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Production of Metastable Ions in Cesium-Atom-Electron Collisions*

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The structure in the total electron-impact ionization cross section in cesium can be partially accounted for by the mechanisms of autoionization and excitation ionization of $5p$ electrons. For electron energies above 17 eV a large fraction of the ions are metastable and can de detected by Auger emission from a metal surface. The experiment was performed in a cesium-atom–electron crossed-beam apparatus, and the metastable ions were counted with a channel electron multiplier. The metastable-ion count rate was a factor of 100 higher than that due to photons from atomic and ionic transitions. We have measured the over-all excitation function for a number of unresolved Cs^+ metastable levels, the lowest being $5d\{[3\frac{1}{2}], 3\}$ at 17.02 eV and $5d\{[\frac{1}{2}], 1\}$ at 17.06 eV.

I. INTRODUCTION

In recent years technological developments in the fields of plasma physics,[1] astrophysics,[2] laser physics,[3] and energy-conversion devices[4] have resulted in a number of investigations of the ionization cross section for cesium.[5-11] Figure 1 is a summary of reported Cs ionization cross sections by electron impact. In all of the curves, we notice a sharp onset at 3.9 eV followed by two maxima around 15 and 28 eV.[12] The initial onset is due to the removal of $6s$-valence electrons in a direct impact, i.e.,

$$\mathrm{Cs}(5p^6 6s) + e \rightarrow \mathrm{Cs}^+(5p^6) + 2e\,. \tag{1}$$

The structure peaked around 15 eV is a result of autoionization in Cs. We have previously reported on the significance of autoionization in the total ionization cross section of cesium,[13] which results from excitation of $5p$ electrons followed by electron emission in a nonradiative transition. A typical example discussed in our earlier paper is

$$\mathrm{Cs}(5p^6 6s) + e \rightarrow \mathrm{Cs}^*(5p^5 6s^2) + e \rightarrow \mathrm{Cs}^+(5p^6) + e + e(\mathrm{Auger})\,. \tag{2}$$

In reaction (2) the ejected Auger electron carries off the excess energy from the doubly excited state. The lifetime of the intermediate excited state Cs* may be as short as 10^{-14} sec or as long as 10^{-4} sec.[14]

The broad maximum around 28 eV has been attributed to removal of inner-shell electrons by mechanisms different from autoionization.[5,8-10,13] The objective of the present paper has been to study the production of metastable cesium ions and how it contributes to the second maximum. The generation of metastable ions by electron impact of ground-state atoms is exemplified in

$$\mathrm{Cs}(5p^6 6s) + e \rightarrow (\mathrm{Cs}^+)^m + 2e\,, \tag{3}$$

where m symbolizes a metastable species. Another possibility is the excitation of a short-lived excited ion, i.e.,

$$\mathrm{Cs}(5p^6 6s) + e \rightarrow (\mathrm{Cs}^+)^* + 2e\,, \tag{4}$$

where the reaction product will decay by photon emission to lower states, which may include the metastable states discussed above.

The apparatus used in this investigation consists of a Cs atomic beam intersected at 90° by an electron beam and a channel electron multiplier (Channeltron[15]) for detecting ions and emitted photons. Since the Channeltron counting efficiency was found to be selectively higher for the metastable ions than for ground-state ions or photons, an "onset" in the region of the two lowest metastable states could be explained. The electron energy range studied was 3–45 eV, and the energy resolution of the electron beam was about 0.2 eV.

In the following section we discuss the energy levels of Cs II. The apparatus is described in Sec. III, and the results are presented and discussed in Sec. IV.

