Structure of the cross sections for the excitation of alkaline-earth metal ions by monoenergetic electrons

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A detailed investigation was made of the excitation of the resonance lines and the first terms of the sharp and diffuse series of alkaline-earth metal ions in the energy interval from the threshold of the process to 15 eV. The technique of intersecting modulated electron and ion beams with electron beams of high energy uniformity ($\Delta E_{1/2} = 0.1-0.4 \text{ eV}$) was used. The energy dependence of the excitation cross sections was determined for 13 spectral lines. A clear structure of the excitation cross sections of the investigated spectral transitions was observed near the threshold. The origin of this structure was accounted for.

INTRODUCTION

Excitation of metal ions and atoms by electron impact is attracting increasing interest in atomic physics as well as in plasma physics, including thermonuclear research and astrophysics. The excitation of levels and spectra of alkalineearth ions is of special interest in astrophysics and in the physics of the upper atmosphere of the earth.

The first laboratory studies of such excitation processes in intersecting electron and ion beams were reported in the early seventies.¹⁻⁴ The excitation cross sections were determined for resonance lines and levels of the ions of magnesium, calcium, strontium, and barium for incident-electron energies from the threshold of the process to hundreds (or more) of electron volts, but the energy homogeneity of the electron beams was not very high (the energy scatter of the electron beams was 1.0–1.5 eV). The resultant insufficient energy resolution did not reveal clearly the characteristic features of the dependences of the excitation cross sections of these ions on the interaction energy and thus failed to provide a better understanding of the excitation mechanism.

The progress in the experimental techniques made in the decade since these experiments has made it possible to carry out more precise and satisfactory experiments on electron-ion collisions. Alkaline-earth metal ions are convenient objects for detailed investigations when monoenergetic lowintensity beams are used. In fact, the spectral transitions from the lower levels of these ions lie conveniently in the visible range and the excitation cross sections of the lower levels^{1,2,4} are relatively large $(10^{-15}-10^{-16} \text{ cm}^2)$.

Our aim was to carry out precision investigations of the excitation of alkaline-earth ions using electron beams with a higher energy homogeneity (tenths of an electron volt) and an automated system for the control of the measurements and for the analysis of the acquired data.

EXPERIMENTAL TECHNIQUES AND INVESTIGATION METHODOLOGY

The excitation of alkaline-earth ions by monoenergetic electrons was investigated by an optical method using the technique of modulated electron and ion beams.⁵ The apparatus shown schematically in Fig. 1 was used. The main components were electron and ion beam sources placed inside an ultrahigh-vacuum chamber (where the pressure was down to 1×10^{-9} torr) in such a way that the beams inter-

sected at 90° in an equipotential region. The radiation representing the investigated lines was selected by a high-luminosity MDR-2 monochromator at right angles to the plane of intersection of the beams and was detected using a liquidnitrogen-cooled FÉU-106 photomultiplier operating in the photon-counting regime.

Beams of monoenergetic electrons were used by us for the first time in the excitation experiments. These beams were formed in a source with an electron energy selector utilizing an electrostatic field in a 90° cylindrical capacitor (Fig. 1). In the electron energy range 2–20 eV when the current density in the collision zone was $(0.5-8.0) \times 10^{-4}$ A/cm² the electron energy scatter was 0.1-0.4 eV (at the half-maximum of the distribution function). The electron energy scatter was determined using a 127° electron-energy analyzer with a resolution better than 0.1 eV.

The ion beams were created in a source similar to that described in Ref. 6, which operated reliably under the surface ionization conditions (in the experiments on calcium, strontium, and barium ions) and under the conditions of a low-voltage discharge (magnesium ions). The ions were separated from the neutral component employing a 90° electrostatic capacitor. The energy of the beam ions was 1 keV, and the current density and the density in the collision zone were $(1-6) \times 10^{-5} \text{ A/cm}^2$ and $10^6-10^7 \text{ cm}^{-3}$, respectively.

