01 Jan 1968

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Recommended Citation

K. J. Nygaard, "Electron-impact Lonization Cross Section In Cesium," *The Journal of Chemical Physics*, vol. 49, no. 5, pp. 1995 - 2002, American Institute of Physics, Jan 1968.
The definitive version is available at https://doi.org/10.1063/1.1670359

RESEARCH ARTICLE | SEPTEMBER 18 2003

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J. Chem. Phys. 49, 1995–2002 (1968)
https://doi.org/10.1063/1.1670359

Electron-Impact Ionization Cross Section in Cesium*

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(Received 1 May 1968)

The total ionization due to the passage of an electron beam in cesium vapor has been measured with a Tate and Smith-type apparatus. The retarding potential difference method was used in the electron gun to obtain energy resolution better than 0.1 eV. The density of Cs atoms was determined from the Taylor and Langmuir formula and also measured with a surface-ionization detector. The two methods gave the same density to within ±3% when the apparatus was in thermodynamic equilibrium with the Cs reservoir. The cross section for production of Cs^+ has been determined from threshold to 100 eV. For energies above 28 eV, the results agree closely with those of McFarland and Kinney. At threshold the slope of the cross-section-vs-energy curve was measured to be 2.7 Å²/eV.

I. INTRODUCTION

The interpretation of many plasma experiments using cesium (for instance, thermionic energy converters, ion propulsion devices, and vapor release in the atmosphere) rests upon a full understanding of the various mechanisms of ionization of cesium atoms by electrons. Optical-absorption measurements by Kratz[1] have given the series limit in cesium at 3.8926 eV. Electron-beam measurements agree with this value, but are, of course, not as accurate. The efficiency of ionization (in arbitrary units) of the cesium atom by electron bombardment was first measured by Tate and Smith[2] with energies ranging from threshold to 700 eV. They discriminated between singly and multiply charged ions with a mass spectrometer. The absolute magnitude of the cross section was first determined in Brink's[3] crossed-beam experiment, which was followed by more measurements in another apparatus of the same type by McFarland and Kinney.[4] In the crossed-beam experiments, the data were obtained for energies between 30 and 500 eV in steps of 100 eV above 100 eV. These high-energy results were later supplemented by the threshold and low-energy measurements of Heil and Scott[5] (up to 50 eV) and Korchevoĭ and Przonski[6] (up to 25 eV), all of whom used systems in which cesium vapor was in thermodynamic equilibrium with a liquid-phase reservoir.

The ratio between the highest[3,4,6] and lowest[5] cross-section values reported is about a factor of 2. The reasons for this discrepancy are not completely understood. On this basis, we found it desirable to make a new determination of the ionization cross section from threshold to 100 eV in order to get an overlap between the low- and high-energy measurements discussed above.

We used a Tate and Smith[2]-type apparatus modified to include the feature of retarding potential difference[7] (RPD) in the electron gun. The density of cesium atoms in the collision region was measured with a surface-ionization detector[8] and calculated from the formula of Taylor and Langmuir.[9]

The material in this paper is presented in two major sections, one section describing the experimental apparatus and the other discussing the results and comparing them critically with those of other workers.

II. EXPERIMENTAL

A. General

The major components of the experiment were as shown in Fig. 1. The electron gun and ionization region (to be described later) were located in the middle of a vertically hanging tube with a pool of cesium at the bottom. An ionization gauge for measuring background pressure during bakeout and pumping and a surface-ionization detector for determination of cesium density were mounted on the flanges below valve V_1. The vacuum parts were all made from stainless steel and copper. During bakeout, the vertical tube, valves V_1 and V_2, and the VacIon pump to the left were heated to 300°–400°C while pumping was done with the other VacIon pump. Cesium[10] was then evaporated into the pool through a small sidearm (not shown in the illustration). For normal operation the high-vacuum valves were closed, and the "clean" VacIon pump to the left in Fig. 1 acted on the experimental volume through a small-diam copper tubing from the cesium pool. Part of this tube was water-cooled to about 35°C in order to prevent cesium from entering the pump. The temperature of the Cs pool was kept constant to within ±0.05°C

* Supported in part by U.S. Office of Naval Research under Contract No. 5154(00).
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[10] Cesium impurities of consequence in this experiment are: Na—5 ppm, Rb—2 ppm, and K—1 ppm.

