

Thus, the results of our investigations show that the quadratic dependence of W on E_0 , observed in Ref. 6 for XTR in tin granules, does not appear in the case of a layered radiator made of the same material. It is possible that this disparity is due to the different methods of generation and registration of the XTR.

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¹Proc. Internat. Symp. on Transition Radiation of High-Energy Particles, Erevan Phys. Inst., 1977.

²E. S. Belyakov, M. P. Lorikyan, K. Zh. Makaryan, M. M. Muradyan, and K. K. Shikhlyarov, Nauchnoe Soobshchenie EFI (Scient. Communication, Erevan Phys. Inst.) 44-(73), 1973.

³A. I. Alikhanyan, E. S. Belyakov, G. M. Garibyan, M. P. Lorikyan, K. Zh. Markaryan, and K. K. Shikhlyarov, Pis'ma Zh. Eksp. Teor. Fiz. 16, 315 (1972) [JETP Lett. 16, 221 (1972)].

⁴F. R. Artyunyan, K. A. Isiryan, A. G. Oganesyan, and A. A. Frangyan, Pis'ma Zh. Eksp. Teor. Fiz. 4, 277 (1966) [JETP

Lett. 4, 187 (1966)].

⁵F. R. Arutyunyan, K. A. Isiryan, and A. G. Oganesyan, Zh. Eksp. Teor. Fiz. 52, 1121 (1967) [Sov. Phys. JETP 25, 743 (1967)].

⁶A. K. Drukier, C. Valette, G. Waysand, L. C. L. Yuan, and F. Peters, Lett. Nuovo Cimento 14, 300 (1975).

⁷M. P. Lorikyan, Nauchnoe soobshchenie EFI 58-(74), 1974.

⁸A. I. Alikhanyan, E. S. Belyakov, G. M. Garibyan, M. P. Lorikyan, K. Zh. Markaryan, and K. K. Shikhlyarov, Pis'ma Zh. Eksp. Teor. Fiz. 18, 35 (1973) [JETP Lett. 18, 18 (1973)].

⁹A. I. Alikhanyan, Ref. 1, p. 41.

¹⁰L. A. Vardanyan, G. M. Garibyan, and Yan Shi, *ibid.* p. 374.

¹¹A. L. Avakyan, M. P. Lorikyan, Yu. L. Margaryan, and K. Zh. Markaryan, *ibid.*, p. 287.

¹²G. M. Garibyan and Yan Shi, Zh. Eksp. Teor. Fiz. 70, 1627 (1976) [Sov. Phys. JETP 43, 848 (1976)].

¹³L. A. Vardanyan, G. M. Garibyan, and Yan Shi, Izv. Akad. Nauk Arm. SSR, Fizika, 11, 329 (1976).

¹⁴G. M. Garibyan, and Yan Shi, Izv. Akad. Nauk Arm. SSR Fiz. 12, 105 (1977).

¹⁵Yan Shi, Ref. 1, p. 102.

¹⁶K. Liden and N. Starfelt, Ark. Fys. 7, 427 (1953).

¹⁷J. W. Motz, Phys. Rev. 100, 1560 (1955).

Translated by J. G. Adashko

Collapse of 4f-electron in the configuration $3d^9 4f$ in xenonlike ions

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The $M_{4,5}(3d)$ absorption and emission spectra of the xenonlike ions I^- , Cs^+ , Ba^{2+} , and La^{3+} were measured in ionic compounds (spectral range 600-1100 eV). It is shown that the form of the spectrum characterizes mainly the absorbing ion and depends little on its surrounding. The absorption spectra of Cs^+ , Ba^{2+} , and La^{3+} contain an intensive doublet near the ionization threshold of the $3d$ shell, and their emission spectra contain bands that are at resonance with the absorption bands. It is concluded that in the Ba^{2+} and La^{3+} ions the $4f$ orbit in the configuration $3d^9 4f$ is collapsed and that its collapse takes place on going from Xe to Cs^+ . This conclusion is confirmed by a calculation of the energies and cross sections of the $3d^{10} \rightarrow 3d^9 4f$ transitions in the Hartree-Fock-Pauli approximation.

