

Emission Continua in $M^* + M$ Collisions ($M = \text{Zn, Cd}$) *

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Strong UV and weak visible continua of Zn_2 , Cd_2 and ZnCd have been observed in emission when a discharge-excited atomic beam of zinc or cadmium is crossed with an unexcited beam of zinc or cadmium. It has been found that the discharge-excited beams of Zn and Cd contain also atoms in autoionizing states with lifetimes equal to (140 ± 30) and (110 ± 20) μsec , respectively.

Introduction

Gas-phase excimer spectra of the elements were intensively studied in the twenties and thirties, both in emission and absorption, and several bands were discovered (The most complete list of references for the early studies had been given by Finkelnburg [1]) that were later assigned to corresponding electronic states by Mrozowski [2]. Gas-phase studies of group II B dimers could not, however, give molecular constants due to the almost unstructured character of the bands observed.

The last decade brings revived interest in studies of group II B homo- and heteronuclear dimers in matrices [3–6] as well as in gas-phase by absorption [7] and fluorescence techniques [8–11].

In this paper we report on an effort to obtain luminescence from group II B excimers (or diatomic exciplexes) formed in the collision of the excited atom with an unexcited one. The experiment was carried out by crossing a well collimated discharge-excited atomic beam with another atomic beam. This arrangement enables one to take molecular spectra for the lowest possible metal vapor pressures and also allows to vary independently (and thus keep comparable) the concentrations of the metal atoms from both beams in the collision zone. The latter possibility is very important in the studies of heteronuclear dimers formed from metals that have very different vapor pressures

at given a temperature (E.g. in the Hg-Cd-mixture conventional heating in a closed cell gives an Hg/Cd concentration ratio higher than 10^3).

At pressures in the collision zone below 1 Torr we have observed continua of Zn_2 and Cd_2 as well as continua that differ from the above and result from the luminescence of ZnCd . To our knowledge there is no previous report on emission from the heteronuclear dimer of this composition.

During the experiment it has been discovered also that electron-bombarded atomic beams of Zn and Cd contain highly energetic ($\sim 180\,000\text{ cm}^{-1}$) neutral species, which we believe are atoms in metastable autoionizing states. Additional measurements gave lifetimes of these autoionizing states of Zn and Cd equal to (140 ± 30) and (110 ± 20) μsec , respectively.

Experimental

The scheme of the experimental set-up to obtain the molecular spectra is given in Figure 1. The cylindrical vacuum chamber (30 cm dia, 60 cm ht.), painted black velvet inside, was continuously pumped by a 2000 l/s diffusion pump backed by a rotary pump; the typical background pressure was of the order of 10^{-6} Torr. Inside the chamber two atomic beam sources were mounted. The vertical atomic beam effusing from a stainless steel oven containing metal lumps (purity 99.999%) was excited in the pulsed discharge (45 V, 0.4 A, 9 Hz, square pulses) region between a hot cathode (100 W) and the grounded conically shaped oven orifice. The beam was later passing two slits, a pair of parallel plates connected to the power supply at $\pm 100\text{ V}$ in order to deflect charged particles, and another couple of slits. The excited beam formed in

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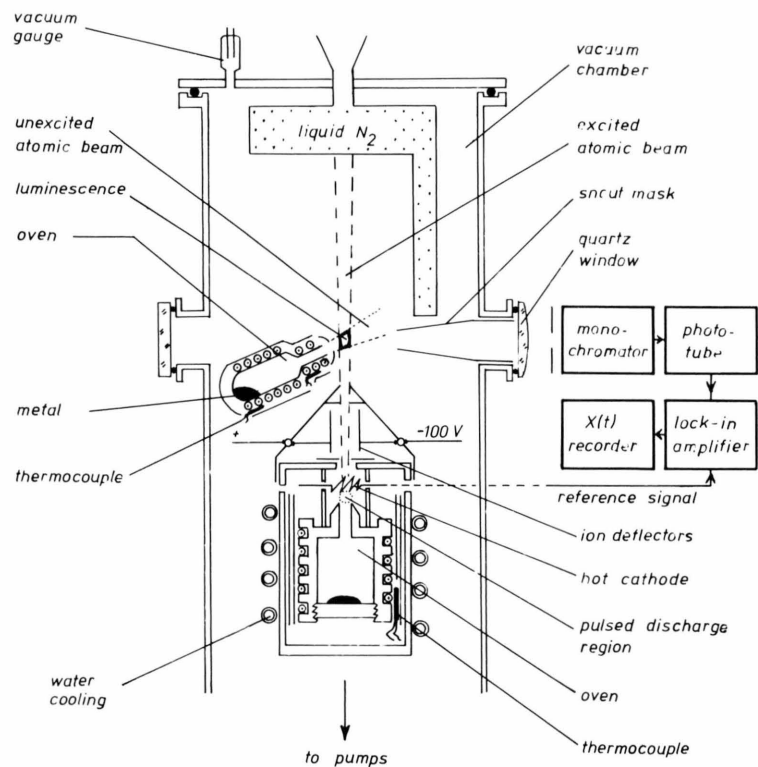


