Excitation of the Mg^+, Ca^+, Sr^+, and Ba^+ resonance levels in electron-ion collisions

I. P. Zapesochnyĭ, V. A. Kel'man, A. I. Imre, A. I. Dashchenko, and F. F. Danch

Uzhgorod State University
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A systematic study of electron excitation of alkaline earth ions at low collision energies (2–100 eV) was carried through for the first time, using the technique of crossed, modulated, charged-particle beams. The cross sections for excitation of the resonance lines and senior terms of the subordinate series were measured for Mg^+, Ca^+, Sr^+, and Ba^+ ions, and the polarization of the strong component of the resonance doublet was measured for the last three ions. The cross sections for excitation of the resonance levels of the ions were measured; their values near the threshold were found to be 2.2 ± 0.4, 2.9 ± 0.5, 3.2 ± 0.6, and 4.4 ± 0.7 in units of 10^{-15} cm^2 for Mg^+, Ca^+, Sr^+, and Ba^+, respectively. The experimental results are compared with various theoretical calculations of the cross sections for excitation of the resonance levels.

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INTRODUCTION

The elementary processes of electron-impact excitation[1] and ionization[2] of neutral alkaline earth atoms have been studied experimentally in recent years. Until very recently, however, only the first steps had been taken in the study of electron-impact excitation of the alkaline earth ions. The published papers are concerned mainly with electron excitation of the resonance radiation of calcium[3] and barium[4-6] ions. The main difficulties here are associated with the low ion concentration in the region where the beams cross (the ion concentrations are four or five orders of magnitude lower than the concentrations in beams of neutral atoms), which makes it necessary to detect very weak radiation (the useful signal) against a strong background of the same wavelengths from a number of accompanying processes. In addition, the levels have low excitation energies (e.g., the excitation potentials of the resonance levels range from only 4.4 eV for Mg^+ down to 2.5 eV for Ba^+), and this also complicates the experiment.

The useful signal can be extracted by using a very effective technique for recording the radiation, which involves simultaneous modulation of both the electron beam and the ion beam. This technique has been discussed in detail by Harrison[7] in connection with the excitation of the metastable 2S level of He^+, by Bacon and Hooper[4] in connection with the excitation of the visible resonance radiation of Ba^+, and by the present authors[8] in connection with the excitation of the resonance radiation of He^+, which lies in the vacuum ultraviolet.

The purpose of the present work is to investigate the cross sections for excitation of the low-lying levels of Mg^+, Ca^+, Sr^+, and Ba^+ ions in collisions with slow electrons, to investigate the polarization of the radiation from those levels, and to determine the cross sections for excitation of the resonance levels of those ions.

NOTES ON EXPERIMENTAL TECHNIQUE

The experimental setup is similar in principle to the one we described earlier[8]. However, the work with metallic ions required the use of an original device for producing, shaping, and fully collecting the crossed ion and electron beams under ultrahigh vacuum conditions (10^{-8}–10^{-9} Torr). The ion beams were produced with a source similar to the one described in[9], which operated equally well in the arc discharge mode (in the experiments with Mg^+) and in the surface ionization mode (in the experiments with the other alkaline earth ions). The ion current was 10^{-7}–10^{-6} A, corresponding to a current density of 10^{-3}–10^{-2} mA/cm^2. The current density in the electron beam was considerable (0.5–5 mA/cm^2), and the energy spread was 1.0–1.5 eV at half maximum (for 90% of the electrons the energy spread did not exceed 2 eV).

A spectroscopic method was used to study the excitation of the ions, the flux of photons emitted by the ions being recorded. The radiation was brought out of the apparatus through a small quartz window and was directed by a two-lens focusing system onto the entrance slit of a standard type MDR-2 high-transmission diffraction monochromator. After the photons from a specific transition were separated in the monochromator they were recorded by a photomultiplier cooled with liquid nitrogen and operated as a counter (photomultipliers of types FÉU-39, -64, -79, and -106 were used).

The techniques used to modulate the two beams and to extract the useful signal have been described in general terms elsewhere[8,10]; further improvements in the technique were introduced in the present experiments. Control measurements showed that the useful signal depended linearly on the electron and ion currents and, over a wide range of the varied parameters, was independent of the pressure, beam modulation frequencies, and operation modes of the ion source and electron gun.