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1. INTRODUCTION

The phenomenon of sudden compression of the radial wave function of an excited electron in a number of neutral atoms or in an isoelectronic sequence, which was named electron collapse, was predicted by Fermi in 1928.¹ Only in the last decade, however, in connection with the extensive studies of excited configurations of atoms and ions, did it attract considerable attention and made it possible to explain a number of interesting effects in atomic spectra and in the physics of atomic collisions.^{2,3}

The effective potential in the centrosymmetric field in the Hartree-Fock equation for the electron nl consists of two terms:

$$V_{\text{eff}}(nl|r) = V(nl|r) + l(l+1)/r^2,$$

where $V(nl|r)$ is the potential of the Coulomb field of the nucleus and of the other electrons, while the second term is centrifugal. In the interval $r \approx 1-5$ a. u., $V(nl|r)$ varies approximately like r^{-2} , and in the case of an electron with $l \geq 2$ these two terms compete with each other in a certain interval of r .² This leads to a specific form of the effective potential, with two minima separated by a positive potential barrier. The localization of the electron in the field of this potential is highly sensitive to a change in the charge of the nucleus or of the states of the other electrons. Whereas in a certain configuration of the atom Z the wave function of the excited electron is localized predominantly in the region of the outer potential well, for the same configuration of

the atom $Z + 1$, or even for another multielectron state of the atom Z ,⁴ it can be localized already in the region of the internal well, and this leads to a radical change—even by several orders of magnitude—in the values of the different characteristics of the excited electron and manifests itself in the spectra by a nonmonotonic change of the type of coupling and of the energy positions of the lines, as well as by a redistribution of the intensity in the spectrum.^{3,5}

The electron collapse is more clearly pronounced the larger the orbital quantum number of the electron. One can therefore expect a strong influence of the effect of the collapse of an $n'f$ electron in the configuration $nd^n n'f$ on the structure of the corresponding absorption and emission x-ray spectra. In a number of papers^{3,4,5} the collapse of the $4f$ electron in the configuration $4d^9 4f$ (which occurs near $Z = 55$) and its influence on the $4d$ absorption spectra were considered. The intensity of the spectrum should become redistributed among the channels $4d - 4f$ and $4d - \epsilon f$. In the indicated spectra, however, owing to the strong multielectron effects, a broad maximum predominates and masks the collapse effect. An interesting result of the experimental investigations is the establishment of the fact that the form of the $4d$ absorption spectra of elements that follow xenon in the periodic table is mainly of atomic origin, and the spectra of the vapors, metals, and solid-state compounds are very similar.⁷

In the present paper we present the results of experimental and theoretical investigations of the collapse of the $4f$ electron in the configuration $3d^9 4f$ of the xenon-like ions I^- , Cs^+ , Ba^{2+} , La^{3+} . Owing to the lesser role of the multielectron effects in this configuration, compared with the configuration $4d^9 4f$, one should expect the possibility of a more unambiguous interpretation of the spectra. As shown previously,⁸ collapse in an isoelectronic sequence should be more rapid than in a sequence of neutral atoms, and the fact that the ions with different values of Z are isoelectronic allows us to attribute the nonmonotonic variation of the spectra in the indicated sequence exclusively to the effect of the collapse.

We begin the article with a report of the results of experimental investigation of the $3d$ absorption and emission spectra of the ions I^- , Cs^+ , Ba^{2+} and La^{3+} in ionic compounds, followed by an analysis of the transitions $3d^{10} - 3d^9 4f$ in the Hartree-Fock-Pauli (HFP) approximation and calculation of the cross section for the photoionization of the $3d$ shell. In the last section we discuss the results and conclude that collapse of the $4f$ electron in the configuration $3d^9 4f$ takes place, at least partially, in the transition from Xe to Cs^+ .

2. $3d$ ABSORPTION AND EMISSION SPECTRA OF I^- , Cs^+ , Ba^{2+} AND La^{3+}

We have measured the absorption spectra of alkali iodides and of the halides of cesium, barium, and lanthanum in the spectral region from 600 to 1100 eV. The measurements were performed with an RSM-500 x-ray monochromator spectrometer, with a glass diffraction grating (600 lines/mm, curvature radius 6 m). An x-

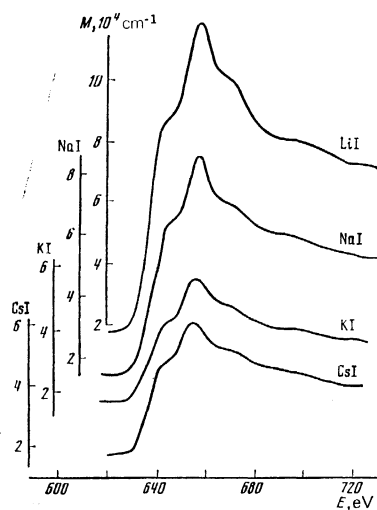


FIG. 1. $M_{4,5}$ absorption spectra of I^- in alkali iodides.

