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A Study of the First Spark Spectrum of Caesium as Excited by Electron Impact

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An apparatus with which one may study the controlled excitation of spectra of volatile metals is described. Certain aspects of the optical excitation functions for several Cs II lines are given. Onset potentials have been compared with those predicted by existing energy level schemes. Possible transitions are suggested for two unclassified lines $\lambda\lambda$4264.7 and 4763.6. Of the two groups into which the Cs II spectrum divides itself, the lines coming from those terms built upon the $^2P_{\frac{1}{2}}$ state of Cs III show very broad excitation function maxima, while the lines coming from terms built upon the $^2P_{1\frac{1}{2}}$ state of Cs III show relatively sharp maxima.

INTRODUCTION

THE purpose of this paper is to show some of the features of the optical excitation functions for certain lines of the caesium II spectrum. The expression, *optical excitation function,* which designates the relation between the intensity of a spectral line and the energy of the bombarding electron which caused it to be emitted was first used in 1919 by R. Seeleger[1] in order to avoid confusion with the expression, *electrical excitation function,* which designates the relation between the probability of excitation of a spectral term and the energy of the bombarding electron. Since that time the functions for several atomic lines of different elements and also for some molecular bands have been measured by different workers. Survey articles on the subject of optical excitation functions have been written by W. Hanle and K. Larche.[2]

The theory of impact excitation has been attacked from the point of view of quantum mechanics and has been worked out for the simplest cases such as hydrogen-like atoms and helium atoms. Although approximate methods have been used agreement with experiment has been good.[3]

APPARATUS AND MATERIALS

The tube

In this experiment the spectra were excited in a Pyrex tube whose design is shown in Fig. 1. Essentials of the tube are the bank of equipotential cathodes, the acceleration grids, the electron collecting cage, the re-entrant quartz window, and the light horn. With the exception of the oxide-coated nickel cylinder cathodes, the metal parts of the tube were of tantalum. The complete tube was covered with an oven.

The electron emitting surface having an effective area of approximately 5 cm^2 consisted

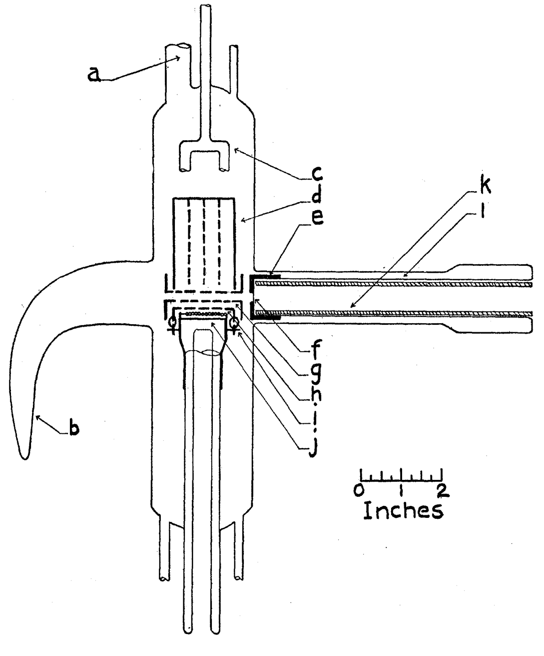

FIG. 1. Sketch of the excitation tube. *a,* pump outlet; *b,* light horn; *c,* glass cane support; *d,* collector cage; *e,* tantalum cap; *f,* quartz window; *g,* second grid; *h,* first grid; *i,* insulating glass bead; *j,* cathode assembly; *k,* aluminum tube; *l,* region of quartz-Pyrex seal.

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[1] R. Seeleger, Ann. d. Physik **59**, 613 (1919).

[2] W. Hanle and K. Larche, Ergeb. d. exakt. Naturwiss. **10**, 285 (1931). See also Physik. Zeits. **33**, 884 (1932); W. Hanle, Die Physik **2**, 85 (1934).