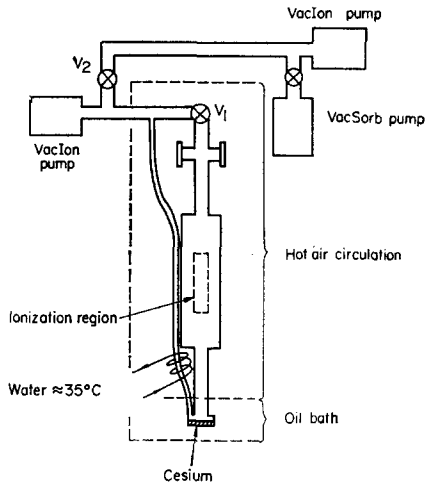

FIG. 1. Schematic diagram of vacuum system and cesium reservoir. Surface-ionization detector and ionization gauge were mounted on the two flanges above the ionization region.

by means of a thermostatically controlled oil bath. Notice that Cs atoms effused out of the lower orifice of the small-diam pumping tube with the temperature T_{Cs} since that part of the tube was immersed in the oil bath. The length immersed was actually helix shaped, thereby making the constant-temperature region much longer than indicated in Fig. 1.

An end vacuum of 10^{-9} torr was easily obtained after the bakeout procedure. The apparatus shown in Fig. 1 could be moved up and down as one unit, facilitating the lowering of the tube into a solenoid. Circulating hot air kept the temperature of the tube and the valve V_1 at about 120°C, thereby avoiding undesirable cold spots where the cesium could condense.

B. Cross-Section Apparatus

The electron gun, depicted in Fig. 2, was constructed according to the RPD principle of Fox *et al.*[7] All electrodes were made from copper. Electrons were emitted from an indirectly heated Philips dispenser cathode of type A. The emission current from this cathode in the presence of cesium was found to be very stable, so that stabilization of the current by electronic means was

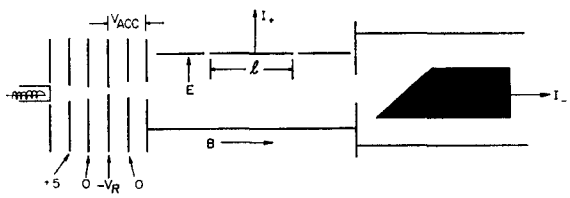

FIG. 2. Cross-section apparatus. The spacing between the electrodes in the gun was 1 mm, the height of the aperture in the retarding electrode 0.2 mm, and the length of the ion collector $l=26.6$ mm. The size of the gaps between this collector and the guard plates is strongly exaggerated. This apparatus was mounted with the axis in the vertical position inside the ionization region in Fig. 1.

unnecessary. The potentials indicated below the gun in Fig. 2 are all with respect to the cathode. All voltages were supplied from batteries. The narrow-slit retarding electrode was at a potential $-V_R$ so that only electrons with energies above V_R could enter the acceleration region and gain an energy V_{acc} before entering the collision region between the parallel plates. A small change ΔV_R in the retarding potential gives a change ΔI_- in the electron current and a corresponding change ΔI_+ in the ion current. If only singly charged ions are produced, the cross section can be determined from the relation

$$\sigma=(\Delta I_+/\Delta I_-)\,(1/Nl), \qquad (1)$$

where N is the cesium atom number density and l is the length of the interaction region. The energy resolution obtained in this mode of operation is better than 0.1 eV, which is sufficient for studying threshold behavior and fine structure on the ionization curve. At higher

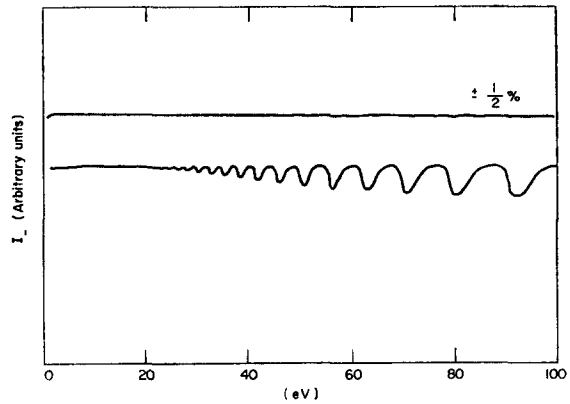

FIG. 3. Electron current I_- as a function of energy before (lower curve) and after alignment (upper curve) in the magnetic field. $B=500$ G.

energies, where no fine structure prevails, the high resolution of the RPD method is not needed. Therefore, for energies above 30 eV we held V_R constant and used the ratio I_+/I_- instead of $\Delta I_+/\Delta I_-$ in Eq. (1).

The potential of the electron collector was made sufficiently high to ensure saturation of electron current at all energies. The high electric field at the collector surface also prevented secondary electrons from entering the collision region. The performance of the electron beam is demonstrated in Fig. 3. After the electron beam was aligned in the magnetic field, the current was independent of energy to within $\pm\frac{1}{2}\%$. Typical electron currents used in this investigation were from 0.1–1 μA.