ray tube with a tungsten anode operated at 5 kV and 90 mA. The higher orders of the bremsstrahlung were suppressed by a focusing mirror. The x-rays were registered with an argon-methane flow-through proportional counter having a nitrocellulose window. Thin films of the investigated substances, whose thickness was measured with the aid of a quartz oscillator accurate to $\sim 20\%$, were evaporated on the nitrocellulose films in vacuum in the measuring chamber of the spectrometer. The width of the spectrometer slits was 15 μm , thus ensuring monochromatic radiation in the employed spectral range with intensity ~ 1000 quanta/sec and a spectral gap width ~ 2 eV.

The absorption spectra in the region of the $M_{4,5}(3d)$ edges of iodine, cesium, and barium are shown in Figs. 1, 2, and 3. In all cases there is a well pronounced albeit not very rich near-edge structure. The general form of the spectra is practically independent of the second component of the compound, and the chemical

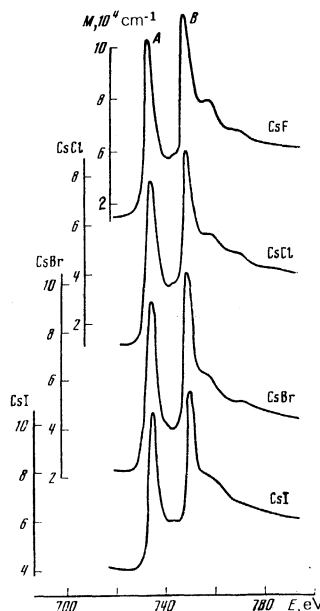


FIG. 2. $M_{4,5}$ absorption spectra of Cs^+ in cesium halides.

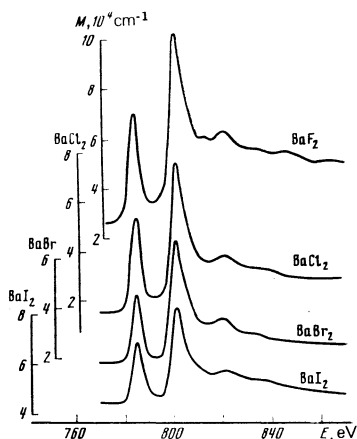


FIG. 3. $M_{4,5}$ absorption spectra of Ba^{2+} in barium halides.

shifts do not exceed 1.5 eV. This demonstrates convincingly that the main structural singularities of the spectra are of quasi-atomic character. They characterize the corresponding ion, which is possibly slightly perturbed by the crystal field. Therefore in first-order approximation we can use the presented spectra to discuss the optical transitions of the $3d$ electrons in the corresponding isolated ions.

For a detailed interpretation, the spectra of the isoelectronic ions I^- , Xe , Cs^+ , Ba^{2+} and La^{3+} are gathered together in Fig. 4. The Xe spectrum was borrowed from Ref. 9. The photoabsorption cross sections are marked on the ordinate scale in the same scale for all ions. The spectra have the same energy scale, the origin of which coincides with the binding energy of the

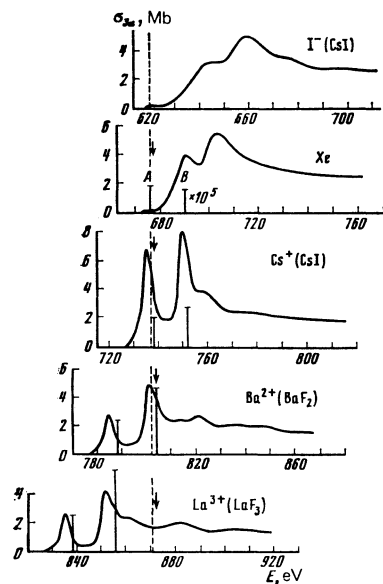


FIG. 4. Partial photoabsorption cross sections of the $3d$ shell of xenon-like ions. The spectra coincide in position at the ionization energies of the $3d_{5/2}$ shells of the corresponding ions (see the text), namely 620, 676, 735, 802, and 871 eV for I^- , Xe , Cs^+ , Ba^{2+} , and La^{3+} , respectively. The theoretical values (see the table) of the intensities (decreased by a factor 1.3) and of the energies of the $3d^{10} \rightarrow 3d^9 4f$ lines are marked by vertical lines, while the theoretical ionization energies are marked by arrows.