II. Cs II ENERGY LEVELS

Energy levels of Cs II were first studied by Wheatley and Sawyer[16] using a spark spectrograph, and many of the lines were classified. The results of this and some of the later studies have been summarized by Moore.[17] To our knowledge, the lifetimes of the resonance lines in Cs II have not been reported in the literature. However, the corresponding lines in Xe I are known to be of the order of 10^{-8} sec.[18] Another method yielding information on the resonance lines of Cs II has been to slow down fast cesium ions in targets of He, Ne, and Ar.[19-21] The present paper represents a first attempt to study metastable cesium ions

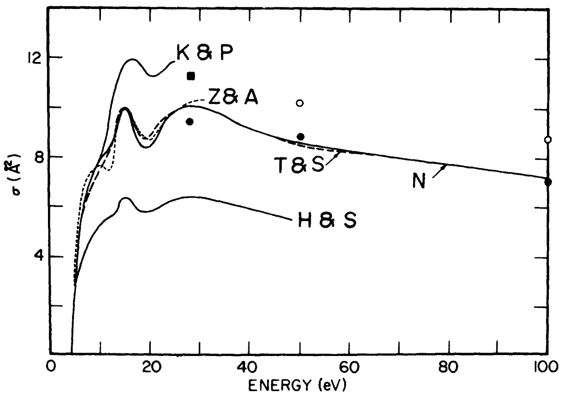

FIG. 1. Compilation of cross-section data for production of Cs^+ ions from cesium by electron impact. H & S, Heil and Scott (Ref. 7); K & P, Korchevoi and Przonski (Ref. 8); T & S, relative measurements of Tate and Smith (Ref. 24) normalized to the absolute measurements of Nygaard (Ref. 10); N, Nygaard (Ref. 10); Z & A, Zapesochnyi and Aleksakhin (Ref. 9); closed square, Brink (Ref. 11); closed circle, McFarland and Kinney (Ref. 5); open circle, McFarland (Ref. 6).

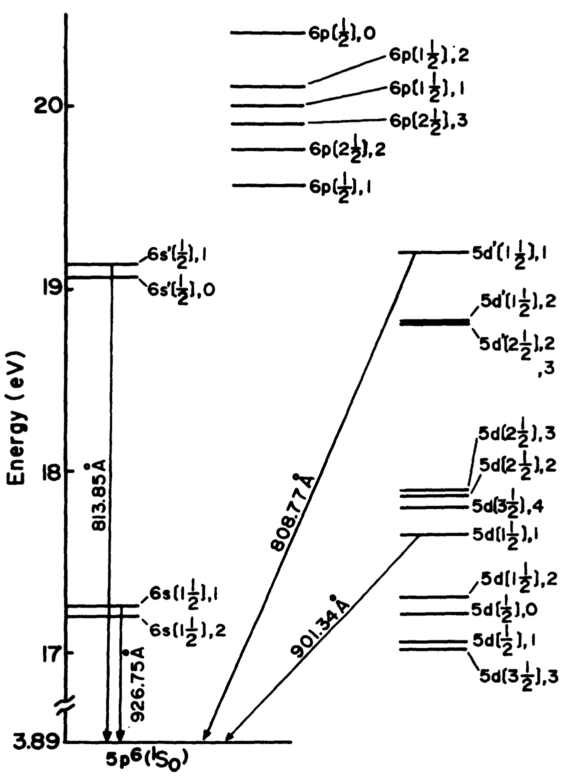

FIG. 2. Simplified Cs II term diagram. All of the lower-lying levels between 3.89 and 21 eV are included. The arrows indicate resonance transitions with respective wavelengths.

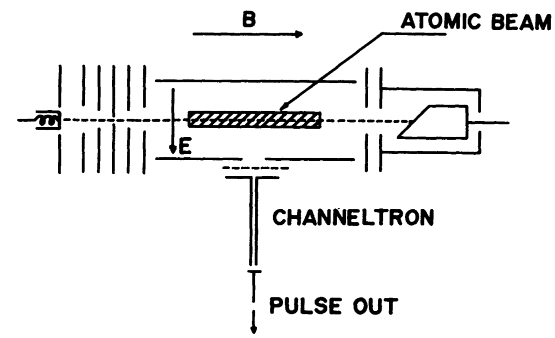

FIG. 3. Total ionization apparatus with channel electron multiplier for detection of Cs^+ ions. The direction of the atomic beam is perpendicular to the plane of the paper. The atomic beam, electron beam, and ion extraction field are orthogonal to each other.

produced by electron impact of ground-state cesium atoms.