[3] Mott and Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1933); Massey and Mohr, Proc. Roy. Soc. **A132**, 605 (1931); **A140**, 613 (1933); **A146**, 880 (1934).

of the upper areas of 13 cylindrical oxide-coated cathodes. These cathodes were of the indirectly heated type, the heaters being connected in parallel. The acceleration grids were woven to a one millimeter mesh from 0.05-mm tantalum wire. The interior of the cage was equipped with a set of partitions to aid in the collection of the very wide electron beam. The leads and supports from the cage were carefully equipped with guard rings to collect any electrical leakage over the glass surface of the tube walls.

The quartz-to-Pyrex seal in the one-inch tubing was necessarily rather long so the re-entrant seal was made in order that the light path from the excitation chamber through the vapor to the exit window would be short. This path was approximately 1.5 cm. In order to cut down reflections and stray radiations the window was equipped with a tantalum cap having an opening 2.54 cm long and 0.3 cm high. Reflected light which traveled down the walls of the re-entrant tubulation was eliminated by means of an aluminum tube placed in the position shown in the diagram. The oven around the tube shut out other stray light.

A smoothly tapering Pyrex tube gradually bent through a 90° angle served as a light trap to provide a black background opposite the quartz window.

Caesium supply

The caesium, prepared by heating a mixture of caesium chloride and calcium under vacuum in a hard glass tube, was distilled into a small tube attached to the lower end of the excitation tube. This small tube was equipped with an oven. Thus by adjusting the temperature of the caesium supply, the large tube could be kept filled with caesium vapor of the proper pressure. The large tube was kept at 100°C or more above the temperature of the caesium source. A steel ball which by means of a magnet could be rolled over the opening between the large tube and the pumps prevented excessive escape of the caesium vapor and yet allowed connection with the pumping system to be made when desired.

Spectrographs

Both a Hilger E-2 and a Hilger E-1 were used during the work. The slit of the E-2 was illuminated by placing it at the end of the re-entrant tubulation of the excitation tube. The slit of the E-1 was illuminated by means of a double convex quartz lens.

Rotating sector

For calibration of the photographic plates a rotating aluminum sector of variable aperature was placed between the tube and spectrograph.[4] This sector consisted of two similar parts, movable with respect to each other, which allowed a continuous range of opening from 0° to 180°.

Plates and development

Eastman 40, Eastman 50, and Wratten and Wainwright panchromatic plates were used. They were developed for five minutes at 21°C in a developer described by Valasek.[5] Both rocking of the tray and brush development were tried with about equal results. Plate densities[6] were measured by means of a Moll microphotometer. For most of the measurements the self-recording device was not used, a galvanometer with a 50-cm swing being used in its place.

Operation

After the parts of the tube were adequately outgassed by baking and pumping and the drawing of current from the cathodes, the steel ball was rolled over the pump outlet and the tube filled with caesium vapor. The caesium oven and the cathode heaters were heated with a.c. current taken through step-down transformers from a voltage regulator. This was done so that the oven and the heaters might be operated at a constant temperature for a long period of time. (The ten to twelve amperes needed to heat the cathodes were admitted to the tube through eight lead-in wires at the bottom of the tube.) Electron accelerating voltages were taken directly from batteries, there being only very low resistances in the external part of the tube-current circuit. Electron emission currents up to 150 milliamperes were used in

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[4] See G. R. Harrison, J. Opt. Soc. Am. **24**, 59 (1934); **11**, 341 (1925) concerning use of sectors for calibration purposes.

[5] J. Valasek, Phys. Rev. **29**, 817 (1927).

[6] Density is defined as $\log_{10}$ opacity. The opacity of a given area is defined as the ratio of the light passing an equal area of clear plate to that passing the given area when both are intercepting beams of equal intensity.

exciting the spectra. It was found that the steadiest conditions were obtained after continuous operation of the tube for several days.

