

Use of Space-Charge-Amplification Techniques in the Absorption Spectroscopy of Cs and Cs₂[†]

D. Popescu and M. L. Pascu
Institute of Physics, Bucharest, Romania

C. B. Collins and B. W. Johnson
The University of Texas at Dallas, Dallas, Texas 75230

Iovitzu Popescu
University of Bucharest, Bucharest, Romania
(Received 26 March 1973)

Space-charge amplification of the direct and indirect ionization resulting from photoabsorption in alkali-metal vapor is shown to provide a useful complement to the conventional techniques of absorption spectroscopy. Because of its inherently greater sensitivity, this technique is particularly useful in spectroscopic applications involving weak transitions such as those to highly excited states or absorptive transitions from excited states of low population. This paper reports the use of this technique to extend prior measurements of the oscillator strengths of the ($6^2S \rightarrow n^2P$) series in Cs, the n^2D doublet separations, and the photoionization spectrum of Cs₂.

I. INTRODUCTION

Space-charge detection of the products of photoionization and associative ionization gives a technique for extending the sensitivity of classical atomic absorption spectroscopy by several orders of magnitude. It has been recently utilized in alkali-metal-vapor systems to investigate a variety of atomic and molecular absorption spectra,^{1,2} including those from excited states,³ multiphoton processes,^{4,5} and molecular satellites of atomic cesium lines.⁶ This paper presents some new spectroscopic data obtained with these techniques for both atomic and molecular cesium. In particular, the measurements reported here concern the determination of oscillator strengths for the $6^2S \rightarrow n^2P$ series for atomic cesium in the limit of large n , measurement of the n^2D doublet intervals for highly excited states, and a more precise determination of the photoionization cross section of Cs₂ as a function of wavelength.

In contrast to the techniques of standard absorption spectroscopy which are based on the measurement of relatively small attenuations of large signals, the method used in this and the previously cited works is based on the measurement of positive ions produced either directly or indirectly by the photon absorptions. The positive ions produced in this way enhance the output signal of a thermionic diode containing the absorbing gas by partially neutralizing the negative space charge surrounding the diode filament. The relatively long time which the positive ions spend traversing the potential well of the space-charge region provides for the release of 10^4 – 10^6 electrons per ion

from that region.^{7,8} Essentially this technique, when coupled with light modulation and synchronous detection, represents a modernization of the early experiments on photoionization⁹⁻¹² and is now sufficient to allow detection of ion signals as small as a few ions per second.

II. EXPERIMENTAL APPARATUS

The experimental absorption cell used in these cesium studies was made of Pyrex glass with quartz windows and filled with cesium vapor at a pressure controlled by a two-chamber oven according to standard techniques.³ The diode included in the cell consisted of a 0.15-mm-diam tungsten wire filament and a silver disk anode, both properly activated with cesium and separated by 1.5 mm. They were aligned so that the conduction path lay transverse to the optical axis. The exact position of the focal volume within the diode structure was not found to be particularly critical, and only required that the positive ions produced by the absorption process under investigation be able to diffuse or drift into the space-charge cloud surrounding the filament.

For investigation of absorption from ground-state cesium species the diode was used as described above. However, for processes involving photoabsorption from excited states, such as 6^2P or 5^2D , it was necessary to use the diode to produce a discharge to populate these states, but at a sufficiently low power to minimize the direct production of ions. In this case the detection of the ions produced from the subsequent photoabsorption occurred in a second diode of

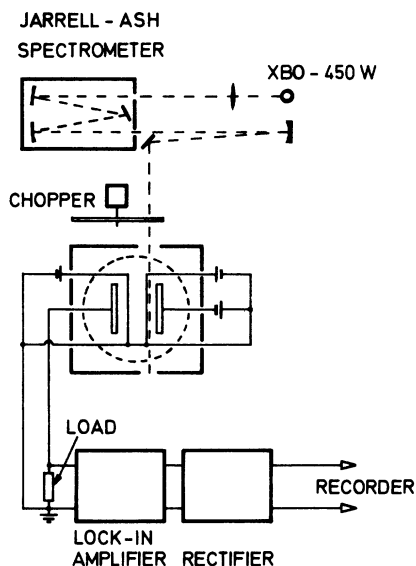


FIG. 1. Block diagram of the experimental apparatus.

identical construction and placed in sufficient proximity, about 3 mm, from the excitation diode to allow the diffusion of ions between them.