Under these conditions the intensity of the useful signal (representing the radiation induced by the electron-ion collisions) generated even in ultrahigh vacuum was not just comparable with, but well below the combined background due to the other collisional processes (collisions of beam ions and electrons with the atoms of the active substance, with the molecules of the residual gas, and with the surfaces of the components of the apparatus). The technique for modulating both beams (by rectangular voltage pulses phase-shifted by one-quarter of a period) and synchronous (with the beam modulation pulses) switching of the photomultiplier signal between two signals made it possible to separate the useful signal from the background reliably when the latter exceeded the signal by a factor up to 100.

An important component of the improved apparatus was a measuring and control system based on an Élektronika 100-I microcomputer⁷ with suitable programs for the control of the measurement process and for the analysis of the experimental data. The system was tested by an investiga-



FIG. 1. Schematic diagram of the apparatus: 1) reservoir with the working substance; 2) ionization chamber; 3) ion-optical system; 4) electrostatic ion selector; 5) traps for atoms; 6) electron collector; 7) source of electrons; 8) ion collector; 9) intersecting beam configuration (*e* denotes electrons, A^+ denotes ions, and hv is the emitted radiation).

tion of the excitation of singly and doubly charged sodium ions,⁸ and of helium atoms and ions⁹ in electron-atom collisions; the results confirmed the high reliability and effectiveness of the system. All this made it possible to greatly increase the precision of the measurements and to greatly reduce the duration of the experiments and of the time needed for analysis of the data.

In the course of prolonged experiments we carefully determined the energy dependence of the excitation cross sections (excitation functions) of the resonance lines of the Mg^+ , Ca^+ , Sr^+ , and Ba^+ ions, and also of the head terms of the secondary series of the Mg^+ , Sr^+ , Ba^+ ions. In the case of the magnesium ion the resonance lines were investigated without resolution into their components, but in the case of calcium, strontium, and barium the components of the resonance doublets were separated and investigated separately. The resonance radiation emitted by the last three ions was located in the most convenient part of the spectrum $(\lambda = 350.0-500.0 \text{ nm})$, where the recording apparatus had a higher sensitivity (the signal/background ratio ranged here from 5/1 to 1/1), so that we were able to investigate the excitation functions with a higher precision than in the case of the corresponding Mg⁺ ($\lambda \approx 280 \text{ nm}$) radiation in the near ultraviolet (where the signal/background ratio ranged from 1/1 to 1/5). In the case of the lines of the secondary series the useful signal was an order of magnitude less (the signal/background ratio was correspondingly poorer and it ranged from 1/5 to 1/20).

Investigations of the general behavior of the excitation functions carried out in a wide energy range (2-100 eV)showed that our measurements and those reported earlier^{1,2,4} were in full mutual agreement with the range 15–100 eV. We therefore limited detailed studies of the dependence of the excitation cross sections on the electron energy to the interval from the threshold of the process to 15 eV, i.e., exactly where the behavior of our excitation functions differed greatly from those reported earlier. The absolute values of the excitation cross sections were calculated by normalizing our data at 100 eV to the results obtained in Ref. 1 with an error of at most 30%.

In the present measurements on the resonance lines we were able to vary the scatter of the beam electron energies from 0.3 eV for Mg⁺ down to 0.1 eV for Ba⁺. The rms error of the relative determination of the excitation functions of the resonance lines in a 90% confidence interval was at most 2–8%. The error in determination of the electron energy scale was within \pm 0.1 eV.