We calculated the absolute cross sections for excitation of the investigated transitions using the following well known formula applicable to the case of single collisions:

$$\sigma_\lambda = \frac{C}{\eta_\lambda}\frac{1}{N_e N_i v_e V}.$$

where C is the useful signal (counts/sec), η_λ is the sensitivity of the recording system (i.e., the probability that a photon of wavelength λ emitted in an arbitrary direction in the region scanned by the detector will be recorded), N_e and N_i are the electron and ion concentrations in the collision region, v_e is the velocity of the electrons, and V is the volume of the collision region from which radiation is collected. This formula presupposes that the electron beam passes entirely within the ion beam (the design of the apparatus assures that this condition is met) and that the radiation from the excited particles is isotropic. Actually, however, the radiation emitted by ions as a result of collisions with an electron beam is generally polarized and anisotropically distributed. We therefore investigated the polarization of the radiation under study whenever we could.

In order to determine the absolute excitation cross sections we measured the sensitivity of the recording system over a wide wavelength range encompassing all the investigated transitions, using standard light sources: a type SI-8-200 tungsten filament incandescant lamp, and a type DVS-25 hydrogen arc lamp. The error in the sensitivity calibration does not exceed ±16%.

RESULTS AND DISCUSSION

The conditions realized in the experimental setup enabled us systematically to investigate electron-impact excitation of the alkaline earth ions of magnesium, calcium, strontium, and barium for the first time with fairly high accuracy. The most careful attention was given to the excitation of the resonance lines emitted in ns – np transitions and the lines of the subordinate series emitted in np – (n + 1)s and np – nd transitions[1)]. These transitions form multiplets. In all cases with the exception of Mg^+ we investigated the excitation of the multiplet components individually (in all we studied 25 lines lying in the wavelength range 230–620 nm).

Before turning to the discussion of the results on the excitation functions, let us call attention to the following circumstance. In beams of calcium, strontium, and barium ions, the particles, generally speaking, may be found not only in their ground states, but also in their metastable ^2D states. Calculations using Boltzmann's formula (under the assumption of thermodynamic equilibrium in the surface-ionization source at the working temperature of ~2200 K) showed that fewer than 1% of the Ca^+ and Sr^+ ions would be in the metastable state, and that only for Ba^+ would an appreciable fraction of the particles (13–14%) be in the metastable state. Additional studies of the excitation of the resonance lines of these ions using the source in the discharge mode (which made it possible to vary the yield of metastable ions) enabled us to estimate the cross sections for excitation of the resonance transitions from the metastable states, and this made it possible properly to correct the experimental data on the excitation of transitions from the ground state in Ba^+.

Figures 1–4 show the energy dependence of the cross sections for excitation of the resonance transitions from the $n^2P_{3/2}$ levels, the transitions of both subordinate series ending on $n^2P_{3/2}$ levels, and also the $5^2D_{5/2} - 4^2F_{7/2,5/2}$ transition in Ba^+. Each of the experimental points on the curves was obtained by averaging the measurements of a run, which was continued until adequate statistics had been accumulated; the runs ranged in duration from 100 sec for the resonance lines to 1000 sec for the weakest transitions that we messured. The statistical (but not the absolute) error of the measurements is shown on the figures by vertical bars equal in length to the 90% confidence interval. The energy scale was calibrated to within ±0.5 eV.

As is evident from the figures, the excitation cross section rises sharply in the vicinity of the threshold for all the investigated transitions. This rise is consistent (allowing for the energy spread of the electrons) with the hypothesis that the electron excitation cross sections

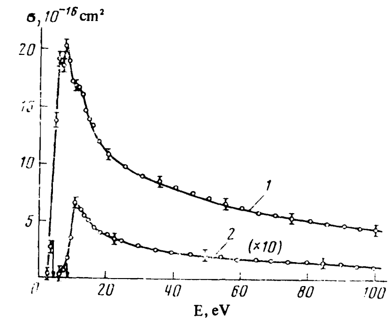

FIG. 1. Energy dependence of the cross sections for excitation of radiative transitions in magnesium ions: 1–λ = 279.6 + 280.3 nm ($3^2S_{1/2}-3^2P_{3/2,1/2}$); 2–λ = 293.6 + 292.9 nm ($3^2P_{3/2,1/2}-4^2S_{1/2}$).

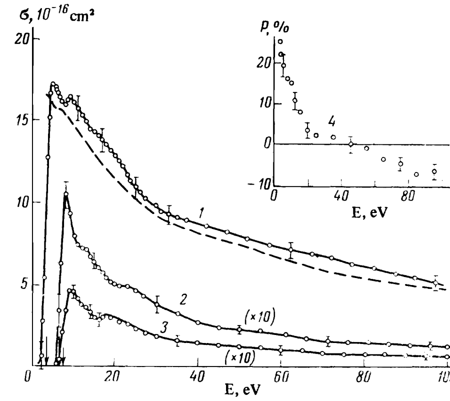

FIG. 2. Energy dependence of the cross sections for excitation of radiative transitions in calcium ions: 1–λ = 393.4 nm ($4^2S_{1/2}-4^2P_{3/2}$) (the dashed curve represents data from [3]); 2–λ = 373.6 nm ($4^2P_{3/2}-5^2S_{1/2}$); 3–λ = 317.9 + 318.7 nm ($4^2P_{3/2}-4^2D_{5/2,3/2}$). Curve 4 shows the polarization of the 393.4 nm line.