Tests of the apparatus

Homogeneity of the electron beam was tested by the retarding potential method. It was found that the spread was approximately 0.6 volt for a 5-volt electron beam and approximately 1.0 volt for 20-volt electrons. A measurement of the optical excitation function for the λ2537 line of mercury gave results which agreed quite well with those of F. Ostensen.[7] This agreement indicated that secondary electrons were not causing trouble, since Ostensen's tube was primarily designed to eliminate all secondary electrons. The agreement was further interesting in view of the fact that Ostensen used graded screens for calibration of his plates while the rotating sector was used here.

The linear relation between electron current and intensity of lines shown in Fig. 2 indicated clearly that, over the range of current given, the excitation was due to single-electron collisions. It also serves to justify the method of intensity calibration.

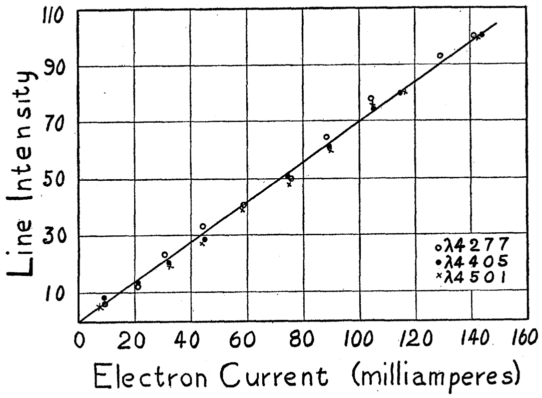

FIG. 2. Line intensities *vs*. electron current in tube.

While experiments showed that exposures of two hours duration could be taken with not any trouble from stray light, it was found that exposures of from five to thirty minutes were sufficient for good plates if a caesium vapor pressure of 2×10^{-3} mm of Hg and an electron current of 50 milliamperes were used.

Corrections to the voltage scale to take care of contact potentials were made by reference to the strong Cs II line, λ4603.7, the scale being shifted so that the onset potential of this line agreed with the theoretical value. This *theoretical value* was obtained by adding to the ionization potential of Cs I the energy of the level in Cs II (measured from the ground state of Cs II) from which the line is known to come.[8] It might be noted here that the correction to the voltage scale varied with the amount of covering of the cathodes by caesium, the correction becoming quite small under conditions where the covering was large.

RESULTS

Table I shows the lines found in caesium vapor with the E-2 spectrograph when the exciting potential was 30 volts.

Figs. 3, 4, and 5 show how the density of different lines (as recorded by the Hilger E-1 spectrograph on Eastman 50 plates) changed with voltage. Ten-minute exposures were used with a tube current of 50 milliamperes in a caesium vapor pressure of approximately 10^{-3} mm of Hg. Fig. 6 gives the optical excitation function for λ4603.7. Data *A* of Fig. 6 were taken from a plate whose exposure time was 5 minutes, while data *B* were taken from a plate whose exposure time was 30 minutes. The densities of the plates were reduced to relative intensities by means of calibration curves, a relative intensity of 100 being taken in each case for the value at 43 volts.

Table II gives a comparison of the experimentally found onset potentials with those predicted by the energy level scheme of Olthoff and Sawyer.[6] The position and character of the excitation function maxima are also indicated. The energy level scheme refered to may be represented by Fig. 7 where it has been separated into two sets of levels, one corresponding to those built upon the $5p^5(^2P_{1\frac{1}{2}})$ state of Cs III and one corresponding to those built upon the $5p^5(^2P_{\frac{1}{2}})$ state of Cs III. By referring to Table II it will be seen that those lines arising from transitions within the first set of levels have relatively sharp excitation function maxima, while those lines arising from transitions within the second set of levels have very broad maxima.

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[7] F. Ostensen, Phys. Rev. **34**, 1352 (1929).

[8] J. Olthoff and R. A. Sawyer, Phys. Rev. **42**, 766 (1932).