RESULTS AND DISCUSSION

1. The results obtained are presented in Table I and are also plotted in Figs. 2–4. It is clear from Figs. 2 and 3 that in the case of all the excitation functions of the resonance lines

Ion	Transition	λ, nm	$E_{ m exc}$, eV	E _{max} , eV	$\sigma_{\rm max},$ 10^{-16} cm ²	$\sigma_{20} eV, 10^{-16} cm^2$	$\sigma_{100} \text{ eV}$ 10^{-16} cm^2
Mg+	$\begin{cases} 3p^2 P_{\frac{1}{2}, \frac{3}{2}} - 3s^2 S_{\frac{1}{2}} \\ 4s^2 S_{\frac{1}{2}} - 3p^2 P_{\frac{1}{2}, \frac{3}{2}} \end{cases}$	279,6+280,3 292,2+293,6	4,42; 4,43 8,63	6,0 11,0	23,0 1,3	12,5 0,5	4,5 0,13
Ca+	$\begin{cases} 4p^2 P_{\frac{1}{2}} - 4s^2 S_{\frac{1}{2}} \\ 4p^2 P_{\frac{3}{2}} - 4s^2 S_{\frac{1}{2}} \end{cases}$	396,8 393,4	3,12 3,15	3,6 3,7	13,5 23,0	6,5 13,0	2,5 5,0
Sr+	$\begin{cases} 5p^2 P_{1'_2} - 5s^2 S_{1'_2} \\ 5p^2 P_{s'_2} - 5s^2 S_{1'_2} \\ 6s^2 S_{1'_2} - 5p^2 P_{s'_2} \\ 5d^2 D_{s'_2} , s'_1 - 5p^2 P_{s'_2} \end{cases}$	421,6 407,8 430,6 346,4+347,9	2,94 3,04 5,91 6,61; 6,62	3,25 3,6 6,4 7,8	19,0 34,0 2,8 1,6	8,0 16,1 0,8 0,5	3,0 6,0 0,2 0,1
Ba+	$\begin{cases} 6p^2P_{1/_2} - 6s^2S_{1/_2} \\ 6p^2P_{3/_2} - 6s^2S_{1/_2} \\ 7s^2S_{1/_2} - 6p^2P_{3/_2} \\ 6d^2D_{3/_2}, s_{1/_2} - 6p^2P_{3/_2} \end{cases}$	493,4 455,4 490,0 413,1+416,6	2,51 2,72 5,25 5,69; 5,72	3,2 2,9 6,0 6,2	27,6 44,3 5,2 2,5	7,0 14,0 1,5 0,9	3,0 6,0 0,25 0,2

TABLE I. Cross sections of electron-impact excitation of spectral transitions in ions of alkalineearth metals.

Note. Here, E_{\max} is the energy at which the cross section has its maximum value σ_{\max} .



FIG. 2. Energy dependence of the excitation cross section of the stronger components of the excitation closs section Mg^+ at 279.5 + 280.3 nm $(3^2P_{3/2,1/2} \rightarrow 3^2S_{1/2})$, where the dashed curve represents the calculations reported in Ref. 17; Ca⁺ at 393.4 nm $(4^2P_{3/2} \rightarrow 4^2S_{1/2})$, where the dashed curve represents the calculations reported in Ref. 17; Ca⁺ at 393.4 nm $(4^2P_{3/2} \rightarrow 4^2S_{1/2})$, where the dashed curve represents calculations reported in Ref. 18 and the symbol \times gives the experimental data from Ref. 2; Sr⁺ at 407.8 nm ($5^5P_{3/2} \rightarrow 5^2S_{1/2}$), where the symbol \bigcirc gives the experimental data from Ref. 1; Ba⁺ at 455.5 nm ($6^2P_{3/2} \rightarrow 6^2S_{1/2}$), where the symbol \times gives the experimental data from Ref. 4.

FIG. 3. Energy dependence of the excitation cross sections of the weaker component of the resonance doublets of Ca⁺ at 396.8 nm $(4^2 P_{1/2} \rightarrow 4^2 S_{1/2})$; Sr⁺ at 421.6 nm $(5^2 P_{1/2} \rightarrow 5^2 S_{1/2})$, where the symbol O gives the experimental data from Ref. 1; Ba⁺ at 493.4 nm $(6^2 P_{1/2} \rightarrow 6^2 S_{1/2})$. The inset shows the decay channels of the higher terms of the series of the autoionizing states of the $6p_{3/2}$ ns configurations of Ba (Ref. 20).

there is a characteristic rise in the excitation efficiency of the n^2P levels at the threshold of the excitation process. This rise is correlated with the scatter of the beam electron energies (the smaller the scatter, the sharper and the stronger the maximum at the threshold). This threshold behavior of the excitation functions of the ionic lines is in good agreement with the finite value of the cross sections for the excitation of the ionic levels by electron impact at the threshold process because of the acceleration of the bombarding electrons by the Coulomb field of the ions.