Fig. 1. Experimental set-up for the luminescence studies.

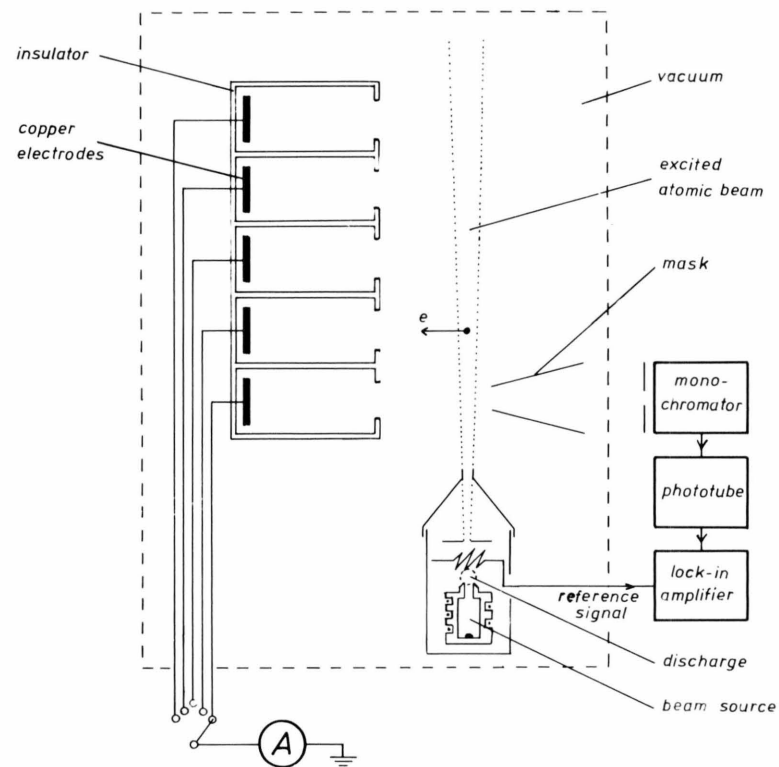


Fig. 2. Apparatus for lifetime measurements of metastable autoionized states.

this way had 3 mm dia at the source exit and its divergence was 3° .

The second atomic beam source was mounted above the first one and tilted to cross the beams at about 75° . In this source the metal was evaporated from a quartz crucible, 40 mm long, 2 mm dia nozzle, all wrapped in zirconia oxide insulation and a tantalum shield. The temperatures of the oven and the nozzle could be varied independently by two separate heaters, and that of the nozzle was always kept 50 K higher. This unexcited beam was poorly collimated by one slit (divergence about 15°), but since the orifice was only about 1 cm from the excited beam, the luminescing crossing zone was limited to a cylinder 5 mm long. Atoms from both beams were deposited on liquid- N_2 -cooled walls.

The luminescence from the collision zone was focused on the entrance slit of a monochromator with either Jobin-Yvon (1800 grooves/mm) grating in the UV or Carl Zeiss Jena (651 grooves/mm) grating in the visible. The signal from M12 FVC51 phototube was fed into a Unipan 232 B lock-in nanovoltmeter with a reference signal supplied by a discharge-driving unit.

In the beginning of the experiment, to check that the discharge excited beams of Zn and Cd did not contain charged particles, a Faraday-cup grounded through a Unitra 219 electrometer was put above the excited beam source. As the voltage on the parallel deflectors of the source was increased, the current through the electrometer was monitored. Unlikely the Mg, Ca and Sr-excited beams from the same source [12], in the case of Zn and Cd a substantial current (several microamps) from the Faraday-cup could not be suppressed by a voltage increase up to 300 V on the deflectors.