Figure 1 shows a schematic representation of this double-diode arrangement together with the supporting optics and electronics.

It was necessary to optimize the light-modulation frequency in terms of transit times of the ions. The optimum was found to lie in the range 8–20 Hz, in agreement with measured¹³ diffusion coefficients of cesium ion Cs^+ and Cs_2^+ in cesium at the working pressure range corresponding to saturated vapor at temperatures of 200–210 °C. Optimal filament temperatures were of the order of 1100 °K for the detecting diode and 800 °K for the excitation diode when the latter scheme was employed.

The light source employed was a 450-W high-pressure xenon arc lamp, the continuum from which was filtered with a 1-m Czerny-Turner monochromator with a 1200-line/mm grating. Slits were selected to give 0.5-Å resolution.

It was found that an external load resistance of $10^5 \Omega$ provided sufficient signal for synchronous detection according to standard techniques.³

III. RESULTS AND DISCUSSION

Typical direct recordings of ion signal are shown in Figs. 2 and 3 for the wavelength ranges corresponding to the principal ($6^2S - n^2P$) and diffuse ($6^2P - n^2D$) series, respectively, of atomic cesium. As mentioned above, the former measurements involving photon absorption from the ground state were made with the single-diode system, while the latter involving absorption from the resonance 6^2P states required the use of the double diode. One diode was used for ion detection and the other for the excitation of the 6^2P states in a low-power dc discharge. It was found that a 2-V bias was sufficient to maintain the discharge in the excitation diode, and larger biases were avoided, as they were found to initiate the anode glow mode of discharge with the production of a considerable continuous ionization which lowered the sensitivity of the detecting diode.

The relative sensitivity of the diode detection method in comparison with conventional absorption techniques can be appreciated by noting that spectra of the same signal-to-noise ratio as shown in Fig. 2 may be obtained in the latter case by use of a multiple-reflection system to give an effective absorption length of 40–50 m, a vapor pressure of a few torr, and several hours integration time of the signal on a film.^{14,15} In contrast,

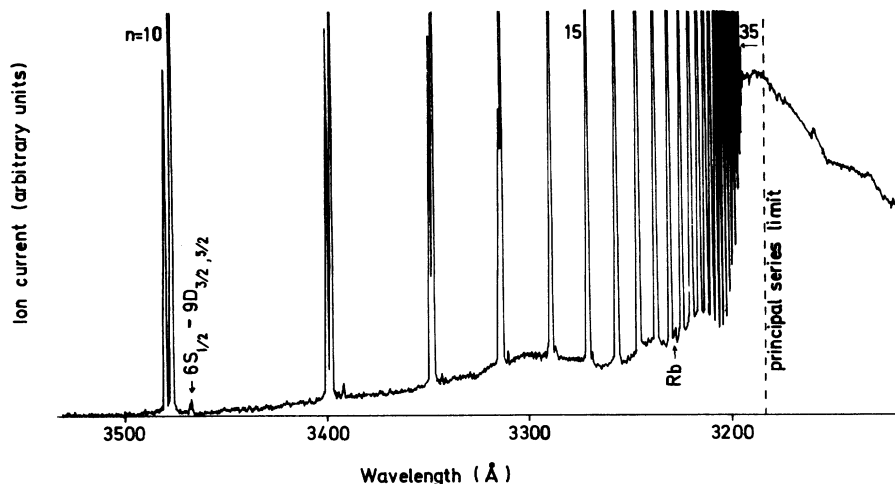


FIG. 2. Typical ion signal spectrum showing the Cs principal series ($6^2S - n^2P$) near the series limit. Both the continuum molecular absorption of Cs_2 and the main continuum of the Cs atom can be seen together with members of the quadrupole series $6^2S - n^2D$.

