CROATICA CHEMICA ACTA CCACAA **66** (1) 217–225 (1993)

ISSN 0011–1643
CCA–2134

Original Scientific Paper

Laser Optogalvanic Spectrum of Cesium in a Radiofrequency Discharge

D. Kumar, P. L. Clancy, L. Klasinc, and S. P. McGlynn*

Department of Chemistry, Louisiana State University,
Baton Rouge, Louisiana 70803

Received February 18, 1993

The laser optogalvanic (LOG) spectrum of cesium vapor at ~50 m Torr in a low power (≤ 1 W), ~30 MHz radiofrequency discharge has been recorded in the range 16,250 to 16,860 cm^{-1}. Members of several Rydberg series (6p → *n*s, 6p → *n*d, 5d → *n*p and 5d → *n*f) that terminate on the first ionization limit have been observed. The line broadening of high-*n* ($n \geq 30$) f- levels in cesium is considerably less than in xenon. The excessive broadening in xenon is attributed in part to interactions of the Rydberg electron with the open-shell core.

INTRODUCTION

The laser optogalvanic (LOG) effect is the change produced in the electrical properties of a gaseous discharge when the discharge is illuminated with light of energy corresponding to an electronic, rotational or vibrational excitation of some species in the discharge. Although the optogalvanic effect has been known for over 50 years,[1] it is only recently, with the advent of high-power, tunable lasers, that the technique has attracted much attention. Green and co-workers, in 1976, sparked this renaisance when they demonstrated the very high sensitivity of LOG signals in hollow cathode lamps.[2] Since that time, many new electronic transitions in both atoms[3–6] and molecules[7–11] have been studied using various modifications of the LOG technique.

Some transient radical species, such as HCO,[12] were studied at the Doppler limit for the first time using a variation of radiofrequency (RF)LOG spectoscopy. Indeed, Lawler *et al.*[13] have developed a two-photon LOG technique for sub-Doppler measurements. This dual beam intermodulated technique was employed by Suzuki and Kakimoto,[8] in conjunction with a ring dye laser, to obtain sub-Doppler measurements

---

*On leave from Ruđer Bošković Institute, Zagreb, Croatia of N_2 Rydberg states. A recent review article by Barbieri *et al.*[14] attests to the high sensitivity and spectroscopic utility of LOG detection.

Efforts have been made to model the optogalvanic effect in a dc discharge.[5,15–17] All of these efforts are based on rate equations for processes occurring within the discharge. Unfortunately, the complexity of the plasma, which is a mixture of several species in various states of excitation in dynamic equilibrium with dc/rf fields and photon absorption /emission fluxes, and a lack of knowledge of rates/cross-sections for the various plasma processes have precluded a modeling capability.

We have recently shown[18–22] that the temporal profiles of LOG signals consist of two distinct components. One component is mediated by changes of equilibrium ionization rates in the plasma. The other component is mediated by the photoacoustic (PA) effect; this component does not require either ionization or mobility rate changes in order to produce a signal. In fact, the PA-mediated LOG signal is generated by a perturbation of the positions of charge carriers (usually ions, such as those in the positive ion sheaths in the vicinity of the electrodes) under the influence of the PA wave. We have also developed a method which disentangles these two complex temporal profiles even when they exhibit temporal overlap. These results have enhanced our understanding of the various plasma processes involved in the generation of a LOG signal.

The motivation for LOG investigations of cesium is provided by our results of pressure dependence, field-ionization and »*l*-mixing« studies of LOG signals in xenon.[6,23,24] The high-*n* Rydberg electron of xenon interacts with the »open-shell« core (*i.e.*, with the five p electrons) and suffers an extrinsic field broadening due to the rf fields in the discharge and an intrinsic broadening due to *l*-mixing. As a result, transitions to high-*n* ($n \geq 30$) Rydbergs in xenon are broad and diffuse and are »washed out« for $n \gtrsim 40$ under our experimental conditions. A cesium high-*n* Rydberg electron, on the other hand, interacts with a »closed-shell« xenon-like core and, consequently, transitions to these high-*n* Rydbergs will suffer little or no broadening due to the rf field-dependent *l*-mixing effects. Therefore, in comparison with xenon, higher-*n* Rydberg series members should be readily observable in cesium.