We have assumed that some Zn- and Cd-atoms pass through our deflectors without changing direction and ionize spontaneously later along the way up. To check this hypothesis, a simple lifetime measurement was performed, as shown in Figure 2. A series of 5 boxes made of insulating material was mounted above the excited beam source along the beam path. On the back wall of each box a thick copper plate was attached and connected through a switch to an electrometer. The aperture of each entrance slit in the boxes was 1 cm. Electrons produced in autoionization are sent in all directions while ions should change their original direction only slightly and have no chance to enter the boxes.

The lifetime of the autoionizing atoms was determined by subsequent measurement of the current coming from each box and simultaneous measurement of the beam velocity. To measure this velocity we used a phase shift method in which the $^3P_1 - ^1S_0$ intercombination line (always seen in the excited beam) was observed at a distance of $\Delta x = 66$ mm from the discharge through a 2 mm slit put on the mask. The phase shift $\Delta\phi$ of the photomultiplier signal with respect to the discharge-driving pulse could be measured by adjustment of the lock-in nanovoltmeter to obtain maximal recovered signal. The most probable beam velocity was later calculated from the formula $v_m = \Delta x \cdot \omega / \Delta\phi$. Different discharge frequencies ω were applied, ranging from 400 Hz to 900 Hz in search for the best peak in phase shift adjustments; the results for sharper peaks were later taken with higher statistical weight.

Results and Discussion

The discharge-excited beams of Zn and Cd themselves had weak visible emission, mostly due to the $^3S_1 - ^3P_1$ triplet, by far the strongest visible feature. Intercombination lines for Zn and Cd at 3076 Å and 3261 Å were relatively weak, as could be expected, since the radiative lifetimes of the lowest 3P_1 are only 20 [13] and 2 [14] μsec , respectively, so in the region observed, 66 mm from the discharge, at a typical beam speed of 500 m/s only a very small part of the original amount of atoms in the lowest 3P_1 state was left. The much longer-lived 3P_0 and 3P_2 should however maintain the original population acquired in the discharge.

When the second beam source was also on, with increase of its temperature more and more light came from the collision zone. First a rich spectrum of atomic and ionic lines of Zn or Cd (or both) appeared, later, when the vapor pressure inside the unexcited beam source was of the order of 10^{-1} Torr, some lines broadened and continua through all UV were observed (Figures 3–6). The spectral resolution of the recordings was unfortunately limited by a relatively high minimal speed of the monochromator's scanning.

The $\text{Zn}^* + \text{Zn}$ continuum (Fig. 3) looks similar to the spark-excited $\text{Zn}_2 (^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+)$ [15] spectrum obtained by Kapuściński [16] for much higher vapor pressures. Though the latter has a structured

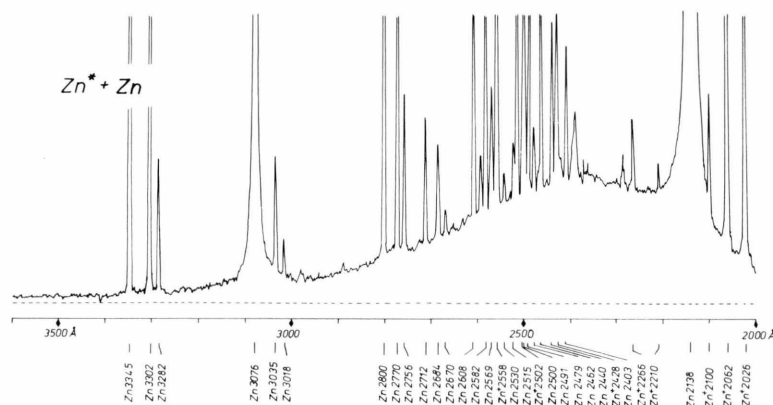


Fig. 3. UV luminescence spectrum observed in $Zn^* + Zn$ collisions: spectral resolution 3.3 Å, sensitivity lower than in Figs. 4–6 by a factor 0.3. Oven temperatures $T(Zn^*) = 805$ K, $T(Zn) = 800$ K correspond to vapor pressures inside the oven equal to 2.5 Torr and 2.2 Torr, respectively. Bottom dashed line is closed-slit-signal level.