Within an interval of several electron volts near the threshold a complex structure in the form of several sharp maxima and minima of the excitation functions is clearly exhibited. Beyond the ionization threshold of a singly charged ion the excitation function is close to the dependence $\sigma(E) \propto E^{-1} \lg E$, which is typical of the optically allowed transitions. The ratio of the excitation cross sections of a resonance doublet at a fixed energy agrees with the familiar ratio of the intensities reported for atoms of alkali metals (excluding the region near the threshold).

An investigation of the polarization of the resonance radiation emitted by alkaline-earth metal ions demonstrated that the degree of polarization of the strong components of the resonance doublets was a maximum near the threshold (20-25%), showed a reversal of the sign near 50 eV, and ranged from -5% to -10% at $100 \,\text{eV}$. The polarization of the weak components was not detected experimentally.

Theoretical calculations of the excitation cross sections of the resonance levels of these ions had been made by a variety of methods: using the second Coulomb-Born approximation,¹⁰ by the method of distorted waves,^{10,11} and using the tight-binding method.¹² These calculations demonstrated the need to allow for the normalization, exchange, and coupling of the various scattering channels. When this allowance was made, it was possible to achieve good agreement with the experimental data beginning from energies amounting to several thresholds, but a largely discrepancy remained between the theory and experiment in the region of the excitation threshold. For example, the most accurate (until recently) calculations¹² carried out by the tight-binding method gave the excitation cross sections of the resonance levels of the Ca⁺ ion over-estimated on the average by 40%, compared with the experimental data. One of the possible reasons for this discrepancy in the threshold region could be the fact that in these investigations the target was described by single-configuration Hartree-Fock wave functions, which in the case of alkaline-earth ions were not very accurate because of the neglect of the effects of the polarization of the ion core by the bombarding electrons. However, as pointed out in Ref. 13, the application of a model polarization potential of the core made it possible to improve the agreement between the calculated excitation cross sections and the experimental data near the threshold.

2. We now consider the origin of the structure of the excitation cross sections of the resonance doublets. Undoubtedly, the nature of the excitation functions of these lines should be influenced by the contribution made to the filling of the upper levels by cascade transitions from the levels of the secondary series, mainly from the head terms of these series. However, in reality this contribution was weak because the efficiency of excitation of the lines in the secondary series was more than one order of magnitude lower than

the corresponding efficiency in the case of the resonance lines.¹⁾

On the other hand, a particularly clear structure of the excitation functions of the resonance lines of the investigated ions is observed also below the excitation threshold of the (n + 1) levels closest to the resonance, i.e., in the range of energies where the cascade contribution is known to be absent. This circumstance and the fairly clear resolution of the maxima of the experimental curves are evidence of a major contribution of the resonances to the excitation of ions by electron impact.

An analysis of our precision experimental data leads, in our opinion, to the unambiguous conclusion that the reason for the structure in the excitation cross section of alkalineearth ions is the capture of a bombarding electron by an ion (involving the long-range Coulomb attraction forces) and the formation of a short-lived autoionizing state of a neutral atom. The capture process is resonant (when the energy of the system formed by an ion and a bombarding electron is equal to the energy of a discrete superexcited state of a neutral atom) in accordance with the scheme

$$A^{+}(ns^{2}S_{lb}) + e \to A^{-}(nl, n_{1}l_{1}^{1,3}L), \qquad (1)$$

where $A^+(ns^2S_{1/2})$ is an ion in its ground state; $A^{**}(nl,n_1n_1^{1,3}L)$ is an autoionizing state of an atom; L is the symbol used for the states; and e is the bombarding electron.