The ions produced between the parallel plates initially have zero kinetic energy and will move to the upper plates in a proper $\mathbf{E}\times\mathbf{B}$ field configuration. The guard plates on either side of the ion collector establish a uniform electric field $\mathbf{E}$ and accurately define the length l of the collision region. The ion trajectories are

cycloidal, with drift in the direction of $\mathbf{E}\times\mathbf{B}$ and generating radius

$$r_c = M\,|\,\mathbf{E}\,|/(Ze\,|\,\mathbf{B}\,|^2), \qquad (2)$$

where e is the electronic charge and M and Z are the ionic mass and charge numbers, respectively. Since the appearance potential for Cs^{4+} is 113 V, these ions will not be produced within the energy range of this experiment. Hence, as long as half of the parallel-plate separation is less than $2r_c$ (i.e., $d<4r_c$) for $Z=Z_{\max}=3$, complete collection of all ionic species is assured. This requirement was always satisfied in the experiment.

The actual measurement of the ion current I_+ is complicated by cesium deposited on all insulator surfaces, thereby forming a leakage path for the current. By using ceramic insulators and a guard ring around the ion-collector feedthrough, we were able to maintain the leakage resistance of this part above 10 MΩ. This is a factor of 100–1000 higher than the effective input impedance of the Keithley 610 B which was used for the measurement of the ion current.

C. Surface-Ionization Detector

When the mean free path of the atoms is much larger than the characteristic dimensions of the apparatus, Knudsen flow can be assumed and the density $N(T)$ in the interaction region at the temperature T can be found from

$$N(T) = N_0[T_0/(T_{Cs}T)^{1/2}]p(T_{Cs}), \qquad (3)$$

where N_0 is the gas number density at 1 torr at temperature $T_0=273°K$, and $p(T_{Cs})$ is the vapor pressure at the surface of the reservoir which is at temperature T_{Cs}. Since $N(T)\propto T^{-1/2}$, it is more than sufficient to keep the temperature T in the collision region constant to within $\pm 5°K$. On the other hand, the strong dependence of the vapor pressure on temperature requires that T_{Cs} be constant to within $\pm 0.05°K$. (A temperature change $\Delta T_{Cs}=0.1°K$ corresponds to a relative change in density $\Delta N/N\approx 1\%$.)

Experimentally, prudence must be exercised in the application of Eq. (3). First, Knudsen, or molecular flow can only be established when all surfaces are covered with cesium.[11] Some workers[12,13] have reported that this might take many days, especially at surfaces where absorption of atoms will obstruct the specular reflection of atoms that is required in Knudsen's theory. Second, in the literature there is disagreement on the values of the cesium vapor pressure in the range of our experiment. By comparison, we find that the values recommended by Honig[14] and by Hultgren *et al.*[15] are 20%–30% below Nesmeyanov's[16] and Taylor and Langmuir's[9] values. Recently, Rozwadowski and Lipworth[17] made optical-absorption measurements of the density of saturated cesium vapor and obtained results in excellent agreement with those of Taylor and Langmuir. Consequently, we have decided to use the latter values and complement these with our own surface-ionization detector measurements.

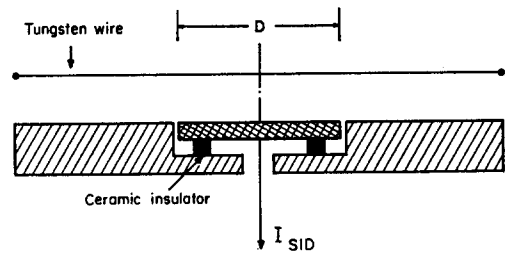

FIG. 4. Surface-ionization detector. The diameter of the wolfram wire was $d_w=1.28\times10^{-2}$ cm and $D=2.44$ cm.

The construction of the surface-ionization detector (SID) is shown in Fig. 4. Above the center of a guarded circular copper plate a hot tungsten wire is stretched parallel to the surface. Positive ions produced over the length D are collected on the central part of the ion collector and give a current

$$I_{SID} = \tfrac{1}{4}eN\langle c\rangle F, \qquad (4)$$

where $\langle c\rangle$ is the average thermal velocity of the cesium atoms and $F=\pi d_w D$. By comparison with another surface-ionization detector equipped with a rectangular collector, we found that all ions generated over the circular collector were measured.

