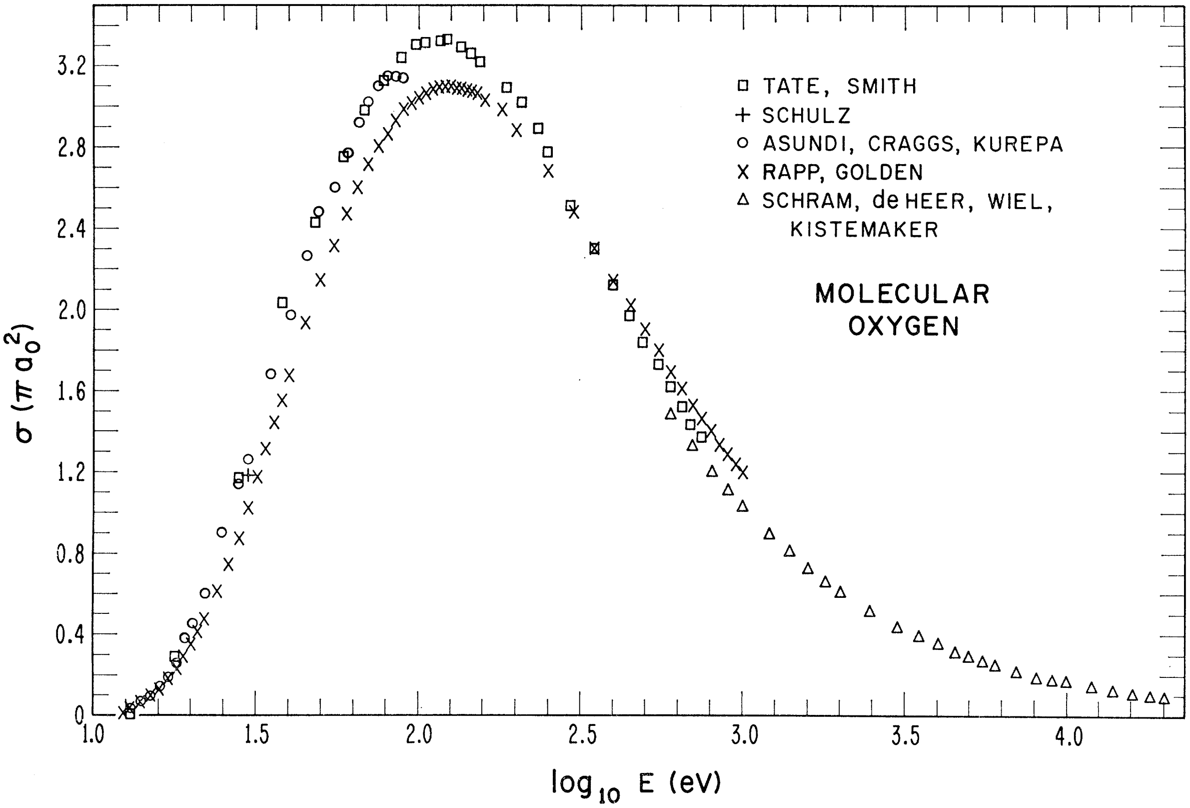

FIG. 17. Total cross sections for the ionization of molecular oxygen. References: Tate (4); Schulz (17); Asundi (6); Rapp (7a); Schram (8).

TABLE III. Total cross sections (Ref. 33) for the ionization of the alkali metals in πa_0^2 units.

E(eV)	50	100	200	300	400	500
Lithium	3.52	2.50	1.71	1.36	1.13	0.94
Sodium	4.68	3.60	2.85	2.29	1.95	1.71
Potassium	7.30	6.82	5.46	4.22	3.52	3.11
Rubidium	9.57	9.32	7.58	6.11	5.13	4.62
Cesium	12.9	12.3	11.0	9.78	8.18	7.10

(3) *Absolute Cross Sections for Ionization of Atomic Ions and Helium Metastable Atoms*

Fite and Brackmann (66) measured the average cross section for ionizing an unknown mixture of metastable helium atoms (2^1S and 2^3S) in a beam from an rf discharge over the electron energy range 10–24 eV and found it to be approximately 3.2 πa_0^2. This was determined by observing the ion current below the spectroscopic threshold for ionization from the ground state. It was assumed that ion current below the threshold for ionization from the ground state was due to ionization of atoms in these two metastable levels. The metastable atom density in the beam was determined from the amount of secondary electron current generated when the metastable helium atoms impinged on a gold surface. The emission coefficients for metastable helium atoms hitting a gold surface in the 2^1S and 2^3S states were assumed to be the same as those measured by Stebbings (67) for the 2^3S state.

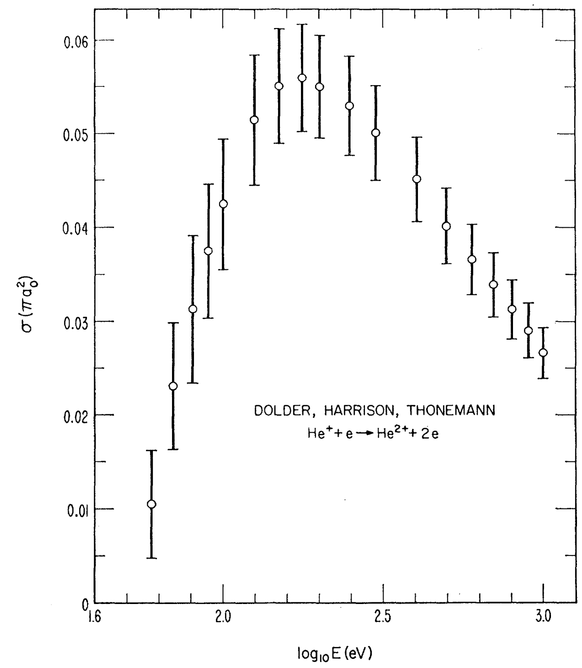

Fig. 18. Cross sections for the ionization of He^+. The error bars indicate the "maximum total error" as listed by the authors (Ref. 25).

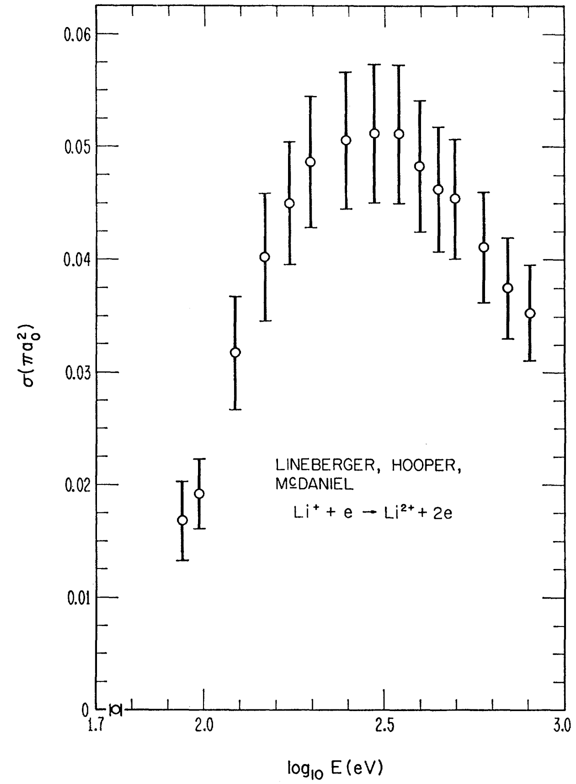

Fig. 19. Cross sections (Ref. 27) for the single ionization of Li^+. The error bars indicate the "maximum total error." This is the sum of the random error and an estimate of the systematic error due to an uncertainty in instrument calibration.

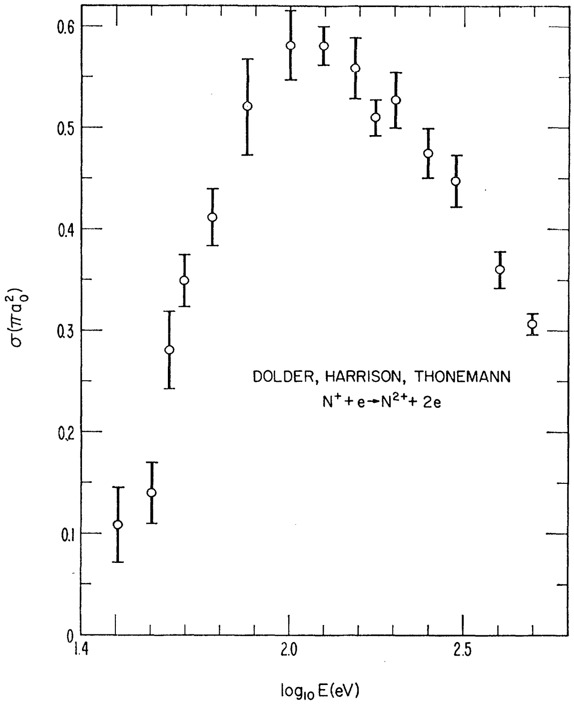

Fig. 20. Cross sections for the single ionization of N^+. These data are the uncorrected points given in Fig. 1 in Ref. 64 and exclude the data below the spectroscopic threshold of 29.6 eV. The error bars indicate a 95% confidence limit for the random errors.