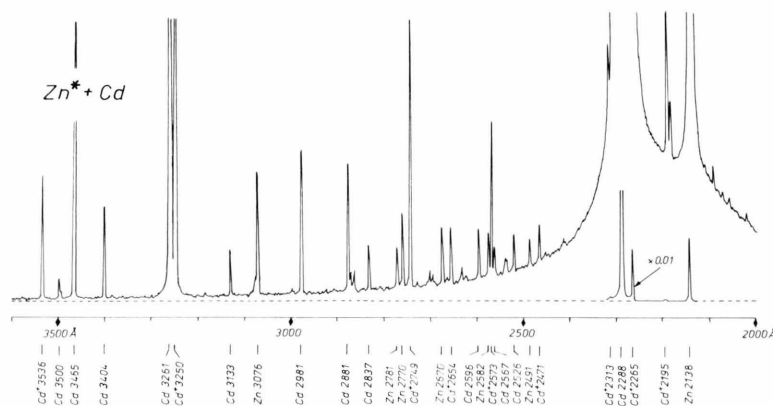
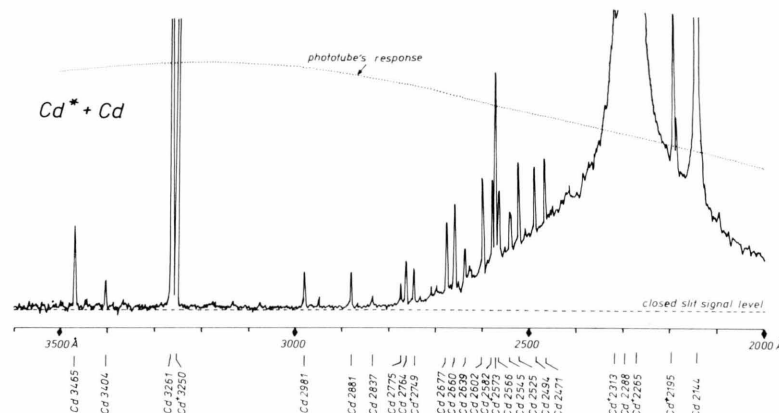


Fig. 5. UV luminescence spectrum observed in $Zn^* + Cd$ collisions: spectral resolution 2 Å. Oven temperatures $T(Zn^*) = 810$ K, $T(Cd) = 690$ K, corresponding vapor pressures inside the oven are 3 Torr and 1.5 Torr, respectively. Insert between 2130 Å and 2320 Å shows the spectrum with sensitivity 100 times lower.



part between 2500 Å and 3000 Å, the maximum for both continua lies at approximately the same wavelength (~ 2400 Å). The spectrum in Fig. 3 goes obviously beyond the 2120–3080 Å limits quoted in [16], since we have no VUV-limitation in excitation energy as it was in the previous studies and therefore emission from excimer states arising from atomic excited states higher than 1P_1 can also contribute to the spectrum.

The $Cd^* + Cd$ continuum (Fig. 4) reminds that obtained by Kapuściński [17] for Cd_2 excited by a Cd-spark at the lowest quoted vapor pressure of cadmium in the cell (800 K). The maximum in both spectra is around the Cd I 2288 Å-line, however the limits differ: in Fig. 4 the continuum starts at 2800 Å and goes deep into the vacuum ultraviolet, while in [17] it lies between 3100 Å and 2250 Å.

The luminescence observed in UV when two different atoms collide is shown in Figures 5 and 6. Here the continuum has a maximum at about 2150 Å, and since the spectrum is different from that for the homonuclear dimer in the same conditions, we believe that this emission comes from the ZnCd heteronuclear excimer (exciplex). ZnCd was observed before only in matrices [4] between 2400 Å and 2800 Å in absorption.

In general, in addition to the continua, a broadening of the atomic lines corresponding to transitions from the lowest 3P_1 to the ground state and the lowest 1P_1 to the ground state is also observed, the latter broadening being stronger.

The visible band of ZnCd between 4000 Å and 5300 Å (see Fig. 7) has a 100 times lower intensity than the UV continuum. This emission is most likely from $^3\pi$ to the ground state. The shape, limits and position of the maximum of the ZnCd-band in the visible are similar to that of Cd_2 [9] and $CdHg$ [8, 11].