The tungsten wire was aged according to the recommended procedure of Taylor and Langmuir.[8] It was first heated to 2400°K for 24 h. The temperature was then increased to 2600°K for a period of 1 h, after which the wire was given 4–6 short flashes at 2900°K. The filament temperatures were determined from the tables of Jones and Langmuir.[18] When tungsten filaments were treated in this way at background pressures of 10^{-9}–10^{-8} torr, we found, from x-ray-diffraction analysis, a layer of tungsten carbide on the surface. The carbon probably comes from impurities in the volume of the material. Suppliers of tungsten have indicated that all wires contain some carbon, at least 10–15 ppm, because of the fabrication procedure. From measurement of the electron emission as a function of filament temperature we found the work function to

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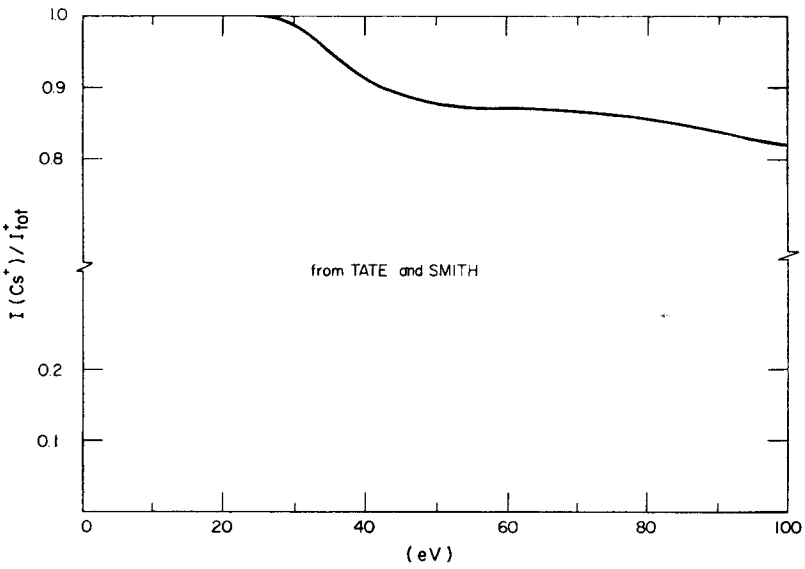

FIG. 5. $I(Cs^+)/I_{tot}^+$ as a function of electron energy as obtained from Tate and Smith (Ref. 2).

about 5.6 V, which is higher than for pure tungsten. When the high-temperature aging took place at much higher pressures (10^{-4}–10^{-5} torr), the x-ray diffraction did not reveal any carbides at all. The explanation of this is probably that carbon at the surface reacts with oxygen to give carbon monoxide. Nevertheless, surfaces with and without carbides gave the same cesium densities when used in surface-ionization detectors.

Absolute measurements of the density of cesium atoms in the vapor phase by means of surface ionization are based on the observation of Langmuir and Kingdon[19] that all atoms leave the surface as ions. (The use of hot wires for density determinations in atomic beams has been studied and discussed by Datz and Taylor[20] and by McFarland and Kinney.[21]) By using Eq. (4) for determination of the density, we found values that agree with those calculated from Taylor and Lanqmuir's formulas[9] to within $\pm 3\%$. A basic requirement for this agreement to occur is that the whole apparatus be in thermodynamic equilibrium with the cesium reservoir. This condition was reached about two weeks after cesium was introduced into the system. The distance between the cesium pool and the top of the tube (about 1 m), combined with the time it takes to cover all surfaces with cesium, accounts for part of the delay. In practice, we found that the density increased very slowly as the equilibrium condition was approached.

D. Consistency Checks

Some of the precautions that must be made in electron-beam ionization experiments have been discussed by Briglia and Rapp[22] and Kieffer and Dunn.[23] First, from Eq. (1) we would expect to find the saturated ion current proportional to the saturated electron current. In cesium this was verified for $0.1 < I_- < 10$ μA. (A test case in helium gave $I_+ \propto I_-$ for $10^{-4} < I_- < 10$ μA.) The collection efficiencies for electrons and ions have already been discussed in Sec. II.B.

Furthermore, proportionality between I_+ and cesium density was found over the density range 5×10^{10}–10^{12} cm^{-3}. At the highest density of 10^{12} cm^{-3}, the electron mean free path is $\Lambda = (n\sigma)^{-1} \approx (10^{12}\times10^{-15})^{-1} = 10^3$ cm, which is much longer than the length l of the interaction region in Fig. 2. Therefore, even at the highest density used, the probability of one electron producing more than one ionization event is negligible.

Beam electrons with perpendicular velocity components will travel in helices parallel to the magnetic field. The path length along one particular helix is, of course, larger than the length l as defined in Fig. 2. Corrections must therefore be made to determine the true path length. Unfortunately, the formula presented by Massey and Burhop[24] is inapplicable to most practical guns, as pointed out by Asundi.[25] In our electron gun the electric lens configuration[26] tends to minimize the perpendicular velocity-beam component and the corresponding increase in path length. Since the increase in path depends strongly on the magnetic field, the best way to check the constancy of the ionization length is to measure I_+/I_- as a function of B, keeping all voltages constant. We found I_+/I_- to be constant for the range of parameters used in the experiment.