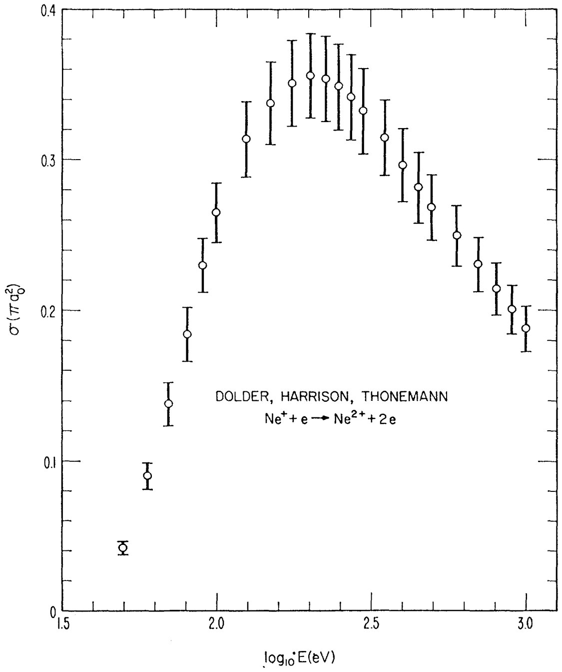

Fig. 21. Cross sections for the single ionization of Ne^+. The bars indicate the "maximum total error" as listed in Ref. 63.

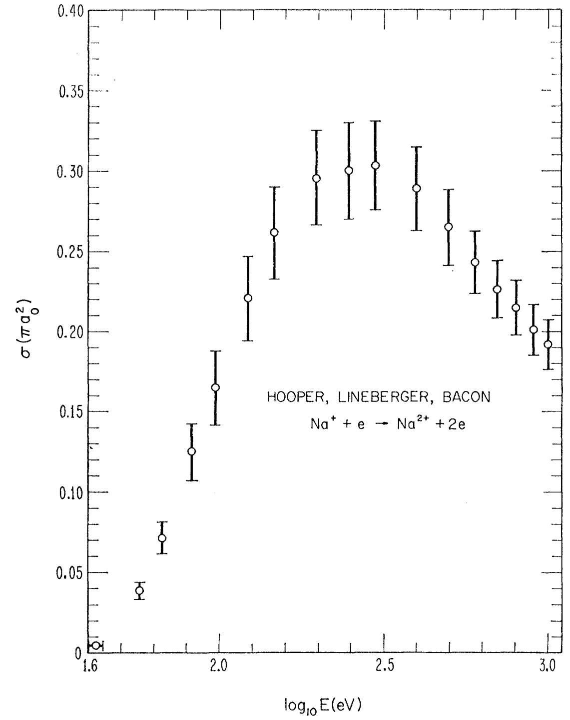

FIG. 22. Cross sections for the single ionization of Na^+. The error bars indicate the "maximum total error." This is the sum of the random error and a estimate of the systematic error due to uncertainty in instrument calibration. The reference for these data is (27).

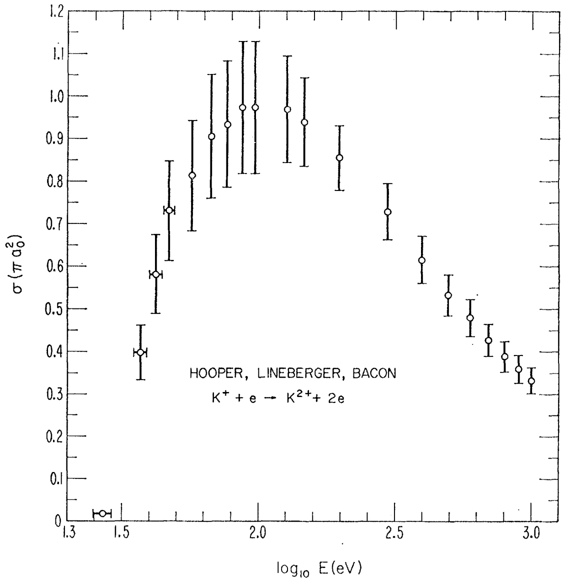

FIG. 23. Cross sections for the single ionization of K^+. The error bars indicate the "maximum total error." This is the sum of the random error and an estimate of the systematic error due to uncertainty in instrument calibration. The reference for these data is (27).

(4) Absolute Cross Sections for Ionization of Atoms and Diatomic Molecules into Excited Final States

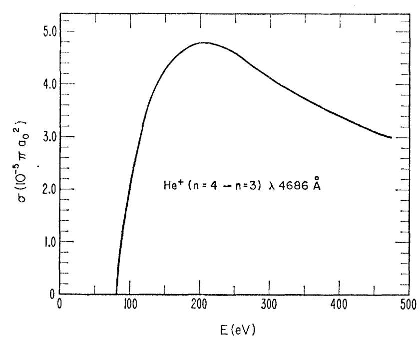

FIG. 24. Cross sections for the emission of λ=4686-Å He^+ radiation when electrons bombard atomic helium. The data were obtained by fitting a smooth curve through the oscilloscope trace given in Fig. 3 in Ref. 53 and the maximum of this line was normalized to 4.2×10^{-21} cm² as quoted by the authors.

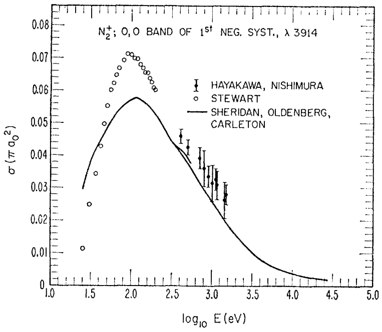

FIG. 25. Cross sections for the emission of λ=3914-Å N_2^+ radiation when electrons bombard molecular nitrogen. References: Stewart (54); Sheridan (55); Hayakawa (56).

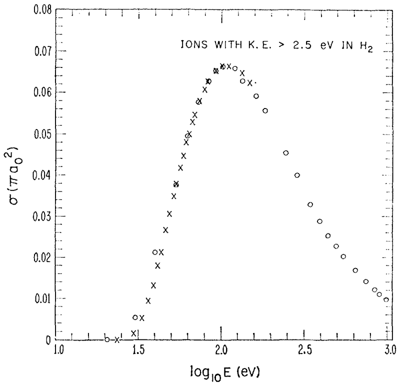

FIG. 26. Cross sections for the dissociative ionization of molecular hydrogen yielding product ions with kinetic energies greater than 2.5 eV. These data were taken from Figs. 43(c, d) in Ref. 7c.

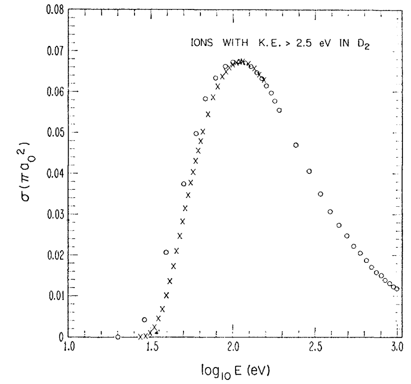

FIG. 27. Cross sections for the dissociative ionization of molecular deuterium yielding product ions with kinetic energies greater than 2.5 eV. Data are from Figs. 43 (f, g) in Ref. 7c. Electron energy values from Fig. 43 (g) were reduced by 9 eV. This correction was communicated to us privately by Dr. Rapp.

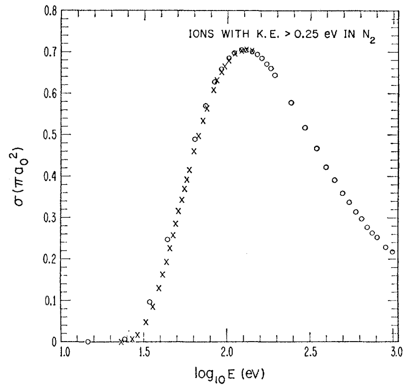

FIG. 28. Cross sections for the dissociative ionization of molecular nitrogen yielding product ions with kinetic energies greater than 0.25 eV. Data are from Figs. 43 (i, j) in Ref. 7c.

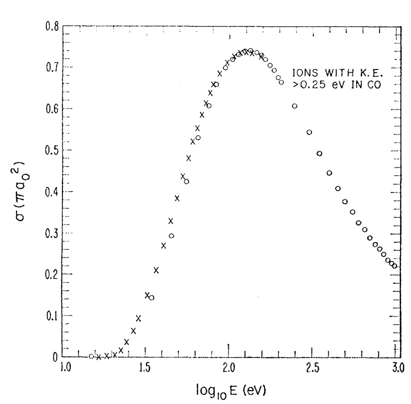

FIG. 29. Cross sections for the dissociative ionization of carbon monoxide yielding product ions with kinetic energies greater than 0.25 eV. Data are from Figs. 43 (o, p) in Ref. 7c.