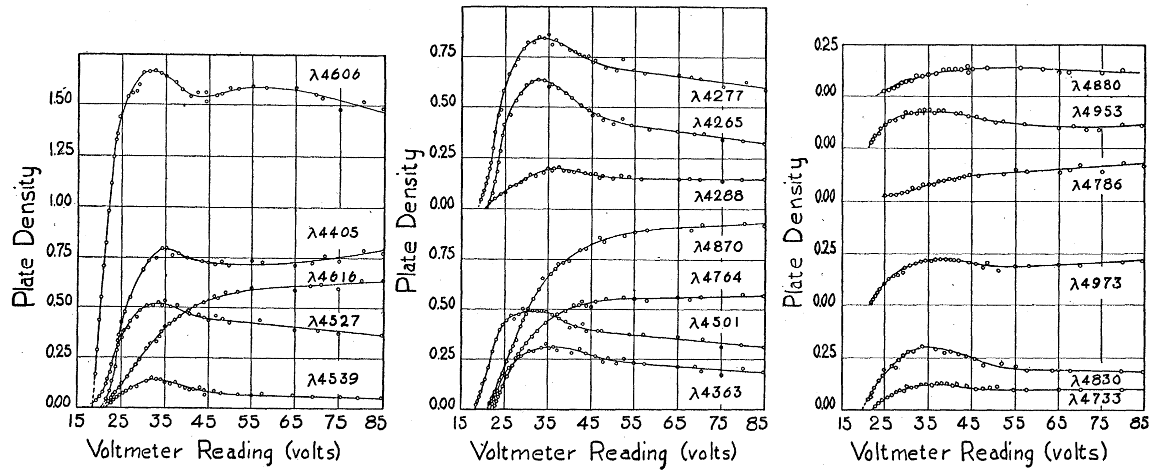

FIG. 3. FIG. 4. FIG. 5.

FIGS. 3, 4 and 5. Line intensities *vs.* the accelerating voltage applied to the tube.

TABLE I. *Caesium lines present in the spectrum excited by 30-volt electrons.*

Cs I 6723.3	Cs II 4870.0	Cs II 4526.7	Cs II 4222.1	Cs I 3888.4	Cs II 2829.4
Cs I 6587.0	Cs II 4830.2	Cs II 4501.5	Cs II 4186.2	Cs I 3876.2	Cs II 2816.9
Cs I 6354.5	Cs II 4786.4	Cs II 4435.7	Cs II 4151.3	Cs II 3805.1	Cs II 2793.3
Cs I 6213.0	Cs II 4763.6	Cs II 4405.2	Cs II 4068.8	Cs I 3611.5	Cs II 2789.8
Cs I 6010.3	Cs II 4732.9	Cs II 4384.4	Cs II 4067.9	Cs II 3368.5	Cs II 2700.0
Cs I 5663.8	Cs II 4646.5	Cs II 4373.0	Cs II 4047.2	Cs II 3268.3	Cs II 2635.9
Cs I 5635.0	Cs II 4623.1	Cs II 4363.4	Cs II 4039.8	Cs II 2970.8	Cs II 2627.9
Cs II 5227.0	Cs II 4616.1	Cs II 4300.6	Cs II 3978.0	Cs II 2968.4	Cs II 2610.1
Cs II 5043.8	Cs II 4603.7	Cs II 4288.4	Cs II 3974.2	Cs II 2940.9	Cs II 2600.4
Cs II 4972.6	Cs I 4593.1	Cs II 4277.1	Cs II 3965.2	Cs II 2931.0	Cs II 2596.9
Cs II 4952.8	Cs I 4555.5	Cs II 4264.7	Cs II 3959.5	Cs II 2859.4	Cs II 2544.0
Cs II 4879.9	Cs II 4538.9	Cs II 4232.2	Cs II 3897.0	Cs II 2846.2	Cs II 2539.2

TABLE II. *Comparison of onset potentials in volts and the upper energy level as given by Olthoff and Sawyer.* In the indicated transitions the odd terms are indicated by the symbol (^{0}) attached as a superscript. In all transitions the term having the highest value is given first.