The first LOG spectrum of cesium in a dc discharge was reported by Bridges.[25] A recent work on cesium, also based on LOG detection in a dc discharge, was published by Roesch.[26] More recent experiments on cesium, not using the LOG technique, have followed along two lines. First, experiments designed to obtain highly accurate measurements of cesium energy levels, ionization limits and quantum defects of *n*g, *n*f, *n*d, *n*p and *n*s states have been performed.[27–32] Second, experiments designed to investigate the behavior of high Rydberg states, experiments that exploit the highly hydrogenic nature of cesium Rydberg states, have been performed in high magnetic fields.[33–35]

In this paper, we present some RFLOG results of line broadening studies of transitions to high-*n* Rydbergs in cesium in the range 16,250–16,860 cm^{-1}.

EXPERIMENTAL

The experimental arrangement for LOG measurement in an rf discharge has been described.[6,23] The minor modifications required to permit heating of the discharge cell to ~190 °C in order to obtain ~50 mTorr vapor pressure of cesium[25] are now described: A quartz cell (or tube), about 20 cm long and 8 mm in diameter, was constructed with a ground glass joint at one end. The cell was attached to a vacuum system consisting of a mechanical roughing pump and an oil diffusion pump. After allowing the cell to degas for several days, a small quantity (~0.1 g) of cesium metal was placed in the cell, and the cell was reattached to the vacuum system. The system was thoroughly degassed and the cell was sealed under vacuum.

In order to attain sufficient Cs vapor pressure for RFLOG studies, one must heat the cell. The maintenance of a constant cell temperature required an oven (Figure 1). The oven (80 × 100 × 350 mm) was constructed of aluminum with the discharge tube mounted inside the oven. Holes were drilled in the oven walls to allow the connections to the rf electrodes to enter the chamber, to allow the connection to the pick-up coil to enter the chamber, to allow the laser beam to penetrate the oven, and to allow the tip of a thermometer to protrude into the chamber. The source of heat was a hot-plate placed on the top of the oven.

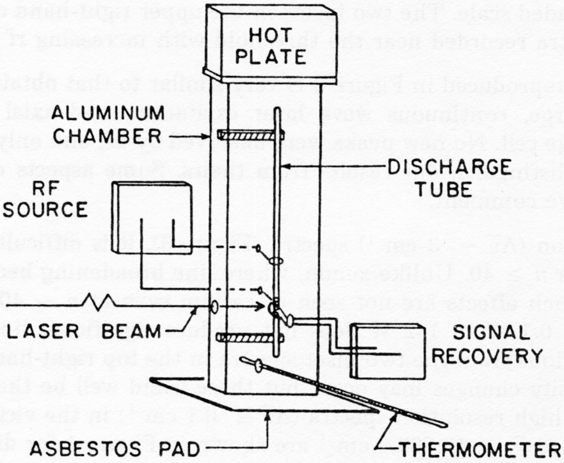

Figure 1. Experimental arrangement for RFLOG studies in a heated discharge tube. See text and Refs. 6, 23 for details.

This device could attain a temperature of 180–190 °C, at which cesium has a vapor pressure of 50–60 mTorr.[25] It took about an hour to stabilize the operating temperature which was measured near the bottom of the quartz cell. This temperature, once attained, remained constant over time and provided a constant vapor pressure of cesium. Temperature control was provided by control of the hotplate. The actual temperature in the region of laser excitation was somewhat higher due to a small temperature gradient along the tube and due to rf heating.

In all other respects, the experiment was conducted as described in Refs. 6, 23. Signal normalization and generation of wavelength calibration markers from a hollow cathode lamp have been described previously.[36,37]

RESULTS AND DISCUSSION

The various transitions observed in the region covered by the scanning dye laser are indicated in the state diagram of cesium in Figure 2. Within this range, several Rydberg series arising from the 5d and 6p states of neutral cesium may be observed.

The four series originating in the 5d states are: $5d_{5/2} \rightarrow nf_{7/2}$, $5d_{3/2} \rightarrow nf_{5/2}$, $5d_{5/2} \rightarrow np_{3/2}$, and $5d_{3/2} \rightarrow np_{1/2}$. Some spectral features of LOG signals from cesium vapor in an rf discharge in the range 16,250–16,860 cm^{-1}, along with the neon calibration markers (top traces), are reproduced in the lower half on Figure 3. The two observed $5d \rightarrow nf$ series are indicated by running indices along the top and the two $5d \rightarrow np$ series by indices running along the bottom of the spectrum. Some other peaks are identified individually. In the upper half of Figure 3, the region $\bar{\nu} > 16{,}620$ cm^{-1} is shown on an expanded scale. The two insets in the upper right-hand corner show portions of LOG spectra recorded near the threshold with increasing rf power values.