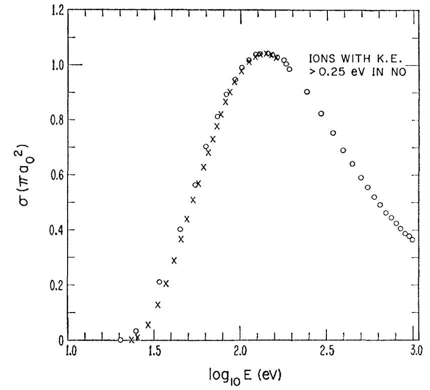

FIG. 30. Cross sections for the dissociative ionization of nitric oxide yielding product ions with kinetic energies greater than 0.25 eV. Data are from Figs. 43 (r, s) in Ref. 7c.

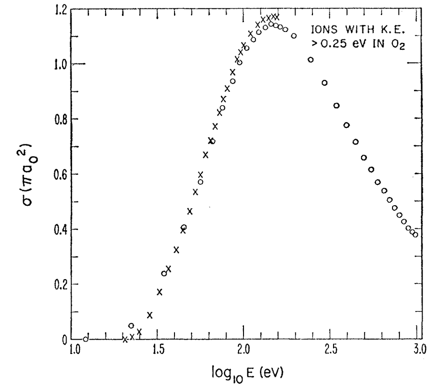

FIG. 31. Cross sections for the dissociative ionization of molecular oxygen yielding product ions with kinetic energies greater than 0.25 eV. Data are from Figs. 43 (l, m) in Ref. 7c.

(5) *Relative Cross Sections for the Production of Multiply Charged Atomic Ions from Atoms*

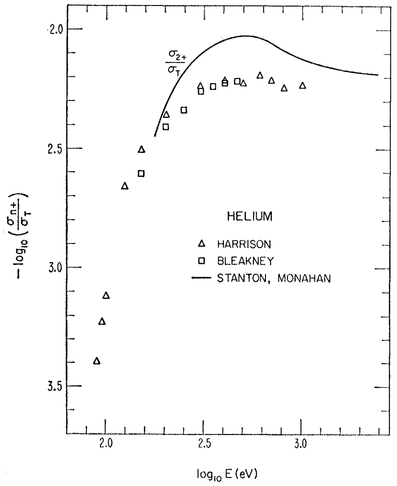

FIG. 32. $\mathrm{Log}_{10}(\sigma_{2+}/\sigma_T)$ vs $\log_{10}E$(eV) for helium, where σ_{2+} is the cross section for production of ions of charge +2, and σ_T is the total ionization cross section. References: Harrison (62); Bleakney (68); Stanton (69).

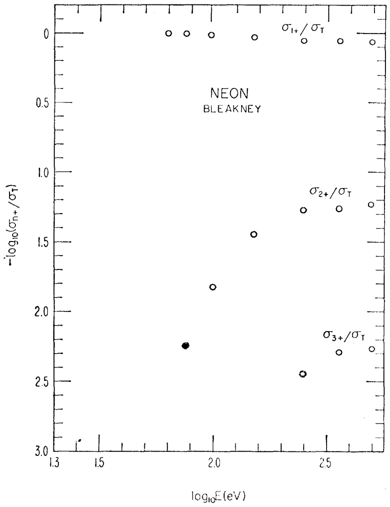

FIG. 33. $\text{Log}_{10}(\sigma_{n+}/\sigma_T)$ vs $\log_{10}E$(eV) for neon (Ref. 70), where σ_{n+} is the cross section for production of ions of charge $+n$, and σ_T is the total ionization cross section.

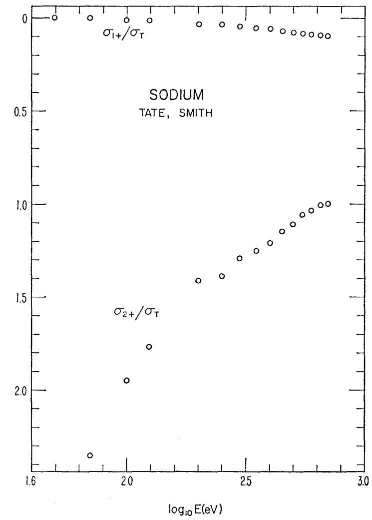

FIG. 34. $\text{Log}_{10}(\sigma_{n+}/\sigma_T)$ vs $\log_{10}E$(eV) for sodium (Ref. 19), where σ_{n+} is the cross section for production of ions of charge $+n$, and σ_T is the total ionization cross section.

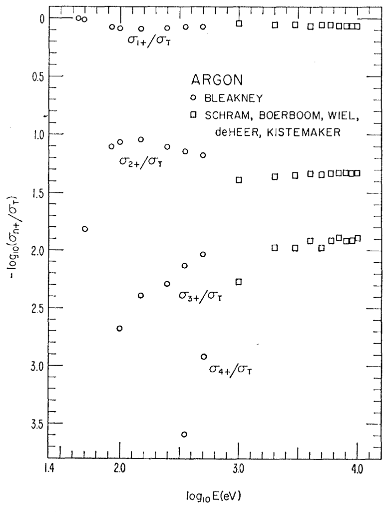

FIG. 35. $\text{Log}_{10}(\sigma_{n+}/\sigma_T)$ vs $\log_{10}E$(eV) for argon, where σ_{n+} is the cross section for production of ions of charge $+n$, and σ_T is the total ionization cross section. References: Bleakney (70); Schram (71).

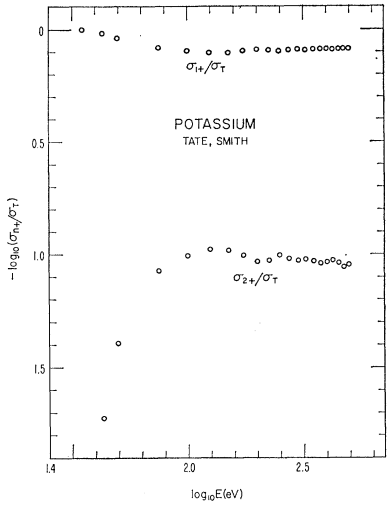

FIG. 36. $\text{Log}_{10}(\sigma_{n+}/\sigma_T)$ vs $\log_{10}E$(eV) for potassium (Ref. 19), where σ_{n+} is the cross section for production of ions of charge $+n$, and σ_T is the total ionization cross section.

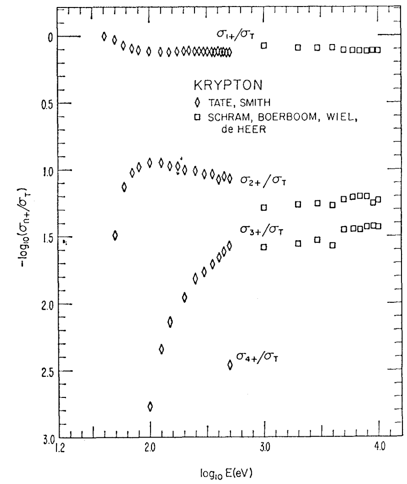

FIG. 37. $\text{Log}_{10}(\sigma_{n+}/\sigma_T)$ vs $\log_{10}E$(eV) for krypton, where σ_{n+} is the cross section for production of ions of charge $+n$, and σ_T is the total ionization cross section. References: Tate (19); Schram (71).

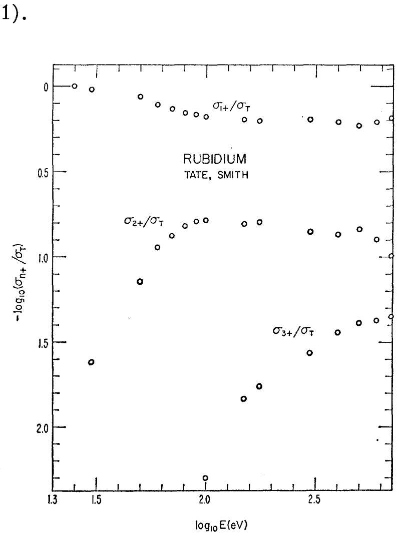

FIG. 38. $\text{Log}_{10}(\sigma_{n+}/\sigma_T)$ vs $\log_{10}E$(eV) for rubidium (Ref. 19), where σ_{n+} is the cross section for production of ions of charge $+n$, and σ_T is the total ionization cross section.

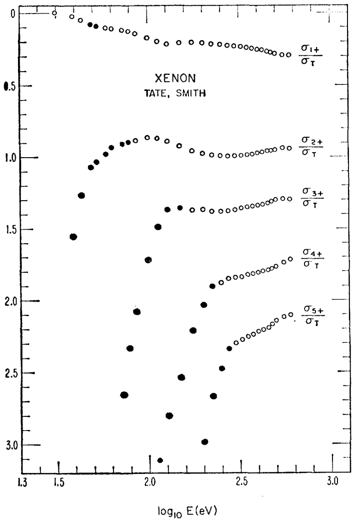

FIG. 39. $\mathrm{Log}_{10}(\sigma_{n+}/\sigma_T)$ vs $\log_{10}E(\mathrm{eV})$ for xenon (Ref. 19), where σ_{n+} is the cross section for production of ions of charge $+n$, and σ_T is the total ionization cross section.