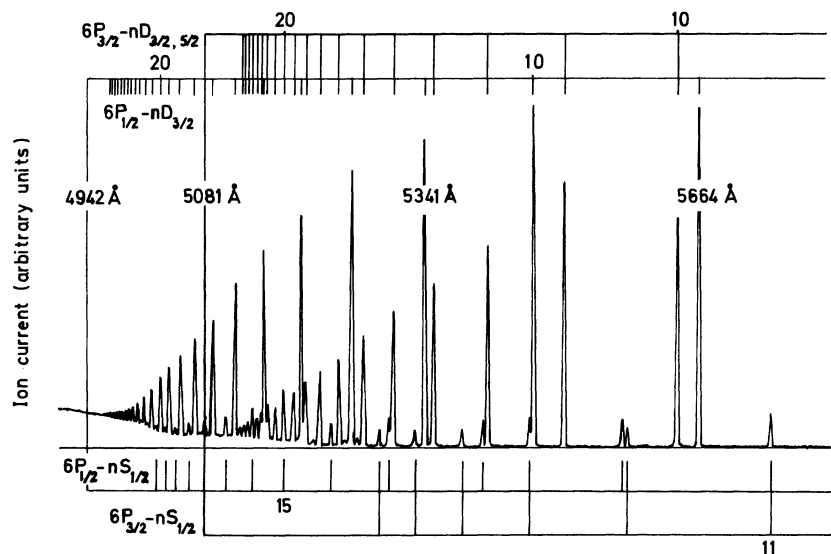
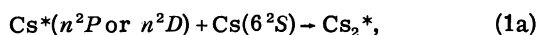


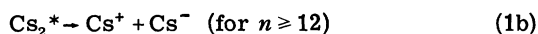
FIG. 3. Ion signal spectrum typical of absorption from excited states. The large signals correspond to sequences of the diffuse-series spectrum arising from transitions from the $6P_{1/2}$ and $6P_{3/2}$ states of atomic cesium.

the space-charge detection of resultant ions employs an optical path of the order of 1.0 mm, 0.1–0.5-torr vapor pressure, and time constants of the order of a second. Absorption from excited atoms such as shown in Fig. 3 is even more difficult by conventional techniques.

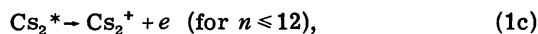
During the work reported in this paper, clearly resolved lines were observed for principal quantum numbers in the range $7 \leq n \leq 55$ for the principal series and $7 \leq n \leq 33$ for the diffuse series. In each case, it is believed that the ionization actually detected results from the photoabsorption event according to one of the mechanisms suggested by Lee and Mahan^{16,17}:



followed by either



or



where Cs_2^* is a highly excited molecular state.

In contrast to the present work, however, in those earlier papers^{16,17} it was necessary to measure absolute photoion currents and the corresponding time of flight which required the minimization of thermal electron emission currents and related space-charge effects. The objective of the present work has been the detection at highest sensitivity of the positive ions produced from the highly excited states resulting from the photoabsorption processes. For this purpose, in addition to the approximately six-orders-of-magnitude internal amplification of the

hot-wire diode, external amplification with standard light modulation and synchronous detection served to give an over-all gain of the order of 10^9 – 10^{11} electrons per ion.

Since the bulk of the data obtained concerns the spectroscopy of the excited states of cesium lying above $n = 12$, the quantitative interpretations first to be discussed were made in terms of the Cs^+ ion spectrum resulting from process (1b).

Oscillator strengths were obtained from the data of Figs. 2 and 3 by using the atomic continuum as a reference. This cross section at the limit of the principal series has been reported¹⁸ to be $\sigma_i(\lambda_0) = 0.22 \text{ Mb}$ ($1 \text{ Mb} = 10^{-18} \text{ cm}^2$). Then, from the ratio of expressions for the ion current integrated over the absorption line S_i , to the ion current S_c , from the portion of the continuum lying within the bandwidth $\Delta\lambda$ of the spectrometer, the f values can be obtained in terms of the photoionization cross section $\sigma_i(\lambda_0)$, at the wavelength λ_0 corresponding to the ionization limit, as

$$f = \frac{mc^2}{\pi e^2} \left(\frac{\lambda_0 \sigma_i(\lambda_0) \Delta\lambda I(\lambda_0) S_i}{\lambda^3 I(\lambda) P_i(\lambda) S_c(\lambda_0)} \right), \quad (2)$$

where $I(\lambda)$ is the relative intensity of the irradiating light at the wavelength λ and $P_i(\lambda)$ is the probability of ionization of the excited state produced by the absorption of the wavelength λ . Collection efficiencies and geometric factors characteristic of the diode have been eliminated in the scaling of the measurement to the photoionization continuum.