Finally, we checked that the current of stray electrons to the entrance and exit electrodes in the ioniza-

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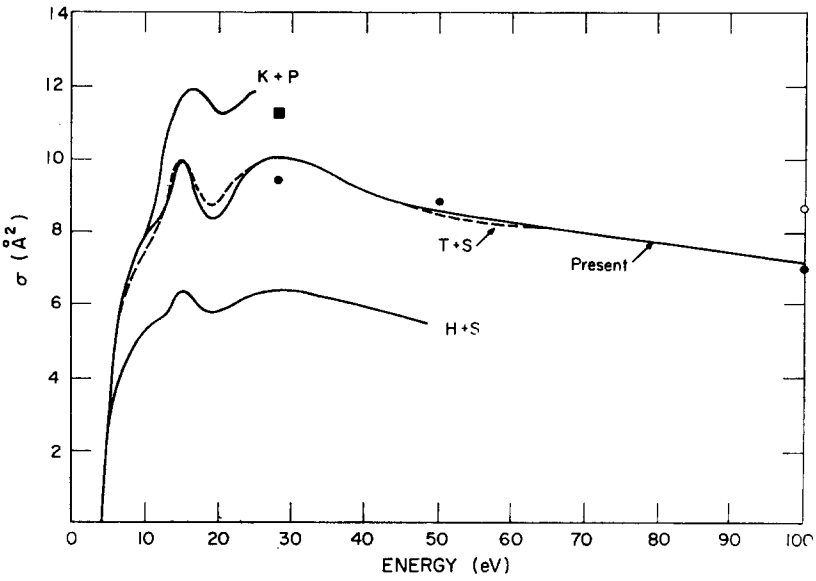

FIG. 6. Ionization cross section for Cs^+ vs electron energy. The fulldrawn curve extending to 100 eV represents the present measurements. Legend: H+S, Heil and Scott (Ref. 5); K+P, Korchevoĭ and Przonski (Ref. 6); T+S, Relative measurements of Tate and Smith (Ref. 2) normalized to the present maximum at 28 eV; ■, Brink (Ref. 3); ●, McFarland and Kinney (Ref. 4); ○, McFarland (Ref. 28).

tion region and to the lower parallel plate was 1000 times smaller than the beam current. Stray electrons were not detected on the ion collector.

Because of the contact potential difference between the retarding electrode in the gun and the collision region the energy scale needs to be calibrated. For this purpose we let helium into the tube together with the cesium and measured the resonance[27] in the elastic scattering cross section at 19.3 eV. The resonance shows up as an increase in transmitted electron current. The other point on the energy scale was taken at the appearance of Cs^+ ions at 3.89 eV. In addition, we plotted the electron-beam current as a function of energy and extrapolated the current to zero[22] to find the contact-potential difference between the collision region and the retarding electrode. All methods gave the same correction of 0.8 V, which includes the contact potential difference in the tube as well as contributions from the leads between the tube and the voltmeter.

A spread in energy in the electron beam arises from thermal spread of electrons leaving the cathode surface and from possible nonuniform distribution of contact potential on electrode surfaces. If the cathode temperature is T_c, the average energy of the emitted electrons is $2kT_c$. The Philips impregnated cathode in our electron gun was operated at about 800°K, corresponding to an average thermal energy of 0.14 eV. By measuring the tail in ion current at threshold we found a spread of 0.07 eV. In addition, a retarding potential measurement of the current to the electron collector resulted in a spread in energy (defined as the full half-width) of 0.1 eV. This spread was independent of the beam energy.

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III. RESULTS AND DISCUSSION

A. Data Analysis

The ion current measured on the collector of our total ionization apparatus is

$$I_{\text{tot}}^+ = I(Cs^+) + I(Cs^{2+}) + I(Cs^{3+}) + \cdots, \quad (5)$$

where the current of Cs^{k+} ions is

$$I(Cs^{k+}) = I_- knl\sigma(Cs^{k+}) \quad (6)$$

and $\sigma(Cs^{k+})$ is the cross section for removing k electrons from the atom. We determined the current of singly ionized atoms by multiplying the measured ion current with the ratio

$$R = I(Cs^+)/I_{\text{tot}}^+.$$

This ratio is identical with the correction factor $[\sum k\alpha_k]^{-1}$ used by Brink,[3] where

$$\alpha_k = \sigma(Cs^{k+})/\sigma(Cs^+).$$

From a careful analysis of Fig. 3 in Tate and Smith's[2] original paper, we obtain the current ratio shown in Fig. 5. According to Tate and Smith the ionization curve for Cs^+ might be 15% too low due to incomplete collection of ions. It should be noted that the Tate and Smith ordinates as presented in their paper can be interpreted in different ways. As will be shown later, different interpretations will give different results for the Cs^+ cross section.