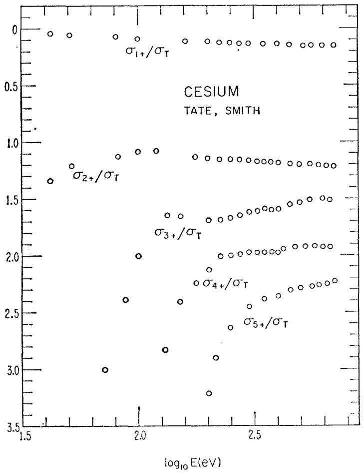

FIG. 40. $\mathrm{Log}_{10}(\sigma_{n+}/\sigma_T)$ vs $\log_{10}E(\mathrm{eV})$ for cesium (Ref. 19), where σ_{n+} is the cross section for production of ions of charge $+n$, and σ_T is the total ionization cross section.

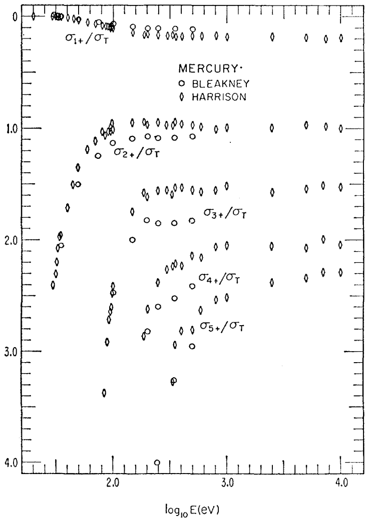

FIG. 41. $\mathrm{Log}_{10}(\sigma_{n+}/\sigma_T)$ vs $\log_{10}E(\mathrm{eV})$ for mercury, where σ_{n+} is the cross section for production of ions of charge $+n$, and σ_T is the total ionization cross section. References: Bleakney (59); Harrison (62).

B. Discussion of Experiments

General

We have attempted to assess the accuracy of the electron impact, ionization cross-section data for atoms and diatomic molecules in the literature, and to present those which appear to be most reliable based on conclusions about likely systematic errors. In some cases only one experiment has been reported and is presented here.

In attempting to determine accuracy, systematic errors are of paramount importance. Authors reporting data almost never report limits of possible systematic errors which are later proved realistic.

There are in general two reasons for this: (1) Experimentors may lack knowledge of the existence of a significant systematic error, possibly because certain parameters cannot be controlled in the experimental arrangement. (2) Empirical tests used to demonstrate the absence of systematic errors are often inadequate. Such tests are necessary but not sufficient, and reliance on them usually means that the quantitative nature of the systematic effect is not understood.

The Rare Gases: He, Ne, Ar, Kr, Xe

Rare gases would appear to be the atomic species most likely to yield consistent measurements, since they are inert and at the pressures involved act as ideal gases. In Fig. 42 the ratios of the total ionization cross sections reported by P. T. Smith (3) to those of Rapp and Golden (7a) for helium, neon, and argon are plotted. The work of Smith has been considered a classic, and his data have been used by numerous authors as a standard for comparing their relative measurements, and also for normalizing their relative data. The experiment of Rapp and Golden is an attempt to repeat the experiments of Smith and to verify his results. The design of the experimental apparatus used by Rapp and Golden is essentially the same as the design used by Smith. Some improvements have been made, such as longer guard plates, differential pumping for the electron gun, and smaller apertures. The trend of the ratios indicates a systematic difference which is a function of electron energy.

One of the systematic errors, which has been discussed as a possibility in Smith's apparatus, is an increase in path length due to off-axis velocity components (Ref. 9). The maximum expected value of the error (see Sec. II) has been plotted in all three figures for $d=1.5$ mm and $B=250$ G which apply to Smith's work. In the case of helium, it does appear to be an upper limit; in the case of neon and argon, it does not. Since it is possible that there are systematic pressure errors in the neon and argon data, the disagreement of the ratios with the predicted upper limit is probably not significant.

The assumption made to derive this formula [see Eq. (2)] is that all the electrons have helical paths of diameter d, which is determined by the apertures in the electron gun. Asundi (10) tried to obtain a more realistic limit to the possible error in Smith's data by calculating an "effective" d, using two separate models for the

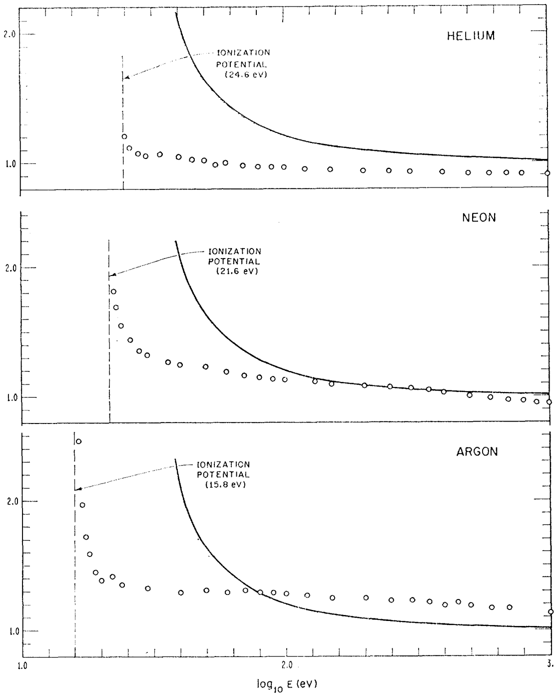

FIG. 42. Comparison of the total cross-section data of Smith (3) and Rapp, Golden (7a) for helium, neon, argon. The line represents the maximum ratio expected [Eq. (2)] if the only systematic error in either experiment was a path length error in Smith's.

mechanism whereby the electrons acquire off-axis velocity components. Both models were based upon geometrical considerations and not on the gas used. An attempt was made to fit this formula to the ratios given in Fig. 42 in order to obtain an "effective" *d*. There was no "effective" *d* which would give a reasonable fit to the ratios. This applies to each of the gases separately. The large ratios, particularly in neon and argon, which are very near threshold can be altered considerably by assuming a difference in the energy scale of the two experiments of a few tenths eV. Since both experimentors used essentially the same value for the ionization potential (within 0.1 eV), it is unlikely that this can completely explain the rather rapid rise in the ratios below 50 eV. It does mean, though, that there is considerable uncertainty in the ratios within 1.0 eV of the ionization potential.

Although the general trend of these ratios for the three gases is the same, the slopes above 100 eV are quite different. This suggests that the effect probably has something to do with the properties of the gases involved.

At their maxima (which are below their respective ionization potentials), the momentum transfer cross sections for He, Ne, and Ar are about a factor of five larger than the ionization cross sections *at their maxima.* Therefore, at electron energies near threshold a small percentage of the electrons in the beam might have collided with the gas atoms and thus have had their momenta significantly changed. Even a very small fraction of the electrons scattered at 90° can have a significant effect on the average path length which the electron takes through the gas. If important, this effect is very dependent on the angular distribution of the scattering. The results of Smith are somewhat more affected by this effect than those of Rapp and Golden; since Smith's data were taken at higher pressures, the apertures defining his electron beam were larger, and he had no differential pumping.

Comparison of other data for the rare gases, particularly those of Tozer and Craggs (65), and Asundi and Kurepa (5) with Rapp and Golden does not reveal any systematic differences of this type. In most cases the data for these experiments differ by a constant percentage which probably results from systematic errors in pressure measurement. This fact tends to add weight to the possibility that Smith's experiment may have had a path-length error.

The original data of Rapp and Golden were presented in an unpublished report (Ref. 7c). These cross section data were put on an absolute scale, using pressures measured with a McLeod gauge. Before publication the authors decided to use a flow technique as a pressure standard. Unfortunately, they did not explore all of the possible systematic effects, so it is not certain whether the new normalization is better than that obtained using the McLeod gauge. We have decided to present the published data, since the data normalized using the McLeod gauge differ essentially from the new data by a multiplicative constant which is given in their published reference (Ref. 7a).

The recent data of Schram *et al.* (8), in the range 0.6–20 KeV, is in general lower than that of the other experiments at the same energies. As they point out, their data also have a significantly different dependence on energy than the other high energy data. In fact, the energy dependence of their measured cross sections is in accordance with a simple law derived by Bethe (72) based on the Born approximation and on the assumption of single electron excitation. Since the theoretical situation regarding multiple ionization is not clear, it is on this basis not reasonable to give these data more weight than the other data.

The rare gas cross sections are generally regarded as well known; the data presented in Figs. 4, 7, 8, 9, and 10 indicate that this opinion is not well founded unless one considers 20–30% as a small uncertainty. The evidence indicates that systematic errors exist both in the shape of these cross-section curves and in their absolute magnitude. The only conclusion which it seems safe to make at present is that the spread in the data gives some indication of the range of possible systematic errors.

Atomic Hydrogen

The three experiments, the data for which are plotted in Fig. 3, are in rather good agreement considering their difficulty and the fact that the experimental techniques used were quite different.