In Fig. 2 are shown some of the lower excited states of the Cs^+ ion.[22] The numbers following the electron configuration of each level are K and J values of the respective state. According to the Racah scheme[23] for electron coupling,

$$\vec{K} = \vec{J}_p + \vec{l}_e \tag{5}$$

and

$$\vec{J} = \vec{K} + \vec{s}_e \; , \tag{6}$$

where $\vec{J}_p$ is the total angular momentum of the core, and $\vec{l}_e$ and $\vec{s}_e$ are the orbital and spin angular momentum of the external electron, respectively.

In the case of Cs^+ ionic levels, it has been reported[17] that there are no exceptions to the transition rule for the J values, namely, $\Delta J = 0$ or ± 1, except that $J=0$ to $J=0$ is forbidden. Transitions from $5d\{[\frac{1}{2}], 1\}$ to $^1S_0$ might be expected, but have never been observed, neither in Cs II nor in the similar Xe I system. The reason for this discrepancy is not completely understood, but the same type of anomaly has also been noted in Ar I.[17]

III. EXPERIMENTAL ARRANGEMENT

We have studied excited ionic states of cesium in a Tate-Smith-type[24] total ionization apparatus modified to incorporate an atomic beam and a Channeltron (Fig. 3). The ions produced are expelled from the interaction region by a transverse electric field and counted by a Channeltron. Magnetic fields of about 200 G were used to collimate the electron beam. The system background pressure was better than 5×10^{-9} torr.

The electron gun shown to the left in Fig. 3 is of the retarding potential difference (RPD) type developed by Fox *et al.*[25] It consists of an indirectly heated cathode and five acceleration and control electrodes. Typically, the electron-beam current was kept within 10^{-7}–10^{-8}A to avoid space-charge effects. The zero point on the energy scale was found from the sharp onset of the electron-beam current at low acceleration voltage and from retarding the electron beam in front of the electron collector. For sufficiently low beam currents, the zero point on the energy scale was found to be independent of the magnitude of the current. Other points on the energy scale were compared with known levels in the autoionization spectrum.[13]

The effect of the helical path of the beam electrons in the collimating magnetic field has been discussed by Massey and Burhop.[26] In the present experiment we were limited to magnetic fields below 200 G in order for the Channeltron to operate properly. Even under this condition the increase in path length for the beam electrons was found to be negligible. Unfortunately, for magnetic fields below 200 G the electron-beam energy resolution was about 0.2 eV, as compared to 0.1 eV at a magnetic field of 700 G. In all cases, the energy spread was determined from the retardation measurements discussed above.

The cesium atomic beam was formed in a linear array of parallel capillaries,[27] each of length 10 mm and inside diameter 0.12 mm. The electron beam was aligned in such a way that it was completely immersed in the atomic beam, and the length of the interaction region was 25 mm. The Cs density in the collision region was 10^{10}–10^{11} atoms per cm^3. It was monitored by measuring the cesium-ion current at a given electron energy and determined by comparison with the absolute ionization cross sections measured by Nygaard[10] in a vapor cell apparatus. In addition, it was measured in the new crossed-beam apparatus with a surface ionization detector.[28] The result of the two methods agreed to within ±5%. The stability of the cesium beam density was excellent, typically constant to within less than 1% over a single data run lasting 100 min.

The Channeltron was located under the ion collector plate in the collision chamber looking into a reaction region through a rectangular hole of 4×1 mm^2. Its input end was operated at a negative potential with respect to the interaction region to prevent any stray electrons from hitting it and also to accelerate ions. The background count rate for a new multiplier was about 1 count/sec, increasing gradually to about 50 counts/sec after about 200 h, due to cesium exposure. An extensive study of Channeltron operating characteristics in magnetic fields has been carried out independently.[29] It was found that the Channeltron exhibited a sufficiently high gain at 200 G when the applied voltage was increased to 4000 V. The long-term stability of the amplification was very good as verified from the reproducibility of the data. The output pulses were amplified and analyzed in a discriminator with lower threshold adjusted to eliminate background counts in the absence of the electron-beam current. The ion count rate was not sensitive to the discriminator setting, since the spread in pulse-height amplitudes for our Channeltron operating in the saturated mode was found to be less than 50% full width at half-maximum (FWHM).