B. Compilation of Results

Absolute data for the Cs^+ cross section as a function of electron energy are shown in Fig. 6. The curve in the middle represents the present measurements. All curves pertain to experimental systems in which cesium vapor

was in supposed thermodynamic equilibrium with a liquid-phase reservoir. Korchevoĭ and Przonski[6] used the cylindrical-collector arrangement developed by Schulz,[28] whereas Heil and Scott[5] modified the Tate and Smith apparatus by depositing the ion collector and guard ring on the inside of a glass tube. The points represent crossed-beam experiments by Brink[3] and by McFarland and Kinney.[4] If McFarland and Kinney take the Tate and Smith ordinates as probabilities of ionization, they get the filled circles as values for the cross section. On the other hand, if the Tate and Smith ordinates are interpreted as ion currents proportional to $k\sigma(Cs^{k+})$, the higher values indicated by the open circles[29] are obtained. No energy values have been assigned to the maximum cross sections reported by Brink[3] and McFarland and Kinney.[4] From the shape of the cross-section curves we see that a rather flat maximum occurs at 28 eV. Accordingly, the maximum points from the crossed-beam experiments have been plotted at this energy. At maximum (filled circle at 28 eV) the probability of ionization is approximately equal to $I(Cs^+)/I_-$, since very few Cs^{++} ions are produced at this energy. The McFarland and Kinney value at maximum is therefore insensitive to interpretation of the Tate and Smith paper.

Our results seem to coincide with those of Korchevoĭ and Przonski[6] for energies up to about 10 eV. Differences in initial slope are not discernible because of the scale used in Fig. 6.

It is interesting to normalize the curve of Tate and Smith[2] to ours at 28 eV and compare the shape of the cross-section curves. The total ion current I_{tot}^+ as reported by Tate and Smith and remeasured here falls off almost linearly by $\frac{1}{2}\%$ per eV from 28 to 100 eV. Since we are using the ratio of $I(Cs^+)/I_{tot}^+$ from Tate and Smith, it is not surprising to find good agreement in this energy range. We notice that the minimum at about 19 eV is 13% below the maximum on the Tate and Smith curve and 17% below on ours. In Heil and Scott's work,[5] the "dip" on the curve is about 10% of the maximum. With low electron currents (0.1–0.5 μA) in our experiment the magnitude of this dip was independent of current. However, at higher beam currents (1–5 μA) the dip decreased in magnitude, presumably because higher currents cause a large spread in energy.

Part of the disagreement between the various results can be understood by analyzing the experimental techniques. Since Korchevoĭ and Przonski[6] had no guard rings outside their ion collector, the effective length of the collision region is larger than l, thereby increasing the apparent value of the cross section.

The lowest cross-section values have been obtained by Heil and Scott.[5] In this experiment there might have been a systematic error in the determination of the cesium density, as discussed by McFarland,[29] or the apparatus might not have been in complete thermodynamic equilibrium.

Basic difficulties in crossed-beam experiments are the measurements of the cesium atom density and the determination of the interaction volume. Brink[3] and McFarland and Kinney[4] were using different experimental systems with different geometry factors. In spite of complicated calibration procedures, their results agree within the experimental accuracy, which lends confidence to the reliability of this type of experiment. In addition, the crossed-beam experiment has the advantage that insulators can be shielded from the cesium flux, thereby eliminating the leakage current problem prevailing in vapor-phase systems.

The accuracy of the present data is about 7%. However, the high-energy part of the curve might be too low due to a systematic error in the correction factor $I(Cs^+)/I_{tot}^+$. It should be noted that the systematic error in the work of Tate and Smith might be energy dependent. Since McFarland[4] and Heil and Scott[5] have been using the same correction factor, the systematic error is also inherent in their results. Korchevoĭ and Przonski[6] avoided this ambiguity by limiting their measurements to the range below the second ionization potential.

C. Ionization Mechanisms

In electrical discharges, atoms are ionized by the electrons on the "tail" of the electron-energy distribution, and for this reason it is important to know the initial slope of the cross section. A linear threshold law for ionization of hydrogen has been predicted by Geltman,[30] Rudge and Seaton,[31] and Kang and Foland.[32] It is reasonable to assume that the same law also applies to the removal of the 6s valence electron of cesium. It has been suggested by Temkin[33] that the asymptotic form of the wavefunction that was used by Rudge and Seaton is inadequate and therefore invalidates the linear threshold law. A nonlinearity would occur within 0.1 eV from threshold, where accurate measurements are difficult to obtain. In many experiments linearity has been found over a range of approximately 1 eV, as shown in Table I. Normalization of Tate and Smith's results[2] to other absolute measurements is considered arbitrary and is therefore not included in Table I. The measurement of Nottingham[34] was made in an electrical discharge in which accurate knowledge of the parameters needed to determine the cross section is difficult to establish. It is surprising to observe that Korchevoĭ and Przonski,[6] who reported the highest