Since atomic hydrogen is not stable at ordinary temperatures, these experiments were done using a beam generated in a high temperature oven or radio frequency discharge. All of these data are relative because of the difficulty in measuring the neutral beam density.

Fite and Brackmann (24) used two methods to normalize their relative cross-section data. The first method, which they called "relative," was to normalize their relative data at 500 eV to a Born approximation calculation. The second was to compare signals of proton current and H_2^+ current from their mass spectrometer, taking into account the amount of dissociation in the neutral beam. They then assumed that the corrected H^{2+} signal corresponded to the total ionization cross section as measured by Tate and Smith. This procedure neglects the energetic protons which result from dissociative ionization of H_2. Above 50 eV these protons represent between 5 and 10% of the total ion current [see Fig. 26]. It is surprising that the agreement between these two sets of data is so good.

The elaborate procedure used by Fite and Brackmann to determine the collection efficiency of the mass spectrometer for thermal ions at all temperatures involved use of a heavy rare gas, Ar. The conclusion they reached was that no detectable transverse momentum was imparted to the thermal ions regardless of their mass and the energy of the impacting electron. This result is somewhat surprising, since they claim that the collection efficiency of their spectrometer was extremely sensitive to very small changes in its position, and since at threshold essentially all of the momentum of the incoming electron is imparted to the ion. An average hydrogen atom from a 1000°C source has only about three times the momentum of an electron with an energy of 13 eV.

Boksenberg (31) normalized his relative data to a Born approximation calculation at 300 eV (his highest energy). The spectrometer used by Boksenberg in determining the relative ionization cross sections for atomic hydrogen had a very high collection efficiency for thermal ions. He presented evidence which indicated it probably was 100% efficient for the collection of thermal protons.

Other relative cross sections measured by Boksenberg with this apparatus, e.g., that for helium, were drastically different from those obtained with total ion collection devices (Ref. 3). After extensive experimental and theoretical analysis, he concluded that the effect resulted from a change in the average electron path due to electron optical effects. He applied an empirical correction to his data by comparing the relative cross section data observed for H_2^+ with the total ionization cross sections observed by Tate and Smith (4). The contribution of dissociative ionization to the shape of the total ionization cross section was ignored.

The work of Rothe *et al.* (29) was different from the two previous experiments in that it was designed to collect all of the ions, including the energetic protons from dissociative ionization. The normalization of these data to those of Tate and Smith would have been correct if both groups had collected all ions. There is considerable doubt that this was so since Tate and Smith (4, 7a) apparently did not have high enough fields to collect all of the energetic ions. In a private communication R. H. Neynaber indicated that in the experiment of Rothe *et al.*, saturation of ion current was achieved. This is somewhat inconsistent with the discussion in their paper, since the fields used to collect the ions were based upon their very low estimate of the maximum energy of the energetic H^+ ions (Refs. 29, 49).

The degree of agreement among these result is, as has been stated, somewhat surprising considering the rather poor agreement among results for the rare gases.

Atomic Nitrogen

The experiment of Smith *et al.* (30), is a relative experiment, and that of Peterson (26) is an absolute experiment. Technically these results should not be compared, since Peterson's apparatus had a mass spectrometer to select the ions, and since he measured the cross section for producing the singly charged atomic nitrogen ion, whereas Smith *et al.* measured the total ion cross section. In any case, the cross section measured by Peterson should have been smaller than that measured by Smith *et al.* Both of these experiments might have had excited atomic species in the neutral atomic beam. The atomic nitrogen used by Smith *et al* was formed in a pulsed dc discharge. Peterson formed his neutral atomic beam by charge exchange of fast N^+ ions with O_2 and Ar.

Peterson also measured cross sections for N_2, Ar, and Ne with this same apparatus. The sum of his partial cross sections should have been very close to the total cross sections measured by Smith (3), and Tate and Smith (4), but was considerably larger except below 60 eV in argon. It is therefore probable that the cross sections that he measured for atomic nitrogen are too large. The measurements are absolute however and do not depend on knowledge of any other cross sections. The assumption that the efficiency of a calorimetric detector is the same for ions as for neutral atoms of the same velocity and mass has never been verified and could lead to large systematic errors.

In the experiment by Smith *et al.* (30), the cross section is obtained from the difference of two ion currents when the beam is completely molecular and

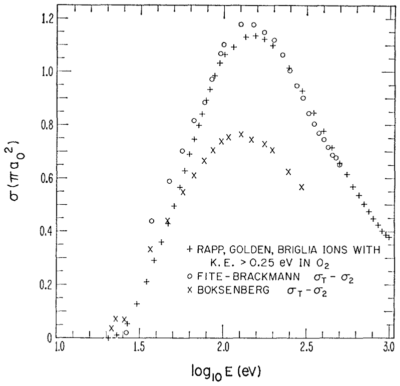

FIG. 43. Comparison of the partial cross sections for dissociative ionization of O_2 measured by Rapp (7c) with approximate cross sections for dissociative ionization deduced from the data of Fite (28) and Boksenberg (31).

when it is partially dissociated. The data were normalized by using the absolute cross sections for molecular nitrogen measured by Tate and Smith (4). Since the dissociation fraction was quite small, about 20%, and the cross section measured for the atom was one half that measured for the molecule, this technique was not very sensitive.

Atomic Oxygen

The experiments of Fite and Brackmann (28), and Rothe *et al.* (29) agree quite well in view of the fact that there is considerable doubt that they had 100% collection efficiency for all ions (see Table II). There is some evidence that the cross sections measured by Boksenberg (31) are too large. All of these experiments were relative and were normalized to the total cross section measurements of Tate and Smith for O_2.

Rapp, Golden, and Briglia (7b) have measured the cross sections for the production of energetic ions from O_2. In Fig. 43 these cross sections as measured by Rapp, Golden, and Briglia, $(\sigma_T-\sigma_2)$ as measured by Fite and Brackmann, and $(\sigma_T-\sigma_2)$ as measured by Boksenberg are plotted. Here σ_2 is the cross section for producing thermal O_2^+ by single electron impact on O_2. Since $(\sigma_T-\sigma_2)$ contains contributions from O_2^{2+}, the close agreement between Fite and Brackmann and Rapp, Golden, and Briglia is possibly fortuitous, but the evidence does indicate that the ratio (σ_2/σ_T) as measured by Boksenberg is probably too large. The total cross sections reported for molecular oxygen by Tate and Smith and by Rapp *et al.* differ by about 10%. This does not affect the agreement between Rapp *et al.* and Fite and Brackmann for the energetic ion cross sections; nor does this affect the discrepancy with the Boksenberg data, since the Rapp, Golden, and Briglia data on dissociative ionization were normalized using a McLeod gauge standard.

If Boksenberg's value for $(\sigma_T-\sigma_2)$ is too small, then his measured cross sections for the ionization of atomic oxygen would be too large (ignoring other possible systematic errors).

Atomic Mercury

All of the data presented in Fig. 9 except that of Liska (61) are absolute and were taken with parallel plate geometry and collection of all ions. The data of Nottingham (38) are not presented because the collection efficiency for positive ions as a function of the electron energy in his apparatus was uncertain and because the data were not corrected for a large number of secondary effects which appear to be systematic.

The data of Jones (2) are here corrected for obsolete mercury vapor pressure data, and for diffusion. [The mercury reservoir and ionization chamber were at 0°C and 70°C, respectively. Bleakney (59) noted these errors.] The vapor pressure data from the International Critical Tables were used instead of those of Smith and Menzies (see Table II).

Harrison (62) had two possible systematic pressure errors. First, he used a secondary standard, an ion gauge, to determine the mercury pressure; and second, he assumed that the temperature of the ionization region was that of room temperature, 27°C. This assumption is probably incorrect. If the temperature of the ionization region were higher than room temperature, which is likely, correcting for this would have the effect of slightly increasing his cross sections. Making this correction would tend to bring his data into better agreement with Bleakney and Jones. Since Liska's data were normalized to that of Smith (60), these are not independent measurements.

Although the cross-section data of Smith are considerably smaller than those of Jones, Bleakney, and Harrison, there appears to be no reason for rejecting Smith's results or giving them less weight.

One of the uncertainties in all of these experiments is the purity of the gas. The mercury vapor was introduced through the pumping line by regulating the temperature of the trap.

Alkali Metals: Li, Na, K, Rb, Cs

The absolute, total ionization, cross-section data for the alkali metals are presented in a small table, since only one set of experimental results, that of McFarland and Kinney (33), was selected for presentation.

The data of Brink (32) are not presented, since only cross sections for production of the single ion were presented, and since these were derived from his total cross-section data, using relative cross sections for the production of multiply charged ions that were not defined. His total cross-section data were not available.

McFarland and Kinney did a crossed-beam experiment. The intensity of the neutral atomic beam was determined, using a surface ionization detector. The efficiency of this detector has not been clearly established for the alkalis (see Sec. II) and is probably the source of the largest systematic error in the experiment.