A similar expression for the f values for the diffuse series requires the additional knowledge of the ratio of populations of the 6^2P and 6^2S states. This was determined from LTE considerations applied to the 800 °K electron temper-

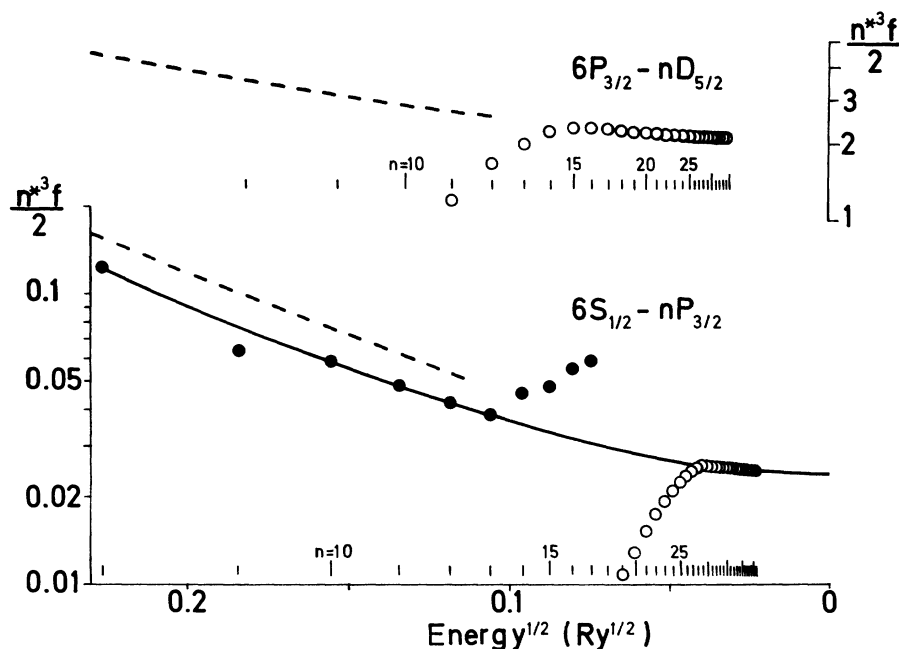


FIG. 4. f values corresponding to the $6^2S_{1/2} - n^2P_{3/2}$ and $6^2P_{3/2} - n^2D_{5/2}$ transitions of cesium atoms. Ordinates are given as $(n^*)^3 f / 2$ where n^* is the effective principal quantum number and abscissas in terms of $(\text{ionization energy})^{1/2}$ for convenience. Open circles, this work; closed circles, Krater and Meister; dashed line, Stone (theoretical); solid line, Marr and Creek (extrapolated).

ature indicated by the relative populations of $6^2P_{3/2}$ and $6^2P_{1/2}$ states.³

Figure 4 collects the results of these computations, assuming that $P_i(\lambda) = 1$ for all λ , although such equality is only approximately achieved in the limit of high quantum numbers. Shown are values of $(n^*)^3 f$, where n^* denotes the effective principal quantum number obtained from the spectroscopically determined energy of the level. It can be seen that the values, uncorrected for the actual behavior of $P_i(\lambda)$, appear to decrease steeply toward lower n at about $n = 30$ for the n^2P states. This is evidently due to the steep decrease of ionization probability in comparison with other possible relaxation branches for the deeper-lying atomic states. At higher principal quantum numbers $(n^*)^3 f$ values reach a nearly constant asymptote and fit well the general shape of the extrapolated and previous experimental and theoretical data.¹⁸⁻²⁰ The essentially unit probability for ionization of these higher states is consistent with the mean lifetime values, which are strong functions of principal quantum number. From the data of Fig. 4 it is possible to compute the ionization probability $P_i(\lambda)$ and correct the f values in the wavelength region spanning the gap between the Marr-Creek¹⁸ values and those of this work. Resulting f values for the principal series are summarized in Table I.