$3d_{5/2}$ electrons in the corresponding free ions (the numerical values of these energies will be estimated in the next section).

In their general appearance, the considered spectra are clearly divided into two groups. In the case of I^- and Xe , the broad smooth maxima are located beyond the ionization threshold, and with further distance from the threshold the absorption decreases, but still remains appreciable. For Cs^+ , Ba^{2+} , and La^{3+} , two intense relatively narrow maxima below the ionization threshold predominate in the spectrum, and the absorption in the region of the continuous spectrum is much weaker than in the cases of I^- and Xe .

Proceeding to an interpretation of these regularities, we note first that the doublet structure separated in all the spectra is due to the spin-orbit splitting of the $3d$ shell. This is evidenced by the proximity of the energy intervals between the components of the doublets and the energies of the spin-orbit splitting of the $3d$ shells obtained by photoelectron spectroscopy (see, e. g., Ref. 10).

There are good theoretical grounds for assuming that the absorption spectrum of Xe is determined entirely by transitions of $3d$ electrons into a continuum of f states, i. e., by $3d-f$, transitions and that their transitions to the p state have small oscillator strengths.^{11,12} Since the f states are retained by the intra-atomic potential barrier in the region of the outer potential well, the transitions $3d-\epsilon f$ become effective only at energies sufficient for the f wave to penetrate into the inner well, and this leads to a quasiresonant concentration of the oscillator strengths of the transitions in the region above the ionization threshold.

Since Z , and hence also $|V(r)|$, is smaller in the case of I^- than in the case of Xe , this interpretation can also be used with assurance for the corresponding spectra of the rare-earth atoms (see, e. g., Ref. 13). Inasmuch as in the latter case the oscillator strength stems primarily from $3d-4f$ transitions and the $3d-\epsilon f$ channel is already much less effective,¹⁴ it must be concluded that the clearly pronounced doublets in the initial regions of the spectra of Cs^+ , Ba^{2+} , and La^{3+} are due to $3d-4f$ transitions.

Thus, a qualitative analysis of the spectra presented in Fig. 4 leads to the conclusion that a collapse of the $4f$ orbital in the configuration $3d^9 4f$ takes place on going from Xe to Cs^+ and Ba^{2+} .

Figure 5 shows the emission $M_{4,5}$ spectra of Cs^+ (in $CsCl$), Ba^{2+} (in BaF_2), and La^{3+} (in LaF_3). They were measured, as usual, by rubbing in the objects into the surface of the anode (Cu or Al) of the x-ray tube of the spectrometer. To display the effects of self-absorption of the radiation in the objects, the spectra were measured in several regimes. Figure 5 shows the spectra measured in two regimes, of which the "weak" and the "strong" ensure respectively maximum and minimum self-absorption. The low-energy part of the spectra contains the so called diagram lines corresponding to the transitions $3d^9 5p^6 - 3d^{10} 5p^5$. The high-energy part of the spectra is at resonance with the absorption spec-

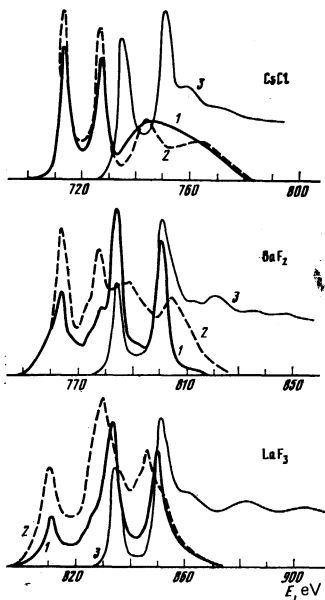


FIG. 5. $M_{4,5}$ emission spectrum of the ions Cs^+ , Ba^{2+} , and La^{3+} in ionic compounds under strong (3 kV, 20 mA) (2) and weak (1 kV, 10 mA) (1) excitation regimes; 3—absorption spectra. The ordinate scale is linear in relative units.

tra and is strongly deformed by self-absorption effects. This part of the spectrum is due to radiative decay of the bound excited states. In the case of La^{3+} and Ba^{2+} they coincide quite accurately with the corresponding absorption bands, and their intensity exceeds that of the diagram lines. This makes it undoubtedly possible to attribute them to the transitions $3d^9 4f \rightarrow 3d^{10}$ and thus confirm the conclusion drawn above that in La^{3+} and Ba^{2+} the orbital $4f$ in the configuration $3d^9 4f$ is localized in the region of the inner potential well.