It is known that most of the autoionizing states have short lifetimes $(10^{-13}-10^{-15} s)$ and they decay nonradiatively through Coulomb autoionization in various channels:

$$A^{+}(ns^{2}S_{12}) + \tilde{e}_{1}, \qquad (2)$$

$$A^{**}(nl, n_1 l_1^{1.3}L) \xrightarrow{\gamma} A^{+*}(n'l'^2L) + \tilde{e}_2, \qquad (3)$$

where $A^{+*}(n'l'^2L)$ is an ion in an excited state; \tilde{e}_1 and \tilde{e}_2 are the electrons emitted as a result of the autoionization.

Recent experimental and theoretical investigations of autoionization phenomena^{14,15} have confirmed that nonradiative decay of autoionizing states to the nearest discrete excited state of an ion, i.e., the process described by Eq. (3), is very effective and sometimes dominant. Consequently, in the case of electron-ion collisions this process is an important channel for filling the excited states of the ionic levels (in addition to direct excitation of ions from their ground state by electron impact) and may give rise to resonances in the excitation functions of the spectral lines of the investigated ions.

3. The fullest information on the autoionizing states of the investigated group of elements in the energy range of interest to us (from the excitation threshold of a resonance level to the ionization potential of a singly charged ion) is available only for the magnesium atom. We therefore consider in greater detail the results obtained for Mg⁺ allowing for the capture of an electron by this ion. The shaded vertical segments in Fig. 2 are the limits where the autoionizing states of the investigated atoms converge. We can see that the structure of the excitation function of the resonance line of the Mg $^+$ ion is particularly clear in the energy interval where the autoionizing states of Mg are located and where convergence of the series to the $4s^2S$, $3d^2D$, and $4p^2P$ levels of the Mg $^+$ is observed. It follows from Ref. 16 that the most probable channel for decay of these states is the emission of an electron to resonant levels of the Mg $^+$ ion:

$$\begin{array}{c} \operatorname{Mg}^{**} (4snl^{1,3}L) \\ \operatorname{Mg}^{**} (3 \, dnl^{1,3}L) \\ \end{array} \\ \end{array} \\ \operatorname{Mg}^{**} (3 \, dnl^{1,3}L) \\ \end{array} \\ \begin{array}{c} \mathcal{M} \\ \end{array} \\ \begin{array}{c} \operatorname{Mg}^{**} (3p^2 P_{\frac{1}{2}, \frac{3}{2}}) + \tilde{e} \,. \end{array}$$
 (4)

It therefore follows that the processes described by Eq. (4) give rise to additional filling of the resonance levels of Mg⁺, so that the excitation function of the resonance radiation exhibits singularities in the form of resonances whose energies are in agreement with the energies of the autoionizing states of the neutral atom, which appear as a result of the capture of a bombarding electron by an ion. Note that the interference between the direct and resonant excitation processes, and also the interference between the latter among themselves, may give rise to constructive (manifested by narrow maxima) and destructive (minima) resonances in the cross sections of the excitation of ions by electron impact.

This interpretation of the structure of the excitation cross sections of the resonance radiation of Mg⁺ is confirmed also by the results of a detailed theoretical calculation carried out by the diagonalization method allowing for the resonances due to the autoionizing states of Mg (Ref. 17). Figure 2 shows the calculated curve obtained in Ref. 17 by averaging over the real scatter of electrons in the beam $(\Delta E_{1/2} \approx 0.3 \text{ eV})$. It is clear from the curves for Mg⁺ in Fig. 2 that there is good agreement between the experiment and theory with respect to both the absolute value of the cross section and the energy positions of the individual resonances. The exception is the first maximum of the structure (E = 5.5 eV) whose existence is not confirmed by these calculations. According to Ref. 11, the main contribution to the structure of the excitation cross sections comes from the triplet ${}^{3}P, {}^{3}D$, and ${}^{3}F$ resonances, and the contribution of the ³F resonances is particularly large in spite of their relatively small width ($\Gamma \approx 0.05 \text{ eV}$).