The spectrum reproduced in Figure 3 is very similar to that obtained by Bridges[25] using a dc discharge, continuous wave laser excitation, and axial excitation in a cylindrical discharge cell. No new peaks were observed by us, and only minor differences of intensities distinguish our results from theirs. Some aspects of the spectrum, however, do deserve comment.

In low-resolution ($\Delta\bar{\nu} \sim 3$ cm^{-1}) spectra (Figure 3), it is difficult to resolve Rydberg transitions for $n \geq 40$. Unlike xenon, where line broadening becomes noticeable for $n \geq 30$,[6,23,24] such effects are not seen in cesium even at $n \simeq 40$. An increase of the rf power from 0.1 W to 1–2 W does not produce significant line broadening in cesium, as it is obvious from the two inset spectra in the top right-hand corner of Figure 3. Some intensity changes may occur but these could well be the result of larger noise levels. Some high resolution spectra ($\Delta\bar{\nu} \simeq 0.1$ cm^{-1}) in the vicinity of the neon calibration marker at $\bar{\nu} = 16{,}769.3$ cm^{-1} are shown in Figure 4 for different rf power levels. Several high-n members ($n \geq 50$) of $5d \rightarrow nf$ and $5d \rightarrow np$ Rydberg transitions are identified in this figure. These high-n Rydberg levels of cesium do not show any

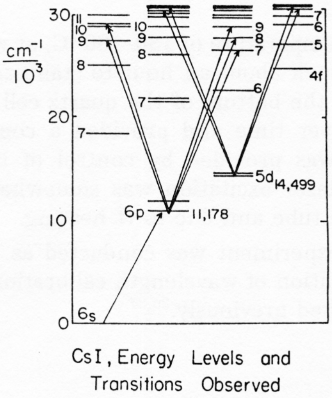

Figure 2. CsI energy levels. The transitions observed in this work are schematized.