IV. RESULTS AND DISCUSSION

In our apparatus, the transit time for the ions to move from the production region to the detecting surface was about 15 μsec. Hence, excited ions with lifetimes less than this value will have decayed to the ion ground state before arriving at the detector. For comparison, it should be

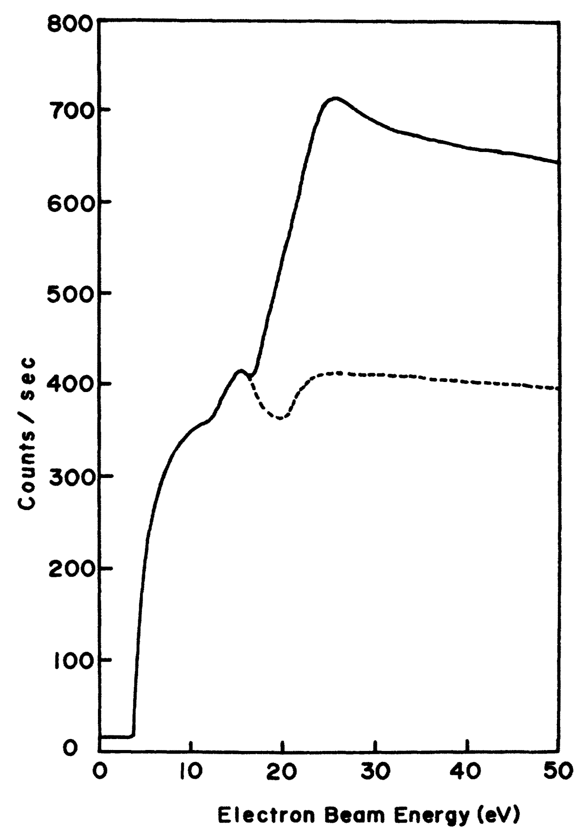

FIG. 4. Cs^+ ion counts vs electron-beam energy (solid line). The dotted line represents the total ion current as measured with an electrometer. The ion count rate was normalized to the total ion current at 15 eV. The electron current was 4×10^{-8} A and the cesium density was 2×10^{10} cm^{-3}.

noted that the lifetimes of excited ions decaying by dipole transitions are of the order of 10^{-8} sec.[18] Typically, the total count rate due to photons and ions (ground state and metastable) was a factor of 100 higher than the net photon count rate under identical experimental conditions. The photon contribution can easily be subtacted from the total, but was usually ignored.

We have been using this method to study the production of both ground-state and metastable cesium ions. A characteristic measurement is shown in Fig. 4 (solid line). It is of interest here to compare this observation with the ionization curve obtained by measuring the total ion current to one of the parallel plates (similar to Tate and Smith[24]) with an electrometer (dotted line). These two *independent* measurements have been normalized to the autoionization peak at 15 eV, and agree in shape to within ±2% from threshold to about 17 eV. Above 17 eV the ionization curve obtained from ion counting rises above the classical current measurement. We ascribe the difference to production of metastable ions, and will in the following discuss this effect in more detail.

One of the major advantages of total ionization measurements using the method of Tate and Smith is that both ground-state and excited ions of identical charge contribute equally to the total ion current I^+_{tot} , provided that sufficient care is taken to suppress secondary electrons. Multiply charged ions will be measured according to

$$I^+_{tot} = \sum_{Z=1}^{Z_{max}} Z I^{Z+} , \qquad (7)$$

where the charge number Z_{max} depends on the energy of the bombarding electrons. Unfortunately, this is not the case in ion counting experiments since the production of secondary electrons by ion impact on a metal surface depends on both the kinetic and internal energy of the ions.

In the present apparatus, when a metastable ion hits the detecting surface, it will be detected with a higher probability because of its higher value of the secondary emission coefficient η^M_+ as compared to the value η_+ for ground-state ions. Therefore, the total count rate can be written as

$$N = n_0(I_-/e)G(\eta_+\sigma_+ + \eta^M_+\sigma^M_+ + \eta_{++}\sigma_{++}) , \qquad (8)$$

where G is a known geometrical factor common for both ground-state and metastable ions, and σ_+ and σ^M_+ are the corresponding cross sections for production of these species. The last term in Eq. (8), $\eta_{++}\ \sigma_{++}$, describes the production and detection of Cs ions above the second ionization potential at 29 eV. We have neglected the contribution due to photons, as justified earlier.