The use of an electron beam with this energy spread enabled us to resolve the maxima of the excitation functions of the Mg⁺ lines dominated by the contributions of the individual resonances. For example, we were able to find a clear peak at 6.7 eV as well as dips at 6.2 and 7 eV due to, respectively, the following autoionizing states of Mg: $3d 4p^3F$ ($\Gamma = 0.04$ eV), $4s3d^{-1}D$ ($\Gamma = 0.27$ eV), and $3d 4p^{-1}F$ ($\Gamma = 0.23$ eV). Beginning at 7.3 eV, the autoionizing states of the 4snl and 3dnl configurations are distributed very densely, and the probability of their formation and the width decrease. For this reason the experimental excitation functions shows only the total contribution from the whole groups of the autoionizing states.

4. A detailed interpretation of the results obtained for the Ca⁺, Sr⁺, and Ba⁺ atoms is at present difficult because of the absence of reliable theoretical values of the ion-excitation cross sections that would allow for the resonances. True, a detailed calculation of the excitation cross sections of the resonance levels of the Ca⁺ ions was made¹⁸ by applying perturbation theory and the tight-binding method to six states (4s, 3d, 4p, 5s, 4d, and 5p). This was done employing semiempirical Hartree–Fock wave functions of the target including one- and two-particle polarization potentials of the core. This calculation predicted the sharp structure of the excitation functions of the resonance levels of the Ca⁺ ion and (after averaging over the instrumental function with $\Delta E_{1/2} \approx 0.3$ eV) agreed satisfactorily with the experimental results near the excitation threshold with the exception of the first maximum (dashed curve in Fig. 2).

It therefore follows that the available theoretical methods for calculating the detailed structure of the cross sections for the excitation of alkaline-earth metal ions by electron impact still fail to provide a full description of the experimental results. It is very likely that the first maxima of the excitation functions of the strong components of the resonant doublets exhibited by this group of ions are due to a different mechanism which is ignored in the above theoretical calculations.

It should be pointed out that the appearance of a new channel of decay of the autoionizing states to the $(n-1)^2D$ levels of the Ca⁺, Sr⁺, and Ba⁺ ions can reduce slightly the contribution of the additional filling of the resonance levels of these ions by the process of formation and decay of the autoionizing states. This should be manifested to a greater extent in the case of the Ca⁺ and Sr⁺ ions than for Ba⁺, because the metastable $(n-1)^2D$ levels of the former are closer in energy to the resonance levels, whereas the $5d^2D$ level of Ba⁺ is, conversely, closer to the ground states of the ion.

It should also be mentioned that the relative contribution of the resonances to the excitation of the resonance levels of alkaline-earth ions is relatively small compared, for example, with the excitation of the resonance levels of the alkali metal ions.¹⁹ This is due to, on the one hand, the very effective direct excitation process ($\sigma \sim 10^{-15}$ cm⁻²) and, on the other, due to the weak filling from the autoionizing states that converge at the levels of the secondary series.²⁾

We may therefore conclude that the observed structure of the excitation functions of alkaline-earth metals near the threshold energies is mainly due to the resonances in the processes of formation and subsequent electron decay of the atomic autoionizing states. This must be allowed for in the determination of the absolute values of the excitation cross sections of the investigated ions in this range of energies.

5. We now consider the characteristics of the excitation of the weaker components of the resonance doublets of the Ca⁺, Sr⁺, and Ba⁺ ions. In contrast to the excitation functions of the stronger components, which exhibit a steep and practically linear rise at the excitation threshold of the $np^2P_{3/2}$ levels, the rising parts of the excitation functions of the weaker components exhibit a structure in the form of an inflection or even a clear maximum (Fig. 3). Moreover, the maxima of the excitation cross sections of the weaker components are reached at somewhat higher energies than in the case of the corresponding curves of the stronger components. It is very likely that these characteristics are due to the superposition of the resonances, which appear directly in the threshold region, on the direct excitation process.