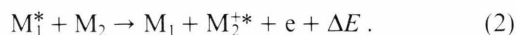
The discrete spectra in Figs. 3–7 consist of many atomic and ionic lines of Zn and Cd. It can be noted that very high atomic states are populated in the collisions, as can be seen in Fig. 6, where for lower resolution ($\Delta\lambda = 5$ Å) a series of lines converging to the Zn I (4^3P_j) ionization limit was recorded. The atomic transitions observed for $Cd^* + Cd$ collisions are given as an example on a Grotrian diagram (Fig. 8), where the thicknesses of the arrows are approximate measures of the line intensities. In the $Zn^* + Zn$ collisions the picture is very much the same, while for $Zn^* + Cd$ (or $Cd^* + Zn$) there are

almost no lines from the singlet states of the neutral atom of the same kind as the one excited in the discharge. It is characteristic that no ionic lines are observed from the levels above a certain energy value; one can also note strong laser lines of Zn II and Cd II, which suggest a high population of the upper laser levels.

Considering the experimental conditions and results described above we assume that the highly excited ionic states are populated in connection with the presence of metastable autoionizing states of Zn or Cd in the excited beam. This is achieved either through the autoionization channel



or through Penning ionization:



The typical autoionization lifetime is 10^{-14} s, but since the selection rules for L and S can not always be fulfilled, it can be as long as 10^{-4} s [24]. If also optical transitions are forbidden, autoionizing states can be metastable, as it was observed by Feldman and Novick [25] for alkali atoms, where the lifetimes against autoionization ranged from 5 to 90 μ sec. The existence of autoionizing levels in group II B-elements (Zn, Cd, Hg) had been confirmed in experiment [18–23]. The last two papers by Mansfield and Connerade [22] and by Mansfield [23] on double electron excitation in zinc and cad-

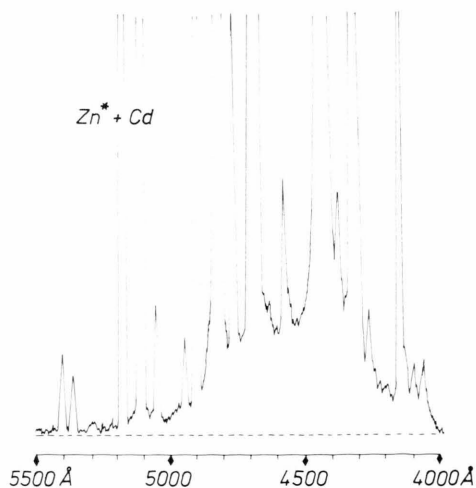


Fig. 7. ZnCd band emission in $Zn^* + Cd$ collisions: spectral resolution 12 Å, $T(Zn^*) = 810$ K, $T(cd) = 705$ K, corresponding vapor pressures inside the ovens are 3 Torr and 2 Torr, respectively.

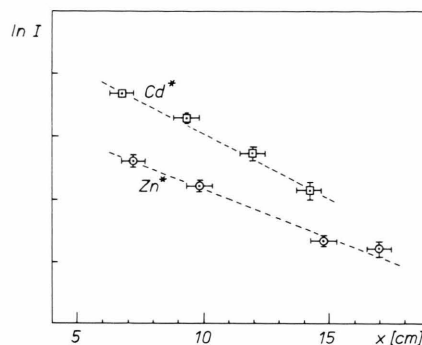
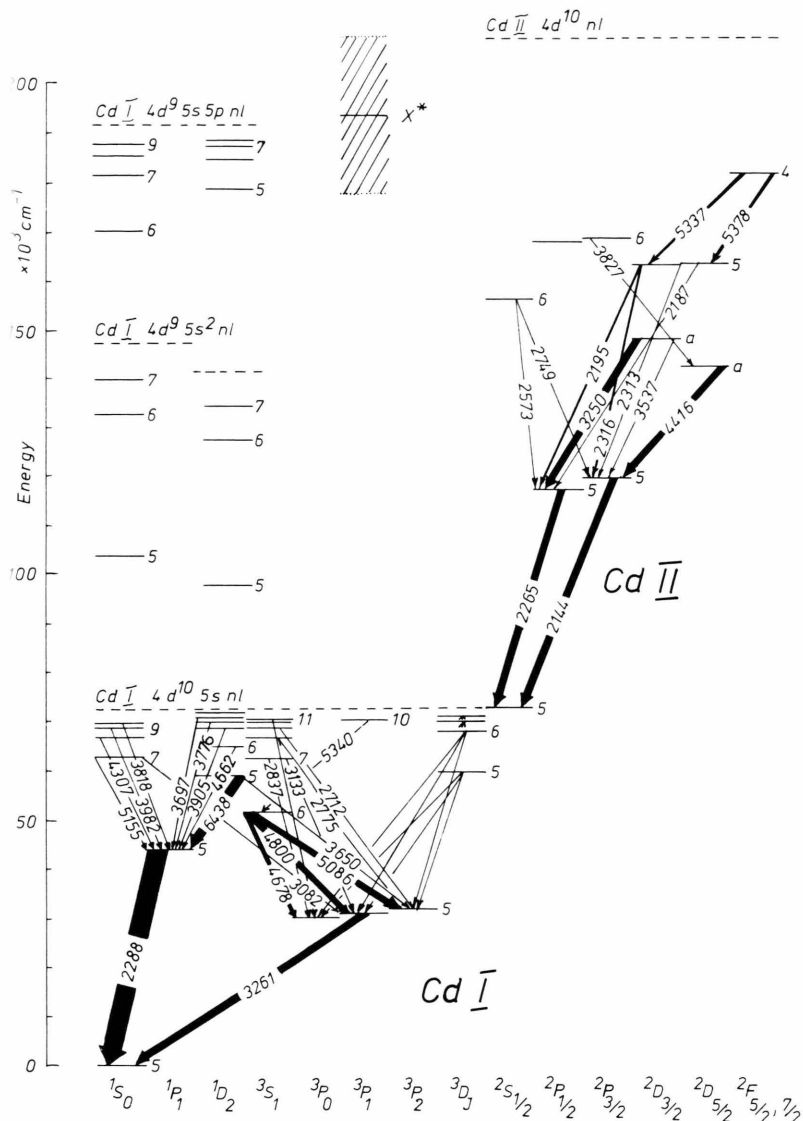