Doublet intervals for the n^2D states were determined directly from data such as shown in Fig. 3. Figure 5 summarizes, together with Kratz's¹⁴ values for the n^2P intervals, the resulting values which show good agreement with

the theoretical expression

$$\Delta\nu_x = \frac{R\alpha^2 Z_{eff}^4}{l(l+1)(n^*)^3}, \quad (3)$$

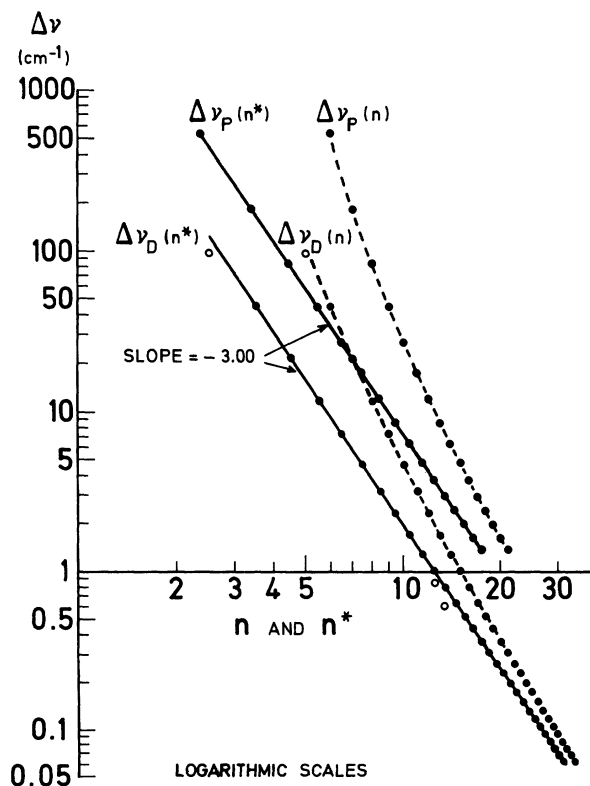


FIG. 5. Doublet intervals in cm^{-1} for the n^2D states of Cs as determined from this work in comparison with published values for the n^2P intervals.

TABLE I. Corrected f values for the principal series $6S_{1/2} - nP_{3/2}$ of cesium.

n	n^*	f	$n^3 f/2$	f values from	$P_1(n)$
6	2.3617	1.094	7.205	Marr and Creek	
7	3.4059	1.461×10^{-2}	0.289	Marr and Creek	
8	4.4208	2.838×10^{-3}	0.123	Marr and Creek	
9	5.4278	9.77×10^{-4}	0.078	Marr and Creek	
10	6.4317	4.41×10^{-4}	0.058	Marr and Creek	4.1×10^{-3}
11	7.4341	2.35×10^{-4}	0.048	Marr and Creek	9.0×10^{-3}
12	8.4360	1.40×10^{-4}	0.042	Marr and Creek	2.1×10^{-2}
13	9.4370	9.15×10^{-5}	0.0384	Marr and Creek	3.8×10^{-2}
14	10.4379	6.24×10^{-5}	0.0352	Marr and Creek	6.6×10^{-2}
15	11.4384	4.45×10^{-5}	0.0333	Marr and Creek	1.1×10^{-1}
16	12.4393	3.28×10^{-5}	0.0320	Marr and Creek	1.6×10^{-1}
17	13.4395	2.50×10^{-5}	0.0304	Marr and Creek	0.224
18	14.4397	1.95×10^{-5}	0.0295	Marr and Creek	0.296
19	15.4406	1.54×10^{-5}	0.0290	Marr and Creek	0.373
20	16.4410	1.25×10^{-5}	0.0282	Marr and Creek	0.457
21	17.4420	1.03×10^{-5}	0.0280	Marr and Creek	0.543
22	18.4427	8.58×10^{-6}	0.0274	Marr and Creek	0.629
23	19.4430	7.21×10^{-6}	0.0271	Marr and Creek	0.712
24	20.4430	6.16×10^{-6}	0.0269	Marr and Creek	0.778
25	21.4430	5.29×10^{-6}	0.0265	Marr and Creek	0.857
26	22.4430	4.56×10^{-6}	0.0264	Marr and Creek	0.899
27	23.4430	4.07×10^{-6}	0.0262	interpolated	0.946
28	24.4430	3.57×10^{-6}	0.0261	between MC	0.980
29	25.4430	3.16×10^{-6}	0.0260	and present	0.990
30	26.4430	2.80×10^{-6}	0.0259	data	1.000
31	27.4430	2.50×10^{-6}	0.0258	present data	1
32	28.4430	2.23×10^{-6}	0.0257	present data	1
33	29.4430	2.00×10^{-6}	0.0256	present data	1
34	30.4430	1.80×10^{-6}	0.0254	present data	1
35	31.4430	1.63×10^{-6}	0.0253	present data	1
36	32.4430	1.48×10^{-6}	0.0253	present data	1
37	33.4430	1.35×10^{-6}	0.0253	present data	1
38	34.4430	1.24×10^{-6}	0.0253	present data	1
39	35.4430	1.13×10^{-6}	0.0252	present data	1
40	36.4430	1.04×10^{-6}	0.0252	present data	1