Molecular Cross Sections: H_2, D_2 N_2, O_2, CO, NO

The cross sections reported by Tate and Smith (4) decrease more rapidly with energy than those of Rapp and Golden (7a) above 100 eV. The cause of this decrease may be the same as that which produced a similar effect in the comparisons of the cross sections for He, Ne, and Ar. The data of Schram *et al.* (8) are again lower than the other available results at the same energies.

In the case of these diatomic molecules, dissociative ionization can make it difficult to collect all of the ions. Rapp, Golden, and Briglia (7b) have estimated [see Sec. III, B(4)] the percentage of total ion current due to energetic ions from dissociative ionization and found it to range at maximum from 36% for O_2 to 7% for H_2. If these ions were not efficiently collected, a significant underestimate of the total ionization cross section would be made. Both Rapp *et al.* (7b) and Schram *et al.* (8) were careful to assure saturation of their collected ion current, and it seems unlikely that their experiments had this systematic error. Tate and Smith may not have used high enough collecting voltages to assure complete collection of the energetic ion current.

The data of Harrison (62) for molecular hydrogen are considerably higher than those of all the other results presented. Harrison may not have collected all of the ion current because the voltage used for collecting the ions, nine volts, was only sufficient to assure total collection of ions with energies less than 4.5 eV. Harrison noted that his cross sections were considerably larger than those reported by Smith. He rechecked the calibration of his ion gauge and found it to be essentially unchanged. Another possible pressure error in this experiment is noted in the discussion of the mercury cross-section data. The likely systematic errors in this experiment would probably tend to increase the cross sections, but there appears to be no valid reason for rejecting Harrison's results.

Ion Cross Sections: He^+, Li^+, N^+, Ne^+, Na^+, K^+

Since each of these experiments was done with mass analysis, the data are cross sections for single ionization of the ions involved. The recent data of Latypov *et al.* (73) are not included because, as they demonstrated, their measured cross sections are so dependent on conditions in their ion source as to be practically meaningless. Only in the case of neon this was not so, which provides strong evidence that their Ne^+ beam was not contaminated with excited species. Dolder *et al.* (63) came to this same conclusion about their own work, when they observed no Ne^{2+} current below the threshold for the appearance of these ions from the ground state of Ne^+. The one data point for Ne^+ from the experiment of Latypov *et al.* was not considered of comparable reliability to the data of Dolder *et al.* and hence is not presented.

Because only one set of data is available for each of these atomic ions, it is difficult to estimate what the magnitude of possible systematic errors might be. For He^+, comparison of the experimental values of Dolder *et al.* (25) with the scaled atomic hydrogen cross sections measured by Fite and Brackmann shows good agreement, i.e., they differ by less than 10% at energies greater than 10 times threshold. At energies less than five times threshold, the agreement is rather poor.

For N^+ it is possible that the beam was contaminated by metastable nitrogen atomic ions, but the evidence presented by Harrison *et al.* (64) seems to indicate that the contamination was quite small. This conclusion was based on an assumed cross section shape for the dissociative ionization of N_2^{2+}, a probable constituent which could give rise to an observed signal below the expected ionization potential. Since their ion beam was mass analyzed, using magnetic deflection, they could not separate N^+ from N_2^{2+} in their primary beam. This possible contamination obviously introduces very large uncertainties in their reported cross sections near threshold.

The experiments of Hooper, Lineberger, McDaniel, and Bacon (27) on the ionization of the singly charged alkali metal ions are significantly different from those of Dolder, Harrison, and Thonemann. The former differ in two ways which tend to reduce systematic errors: First, the experiments were done at much lower background pressure ($\approx 10^{-8}$ Torr) which tended to reduce stripping of the ions on the background gas. Second, the source of ions was thermal emission from a surface, which does not populate metastable excited states.

Again in this case because only one experiment has been reported for each ionic species, it is difficult to predict the magnitude of the systematic errors. The authors have estimated their maximum systematic errors resulting from uncertainties in instrument calibration as ±6%. It is probable that this is a lower limit to the total possible systematic errors.

Absolute Cross Sections for Ionization of Atoms and Diatomic Molecules into Excited Final States

The data of Rapp, Golden, and Briglia (7b, 7c) on the approximate cross sections for production of energetic ions (Figs. 26–31), i.e., dissociative ionization, are the only absolute measurements of these cross sections. These data are quite uncertain for the following reasons:

(1) Because dissociation is not necessarily an isotropic process, an uncertain fraction of the ions was collected.

(2) Since ions of thermal energy were eliminated by retarding, this technique may eliminate some fraction of ions resulting from dissociation.

(3) Under the conditions used, reflection of low energy ions from the collector could be serious.

Rapp *et al.* do not claim that their data are accurate, but these are the only absolute results presently available.

Bleakney in 1930 (59) used this same experimental technique with H_2 to estimate the percentage of total ion current resulting from energetic ions with an appearance potential greater than 30 eV. His estimated percentage rises from threshold to an almost constant 7% at higher energies. Considering the nature of the experiments, this result is in good agreement with the results of Rapp.

Experiments to measure approximate cross sections for ionization into excited electronic states which radiate have been done by St. John and Lin on He (53), by Stewart (54), Sheridan *et al.* (55), and by Hayakawa *et al.* on N_2 (56). The detection mechanism must measure absolutely the intensity of this radiation. These experiments are difficult to evaluate, but since they are the only ones available and are done absolutely, they are presented. They are not cross sections for ionization into a single excited ion state but for the production of radiation of a certain wave length. Cascading and branching ratios were not taken into account in analyzing the data.

Relative Cross Sections for Production of Multiply Charged Atomic Ions

Most of the data in the literature on the relative abundances of multiply charged ions were collected using electron multipliers as detectors. In most cases authors did not take proper account of the fact that the gain (i.e., the number of secondary electrons per ion) is quite different for ions of different charge and mass which have been accelerated through the same potential.

Secondary emission coefficients for ions having the same kinetic energy but having different charge or mass can differ by factors of two or three. We compared data collected using uncalibrated multipliers and those using Faraday cups as collectors. The differences in relative cross sections were typically of the order of two for data taken in these two ways. We concluded that data collected with uncalibrated multipliers could not be considered as reliable as measurements of ion current directly. None of the data presented here except that of Stanton and Monahan (69) were taken using a multiplier as a detector. Stanton and Monahan obtained their helium data by counting ions, which, if properly done, effectively calibrates the multiplier. It is probable that in none of these experiments were there the same collection efficiencies for the different ions. The magnitude of these collection efficiency errors is difficult to estimate, but some idea of it can be obtained by noting the differences between the results of independent experiments. The data on multiple ions are presented as the logarithm of the ratio of the cross section for the production of the ion in question to σ_T. In order to obtain normalized cross sections for the production of an ion per atom and electron, one multiplies the σ_T given in Sec. IIIB(1) by the ratios given in Figs. 32–41.

These relative cross sections are presented as ratios; we decided that the accuracy of these cross sections was so uncertain that it would have been unreasonable to present them in absolute units. The crux of this problem is obvious from the total cross sections given in Sec. IIIB(1). The disparity in the data makes it impossible to decide which σ_T to use, even if one has confidence in the ratios σ_{n+}/σ_T.

IV. STRUCTURE IN AND THRESHOLD BEHAVIOR OF IONIZATION EFFICIENCY

In recent years most of the research in the study of ionization of atoms and molecules by electron impact has been directed at discovering structure in and determining the threshold shape of the ionization efficiency function. Ideally, its shape should be identical to that of the cross-section curve if single collisions are predominant. Unfortunately, observation of the detailed structure of the ionization efficiency has yielded conflicting results. Review of the techniques, as described in the literature, reveals that they all require very careful adjustment of instrumental parameters. Many of these adjustments rely on reproducing results of other investigators using similar techniques. It appears that these techniques cannot in general be compared with the criteria given in Table I which could be considered minimum criteria for assuring reliability. Therefore we have not included data in this section because the experiments compare favorably with the criteria in Table I. The data were selected because they illustrate major points of agreement or conflict.

The focus of attention on structure and threshold may in large part be attributed to the development of techniques for diminishing the effects of the electron energy distribution in obscuring details of the observed ionization efficiencies. Added incentive to threshold ionization studies was given by the theoretical predictions of Wannier (74) and of Geltman (75) and more recently by Rudge and Seaton (76) for the variation of ionization cross sections near threshold. Existence of mechanisms of ionization other than direct transitions of electrons to the first continuum have been demonstrated, although the relative importance of these mechanisms has not been fully demonstrated. Some investigators have correlated structure in the ionization efficiency curves with energy levels of the neutrals or ions under study and thus a form of spectroscopy has developed in ionization studies. This "spectroscopy" will not be discussed here. except when it is pertinent to the discussion of threshold laws and ionization mechanisms.

We emphasize, before discussing some of the experimental results, that instrumental effects such as mentioned in Sec. II and such as analyzed by Marmet (47) may play a large role here in the results. The only apparent theoretical basis for interpreting structure in ionization curves near threshold are the threshold laws noted above. The energy range of validity of these laws is not predicted. However, it is natural (and sometimes apparently irresistible) for the experimentor to try to interpret structure which he observes, and thus a large literature has grown up, demonstrating and interpreting structure in ionization efficiency curves.