In the case of Cs^+ , the high-energy part of the emission spectrum is a broad structureless band that extends over dozens of electron volts in the absorption region in the $3d$ shells. Similar bands were observed by us in the $N_{4,5}$ spectra of emission of lanthanides.¹⁵ We interpret this band as being due to radiative decay of the $3d^9 4f$ configuration of the Cs^+ ions. It is considerably broadened because of the large probability of nonradiative decay of this configuration.

3. INFLUENCE OF COLLAPSE OF $4f$ ELECTRON ON THE TRANSITIONS $3d^{10} \rightarrow 3d^9 4f$

We shall consider theoretically the transitions $3d^{10} \rightarrow 3d^9 4f$ in the Hartree-Fock-Pauli (HFP) approximation (the relativistic effects are taken into account in first order of perturbation theory with Hartree-Fock wave functions starting with Breit operators in the Pauli form). The effectiveness of this approximation in the calculation of the energy characteristics of the inner electrons was demonstrated in Ref. 16. The solution of the Hartree-Fock equations makes it possible to determine sufficiently accurately the values of Z at which collapse of the excited electron takes place (see Table II of Ref. 17). The radial wave functions were defined as the solutions of the Hartree-Fock equation for the average configuration energy (HF-ac), and also as so-

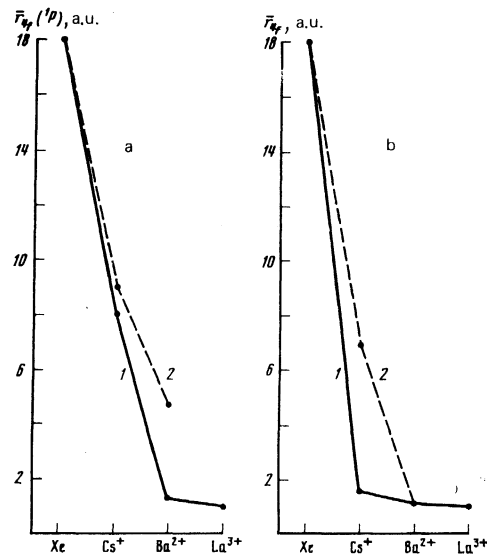


FIG. 6. Variation of the average distance of the collapsing $4f$ electrons from the nucleus in the isoelectronic Xe sequence in the configuration $3d^9 4f$ (1) and $4d^9 4f$ (2), determined by the solutions of the Hartree-Fock equations for the 1P term (a) and for the average energy (b).

lutions for individual terms (HF-t). In the latter case, however, the terms corresponding to the LS -type coupling (in the Hartree-Fock potential only the terms of the electrostatic interaction are taken into account), which is not at all similar to the real type of coupling, close to the jj coupling, in the $3d^9 4f$ configuration.

The results of the calculations are shown in Fig. 6 and in the table. The average distance of the $4f$ electron from the nucleus changes upon collapse of the orbit by approximately one order of magnitude. Its values, determined by the functions HF-av and HF-t (the 3P and 3D terms) are very close and therefore the latter are not cited separately. For Xe (non-collapsed $4f$ electron) and Ba^{2+} and La^{3+} (collapsed $4f$ electron) the results of the solution of the HF-av and HF- 1P equations are practically identical. A substantial dependence on the term is observed only for Cs^+ : according to the solutions of the equations HF-av, the collapse of the $4f$ electron has already taken place, while according to the HF- 1P solutions it has not yet occurred.

TABLE I.

	$I(3d_{5/2}), \text{eV}$			Terms	(LS^1P)	E, eV		$\sigma(3d^{10} \rightarrow 3d^9 4f), \text{Mb}$
	HF	HFP	estimate			HFP	experiment	
Xe	687.6	677.1	676.4	1P	0.72	676.3	—	$2.7 \cdot 10^{-3}$
				3P	0.28	676.3	—	$4.1 \cdot 10^{-6}$
				3D	0.63	688.7	—	$2.1 \cdot 10^{-3}$
Cs^+	749.8	738.6	737.0	3P	-0.06	734.8	—	$2.3 \cdot 10^{-2}$
				3D	-0.65	736.0	735.5	2.67
				1P	0.76	751.4	750.0	3.71
				3P	-0.48	734.6	—	$2.1 \cdot 10^{-4}$
Cs^{2+}	—	—	—	1P	0.63	735.3	—	$3.6 \cdot 10^{-4}$
				3D	0.62	748.3	—	$3.5 \cdot 10^{-4}$
				3P	-0.06	784.0	—	$3.3 \cdot 10^{-2}$
Ba^{2+}	815.8	803.8	802.0	3D	0.59	788.6	785.0	3.21
				1P	0.81	803.7	801.5	6.17
				3P	-0.05	833.2	—	$2.7 \cdot 10^{-2}$
La^{3+}	885.2	872.5	—	3D	0.56	838.8	835.0	3.45
				1P	0.82	855.6	852.5	7.55
				3P	-0.05	833.2	—	$2.7 \cdot 10^{-2}$