By taking the difference between the normalized count rate and ion current measurements we obtain information on the excitation curve for production of metastable ions. The result of this procedure is shown in Fig. 5, and represents the sum of direct excitation and cascading into the lower metastable levels. The very sharp onset at 17 eV is in excellent agreement with the energy of the lowest metastable states of Cs^+, $\{5p^5 5d[3\frac{1}{2}], 3\}$ at 17.02 eV and $5p^5 5d\{[\frac{1}{2}], 1\}$ at 17.06 eV. The general shape of the excitation curve (Fig. 5) resembles closely that of triplet excitation curves,[30] although one has to be very careful distinguishing between singlet and triplet series in the complex Cs II system.

By comparing the ion count with the ion current measurements for energies below 17 eV, the product $G\eta_+$, which enters in Eq. (8), can be determined. If we estimate σ^M_+ to be of the order of 10^{-16} cm^2 and $\sigma^+ \simeq 10^{-15}$ cm^2,[10] we obtain $\eta^M_+/\eta_+ \simeq 10$. One reason for the apparently high value of η^M_+ might be that excitational energy is transferred more efficiently to the surface than translational energy. This effect has been studied by Hagstrum[31] for rare-gas ions, both ground state and metastable, incident on clean and contaminated tungsten surfaces. The difficulty in this kind of investigation is to detect metastable ions in a high background of ground-state ions. However, for electron-beam energies above the onset for metastable-ion production, there is a pronounced increase in the production of secondary electrons

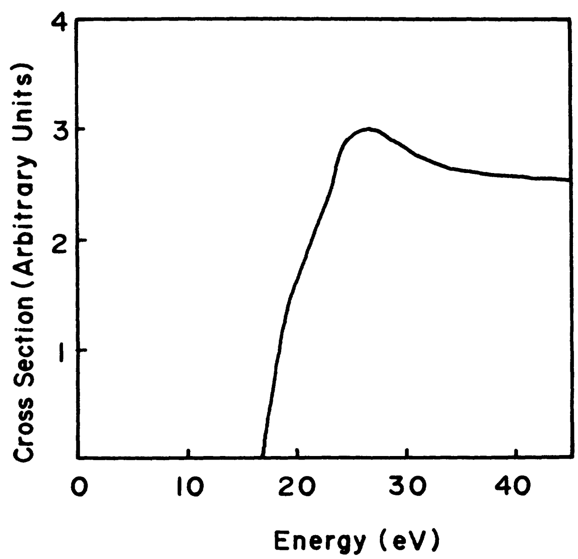

FIG. 5. Relative excitation cross section for metastable-ion production. The curve was obtained by taking the difference between the normalized ion count rate and the total ion current in Fig. 4.

at the surface.

This phenomenon can be better understood by introducing the concepts of potential and kinetic emission of electrons, as discussed and reviewed by Kaminsky.[32] The total secondary-emission coefficient can be written as

$$\gamma = \gamma_{pot} + \gamma_{kin} , \qquad (9)$$

where the two terms on the right-hand side of Eq. (9) refer to the processes mentioned above. For Cs^+ ions in their ground state, $\gamma \simeq \gamma_{kin}$, since the ionization potential I is less than the work function ϕ. This argument is further substantiated by the fact that $\gamma = 0$ for ion energies below a certain threshold value E_{th}. It appears from Fig. 14.3.1.1.2.a in Ref. 32 that $\gamma_{kin} \simeq 0.01$ for ground-state Cs^+ ions of energy 1 keV. No data are available below this energy.