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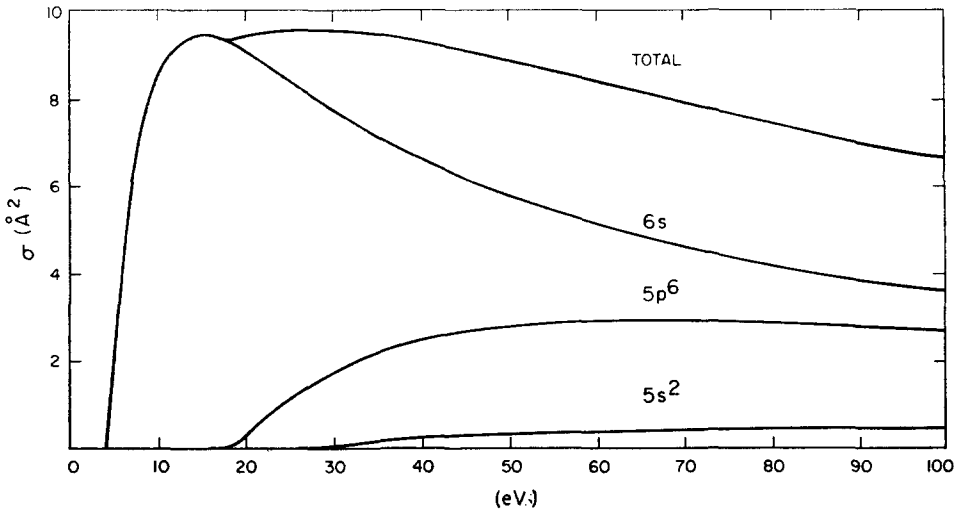

FIG. 7. Cross sections calculated from the Gryzinski formula (Ref. 34)

$$\sigma_i = (\sigma_0/U_i^2)x^{-1}[(x-1)/(x+1)]^{3/2}\{1+\tfrac{2}{3}[1-(2x)^{-1}]\ln[2.7+(x-1)^{1/2}]\},$$

where $x=U/U_i$, and $\sigma_0=6.56\times10^{-14}$ (eV^2·cm^2). We have used $U_i=3.89$, 17.2, and 26 eV for removal of $6s$, $5p$, and $5s$ electrons, respectively. (See McFarland, Ref. 36.) The total cross section $\Sigma_i\sigma_i$ is for the electron configuration $5s^25p^66s$.

maximum cross section among the workers quoted here, obtained the lowest value of the slope, 1.7 Å^2/eV. Since they do not state the range of linearity, there is a slight possibility that because of insufficient energy resolution their number refers to the tailing part of the ionization curve. It has been mentioned already that the maximum of our cross section agrees closely with the results of the crossed-beam experiments, and for this reason we recommend our value of 2.7 Å^2/eV for the slope.

The initial slope of the cross-section curve in hydrogen has been calculated[32] and compared with experimental data. Unfortunately, similar calculations for cesium are not easily available. The Gryzinsky cross section[35] behaves as $(U-U_i)^{3/2}$ at threshold, which is not correct, but very quickly ($U-U_i\approx0.04U$) converts to linear behavior as predicted by quantum mechanics.[30–32] An estimate of the slope from Gryzinsky's formula (see Fig. 7) gives a value of approximately 2 Å^2/eV, which is in good agreement with the lowest experimental values in Table I.

TABLE I. Threshold behavior of ionization cross section.

Author(s)	Slope (Å^2/eV)	Range of linearity above threshold (eV)
Present work	2.7	≈1
Heil and Scott[a]	2.2	0.8
Korchevoĭ and Przonski[b]	1.7	unknown
Nottingham[c]	5.7	≈1.5

[a] Reference 5.
[b] Reference 6.
[c] Reference 34.

As a first attempt to explain the structure (including the two maxima) of the cross-section curve, we have calculated the partial cross sections for removal of $6s$, $5p$, and $5s$ electrons using the Gryzinsky[35] formula (Fig. 7). The inclusion of ionization of core electrons[36] gives a maximum total cross section that agrees very closely with the present experimental result. Most conspicuous is the 2% dip on the Gryzinsky curve, as compared to a value of 17% in the experiment. Furthermore, the energies at which the first maximum and the dip occur in Figs. 6 and 7 do not correspond. We therefore conclude that ionization of valence and core electrons does not provide a complete explanation for the structure of the ionization curves, and that additional mechanisms are needed. (Similar types of structure have also been observed on the ionization curves of Rb^+,[2,3] K^+,[2,3,37] and Mg^+.[37])

It has been suggested by Heil and Scott that the sharp first peak is due to autoionization with a partial cross section for this process of about 1 Å^2. Our data indicate a value of about 1.6 Å^2. Interpreting the first peak in this way implies the existence of a doublet autoionization level (spin$=\frac{1}{2}$) at about 12 eV above the Cs^+ ground state. Feldman and Novick[38] have observed a quartet (spin$=\frac{3}{2}$) autoionization level at 12.6±0.3 eV. Their state is metastable (with lifetime about 40 μsec) because it cannot make a dipole transition to the singlet

[35] M. Gryzinsky, *Atomic Collision Processes*, M. R. C. McDowell, Ed. (North-Holland Publ. Co., Amsterdam, 1964), pp. 226–236. [Notice that the value of σ_0 in Eq. (4) of this reference is a factor of 100 too low.]

