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ELECTRON-IMPACT EXCITATION OF THE $5p^5 5d6s^2$ AUTOIONIZING STATES IN Ba ATOM [1]

The excitation cross-sections for the $5p^5 5d6s^2$ autoionizing states of Ba atoms are studied experimentally and theoretically in an electron-impact energy range from the excitation thresholds of the states up to 600 eV. Experimental data are obtained by determining the intensities of lines in the ejected-electron spectra measured at an observation angle of 54.7°. The incident-electron and ejected-electron energy resolutions are 0.2 eV and 0.07 eV, respectively. The calculations are performed in the distorted wave approximation by using relativistic radial wave functions obtained in the standard Dirac–Fock–Slater method. For all the states, the experimental cross-sections reach their maxima at low impact energies revealing by that predominantly the spin-exchange character of the excitation of autoionizing states. The structure of the near-threshold maxima indicates the formation of strong negative-ion resonances. At high impact energies, the shape and value of the cross-sections are determined by configuration and state mixing effects.

Keywords: atom, excitation, ionization, autoionization, cross-section.

1. Introduction

The excitation of inner electron subshells in atoms results in the formation of a broad class of atomic states located above the first ionization limit. Such quasibound states decay to the continuum by the configuration interaction with the formation of an ion and a free (ejected) electron. This process is known as *autoionization* and shows the important role of electron correlations in intraatomic interactions.

The most valuable source of information on the correlation and cascade processes in the electron-impact excitation of atomic states is the excitation cross-sections measured in a broad impact-energy range. Recently, such experimental data complimented by the large-scale relativistic calculations were obtained for autoionizing states in alkaline atoms (see [1] and references therein). One of the main results of these studies is the detection of strong resonance processes in the electron-impact excitation of the outer p^6 subshells in Na, K, Rb, and Cs atoms.

Barium is the heaviest of the alkali-earth group of atoms. Therefore, the correlations and many-body effects should play an important role in its electron-impact excitation. This was shown by the photoexcitation of the $5p^6$ subshell [2] and by the *R*-matrix calculations for the $6s^2$ valent shell [3]. In [2], due to the high complexity of the photoabsorption spectrum, the authors failed to classify the lines us-

[1] This paper is dedicated to the blessed memory of Dr. Alicija Kupliauskienė (1949–2018), a talented theoretical physicist, our colleague and a good friend, who supported experimental studies of autoionization processes in metal atoms, including barium, with very qualified calculations for many years.

ing the single configuration non-relativistic Hartree–Fock approach. In [3], a strong resonant structure in the excitation cross-sections of the $5p^6 n_1 l_1 n_2 l_2$ states was revealed. Only recently [4], by a combination of the experimental data on the excitation dynamics of ejected-electron spectra and the calculated parameters of the $5p^5 n_1 l_1 n_2 l_2 n_3 l_3$ states, all the lines in electron spectra [5, 6] and many lines in the photoabsorption spectrum [3] were classified.

The present work is a continuation of these studies and is devoted to the excitation dynamics of the $5p^5 5d6s^2$ configuration in barium. In particularly, we report the experimental and calculated excitation cross-sections of the singlet and triplet autoionizing states obtained in an electron-impact energy range from the excitation thresholds up to 600 eV. Both dipole-allowed and dipole-forbidden transitions are studied. In Section 2, we will briefly describe the apparatus and the measurement procedure, as well as the calculation method. In Section 3, the results of the measurements and calculations are considered, and the processes which may influence the shape and value of the excitation cross-sections are discussed. Conclusions are drawn in Section 4.

2. Measuring Procedure and Calculation Method

The measuring and the data processing procedure used for obtaining the excitation cross-sections of the autoionizing states were described earlier [7, 8] in details. In the present study, the ejected-electron spectra corresponding to the decay of the $5p^5 n_1 l_1 n_2 l_2 n_3 l_3$ autoionizing states of Ba atoms were measured by employing an electron spectrometer consisted of a monochromator and an analyzer (both of the 127 ° electrostatic type), and an atomic beam source designed for working temperatures up to 700 °C [4]. The incident- and ejected-electron energy resolutions (FWHM) were about 0.2 eV and 0.07 eV, respectively. The spectra were measured in series, step-by-step for different impact-energy values over the range from the $5p^6$ excitation threshold at 15.61 eV up to 600 eV. Below the 21.5 eV impact energy, the increment step was 0.1 eV. In order to minimize a possible influence of the asymmetry of the angular distribution of Auger electrons on the impact-energy dependence of the intensity of ejected-electron lines, the measurements were performed at an observation angle of 54.7° [9]. The intensity of the spectra was automatically normalized to the intensity of the incident electron beam by a current-to-frequency converter. The examples of ejected-electron spectra at impact energies of 27.5 and 102 eV are shown in Fig. 1. Comparing the spectra shows that low-energy lines 4–17, which reflect the decay of dipole-forbidden states [4], are dominant in the spectrum at 27.5 eV, whereas lines 23–60 associated with dipole-allowed states are most noticeable in the spectrum at 102 eV. However, as will be shown below, the dipole-allowed states possess also the strong excitation maxima at near-threshold impact energies.