There are several experimental results that seem to indicate that the ionization cross section varies with the *n*th power of the excess energy above threshold of the impacting electron where *n* times ionized ions are being formed. The results of Hickam, Fox, and Kjeldaas (77) using the RPD method mentioned in Sec. II for single ionization of He are shown in Fig. 44. A straight line as predicted by Geltman, Rudge, and Seaton can be readily fitted to the points, and these authors show that there are large deviations from a fitted 1.1-power law, the dependence which is predicted by Wannier. Others (78, 79) have confirmed that the first ionization of He is consistent with a first-power law. Fite and Brackmann (24) observe that the ionization cross section for H atoms increases linearly with excess energy with a slope of 0.078 πa_0^2/eV. McGowan and Fineman (80) have recently done the experiment with high energy resolution; and they confirm the linearity, finding a slope of 0.064 πa_0^2/eV.

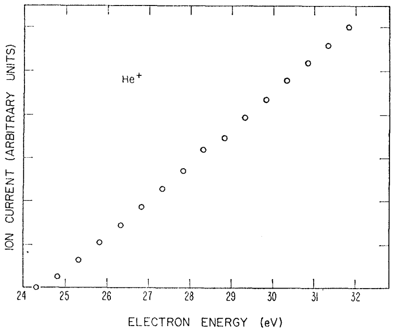

Fig. 44. Data of Hickam *et al.* (77) showing the linear rise with energy of ion current for single ionization of He.

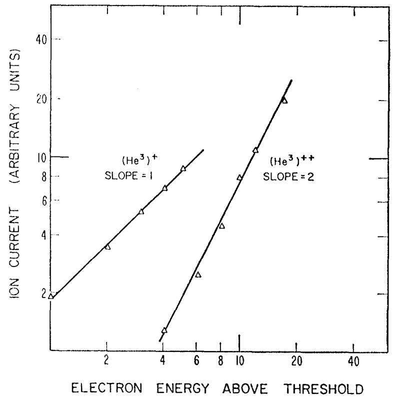

Fig. 45. Data of Fox (81) demonstrating the linear and quadratic threshold laws of single and double ionization, respectively, of He.

Double ionization of He has been shown by Fox (81) and by Krauss, Reese, and Dibeler (82) to be consistent with a threshold law varying as the square of excess energy above threshold. Figure 45 shows Fox's results. Fox used He^3 to avoid complications from H_2^+, while Krauss *et al.* used a high resolution, mass spectrograph to separate H_2^+ from He^{++}. Both groups used the full energy spectrum of electrons emitted from a filament. Dibeler and Reese (83), using the full electron energy width from a filament, showed that the

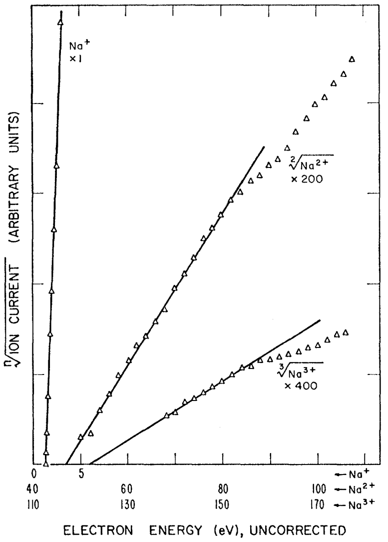

Fig. 46. Data of Dibeler and Reese (83) demonstrating threshold behavior for one, two, and three times ionized sodium.

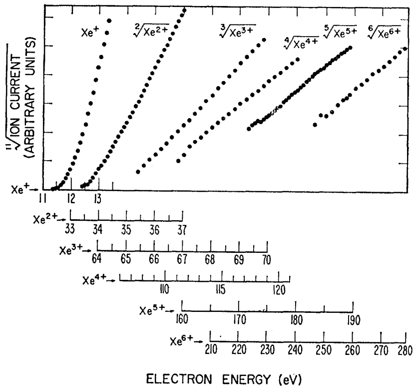

Fig. 47. Data of Dorman *et al.* (85) demonstrating threshold behavior for up to six times ionized xenon.

appearance behavior of one, two, and three times ionized sodium is consistent, respectively, with a linear, square, and cubic dependence on energy above threshold. Their results are shown in Fig. 46. The linear and square laws for single and double ionization, respectively, of sodium and potassium have been demonstrated by Kaneko (84), using the RPD method.

The unique feature of all of these systems studied is the absence of excited states lying near the ground state of the ion. Fortuitously, the use of the natural spread in electron energies in some of the above work does not seem to be a great disadvantage, since the threshold law seems to be obeyed over an energy range which is large compared to the spread.

More severe difficulties of interpretation in terms of threshold laws have occurred for other than the systems mentioned above, and some controversy over these interpretations still exists. This is often attributed to the onsets of other ionization processes relatively near the appearance energy for ground-state ions. However, Dorman *et al.* (85, 86) have pointed out that the greater the degree of ionization, the less important in determining the threshold law will be higher processes *having the same threshold law*, and for ionization of degree four or greater, the effect is completely negligible. They point out (86) that when processes with different threshold laws are present for producing ions of charge n, then an nth root extrapolation of the ionization efficiency curve to the energy axis will give a lower limit to the threshold energy. The energy at which ion current is first detected sets an upper limit on the threshold energy. Multiple ionization of the rare gases has been shown to be consistent with the nth power threshold law by Morrison and co-workers (85–87), Krauss, Reese, and Dibeler (82), and more recently by Kiser (88). Morrison *et al.* also showed that in many cases the derivatives of the ionization efficiency curves were consistent with the threshold laws. All of these workers used the full energy spread of electrons from a filament. Representative results of Morrison are shown in Fig. 47. Clarke (41), using an electrostatic electron energy selector, found that the threshold law for Xe^{++} is consistent with a square-law dependence on excess energy. In contrast to this, Fox (81, 89) and Hickam, Fox, and Kjeldaas (77) found that a series of straight-line segments fits their data most satisfactorily. Although an nth root plot of these data yields reasonable straight lines, extrapolations of such plots do not give threshold energies in agreement with spectroscopic values, in contrast to extrapolation of straight-line segments fitted directly. Similarly, Blais and Mann (90) fitted straight-line segments to double ionization of Au, but Dorman and Morrison (52) pointed out that a plot of the square root of ionization efficiency against energy is also a straight line within experimental error over a range of at least 10 eV. Within the limitations set by higher processes as discussed by Dorman and Morrison (86) and mentioned above, the data of other workers seem to be consistent both with the form of the threshold law and the nth root extrapolated threshold energy. A comparison of threshold energies as found by various workers is given by Kiser (88). Dorman and Morrison (52) have also found that double ionization of NO, CO, N_2, and of some polyatomic molecules increases in a way that is consistent with dependence on the square of the energy above threshold.

Fine structural variation observed in ionization efficiency curves may be interpreted in terms of at least three kinds of mechanisms: (1) Higher lying states of the ion become energetically accessible, and ions formed in these states begin to contribute to the observed current. It is reasonable, and it appears to be borne out, that such states appear with the same kind of threshold law as that of the ground-state ion. (2) The impacting electron may excite the neutral atom or molecule to an energy level lying above the energy of the continuum of the ground-state ion. This excited level may then autoionize with a lifetime as short as 10^{-14} sec. The energy dependence for this kind of excitation is not well established. Dorman, Morrison, and Nicholson (91) had felt there was evidence for a step function thres-

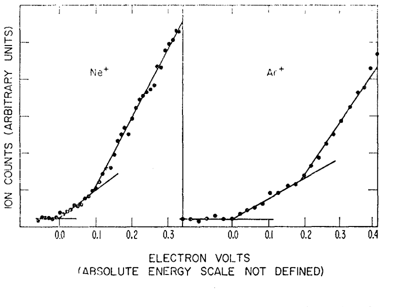

Fig. 48. Data of Marmet and Morrison (101) showing direct ionization efficiency curves of Ne^{+} and Ar^{+}, plotted as a function of energy above threshold.

hold, but in more recent work Morrison (42) notes that there may be pronounced effects due to configuration interaction. (3) Auger processes also account for some observations of structure. In these an inner shell electron is knocked out by the impacting electron; and an outer electron, in transferring into the vacancy, gives the transition energy to another outer electron. If this energy is high enough, the outer electron is ejected, thus leaving the atom ionized to one higher degree.

The first mechanism leading to structure—that of forming ions in excited states—has perhaps been most observed in ionizing noble gases where the ion ground state is a doublet, with $^2P_{\frac{3}{2}}$ higher than $^2P_{\frac{1}{2}}$. This doublet separation is 1.31 eV in xenon, 0.67 eV in krypton, 0.18 eV in argon, and 0.10 eV in neon. Structure which has been attributed to these doublets has been observed many times (Refs. 77, 78, 92–103). Results of Marmet and Morrision (101) for Ne and Ar are shown in Fig. 48. One might expect that with no other ionizing mechanisms present, the ratio of the slopes of lines fitted to the data might be the same as the ratio of the statistical weights of the two states. The various data referenced above, however, do not show consistent results for the ratios of these slopes. That the ratio may not be as predicted can perhaps be explained in terms of autoionization as discussed below. The technique of observing "breaks" in straight-line fits to data has also been applied to some molecules, and interpretation of the results has been made in terms of excited electronic states of the ion (Refs. 41, 93–96, 98, 99, 104–109) and in terms of vibrationally excited states of the ion (Refs. 41, 95, 109, 110). Here again the role of autoionization has probably not been thoroughly accounted for in interpreting the shapes of these ionization efficiency curves.