The mechanism responsible for these resonances is similar to that described above (for the stronger components), but the contribution in the case of the weaker components comes from the atomic autoionizing states located in a narrow energy interval between the levels of the doublet splitting of the resonance $np^2P_{1/2,3/2}$ states of the ions. It is worth noting that the method of multistage excitation of a beam of barium atoms by laser radiation was used in Ref. 20 to study the process of filling and decay of higher terms of the series of autoionizing states of this atom, which converges in particular to the $6p^2P_{3/2}$ level. It was shown there that the dominant ($\approx 70\%$) decay channel of the autoionizing $6p_{3/2}ns$

configurations with principal quantum number $n \ge 12$ is electron decay to the $6p^2 P_{1/2}$ level of Ba⁺ (inset in Fig. 3).

Bearing this point in mind and the fact that the position of an inflection or a maximum in the excitation functions of the weaker components coincides with the energy interval corresponding to the doublet splitting of the resonance levels of Ca⁺, Sr⁺, and Ba⁺, we may assume that the capture of bombarding electrons by ions is an effective process in our experiments and it leads to the formation of the autoionizing states corresponding to higher terms of the series that converge at the resonant $np^2P_{3/2}$ states. The subsequent electron decay to the $np^2 P_{1/2}$ levels by the Koster-Kronig process increases their population and is responsible for some contribution of this group of resonances to the direct excitation process. This was indeed observed in our experiments in the form of an inflection in the case of Ca⁺ or a maximum in the case of Sr^+ and Ba^+ , which appeared in the rising parts of the excitation functions of the weaker components of the reasonable doublets.

6. As pointed out already, in the case of other radiative transitions in this group of ions we investigated in detail only

6,10⁻¹⁶ cm²

the head terms of the sharp and diffuse series of the Mg $^+$ Sr^+ , and Ba^+ ions. This was because the efficiency of excitation of even the head terms of the secondary series was an order of magnitude less than in the case of the resonance line, making it difficult to detect a useful signal with sufficient precision. Reliable recording of the useful signal was possible only by increasing the density of electrons in the beam, but this resulted in some increase in the scatter of the beam electron energies ($\Delta E_{1/2} \approx 0.4 \text{ eV}$), increased the exposure time, and made it necessary to carry out a larger number of measurement cycles.

It is clear from Fig. 4 that in the case of the optically forbidden transitions there was also a rapid rise of the excitation cross section at the threshold of the process. Near the threshold the excitation functions of these transitions had two or three clear maxima. The fall of the excitation cross sections obeyed $\sigma(E) \propto E^{-1}$, typical of the optically forbidden transitions in the case of the ground state of the ion. The real contribution of the cascade transitions from the levels of the secondary series to the populations of the resonance levels could reach, as demonstrated by an analysis of our re-

FIG. 4. Energy dependence of the excitation cross sections of the stronger components of the head terms of the secondary series of Mg + at 292.2 + 293.6 nm $(4^2 S_{1/2} \rightarrow 3^2 P_{1/2,3/2})$, where O gives the experimental data Ref. from 1; Sr ⁺ at 346.4 + 347.9 nm $(5^2 D_{5/2,3/2} \rightarrow 5^2 P_{3/2})$; Sr⁺ at 430.5 nm $(6^2 S_{1/2} \rightarrow 5^2 P_{3/2})$; Ba⁺ at 413.1 + 416.6 nm $(6^2 D_{5/2,3/2} \rightarrow 6^2 P_{3/2})$; Ba⁺ at 490.0 nm $(7^2 S_{1/2} \rightarrow 6^2 P_{3/2})$, where \bigcirc gives the experimental data from Ref. 1. The inset shows the decay channels of the higher terms of the autoionizing series of the $6d_{5/2}$ nd configurations of Ba (Ref. 21).