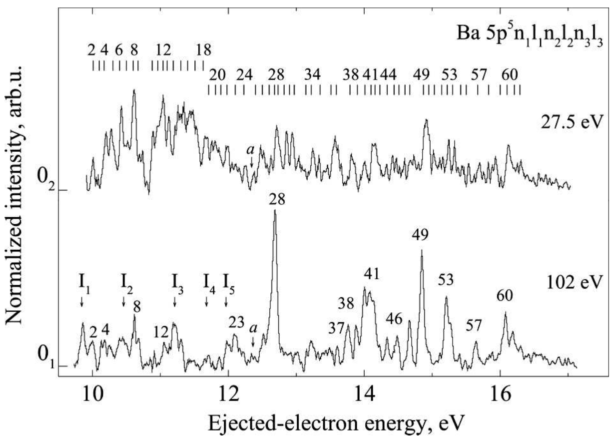

Fig. 1. Ejected-electron spectra of Ba atoms for impact energies of 27.5 and 102 eV. In spectra, a polynomial background function was subtracted from the original data. Bars on the top of the spectra mark the positions of ejected-electron lines. I_{1-5} mark the positions of lines at 9.88, 10.47, 11.22, 11.70, and 11.99 eV which correspond to the decay of the $5p^5 n_1 l_1 n_2 l_2$ ionic autoionizing states [10]. The indexation of lines is in accordance with [6]

In the presented ejected-electron spectra, a new line a at 12.33 eV with the appearance energy of approximately 17.8 eV was revealed. Unfortunately, it remains unclassified, because this requires an additional analysis of the dynamics of its excitation in combination with a possible revision of the entire classification of lines in the electronic spectra of Ba atoms.

The sets of spectra obtained in three independent experiments were processed to subtract an intensity of the background and to derive the line intensities. The typical relative error in determining the line intensities being of statistical character did not exceed the maximum value of 25%. It increased up to 30% for the lowest line intensities observed at low (close to the excitation thresholds) and

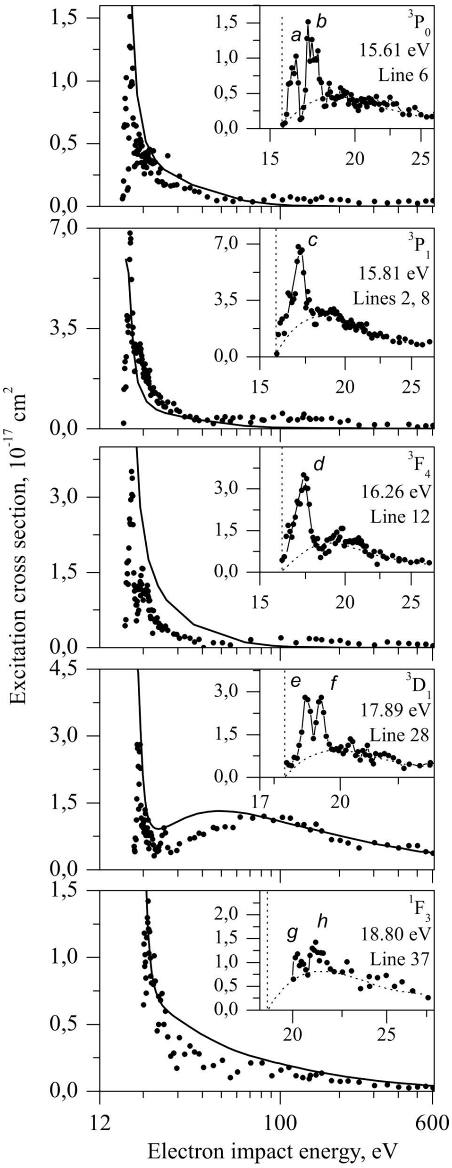

Fig. 2. Electron-impact excitation cross-sections for the autoionizing states in the $5p^55d6s^2$ configuration of Ba atoms. Solid curves represent the present calculations. In the insets, the vertical dashed lines mark the excitation thresholds of states and the dotted curves indicate the broad excitation maxima (see the text)

high (>500 eV) impact energies. The excitation cross-sections of autoionizing states were obtained in the form of the energy dependences of the normalized line intensities. In the case of the multichannel decay mode of a particular state [4], its cross-section was obtained as the sum of the normalized intensities of lines corresponding to the all decay channels of this state.

The calculations of the cross-sections were performed in the distorted wave approximation by using relativistic radial wave functions obtained in the standard Dirac–Fock–Slater method. The Flexible Atomic Code [11] and the relativistic jjJ coupling scheme of angular momenta were used. The obtained expansion coefficients were transformed to the LSJ coupling scheme. A number of configurations used in the superposition to involve the correlation effects both in the initial and final states was 10199. The detailed description of calculations is presented in [4].