where subscript $\times = P$ or D in agreement with the l value for the state. Near the $\Delta\nu_D(n^*)$ line of slope -3 and $\Delta\nu_D(n)$ curve we indicate by open circles the data from Moore's table,²¹ not in agreement with expression (3). For convenience, the resulting $n^2 D_J$ energy levels and $\Delta\nu_D$ doublet intervals are tabulated in Table II.

The photoionization signal contributed by the cesium molecule can be seen to underlie the principal atomic series in Fig. 2. As in the case of determination of the f values, these data can be interpreted to give photoionization cross sections for the cesium molecule by measuring the ratios of ion currents from molecular and atomic continua. Proceeding in an analogous manner, using thermal equilibrium ratios of Cs_2 to Cs , the cross sections presented in Fig. 6 were obtained. These have been plotted as a function of wavelength together with earlier values from the literature.^{1,18} Due to the higher sensitivity of the present method, it was possible to resolve the three bands around 3214, 3239, and 3290 Å, as shown in the wavelength region near the principal-series limit. Previous standard absorption measurements gave only an average

TABLE II. The $n^2 D_J$ levels and $\Delta\nu_D$ doublet intervals shown as they result from present photoionization spectra (until $n=13$ from Moore's table²¹), in cm^{-1} .

n	J	Level	Interval	n	J	Level	Interval
5	$1/2$	14 499.49	97.59	21	$1/2$	31 086.906	0.310
	$3/2$	14 597.08		21	$3/2$	31 087.216	
6	$1/2$	22 588.89	42.94	22	$1/2$	31 118.827	0.265
	$3/2$	22 631.83		22	$3/2$	31 119.092	
7	$1/2$	26 047.86	20.97	23	$1/2$	31 146.197	0.228
	$3/2$	26 068.83		23	$3/2$	31 146.425	
8	$1/2$	27 811.25	11.69	24	$1/2$	31 169.841	0.198
	$3/2$	27 822.94		24	$3/2$	31 170.039	
9	$1/2$	28 828.90	7.16	25	$1/2$	31 190.407	0.198
	$3/2$	28 836.06		25	$3/2$	31 190.579	
10	$1/2$	29 468.54	4.68	26	$1/2$	31 208.406	0.151
	$3/2$	29 473.22		26	$3/2$	31 208.557	
11	$1/2$	29 896.64	3.25	27	$1/2$	31 224.248	0.134
	$3/2$	29 899.89		27	$3/2$	31 224.382	
12	$1/2$	30 197.02	2.33	28	$1/2$	31 238.266	0.118
	$3/2$	30 199.35		28	$3/2$	31 238.384	
13	$1/2$	30 416.06	1.70	29	$1/2$	31 250.727	0.106
	$3/2$	30 417.76		29	$3/2$	31 250.833	
14	$1/2$	30 580.39	1.29	30	$1/2$	31 261.856	0.095
	$3/2$	30 581.68		30	$3/2$	31 261.951	
15	$1/2$	30 707.08	1.00	31	$1/2$	31 271.834	0.086
	$3/2$	30 708.08		31	$3/2$	31 271.920	
16	$1/2$	30 806.720	0.798	32	$1/2$	31 280.816	0.077
	$3/2$	30 807.518		32	$3/2$	31 280.893	
17	$1/2$	30 886.50	0.64	33	$1/2$	31 288.930	0.070
	$3/2$	30 887.14		33	$3/2$	31 289.000	
18	$1/2$	30 951.359	0.527	34	$1/2$	31 296.284	0.063
	$3/2$	30 951.886		34	$3/2$	31 296.347	
19	$1/2$	31 004.805	0.437				
	$3/2$	31 005.242					
20	$1/2$	31 049.365	0.367				
	$3/2$	31 049.732					