Fig. 9. Semilogarithmic plot of autoionization-produced current vs. distance from the discharge.

mium report on autoionizing levels with energies above $180\,000 \text{ cm}^{-1}$. Double electron excitation is expected to be efficient in the discharge and therefore we have put some of the levels and series limits given in [18] and [23] on the diagram in Figure 8. In the $\text{Cd}^* + \text{Cd}$ collisions the lines observed from the highest level are Cd II 5337 \AA and Cd II 5378 \AA from Cd II (4^2F) (energy $\sim 181\,000 \text{ cm}^{-1}$), however we failed to observe twin Zn II 4912 \AA and Zn II 4924 \AA lines from Zn II (4^2F) (energy $\sim 193\,000 \text{ cm}^{-1}$) in $\text{Cd}^* + \text{Zn}$ collisions. The latter doublet was

very strong in $\text{Zn}^* + \text{Zn}$ collisions and no line appearing from a higher level was observed. We conclude that the energies given above are lower limits of energy of the highest involved metastable state in cadmium and zinc. These results get some support from experiments of Bogdanova et al. [26–28], where the formation of enigmatic cadmium metastables was discovered in electron-atom collisions at energies of $(193\,500 \pm 16\,000) \text{ cm}^{-1}$ [27], as marked in Fig. 8 by X^* , although the nature of the metastable was there finally explained in a

Table I

	Measured beam velocity	Calculated beam velocity	Lifetime of metastable autoionizing state τ (10^{-6} s)
	v_m (m/s)	v_c (m/s)	
Zn*	490 ± 30	540	140 ± 30
Cd*	415 ± 60	393	110 ± 20

different way. It can be noted in Fig. 8 that the value given by Bogdanova et al. and the value deduced by us from the appearance of Cd II 5337 Å and 5378 Å lines are close to the Cd I $4d^9 5s 5p n1$ series limit. Longer-living states are expected there, as the lifetimes increase approaching the series limit [29]. Identification of the metastable autoionizing states as belonging to the $4d^9 5s 5p n1$ series would explain the difference between the excited beams of group IIA (examples: Mg, Ca, Sr) and group IIB (examples: Zn, Cd); in the latter one of the electrons of the outermost closed shell is excited in the discharge and this brings in the autoionizing metastables.

We have measured the lifetimes of the metastable autoionizing atoms using the method described above in the experimental section. Semilogarithmic plots of electron current vs. the distance from the source are given in Fig. 9, where the experimental points for Zn* are moved down by unity. The horizontal error bars equal to the slitwidths of the insulated boxes; the vertical error bars are standard deviations as obtained from normalized data for different experimental runs. The measured beam

velocities v_m together with the most probable beam velocities calculated from the oven temperature $v_c = \sqrt{3RT/m}$ (where m = atomic mass) and the lifetimes of the metastable autoionization levels are collected in Table I. For zinc the measured beam velocity is slightly lower than the calculated one, whereas for cadmium the value of v_m is slightly higher than v_c (what could be expected, since the beam passes the discharge region and can be sped up). The lifetimes, derived using measured beam velocities, are of the order of 10^{-4} s, but one has to remember that the experimental method used here is sensitive only in the $(10^{-5} \div 10^{-2})$ s lifetime range. It can not be excluded that atoms in autoionizing states living longer than 10^{-2} s could be present in the beam and pass by boxes undiscovered.