WAVE-LENGTH (A)	TRANSITION AS GIVEN BY OLTHOFF AND SAWYER	ENERGY UPPER STATE (volts)	ONSET POTENTIAL (volts)	APPROXIMATE POSITION OF MAXIMUM (volts)
4830.2	$5p^5(^2P_{1\frac{1}{2}}\,6p)2_2 - 5p^5(^2P_{1\frac{1}{2}}\,6s)^3P_2{}^0$	19.69	21.3	34 sharp
4952.8	$(^2P_{1\frac{1}{2}}\,6p)2_2 - (^2P_{1\frac{1}{2}}\,6s)^3P_1{}^0$	19.69	21.8	36 medium
4603.7	$(^2P_{1\frac{1}{2}}\,6p)3_3 - (^2P_{1\frac{1}{2}}\,6s)^3P_2{}^0$	19.81	19.9	32 sharp
4526.7	$(^2P_{1\frac{1}{2}}\,6p)4_1 - (^2P_{1\frac{1}{2}}\,6s)^3P_1{}^0$	19.88	19.6	33 sharp
4277.1	$(^2P_{1\frac{1}{2}}\,6p)5_2 - (^2P_{1\frac{1}{2}}\,6s)^3P_2{}^0$	19.99	19.8	33 sharp
4501.5	$(^2P_{1\frac{1}{2}}\,6p)6_0 - (^2P_{1\frac{1}{2}}\,5d)1_1{}^0$	20.31	20.0	33 sharp
4879.9	$5p^5(^2P_{\frac{1}{2}}\,6p)2_1 - 5p^5(^2P_{\frac{1}{2}}\,5d,\,6s)4_1{}^0$	21.58	21.8	Very broad
4870.0	$(^2P_{\frac{1}{2}}\,6p)3_2 - (^2P_{\frac{1}{2}}\,5d,\,6s)4_1{}^0$	21.58	21.7	Very broad
4616.1	$(^2P_{\frac{1}{2}}\,6p)4_0 - (^2P_{\frac{1}{2}}\,5d,\,6s)4_1{}^0$	21.70	22.8	Very broad
4786.4	$(^2P_{\frac{1}{2}}\,6p)4_0 - (^2P_{\frac{1}{2}}\,5d,\,6s)5_1{}^0$	21.70	21.3	Very broad
4538.9	$5p^5(^2P_{1\frac{1}{2}}\,6d)2_2{}^0 - 5p^5(^2P_{1\frac{1}{2}}\,6p)5_2$	22.70	22.6	33 sharp
4288.4	$(^2P_{1\frac{1}{2}}\,6d)3_2{}^0 - (^2P_{1\frac{1}{2}}\,6p)4_1$	22.29	22.2	37 medium
4363.4	$(^2P_{1\frac{1}{2}}\,6d)5_3{}^0 - (^2P_{1\frac{1}{2}}\,6p)5_2$	22.84	22.8	36 medium
4264.7	—	—	22.5	33 sharp
4405.2	$5p^5(^2P_{1\frac{1}{2}}\,7s)^3P_2{}^0 - 5p^5(^2P_{1\frac{1}{2}}\,6p)1_1$	22.29	22.5	35 sharp
4732.9	$(^2P_{1\frac{1}{2}}\,7s)^3P_2{}^0 - (^2P_{1\frac{1}{2}}\,6p)2_2$	22.29	22.8	39 medium
4972.6	$(^2P_{1\frac{1}{2}}\,7s)^3P_2{}^0 - (^2P_{1\frac{1}{2}}\,6p)3_3$	22.29	22.8	39 medium
4763.6	—	—	23.8	Very broad