^a Reference 21.

of both atomic and molecular absorption, as shown by the dashed curve in Fig. 6.

It is worthwhile to note that the maximum molecular cross section near the main atomic threshold at 3183 Å is about 21 Mb for 3214 Å, almost 100 times greater than the indicated maximum atomic cross section of 0.22 Mb at the threshold. At the same time, the atomic-to-molecular-concentration ratio at the 490 °K temperature of the saturated vapor is approximately 400, so that the photoionization signal for the molecule would be expected to be about 25% of that from the atom, in general agreement with the data of Fig. 2. Nevertheless, this continues the

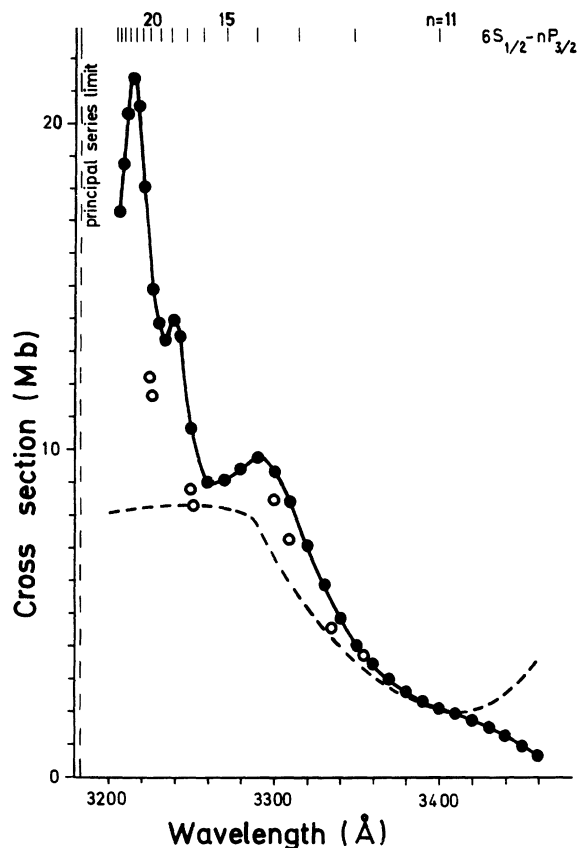


FIG. 6. Photoionization cross section for Cs_2 as a function of wavelength. Closed circles, this work; open circles, Popescu *et al.* (1966); dashed line, Creek and Marr (1968).

disagreement between experiment¹⁸ and recent theory,²² leaving a factor of uncertainty of about 2 between them. Finally, it should be emphasized that, in the present work, both the 6^2S-7^2P and 6^2S-8^2P doublets were observed, but at greatly reduced intensities in comparison with the higher members of the series. Both levels have been suggested to be below the limit for associative ionization according to reaction (1c), and the non-occurrence of associative ionization from these

levels has been used to bound the dissociation energy of the Cs_2^+ molecular ion in past work.² The observation of ionization resulting from absorption to these levels does not appear to affect these conclusions in the current experiment because of the orders-of-magnitude-smaller signals detected in comparison with levels lying above the threshold for associative ionization. Rather, it suggests the necessary involvement of some minority species implying either associative ionization of the $7P$ and $8P$ by collisions with ground-state atoms of high kinetic energy or the Penning ionization by collision with another excited atom or molecule.