The fraction of metastable autoionizing atoms in our beam was not measured, but considering the intensity of luminescence in view of our experience with excited alkaline earth beams we estimate that it could be at least 1%. These atoms can be useful in the collisional production of strong spectral lines from high-lying levels (both neutral and ionic); they might also play a role similar to helium in obtaining population inversion in the group IIB metal ions.

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- [1] W. Finkelnburg, *Kontinuierliche Spektren*, Springer-Verlag, Berlin 1938.
- [2] S. Mrozowski, *Z. Physik* **104**, 228 (1937); **106**, 458 (1937).
- [3] B. S. Ault and L. Andrews, *J. Mol. Spectry* **65**, 102 (1977).
- [4] J. S. Miller and L. Andrews, *J. Chem. Phys.* **69**, 3034 (1978).
- [5] A. Givan and A. Loewenschuss, *Chem. Phys. Lett.* **62**, 592 (1979).
- [6] H. J. Vreede, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.* **27**, 1 (1974).
- [7] J. B. West, H. Komine, and E. A. Stappaerts, *J. Appl. Phys.* **50**, 7929 (1979).
- [8] M. W. McGeoch, G. R. Fournier, and P. Ewart, *J. Phys. B: Atom. Molec. Phys.* **9**, L121 (1976).
- [9] R. E. Drullinger and M. Stock, *J. Chem. Phys.* **68**, 5299 (1978).
- [10] J. G. Eden, *Opt. Commun.* **25**, 201 (1978).
- [11] M. W. McGeoch, *J. Chem. Phys.* **72**, 140 (1980).
- [12] A. Kowalski and M. Menzinger, *J. Chem. Phys.* **78**, 5612 (1983).
- [13] F. W. Byron Jr., M. N. McDermott, R. Novick, B. W. Perry and E. B. Saloman, *Phys. Rev. A* **134**, 47 (1964).
- [14] F. W. Byron Jr., M. N. McDermott, and R. Novick, *Phys. Rev. A* **134**, 615 (1964).
- [15] P. J. Hay, T. H. Dunning Jr., and R. C. Raffanetti, *J. Chem. Phys.* **65**, 2679 (1976).
- [16] W. Kapuściński, *C. R. Soc. Pol. de Phys.* **5**, 401 (1930).
- [17] W. Kapuściński, *C. R. Soc. Pol. de Phys. Fasc.* **VIII**, 5 (1927).

- [18] H. Beutler, *Z. Physik* **87**, 19 (1933).
- [19] H. Beutler and K. Guggenheimer, *Z. Physik* **87**, 176 (1934).
- [20] W. R. S. Garton and J. P. Connerade, *Appl. J.* **155**, 667 (1969).
- [21] W. R. S. Garton and A. Rajaratnam, *Proc. Phys. Soc. London* **A68**, 1107 (1955).
- [22] M. W. D. Mansfield and J. P. Connerade, *Proc. Roy. Soc. London* **A359**, 389 (1978).
- [23] M. W. D. Mansfield, *Proc. Roy. Soc. London* **A362**, 129 (1978).
- [24] H. G. Kuhn, *Atomic Spectra*, Academic Press, New York 1969.
- [25] P. Feldman and R. Novick, *Phys. Rev. Letters* **11**, 278 (1963).
- [26] I. P. Bogdanova, S. V. Ryazantseva, and V. B. Yakhontova, *Opt. Spektrosk.* **45**, 651 (1978); **49**, 478 (1980); **49**, 851 (1980); **51**, 444 (1981).
- [27] I. P. Bogdanova, S. V. Ryazantseva, A. B. Tsyganov, and V. B. Yakhontova, *Opt. Spektrosk.* **50**, 1009 (1981).
- [28] I. P. Bogdanova and S. V. Ryazantseva, *Opt. Spektrosk.* **54**, 752 (1983).
- [29] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, Cambridge 1963.