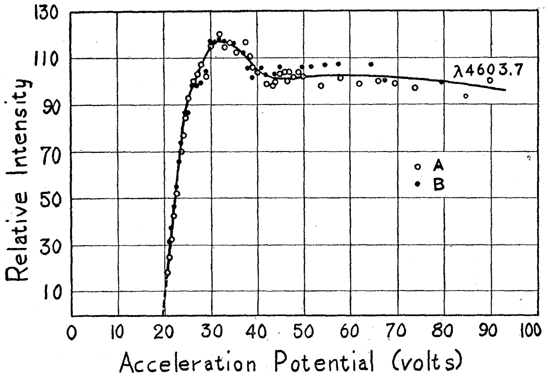

FIG. 6. Excitation function for λ4603.7. *A*, 5-min. exposure; *B*, 30-min. exposure. Relative intensity of 100 taken at 43 volts.

For the two lines, λλ4264.7 and 4763.6 whose classifications are not given in Table II a consideration of the forms of their optical excitation functions, of their onset potentials, and of their wave-lengths when considered in the light of the energy level scheme leads to the suggestion that they may be due to transitions of the types, $5p^5(^2P_{1\frac{1}{2}})6d$, $7s-5p^5(^2P_{1\frac{1}{2}})6p$ and $5p^5(^2P_{\frac{1}{2}})6d$, $7s-5p^5(^2P_{\frac{1}{2}})6p$, respectively.

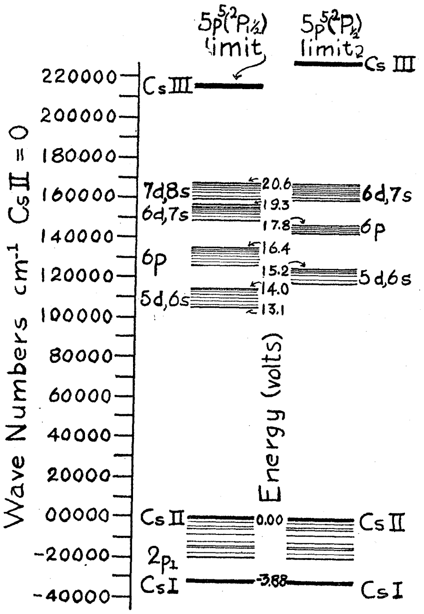

FIG. 7. Energy level scheme.

In conclusion I wish to express my thanks to Dr. J. T. Tate who suggested the problem, to Dr. J. Valasek for helpful suggestions, to Dr. H. A. Erikson for the use of apparatus, and to the RCA Radiotron Corporation and the Bell Telephone Laboratories who furnished me with the necessary oxide-coated cathodes as well as some oxide-coated ribbon.

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Isotopic Constitution of Lead from Hyperfine Structure

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The relative abundance of the isotopes of lead was determined from intensity measurements of the hyperfine structure components of the lead spark line λ5372. With eleven calibrated wire screens a single order of the Fabry-Perot interference pattern was photographed with the same exposure time for each screen. The following results from densitometer measurements were obtained for the percentage abundance of the isotopes of ordinary lead: 51.5, 26.3, 21.4 and 0.8 for Pb^{208}, Pb^{206}, Pb^{207}, and Pb^{204}, respectively. For integral masses of the isotopes the mean mass number is 207.22_8. Assuming a packing factor of +1, this number when converted to the chemical atomic weight scale becomes 207.20.

It has been shown by several investigators[1–4] that spectral lines for the isotopes Pb^{204}, Pb^{206} and Pb^{208}, each with nuclear spin $I=0$, are always single but the lines for Pb^{207}, with spin $I=\frac{1}{2}$, may have as many as four components depending on the J values and splittings of the initial and final atomic energy levels. It has been possible to make very rough esti-

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[1] H. Kopfermann, Zeits. f. Physik **75**, 363 (1932).

[2] J. L. Rose and L. P. Granath, Phys. Rev. **40**, 760 (1932).

[3] H. Schüler and E. G. Jones, Zeits. f. Physik **75**, 563 (1932).

[4] J. L. Rose, Phys. Rev. **47**, 122 (1935).