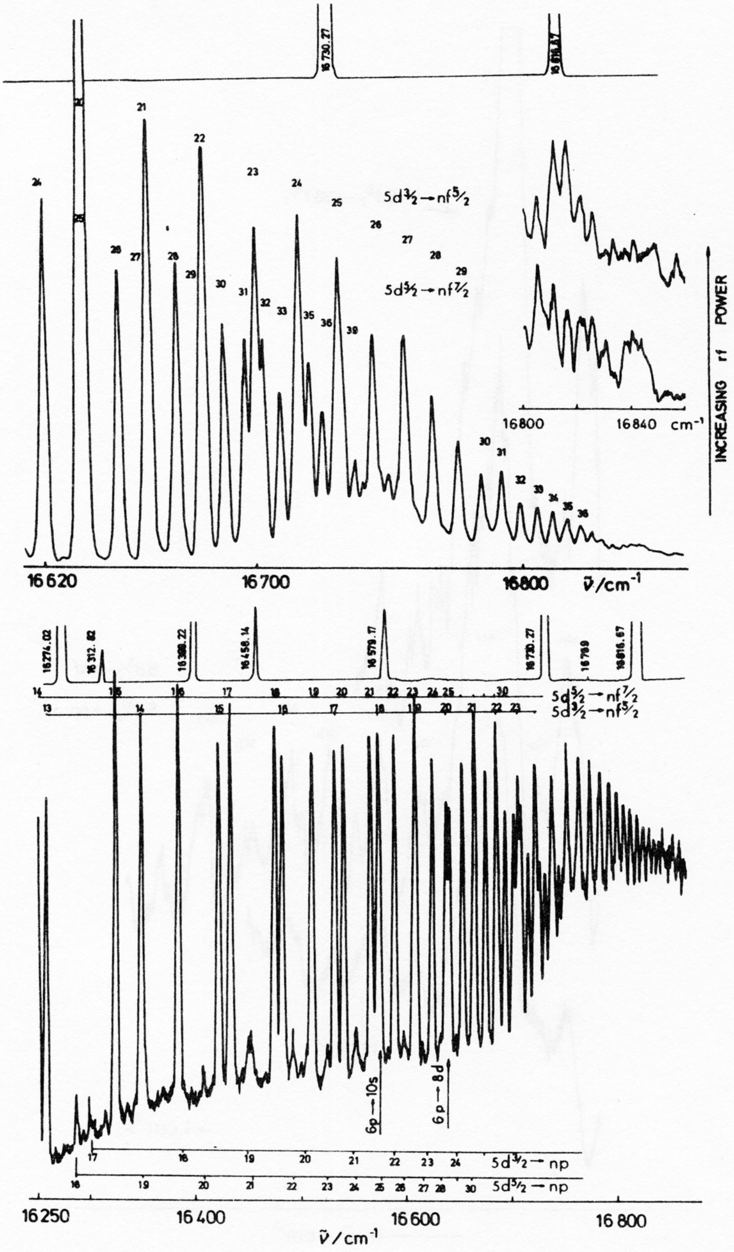

Figure 3. Low-resolution ($\Delta\bar{\nu} \sim 3\text{cm}^{-1}$) LOG spectra of cesium from 16,250–16,680 cm^{-1}. The four Rydberg series observed here are labeled. The upper half shows a low-speed scan from 16,620 to 16,860 cm^{-1}, with two insets depicting part of the spectrum near ionization threshold recorded with increasing rf power. The wavelength calibration markers generated from a hollow-cathode discharge lamp, neon being the filler gas, are also displayed in the upper part of each half.

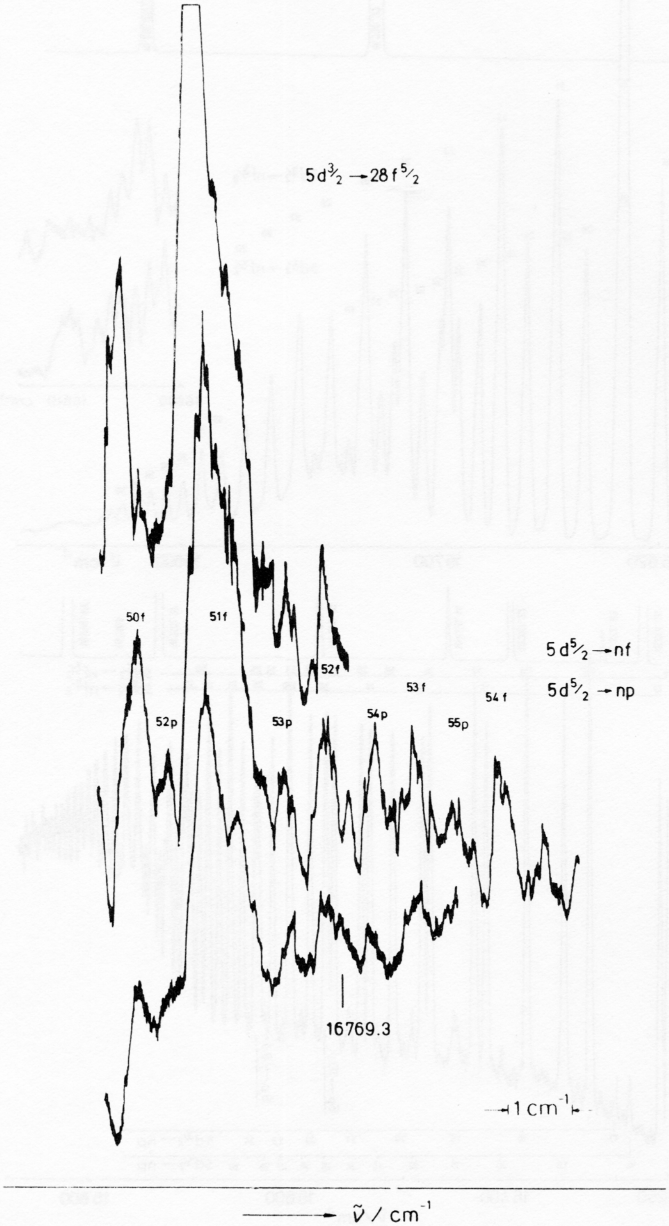

Figure 4. High-resolution ($\Delta\tilde{\nu} \sim 0.1$ cm^{-1}) LOG spectra of cesium in the vicinity of the neon calibration marker at 16,769.3 cm^{-1} recorded with increasing rf power levels (upper trace: highest rf power). Transitions to several high-*n* Rydberg states are identified. No noticeable broadening of these states is observed.

significant broadening. In contrast, the 31f state in xenon is found to have a width >1.0 cm^{-1} under similar conditions.[6]

The ground state term for cesium is ^{2}S. The excited energy levels of the optical electron are all built upon the $[5_p{}^6]$ $^1S_0$ core, and all series converge to the singly ionized $^1S_0$ state of CsII, which corresponds to complete removal of the single s electron. All of the excited states, except for the excited s states, are split by the spin-orbit coupling of the optical electron. The energy levels are designated $^2L_{l+s}$ and $^2L_{l-s}$, in which L is the total orbital angular momentum (which is equal to l, the orbital angular momentum of the optical electron) and s (= 1/2) is the spin angular momentum of the optical electron.