IV. CONCLUSIONS

Owing to a very high sensitivity for the detection of positive ions extending to a few ions/s, the space-charge-amplification system discussed in this work may be used as a detector for a large variety of reactions leading to the ionization of alkali-metal atoms and molecules. The agreement between spectroscopic constants obtained by this technique and those available from conventional absorption methods over the overlapping range of sensitivity tends to confirm the basic accuracy of the system in evidencing photon absorption through the detection of direct and indirectly produced ionization. In contrast to the standard optical methods, the diode detection scheme is best suited to the investigation of reactions involving highly excited states, and in this case appears to form a valuable complement to conventional absorption spectroscopy.

ACKNOWLEDGMENTS

The authors are indebted to Professor Dr. Walter Lochte-Holtgreven, Professor Dr. Johannes Richter, and Dr. Kay Niemax of the Institute of Experimental Physics of the Kiel University for their interest in this work and their valuable comments.

†Work conducted as part of the U. S.-Romania Cooperative Program in Science and Technology in association between the University of Texas at Dallas and the Institute of Physics of Bucharest. Financial support was provided in part by the U. S. National Science Foundation under Grant No. GF443 and in part by the Romanian Comitetul de Stat pentru Energia Nucleara and the Consiliul National pentru Stiinta si Tehnologie.

¹I. Popescu, C. Ghita, A. Popescu, and G. Musa, *Ann. Phys.* **18**, 103 (1966).

²G. V. Marr and S. R. Wherrett, *J. Phys. B* **5**, 1735

(1972).

³D. Popescu, I. Popescu, and J. Richter, *Z. Physik* **226**, 160 (1969).

⁴D. Popescu, *Rev. Roum. Phys.* **15**, 859 (1970).

⁵C. B. Collins, B. W. Johnson, D. Popescu, G. Musa, M. L. Pascu, and I. Popescu, *Phys. Rev. A* (to be published).

⁶K. Niemax, *Phys. Lett.* **38A**, 141 (1972); Ph.D. thesis (Institute of Experimental Physik der Universite Kiel, 1972) (unpublished).

⁷K. H. Kingdon, *Phys. Rev.* **21**, 408 (1923).

- ⁸G. Z. Hertz, *Z. Physik* 18, 307 (1923).
- ⁹F. L. Mohler, P. D. Foote, and R. L. Chenault, *Phys. Rev.* 27, 37 (1926).
- ¹⁰F. L. Mohler and C. Boeckner, *J. Res. Natl. Bur. Std.* 3, 303 (1929); *J. Res. Natl. Bur. Std.* 5, 51 (1930); *J. Res. Natl. Bur. Std.* 5, 399 (1930); *J. Res. Natl. Bur. Std.* 5, 831 (1930).
- ¹¹E. O. Lawrence and N. E. Edlefsen, *Phys. Rev.* 34, 233 (1929).
- ¹²K. Freudenberg, *Z. Physik* 67, 417 (1931).
- ¹³I. Popescu, N. Niculescu, and A. Popescu, *Brit. J. Appl. Phys.* 1, 313 (1968).
- ¹⁴H. R. Kratz, *Phys. Rev.* 75, 1844 (1949).
- ¹⁵T. Z. Ny and S. P. Choong, *J. Phys.* 6, 147 (1935); *J. Phys.* 6, 203 (1935).
- ¹⁶Yuan-Tseh Lee and B. H. Mahan, *J. Chem. Phys.* 42, 2893 (1965).
- ¹⁷Yuan-Tseh Lee and B. H. Mahan, *J. Chem. Phys.* 42, 2016 (1965).
- ¹⁸G. V. Marr and D. M. Creek, *Proc. R. Soc. Lond.* A304, 233 (1968); *J. Quant. Spektrosk. Radiat. Transfer* 8, 1431 (1968).
- ¹⁹P. M. Stone, *Phys. Rev.* 127, 1151 (1962).
- ²⁰As presented in Ref. 16.
- ²¹C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (USGPO, Washington, D.C., 1958), Vol. III, p. 124.
- ²²J. C. Weisheit, *Phys. Rev. A* 5, 1621 (1972).