Whereas the kinetic ejection is completely governed by the kinetic energy of the incident particle, the potential ejection, as implied by the name, depends on the state of excitation of the incident particle. Hence, for metastable ions with kinetic energy $E < E_{th}$, one would expect $\gamma \simeq \gamma_{pot}$. Unfortunately, this phenomenon has not been studied for metastable Cs^+ ions, but by making comparison with heavy noble gases[31] we arrive at a rough estimate of $\gamma_{pot}(Cs^{+M}) \simeq 0.1$. Taking the ratio $\gamma_{pot}(Cs^{+M})/\gamma_{kin}(Cs^+)$, we obtain a value of about 10 at an ion kinetic energy of 250 eV. This finding is in reasonable agreement with $\eta_+^M/\eta_+ \simeq 10$, which was arrived at above from

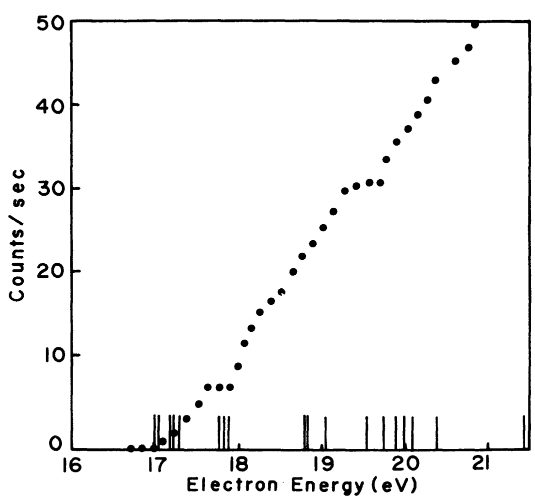

FIG. 6. Metastable-ion count rate vs electron-beam energy near threshold. Vertical lines are the levels of Cs II. The four levels decaying by emission of resonance radiation (see Fig. 2) are not included. Excited states above 19.5 eV decay to one of the lower states followed by production of either vacuum-ultraviolet photons or metastable ions.

analysis of our experimental data.

If the ion energy is reduced from 250 to only 50 eV, we have experimental evidence that $\gamma_{kin} \rightarrow 0$, i.e., $\gamma \simeq \gamma_{pot}$. We have taken advantage of this effect to study the threshold behavior for production of metastable ions, as shown in Fig. 6. Notice that the count rate is zero for electron energies below 17 eV, which means that the ground-state ions are not detected at all. The total count rate is due primarily to ions, with the photon count amounting to less than 1% of the total. The lowest metastable states in Cs II are $5p^5 5d\{[3\frac{1}{2}], 3\}$ at 17.02 eV and $5p^5 5d\{[\frac{1}{2}], 1\}$ at 17.06 eV. Within the limits of the experimental resolution and accuracy of the energy scale, a positive identification of the lowest level could not be made. For energies above the threshold values of 17.02 and 17.06 eV, the count rate does not increase uniformly with electron energy, but shows some very characteristic discontinuities. The plateaus observed in Fig. 6 below 18 eV and at about 19.5 eV can only be explained by some competing process. As a possible mechanism we suggest the existence of negative-ion states, since such states have been capable of explaining structure on ionization curves in the noble gases.[33] Manson[34] has suggested that the very characteristic minimum in the total ionization cross section in cesium[7-10] can be accounted for by such states. There are indications from our observations that such levels appear at 17.6 ± 0.2 and 19.3 ± 0.2 eV. The first of these levels is interestingly close to an unidentified structure at 17.95 eV that we observed in a previous investigation on autoionization[13] using the trapped-electron method of Schulz.[35]

Another possibility for explaining the structure on the metastable-ion production curve is the onset of additional metastable excitation coupled with turnover of excitation of lower states. With a counting statistics of ±1 count/sec for each data point combined with an electron energy distribution of 0.2 eV, a final conclusion relative to the observed structures cannot be made.

In the course of this experiment, the following consistency checks were conducted.

(i) The count rates corrected for background were found to be proportional to the electron-beam current from 2×10^{-8} to 5×10^{-7} A. For currents below 5×10^{-7} A the electron-beam current was independent (to within ±1%) of the electron energy up to about 50 eV.

(ii) The count rates were proportional to the atomic-beam density from 10^{10} to 10^{11} cm^{-3}.

Since the absolute sensitivity of the detector was not known, only relative cross sections could be obtained.

In conclusion, we note that total ionization cross sections obtained from a simple measurement of ion currents are more reliable than ion counting measurements, since the secondary electron coefficient due to excited ions is much higher than that due to ground-state ions. Our general observation in Cs^+ also applies to other atomic systems. Therefore, a great care should be exercised when analyzing the data of ion counting experiments for the purpose of obtaining absolute cross sections.

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