A comparison of the average distance \bar{r}_{4f} for the configuration $3d^9 4f$ with the corresponding results⁴ for $4d^9 4f$ shows (Fig. 6) that collapse in the isoelectronic sequence of $3d^9 4f$ proceeds more rapidly with changing Z , and complete collapse, both in the HF-av and HF-t approximations, is completed one term of the series sooner. In the case of a collapsed electron, the localization of the electron is highly sensitive to the change of the potential, and therefore for the transition cases ($Cs^+ - 3d^9 4f$ and $Cs^+, Ba^{2+} - 4d^9 4f$) refinement of the calculation (allowance for the wave functions of the spin-orbit interaction, and for the correlation and relativistic effects in the calculation) can change the results somewhat.

Localization of the radial wave function influences strongly the integrals of the electrostatic interaction between the $3d^9$ and $4f$ shells, the spin-orbit interaction constant η_{4f} , and the integral of the dipole transition ($3d | r | 4f$). They are changed by 3–5 orders of magnitude by the collapse. At the same time, the spin-orbit interaction constant η_{3d} is practically independent of the localization of $4f$ electron.

The wave functions in the intermediate type of coupling were determined in the basis of the LS -coupling functions and designated $\langle \widehat{LS} |$ in accord with the leading component in the expansion. The intensity of the discrete transitions $3d^{10} 1S - 3d^9 4f$ is then proportional to the square of the coefficient of expansion of the function $\langle \widehat{LS} |$ for the component $\langle {}^1P | - \langle \widehat{LS} | {}^1P \rangle$. For the Cs^+ ion, a calculation of the intensity was carried out both with the wave function HF- 1P and with the function HF-av. In the remaining cases, the function HF-av was used.

The binding energies $I(3d_{5/2})$ of the $3d_{5/2}$ electrons in the energies of the dipole transitions $3d^{10} - 3d^9 4f$ were determined as the differences between the corresponding total energies

$$E(\widehat{LS}) = E(3d^9 4f \widehat{LS}) - E(3d^{10}),$$

$$I(3d_{5/2}) = E(3d_{5/2}^9) - E(3d^{10}).$$

Experimental estimates of the binding energies were obtained in the following manner. For the Xe atoms their direct measurements by the photoelectric spectroscopy method.¹⁰ For the Cs^+ and Ba^{2+} ions we used the quality

$$I(3d_{5/2}) = +E(M_5 O_{2,3}) + I(5p).$$

The energies of the $M_5 O_{2,3}$ lines were taken from the $M_{4,5}$ emission spectra (Fig. 5), the ionization potential $I(5p)$ for Cs^+ was taken from Ref. 18, and for Ba^{2+} from the tables of Ref. 19. The calculated energies of the principal transitions $3d^{10} - 3d^9 4f$ agreed with the measured absorption peaks in Cs^+ , Ba^{2+} and La^{3+} accurate to several electron volts. The deviation is determined from the correlation effects and from the inadequacy of the model of the free ion in the ionic crystals have the same sign and approximately the same magnitude as for the binding energy.

Upon collapse of the $4f$ electron, the intensities of the ground $3d^{10} - 3d^9 4f$ lines change by six orders of magnitude. For Xe (and all the more for I⁻) these transitions take not part whatever in the formation of the

absorption spectra. For Ba^{2+} and La^{3+} , the calculation already predicts a dominant role of the discrete transitions. For the Cs^+ ion, as expected, the results with HF-av functions and with HF- 1P functions (Cs^* in the table) differ greatly. In the former case the Cs^+ spectrum is similar to the spectra of Ba^{2+} and La^{3+} , and in the latter case to the Xe spectrum. Comparison with experiment (the results of the calculation are represented by the vertical lines in Fig. 4) shows that more adequate results are obtained with the first variant. This is attested both by the energy positions of the $M_{4,5}$ peaks and by the ratio of their intensities.