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(spin=0) continuum states. However, the presence of a quartet state at this energy strongly suggests that there is also a doublet state very near in energy, for instance with the $6p^5 6s^2$ electron configuration proposed by Beutler and Guggenheimer.[39] Therefore, attributing the first peak to autoionization is probably justified. The cross section for excitation of the doublet autoionization level is expected to be larger than for excitation of the quartet metastable level because the latter requires a spin change of the $5p$ core electron of the cesium atom. This is consistent with Feldman and Novick's values[38] of the cross section as 10^{-2}–10^{-3} Å^2 for quartet excitations and our observation of about 1.6 Å^2 for the doublet excitation. Notice that the lifetime of the doublet state is too short to be detected in the time-of-flight-type experiment of Feldman and Novick.

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In conclusion, it should be pointed out that the ionization mechanisms of the cesium atom are not completely understood. Experimentally, one can get information about autoionization by studying the kinetic energy (12.6–3.9=8.7 eV) of the electron ejected from the autoionizing level. This will be the objective of another investigation.

ACKNOWLEDGMENTS

The author is indebted to Dr. W. D. McBee, Manager of the Radiation and Information Sciences Laboratory, for the interest he has shown in this project. He also wishes to thank many of his colleagues, in particular Dr. P. M. Stone, presently at the University of Pittsburgh, for discussions and comments on the manuscript. It is a great pleasure to thank Mr. P. J. Engel and Mr. G. H. Parsons for construction of the apparatus and Mr. K. R. Gordon for assistance in the laboratory.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 5 1 SEPTEMBER 1968

Use of Green Functions in Atomic and Molecular Calculations. II. The Green Function of the Helium Atom*

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(Received 8 April 1968)

We derive an analytical expression for the Green function of the helium atom, that is to say for the helium atom where the electron repulsion term (e^2/r_{12}) has been neglected. It is outlined that this Green function may be used as a basis for a numerical iterative procedure to derive the exact eigenfunctions of the helium atom.

I. INTRODUCTION

In the first paper of this series[1] we have shown that the Schrödinger equation for an atom or molecule may be transformed to an integral equation by introducing the Green function. In particular, we have shown that perturbation calculations are conveniently performed by making use of this Green function. As an example we derived the second-order perturbation energy of a hydrogen atom, perturbed by a point charge λ.[2]

In the present paper we wish to investigate the possibility of deriving the eigenfunctions and eigenvalues of the helium atom by means of the Green function techniques. In particular, we derive an analytical expression for the Green function that is needed for such a treatment.

The Hamiltonian of the helium atom and of the analogous helium-type atoms is given by

$$\mathcal{H}=-(\hbar^2/2m)(\Delta_1+\Delta_2)-Ze^2(r_1^{-1}+r_2^{-1})+(e^2/r_{12}). \quad (1)$$

We rewrite this Hamiltonian by introducing the unit of length a_0 and the unit of energy ϵ_0, which are defined as

$$a_0=\hbar^2/me^2Z, \qquad \epsilon_0=-Ze^2/2a_0. \quad (2)$$

The Hamiltonian becomes then

$$H=\Delta_1+\Delta_2+2(r_1^{-1}+r_2^{-1})-(2/Zr_{12}), \quad (3)$$

and we write it as

$$H=H_0+\lambda W,$$
$$H_0=\Delta_1+\Delta_2+2(r_1^{-1}+r_2^{-1}),$$
$$W=1/r_{12}, \qquad \lambda=-2/Z. \quad (4)$$

It is readily seen that we can transform the Schrödinger equation of the helium atom to an integral equation where the perturbation is the term W of Eq. (4) if we can derive the Green function of the operator H_0. In this paper we discuss the evaluation of this Green function.

The Hamiltonian H_0 may be written as a sum

$$H_0=H_0(1)+H_0(2)=(\Delta_1+2r_1^{-1})+(\Delta_2+2r_2^{-1}). \quad (5)$$

We have seen in I that each operator $H_0(i)$ has a set

* This research was supported by the Advanced Research Projects Agency and by the National Science Foundation.
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