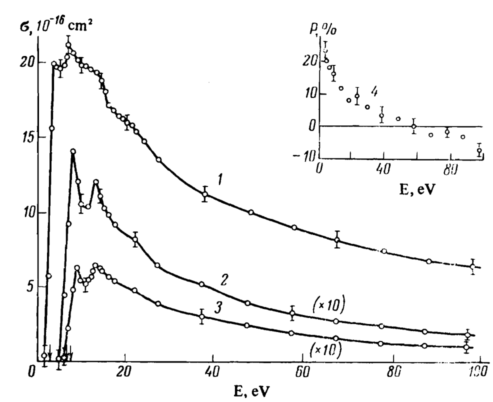

FIG. 3. Energy dependence of the cross sections for excitation of radiative transitions in strontium ions: 1–λ = 407.8 nm ($5^2S_{1/2}-5^2P_{3/2}$); 2–λ = 430.5 nm ($5^2P_{3/2}-6^2S_{1/2}$); 3–λ = 346.4 + 347.5 nm ($5^2P_{3/2}-5^2D_{5/2,3/2}$). Curve 4 gives the polarization of the 407.8 nm line.

of the ions are finite at the thresholds. It is interesting that the excitation cross section has its principal maximum at the threshold and that in most cases this maximum is followed by others, which gradually give way to a monotonically falling excitation curve at higher energies.

We note here that a comparison of our results for the strong components of the Ca^+ and Ba^+ resonance doublets with analogous published curves[3,6] (see Figs. 2 and 4) reveals satisfactory agreement both in the

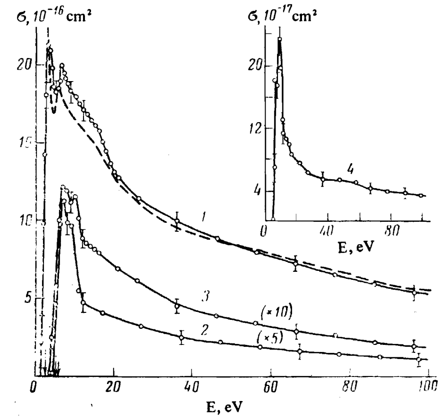

FIG. 4. Energy dependence of the cross sections for excitation of radiative transitions in barium ions: 1—λ = 455.4 nm ($6^2S_{1/2}-6^2P_{3/2}$) (the dashed curve represents data from [6]); 2—λ = 490.0 nm ($6^2P_{3/2}-7^2S_{1/2}$); 3—λ = 413.1 nm ($6^2P_{3/2}-6^2D_{5/2}$); 4—λ = 233.5 nm ($5^2D_{5/2}-4^2F_{7/2,5/2}$).

shape of the excitation curve and in the absolute value of the cross section.

Analysis of the excitation functions presented in Figs. 1—4 shows that the excitation cross sections for the lines of the subordinate series fall off faster at high electron energies than do those for the resonance lines. This is due to the fact that the ns $\rightarrow$ (n + 1)s and ns $\rightarrow$ nd transitions, and also the ns $\rightarrow$ (n − 2)f transitions, are optically forbidden, and their electron excitation cross sections must fall off as E^{-1}, where E is the electron energy, whereas the excitation cross sections for the optically allowed ns $\rightarrow$ np transitions fall of as $E^{-1}\ln E$.

Further, in our experiments it was established that in all cases the ratios of the excitation cross sections for multiplet components are close to those expected on the basis of LS coupling. In particular, this ratio is two for the components of the Ca^+, Sr^+, and Ba^+ resonance doublets. Only in the threshold region for Ba^+ is the ratio somewhat different (as was also established in[6]), and this can be understood in view of the comparatively large (0.2 eV) multiplet splitting of the 6^2P term.

The degree of polarization of the electron-beam excited resonance radiation was examined in the case of the Ca^+, Sr^+, and Ba^+ ions. The results (Figs. 2 and 3) show that the degree of polarization of the strong components of the resonance doublets is greatest (20—25%) at the threshold; the polarization changes sign at 50—60 eV and reaches values of 5—10% at 100 eV (no analysis of the isotopic composition of the ion beams was made). The presence of polarization shows that the magnetic sublevels of the $n^2P_{3/2}$ resonance states of the alkaline earth ions are nonuniformly populated.