Thus, atomic calculation confirms the conclusion drawn above that for Cs^+ , Ba^{2+} , La^{3+} the and principal absorption peaks are connected with the transitions $3d^{10} - 3d^9 4f$. The experimentally observed redistribution of the oscillator strengths among the continuous and discrete spectra in the isoelectronic sequence $I^- - Xe - Cs^+ - Ba^{2+} - La^{3+}$ is direct evidence of the collapse of the $4f$ electron in the $3d^9 4f$ configuration in the middle of the sequence.

4. CALCULATION OF THE $3d$ -SHELL PHOTOIONIZATION CROSS SECTIONS

The collapse of the $4f$ electron should be accompanied by a drastic change in the $3d$ -shell photoionization cross section. As shown by Amus'ya and co-workers,²⁰ for atoms of inert gases and of their neighboring elements (i. e., for Z values near which collapse of the excited electron as well as the associated change in the free-electron function take place), it is important to take into account multi-electron effects in the calculation of the photoionization cross sections. Therefore the results presented below on the calculation of the $3d$ photoionization in the single-electron approximation are more readily estimates.

The calculations were performed using the tabulated single-electron orbitals of Herman and Skillman.²¹

The volume potential was reduced to a local form by dividing the exchange term of the Hartree-Fock equation by the solution of the inhomogeneous equation. The free-electron functions were calculated both in the frozen field of the atomic core and with allowance for the relaxation of the core (this was approximately taken into account by using for the outer electron shells the Herman-Skillman wave functions of the next atom in the periodic system, while the orbitals of the considered atoms were used for the $3d$ and deeper shell). As noted in a number of papers (see Refs. 22, 20 and others), allowance for the relaxation of the core in the single-electron approximation at low energies of the photoelectron usually gives a better approximation.

The results using the ionization energies of the preceding section are shown in Fig. 7. It is important that the character of the photoionization spectrum in the considered isoelectronic sequence changes qualitatively. A quaresonant structure exists for I⁻, Xe, and Cs^+ appearing for Cs^+ only when the relaxation of the core is taken into account. For the succeeding elements it vanishes—this can be attributed to the vanishing of the

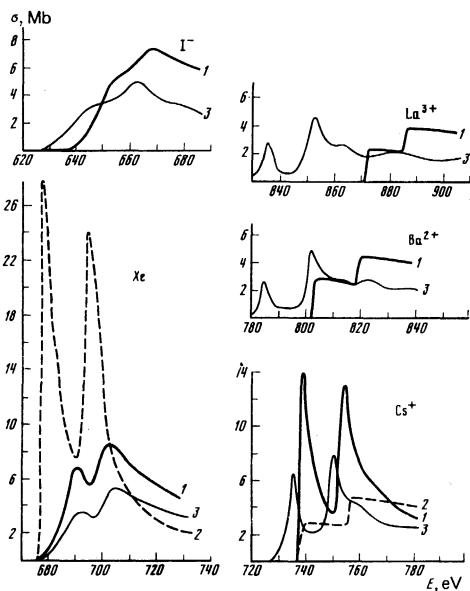


FIG. 7. Partial photoionization cross sections of the 3d shell of xenon-like ions with (1) and without (2) allowance for the relaxation of the atomic core; 3—measured absorption spectra.

effective potential barrier for the ϵf states with increasing degree of ionization.⁹ The calculated quasi-resonant structure in the $3d-\epsilon f$ spectrum of Cs^+ is similar to the experimental spectrum (see Fig. 4), but it is more probable that this a pseudoresonance due to the inaccuracy of the model, just as in the case of calculation of the photoionization of the 4d shell in the single-electron approximation.²³ On the other hand, the results of the calculation with a nonrelaxed core can explain the additional maximum in the Cs^+ spectrum on the high-energy side of the maximum B (another additional maximum may be masked by the maximum A). This would be evidence of simultaneous manifestation of both for absorption channels in the case of a collapsing 4f electron.

5. CONCLUSIONS

The results presented above demonstrate convincingly that the model of the isolated ion is suitable for the interpretation of the main singularities of the 3d absorption and emission spectra of the xenon-like ions I^- , Cs^+ , Ba^{2+} , and La^{3+} , which are contained in compounds with high degree of ionicity. The influence of their surrounding probably manifests itself to a greater degree in the spectral region beyond the ionization threshold of the 3d shell.