The value of the spin-orbit interaction decreases with increasing l: for the 6p states, the spin-orbit splitting is equal to 554.11 cm^{-1}; for the 5d states it is 97.59 cm^{-1}; and for the 6f states, it is 0.10 cm^{-1} (The splitting in the f-states is below the resolution of our equipment). The spin-orbit splitting also decreases with increasing n: Fo example, compare the value for the 6p states with that of the 20p states, namely 1.59 cm^{-1}.[38]

With these values for the spin-orbit splitting in mind, one might expect that cesium spectra in the range 16,250–16,860 cm^{-1} should consist of doublets, representing the spin-orbit splitting of the lower states. Transitions within this range include (see Figure 2) 5d–nf, 5d–np, 6p–nd ($n>8$). In all cases, the spin-orbit splitting of the lower state is appreciable, whereas the spin-orbit splitting of the upper state is small. The result is, indeed, a doublet structure with essentially constant splitting. Upper state splittings either do not occur because of the nature of the upper state (*i.e.*, an s-state) or exhibit a very small unresolved splitting at lower values of n (*i.e.*, nd and nf for $n<8$).

CONCLUSION

The LOG effect provides a sensitive and powerful spectroscopic technique. RFLOG spectra of cesium vapor in the range 16,250–16,860 cm^{-1} contain several Rydberg series originating in 6p and 5d levels and terminating at the first ionization limit. All the observed transitions are assigned. The high-n members (n~40–60) of these series do not exhibit any significant line broadening. The line broadening for high-n ($n \geq 30$) Rydberg states in xenon,[6] consequently, is attributed to intrinsic broadening due to interaction with the open-shell core. We are at present unable to make exact measurements of the rf fields and electron densities in xenon and cesium discharges. Hence our inability to make any quantitative correlations.

Acknowledgement. – This work was supported by the U.S. Department of Energy (Office of Health and Environmental Research) and the LSU Center for Energy Studies.

REFERENCES

1. F. M. Penning, *Physica* **8** (1928) 137.
2. R. B. Green, R. A. Keller, G. C. Luther, P. K. Schenck, and J. C. Travis, *Appl. Phys. Lett.* **29** (1976) 727.
3. D. H. Katayama, J. M. Cook, V. E. Bondybey, and T. A. Miller, *Chem. Phys. Lett.* **62** (1979) 542.
4. D. J. Jackson, E. Arimondo, J. E. Lawler, and T. W. Hansch, *Opt. Comm.* **33** (1980) 51.
5. R. A. Keller, R. Engleman, Jr., and E. F. Zalewski, *J. Opt. Soc. Amer.* **69** (1979) 738.