Our results on the polarizations of the strong components of the resonance doublets of calcium and barium ions are confirmed (within the experimental error) by earlier measurements[3,6]. No appreciable polarization of the weak components was detected. All these results on the polarization of the resonance radiation of alkaline earth ions are in agreement with the predictions of the general theory of the polarization of radiation induced by collisions with an electron beam[12]. Thus, no correction to the cross section for excitation of the resonance lines need be made except in the vicinity of the threshold (and there the correction does not exceed 7—8%).

Another important point involved in determining the cross sections for direct excitation of the resonance levels of alkaline earth ions is the presence of not just one channel for the radiative decay of the resonance n^2P states (as is observed for the isoelectronic alkali metal atoms), but of two such channels: to the n^2S ground states, and to the metastable $(n-1)^2D$ states (the only exception is the Mg^+ ion, which does not have the second channel). The reliable published experimental data on the relative probabilities for the radiative transitions from the resonance levels[13] makes it possible easily to take this branching ratio of the resonance radiation into account[2)].

Taking what was said above into account, we used our results on the radiative transitions to find the absolute cross sections for excitation of the resonance levels of the alkaline earth ions. To do this we first calculated the cross sections for excitation of all the radiations emitted from the resonance levels with allowance for the probabilities for radiative deexcitation of these levels, and then we graphically subtracted the cascade contributions to the populations of these levels. In calculating the populations of the levels via cascade transitions from the $(n+1)^2S$ and n^2D levels we assumed that the main contribution comes from the senior transitions of the subordinate series that we investigated, neglecting transitions from higher-lying states. This neglect is quite justified since the total contribution from cascade transitions to the populations of the resonance levels does not exceed 10—15% (and in addition the cross sections for the excitation of lines of the subordinate series fall off very sharply with increasing principal quantum number).

The final results on the electron excitation of the resonance levels are presented in Fig. 5.[3)] One notices at once that the second maxima have almost entirely disappeared from the excitation functions for the resonance levels; this is obviously due to the exclusion of the cascade transitions.

Now let us examine the results in the light of the available theoretical calculations. The most widely used calculation method for this problem is the Coulomb-Born approximation. Specific calculations of excitation cross sections have been made in various modifications of the Coulomb-Born approximation for Mg^+ by Blaha[15], for Ca^+ and Mg^+ by van Regemorter[16], and for Ca^+ and Ba^+ by Petrini[18]. Vaĭnshteĭn et al.[19] proposed an interpolation formula and tables for calculating excitation cross sections of ions in the Coulomb-Born approximation with allowance for normalization. We used this formula to calculate the cross sections for excitation of the resonance levels of all four ions, and the results of these calculations are also presented in Fig. 5. It will be seen that there is good agreement between experiment and theory at energies above (20—30)E_{thresh}. At low energies the cross sections given by this method are too high, as should be expected; at the threshold, the Coulomb-Born cross section exceeds the experimental cross section by a factor of 1.5—2.

In the low-energy region the theoretical treatment is more complicated. We are aware only of the paper by Burke and Moores[20], who used the strong coupling method (with and without exchange) to calculate excita-

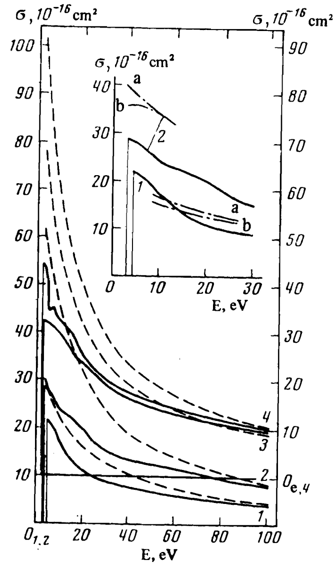

FIG. 5. Cross sections for excitation of resonance levels of alkaline earth ions: 1–3^2P, Mg^+; 2–4^2P, Ca^+; 3–5^2P, Sr^+; 4–6^2P, Ba^+. The full curves represent our experimental data; the dashed curves were calculated in a modified Coulomb-Born approximation with allowance for normalization; the dash-dot curves were calculated in the strong coupling approximation neglecting (a) and including (b) exchange.

tion cross sections for Mg^+ and Ca^+ ions. Although the correlation between theory and experiment is not bad in the first case, in the second case the theoretical results are somewhat too high.

[1)]The first data on the excitation of the Mg^+ resonance radiation were published in a brief communication [11].

[2)]We made direct measurements of the cross section for one of the lines involved in the branching (λ614.2 nm, ($5^2D_{5/2}$–$6^2P_{3/2}$)Ba^+), and the results confirm the relative probabilities given in [14].

[3)]The first data on the cross section for excitation of the Ca^+ resonance level were published in a brief communication [14].

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210