A comparison of the measured spectra with one another and with results of the calculation shows also that the 4f electron in the $3d^9 4f$ configuration is localized in the outer well of the effective potential in the case of the I^- ions and Xe atoms, and in the inner well in the case of the ions Ba^{2+} and La^{3+} . This spatial redistribu-

tion of the charge density of the electron leads to a substantial redistribution of the oscillator strength from the continuous region of the 3d absorption spectrum into the region of discrete transitions.

The transition element from the point of view of the collapse of the 4f orbital in the $3d^9 4f$ configuration is cesium, whose 3d absorption spectrum and its interpretation on the basis of a calculation in the HFP approximation support the conclusion that in the case of Cs^+ the collapse has already taken place. An approximate single-electron calculation of the photoionization cross section points to the possibility of the appearance of transitions of a type $3d-\epsilon f$ in the 3d absorption spectrum of Cs^+ , but the similarity of this spectrum to the corresponding spectra of Ba^{2+} and La^{3+} indicates that the main structure in the Cs^+ spectrum is due to discrete transitions $3d^{10}-3d^9 4f$. The form of the 3d emission spectra of Cs^+ in cesium halides agrees with this conclusion if it is assumed that the nonradiative decay of the $3d^9 4f$ configuration has a high probability.

- ¹E. Fermi, in: *Quantentheorie und Chemie*, Leipziger Vortrage, S. Hirzel Verlag, Leipzig, 1928, p. 95.
- ²U. Fano and J. W. Cooper, *Rev. Mod. Phys.* **40**, 441 (1968).
- ³J. P. Connerade, *Contemp. Phys.* **19**, 415 (1978).
- ⁴S. A. Kuchas, A. V. Karosene, and R. I. Karaziya, *Izv. Akad. Nauk SSSR Ser. Fiz.* **40**, 270 (1976).
- ⁵R. D. Cowan, *J. Opt. Soc. Amer.* **58**, 924 (1968).
- ⁶J. E. Hansen, A. W. Fliflet, and H. P. Kelly, *J. Phys.* **B 8**, L127 (1975).
- ⁷K. Radler and B. Sonntag, *Chem. Phys. Lett.* **39**, 371 (1976). E. R. Radke, *J. Phys.* **B 12**, L71 (1979).
- ⁸A. V. Karosene, A. A. Kiselev, and R. I. Karaziya, *Lit. Fiz. Sb.* **13**, 363 (1973).
- ⁹R. D. Deslattes, *Phys. Rev. Lett.* **20**, 483 (1968).
- ¹⁰*Handbook of Spectroscopy*, Vol. 1, ed. by J. W. Robinson, CRC Press, Cleveland, Ohio, 1974.
- ¹¹S. T. Manson and J. W. Cooper, *Phys. Rev.* **165**, 165 (1968).
- ¹²M. Ya. Amusia and V. K. Ivanov, *Sixth Intern. Conf. on Atomic Physics*, Abstracts, Riga, 1978, p. 446.
- ¹³C. Bonelle, R. C. Karnatak, and J. Sugar, *Phys. Rev.* **A9**, 1962 (1974).
- ¹⁴J. Sugar, *Phys. Rev.* **A6**, 1764 (1972).
- ¹⁵V. A. Fomichev, S. A. Gribovskii, and T. M. Zimkina, *X-Ray Spectra and Electronic Structure of Matter*, München, 1973, Vol. 2, p. 197.
- ¹⁶S. A. Kuchas, A. V. Karosene, and R. I. Karaziya, *Lit. Fiz. Sb.* **18**, 593 (1978).
- ¹⁷D. C. Griffin, K. L. Andrew, and R. D. Cowan, *Phys. Rev.* **177**, 62 (1969).
- ¹⁸A. Reader, *Phys. Rev.* **A13**, 507 (1976).
- ¹⁹*Svoistva elementov (Properties of Elements)*, G. V. Samsonov, ed., Part 1, M., 1976, p. 22.
- ²⁰M. Ya. Amusia, *Proc. of the Fourth Intern. Conf. on Vacuum Ultraviolet Radiation Physics*, Hamburg, 1974, p. 205.
- ²¹F. Herman and S. Skillman, *Atomic Structure Calculation*, Engelwood Cliffs, New Jersey, 1963.
- ²²J. W. Cooper, *Phys. Rev.* **128**, 681 (1962).
- ²³F. Combet-Farnaux, *Proc. Intern. Conf. on Inner Shell Ionization Phenomena*, Atlanta, 1972, Vol. 2, p. 1130.

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