E, eV

sults, values ranging from 6% for the Mg⁺ ion to 20% for the Ba⁺ ion when the electron energy corresponded to the maximum of the excitation function of the cascade transitions. Therefore, some of the features of the excitation functions of the resonance doublets of alkaline-earth ions could be regarded as due to additional resonant filling of the initial levels of the ions by cascade transitions from the levels of the secondary series. Note that the excitation cross sections of monotypic transitions increase from the Mg⁺ to the Ba⁺ ion, and for the same ion the lines corresponding to the transitions from the $(n + 1)^2 S_{1/2}$ levels are excited more effectively than the lines from the $n^2 D_{3/2,5/2}$ levels.

The nature of the structure which appeared also in the excitation functions of the first terms of the secondary series indicated that it was due to the same phenomenon of strong capture of bombarding electrons by ions, accompanied by the formation of the autoionizing states of the corresponding neutral atoms and their subsequent electron decay to the excited levels of the ion. In this case the dominant role was played by the autoionizing states converging to the excited levels of the principal series of the ion.

As in the case of the weaker components of the resonance doublets, the appearance of near-threshold inflections in the excitation functions of the lines from the n^2D levels of the Sr⁺ and Ba⁺ ions (Fig. 4) was due to decay of the autoionizing states of Sr and Ba located in a narrow energy interval between the levels of the split doublet $nd^2D_{3/2.5/2}$. This was confirmed by the results reported in Ref. 21, which were obtained by the method of multistage excitation of a beam of barium atoms by laser radiation. It was found that in the case of the autoionizing states of Ba, converging in series to the 6d $^{2}D_{5/2}$ level Ba $^{+}$, only up to 30% of the autoionizing states of the $6d_{5/2}nd$ configuration ($n \ge 26$) of Ba decayed by the autoionization process to the lower $6d^2D_{3/2}$ level of Ba⁺, because of the appearance of additional competing channels of decay of the autoionizing states to the excited ionic levels (inset in Fig. 4). Clearly, this is why we observed only inflections of the excitation functions of the lines from the n^2D levels of the Sr⁺ and Ba⁺ ions.

CONCLUSIONS

The smaller scatter of the beam electron energies (0.1-0.4 eV) achieved in our experiments ensured clear resolution of the structure of the excitation functions of the spectral transitions, practically undetectable in previous investigations. A qualitatively new and important result was the existence of a considerable contribution of the resonance processes to the excitation of the lower levels of the ions of alkaline-earth elements at electron energies near the excitation threshold. The results demonstrated unambiguously that these resonance processes were due to the effective capture of the bombarding electrons by the Coulomb field of an ion resulting in the formation of the autoionizing states of the corresponding neutral atoms and the subsequent electron decay of these states to excited levels of the ion.

It was also found that, in the case of the group of ions investigated, the contribution of the resonance processes to the excitation cross section of the lower levels gave rise to a structure with deep maxima and minima (which should be compared, for example, with the structure of the excitation functions of the levels of alkali metal ions). The reason for this observation was the high effectiveness ($\sigma \sim 10^{-15} \,\mathrm{cm}^2$) of the direct electron-impact excitation of the lower levels of these ions and also the overlap of groups of narrow resonances (with a true width less than 0.1 eV), which caused relatively wide maxima to appear in the excitation curves. On the other hand, our investigation showed that the role of the resonance effects became greater along the series of these ions from Mg $^+$ to Ba $^+$. This could be a manifestation of the relativistic effects in the outer shells of the heavy ions, in which the process of the direct excitation of the levels of these ions was influenced significantly by the polarization of the core by the bombarding electrons, while the role of the relativistic effects was slight.

- ¹⁾ This will be discussed in greater detail in subsection 6 in the present section.
- ²⁾ This can explain why in some of the earlier studies^{1,2,4} of the excitation of ions of alkaline-earth elements by an electron beam with an energy scatter $\Delta E_{1/2} \approx 1,2$ eV even the combined contribution was not detected.
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