The ionization efficiency curve of H_2 near threshold is an interesting case in point. Figure 49 shows the data of Marmet and Kerwin (110) who used a 127° selector and a volume gas sample in conjunction with a mass spectrometer, the data of Briglia and Rapp (111) who used the RPD method in a total ionization tube, and the data of McGowan and Finemann (80) who used a 127° selector and a molecular beam in conjunction with a mass spectrometer. Marmet and Kerwin interpret their curve in terms of breaks at the thresholds for individual vibrational states of H_2^+. They compare the slopes at the breaks and find reasonable agreement with the Franck–Condon factors between H_2 and H_2^+. Briglia and Rapp observe a nearly straight line and conclude that a direct ionization model of H_2 for which the Franck–Condon factors predict the relative populations of vibrational levels is not valid. McGowan and Fineman also observe a nearly straight line, but look at the first and second derivative of the ionization efficiency curve as well as the curve itself. Comparison of the derivative curve (see below) with photoionization data (Refs. 112, 113) on H_2 shows many similarities. Many peaks which can be traced to autoionization occur in the photoionization data. Similar peaks occur in the derivative of the electron impact curve. The disagreements (Fig. 49) demonstrate and emphasize the extreme difficulties faced in measuring and interpreting ionization efficiency curves near threshold.

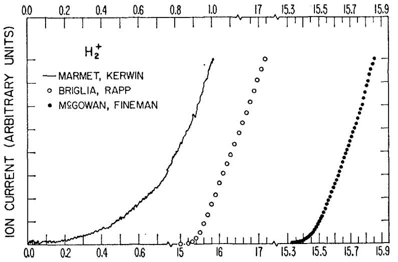

Fig. 49. Ionization curves near threshold for H_2. Data of Marmet and Kerwin (110) are plotted on an energy scale with an arbitrary zero reference. Data of Briglia and Rapp (111) and McGowan and Fineman (80) are plotted on absolute energy scales.

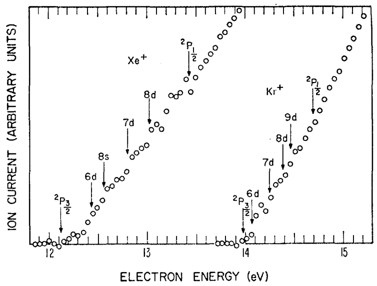

Fig. 50. Data of Morrison (103) on ionization efficiency of Xe and Kr near threshold, reduced by an analytical method. The $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ ionization limits and some excited neutral levels lying between these states are shown by arrows.

The mechanism of autoionization has long been known from interpretation of spectra (Refs. 114), but it appears that Fox, Hickah, and Kjeldaas (92) were the first to use the process to explain structure in ionization efficiency curves. They invoked the mechanism to explain their inability to fit two straight lines as above to the ionization efficiency curves of krypton and xenon. This mechanism has since been suggested as an explanation of features in the ionization efficiency curves of Zn, Cd, Hg (Ref. 115), of O_2 (Refs. 91, 116) and N_2 (Refs. 41, 91, 98, 99) of Mg (Ref. 84) and Ca (Ref. 44), of K, Rb, and Cs (Ref. 117), and of Cu, Ag, and Au (Ref. 90). Recent data of Morrison (103) and of Burns (102) show more clearly the apparent effects of autoionization in the ionization of Kr and Xe. The data of Morrison (103) are shown in Fig. 50. He has pointed out a great similarity between the ionization efficiency curve for Xe and the integral over energy

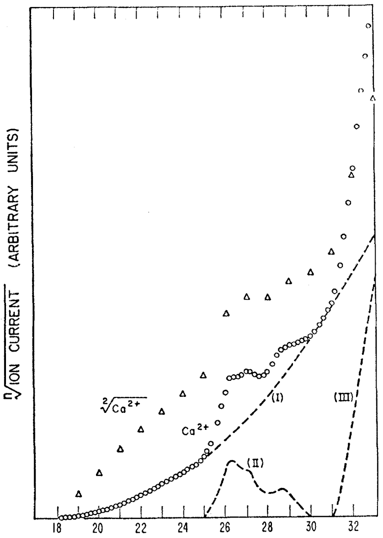

FIG. 51. Data of Kaneko and Kanomata (44) showing double ionization of Ca near threshold. Circles represent the ion current directly, and triangles represent the square root of this current. Dashed curves II and III are the difference between a curve through the circles and a quadratic curve I deduced from a straight line fit to the triangles below 25 eV.

of the photoionization curve. An equivalent similarity has been noted in recent high resolution data (Ref. 116) for O_2 and in H_2 as noted above (Ref. 80). There seems to be no theoretical basis at present upon which such comparisons can be made, so the meaning of the comparisons is doubtful.

Autoionizing lifetimes are usually thought to be of the order of 10^{-13}–10^{-14} sec. However, lifetimes of nearly 10^{-4} sec have been observed (Ref. 118) for some autoionizing levels of alkaline metals. Such a spread in lifetimes can contribute to difficulties in getting consistent results in ionization efficiency curves. Thus it has been observed (Ref. 45) that the shapes of some curves are very sensitive to the ion-source, drawout field; and reasonably long-lived autoionizing levels are suggested as an explanation.

Fox (81) suggested the Auger process as a means of explaining the anomalous shape of his multiple ionization data. It has since been observed more conclusively (Refs. 44, 45, 119), and data of Kaneko (44) for double ionization of Ca are shown in Fig. 51. A portion of the curve shows a quadratic energy dependence, followed by an irregular portion between 25 eV and 30 eV, and a linearly increasing portion starting at 31 eV. This latter portion has been attributed according to a suggestion by Fayard *et al.* (45) to Auger ejection caused by ionization of a $3p$ electron. The Auger process results in a probability for creating Ca^{++} which is comparable to that for Ca^{+}. The threshold law appears to be linear, even though the resultant ion is Ca^{++} because the electron collision produces $(Ca^{+})^{*}$.

V. CONCLUSIONS

The conceptual simplicity of ionization measurements by no means implies that such measurements will be reliable. Although in many of the experiments (particularly total ionization) random errors are small, systematic errors seem often to be serious. There are two main observations leading to this conclusion:

(1) There are large systematic differences in the number density standards used in the various experiments to obtain absolute cross sections. Several recent efforts (see Sec. II) have been made to eliminate temperature effects observed when using McLeod gauges as standards. Although various procedures have been developed based on empirical tests, these tests are necessary, but not sufficient, to define a reliable standard. There thus seems to be an inadequate basis for strongly recommending some of the more recent results in which attempts to improve the pressure standards were made.

(2) Large systematic differences exist in the cross section shapes as a function of electron energy. The causes of these differences have not as yet been identified with certainty, nor are they quantitatively understood.

Rare gases being nonreactive should behave like "ideal" gases. Even for the rare gases, however, systematic differences among the experimentally measured cross sections range from about 10% in helium to 30% in xenon (excluding the threshold region). At this point one must accept these differences as a reasonable measure of the possible range of systematic errors.

Crossed-beam experiments for neutral ground-state species are probably less accurate than the total ionization experiments for the following reasons:

(1) Crossed-beam experiments rely for normalization on the cross sections measured which use the Tate and Smith technique.

(2) The techniques for collecting ions and determining number density of scatterers are less reliable than that of the total ionization tube.

(3) Random errors are large, and it is difficult to determine whether any systematic errors exist, much less to determine the magnitude of the errors.

A strong exception to these comments on crossed-beam experiments would have to be made in the case of crossed charged beams in which the standards for determining target density (electric current and distance) are accurate and easily accessible. However, in these experiments the random errors are quite large, and systematic errors of a subtle nature may be obscured. Reliable independent experiments have never been performed using crossed charged beams, and it is thus not reasonable to speculate about the probable range of systematic errors.

There is a very decided lack of cross-section measurements for individual processes, i.e., cross sections from a known initial state to a single known final state. Fluorescence techniques have been applied in only a small number of experiments on ionization, and it is not yet clear what role is played by structure near the ionization threshold in determining the relative magnitudes of cross sections to individual final states. Mass spectrometers have been used to determine the relative cross sections for going to different final charge states, but in general the assumption of a constant collection efficiency of a mass spectrometer for different charge states has not been demonstrated, and one cannot look upon the relative cross-section data as more than approximate. Clearly, these measurements await new techniques, or imaginative use and interpretation of old techniques.

One final comment which, although it may appear obvious, is worth emphasizing. Consideration of all the data shows that none of the cross sections discussed are reliable to within 10% at best; therefore, any comparison of theoretical calculation with the data should take this uncertainty into account.

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