6. D. Kumar, L. Klasinc, P. L. Clancy, and S. P. McGlynn, *Int. J. Quant. Chem. Symp.* **19** (1986) 403; *Int. J. Quant. Chem.* **31** (1987) 327.
7. P. K. Schenck and K. C. Smyth, *J. Opt. Soc. Amer.* **68** (1978) 626.
8. T. Suzuki, and M. Kakimoto, *J. Mol. Spectrosc.* **93** (1982) 423.
9. C. R. Webster and C. T. Rettner, *Laser Focus* **19** (1983) 41.
10. D. Feldmann, *Opt. Comm.* **29** (1979) 67.
11. D. Kumar, L. Klasinc, P. L. Clancy, R. V. Nauman, and S. P. McGlynn, *Int. J. Quant. Chem. Symp.* **20** (1986) 635.
12. R. Vasudev and R. N. Zare, *J. Chem. Phys.* **76** (1982) 5267.
13. J. E. Lawler, A. I. Ferguson, J. E. M. Goldsmith, D. J. Jackson, and A. L. Schawlow, *Phys. Rev. Lett.* **42** (1979) 1046.
14. B. Barbieri, N. Beverini, and A. Sasso, *Rev. Mod. Phys.* **62** (1990) 603.
15. D. M. Pepper, *IEEE J. Quant. Electron.* **QE–14** (1978) 971.
16. G. Erez, S. Lavi, and S. E. Miron, *ibid.* **QE–15** (1979) 1328.
17. R. D. May, *J. Appl. Phys.* **58** (1985) 1169.
18. D. Kumar and S. P. McGlynn, *J. Chem. Phys.* **93** (1990) 3899.
19. D. Kumar and S. P. McGlynn, *Chem. Phys. Lett.* **176** (1991) 536.
20. D. Kumar, and S. P. McGlynn, *Nature of Laser Optogalvanic Signals,* Proceedings of the International Conference on LASERS'89, D. G. Harris and T. M. Shay, Eds, STS press, 1990, pp. 757–760.
21. D. Kumar, R. R. Zinn, and S. P. McGlynn, *Optogalvanic Effect as a Probe for Plasma Processes,* 45th Annual Gaseous Electronics Conference, Boston, Massachusetts, 1992.
22. S. P. McGlynn and D. Kumar, *Laser Optogalvanic (LOG) Effect in a Capacitively Coupled Plasma,* 14th IUPAC Symposium on Photochemistry, Katholieke Universiteit, Leuven, Belgium, July 1992.
23. L. Klasinc, D. Kumar, P. L. Clancy, and S.P. McGlynn, *Croat. Chem. Acta* **59** (1986) 643.
24. S. P. McGlynn, L. Klasinc, D. Kumar, P. L. Clancy, S. W. Felps, and J. A. Dagata, *Giant Atoms and Molecules* in Mathematics and Computational Concepts in Chemistry, N. Trinajstić, Ed., Ellis Horwood, Chichester, 1986.
25. W. B. Bridges, *J. Opt. Soc. Amer.* **68** (1978) 352.
26. L. P. Roesch, *Opt. Commmun.* **44** (1983) 259.
27. M. S. O'Sullivan and B. P. Stoicheff, *Can. J. Phys.* **61** (1983) 940.
28. C. -J. Lorenzen and K. Niemax, *Z. Phys. A: Atoms and Nuclei* **311** (1983) 249.
29. P. Goy, J. M. Raimond, G. Vitrant, and S. Haroche, *Phys. Rev. A* **26** (1981) 2733.
30. C. J. Sansonetti, K. L. Andrew, and J. Verges, *J. Opt. Soc. Amer.* **71** (1981) 423.
31. C. J. Sansonetti and C. J. Lorenzen, *Phys. Rev. A* **30** (1984) 1805.
32. K. H. Weber and C. J. Sansonetti, *ibid.* **35** (1987) 4650.
33. J. C. Castro, M. L. Zimmerman, R. G. Hulet, D. Kleppner, and R. R. Freeman, *Phys. Rev. Lett.* **45** (1980) 1780.
34. D. Delande, C. Chardonnet, and J. C. Gay, *Opt. Commun,* **42** (1982) 25; C. Chardonnet, D. Delande, and J. C. Gay, *ibid.* **51** (1984) 249.
35. M. L. Zimmerman, M. M. Kash, and G. R. Welsch, *J. de Phys. (Colloq.C2)* **43** (1982) 113.
36. D. Kumar, R. V. Nauman, R. Mohanty, G. L. Findley, and S. P. McGlynn, *Rev. Sci. Instrum.* **54** (1983) 463.
37. D. Kumar, R. V. Nauman, and S. P. McGlynn, *ibid.* **57** (1986) 365.
38. C. E. Moore, *Atomic Energy Levels,* **3** (U.S. Govt. Printing Office, Washington, D.C., 1958).

SAŽETAK

Laserski optogalvanski spektar cezija u radiofrekventnom izboju

D. Kumar, P. L. Clancy, L. Klasinc, i S. P. McGlynn

Laserski optogalvanski (LOG) spektar cezijevih para kod ≈50 mTorr u radiofrekvencijskom izboju niske snage (≤1W) i frekvencije od ~30 MHz, zapisan je u spektralnom području od 16,250 do 16,860 cm^{-1}. Opaženi su članovi nekoliko Rydbergovih serija (6p → *n*s, 6p → *n*d, 5d → *n*p, 5d → *n*f) koje završavaju kod prve granice ionizacije. Širenje spektralnih linija pri visokim-*n* ($n \geq 30$) f-razinama u ceziju znatno je manje nego u slučaju atoma ksenona. Jače širenje u ksenonu dijelom se pripisuje međudjelovanju Rydbergova elektrona sa strukturom otvorene ljuske što ju tvore ostali elektroni.