3. Results and Discussion

Of eleven states of the $5p^55d6s^2$ configuration, the experimental excitation cross-sections were obtained for $^3P_1$, $^3D_1$ dipole-allowed states and for $^3P_0$, $^3F_4$, and $^1F_3$ dipole-forbidden states. The corresponding ejected-electron lines 2, 6, 8, 12, 28, and 37 have remarkable intensity and are well resolved in the spectra. For the state $^3P_1$ which possesses two decay channels [4], the excitation cross-section was obtained by summing the intensities of lines 2 and 8. The relative experimental data were put on the absolute scale by normalizing the excitation function of the $^3D_1$ state to the calculated cross-section at 600 eV. The absolute excitation cross-sections for other states were obtained by using the ratio of line intensities in the ejected-electron spectrum at 102 eV. In Fig. 2, the measured excitation cross-sections are shown together with the calculated data in the impact-energy range from the excitation thresholds of the states up to 600 eV.

Considering the experimental cross-sections, one may see that all the states have the main excitation maxima at near-threshold impact energies. The behavior of the cross-sections in this energy region is shown in the insets in detail. As can be seen, the broad maxima located at approximately 18–22 eV (dotted curves are used to guide the eye) reflect the spin-exchange excitation character of triplet states. However, a similar broad maximum is observed also for the dipole-forbidden singlet $^1F_3$.

As the impact energy decreases to the excitation thresholds of states, the strong resonance structure $a-h$ appears in all cross-sections (see Table 1). Most of the features $a-h$ possess an asymmetric shape, and their widths are visibly larger of the present incident-electron energy resolution equal to 0.2 eV. Therefore, they are, in fact, a superposition of several narrow resonances associated with the formation of short-lived states of Ba^- ions. The high efficiency of this process in the $6s^2$ excitation [3] confirms this assumption. At present, it is difficult to say something about the spectroscopic classification of the observed resonances $a-h$, since this can be done only on the basis of the corresponding theoretical calculations. However, as shown by our theoretical studies of the excitation of the $5p^6$ subshell in a neighboring cesium atom [12,13], the calculation of the near-threshold excitation of the $5p^6$ subshell in barium (e.g., by using the R-matrix approach) will be a very difficult task.

Considering the calculated data, it should be noted that the accuracy of the distorted-wave approximation is low in the region of threshold impact energies. However, as can be seen from the comparison of the data in Fig. 2, the calculated cross-sections for impact energies above 40 eV describe well the experimental ones for all the states. For analyzing the excitation behaviors of the states in this impact energy region, let us consider their eigenstate expansions. These data are presented in Table 2. Note that, due to the strong mixing effects, the distribution of the excitation efficiency is approximately equal over a number of states; therefore, for each state, only three configurations with the largest coefficients are given.

Table 1. **Energy positions of resonance features observed in the excitation cross-sections of the $5p^5 5d6s^2$ autoionizing states**

Feature	a	b	c	d	e	f	g	h
Energy, eV	16.39	17.08	17.19	17.39	18.63	19.25	20.22	21.18

Table 2. **LSJ mixing coefficients for the states in the $5p^5 5d6s^2$ configuration**

State	Mixing coefficients
$^3P_0$	$0.971(5d6s^2\ ^3P_0)+0.122(5d6p^2\ ^3P_0)+0.105(5d^2 6s\ ^3P_0)$
$^3P_1$	$0.744(5d6s^2\ ^3P_1)–0.462(5d^2 6s\ ^5D_1)–0.343(5d6s^2\ ^3D_1)$
$^3F_4$	$0.946(5d6s^2\ ^3F_4)+0.176(5d^2 6s\ ^5F_4)–0.133(5d^2 6s\ ^5D_4)$
$^3D_1$	$–0.711(5d6s^2\ ^3D_1)–0.335(5d^2 6s\ ^3P_1)+0.232(5d6s^2\ ^1P_1)$
$^1F_3$	$–0.604(5d6s^2\ ^1F_3)+0.448(5d6s^2\ ^3D_3)+0.440(5d6s^2\ ^3F_3)$

As follows from the analysis of the dominant configurations in Table 2, the mixing effects for the states $^3P_0$ (0.971) and $^3F_4$ (0.946) are minimal. Therefore, their excitation dynamics fully corresponds to the spin-exchange and dipole-forbidden types of transitions. The same can be said about the excitation of the high-lying singlet $^1F_3$, which is strongly mixed with triplet states $5p^5 5d6s^2\ ^3D_3$ (0.448) and $5p^5 5d6s^2\ ^3F_3$ (0.440).

The strong mixing with $^5D_1$ (–0.462) and $^3D_1$ (–0.343) states enhances the spin-exchange excitation character of the dipole-allowed triplet $^3P_1$. However, a certain increase in the cross-section near 100 eV may be associated with a small contribution from the $5p^5 5d^2 6s\ ^1P_1$ (–0.147) singlet state. The electron excitation of another dipole-allowed triplet $^3D_1$ at low impact energies is typical of spin-exchange transitions. The strong broad maximum observed around 80 eV is caused by a contribution from the $5p^5 5d6s^2\ ^1P_1$ (–0.2322) dipole-allowed singlet state which does not exist as a single level in the $5p^6$ excitation spectrum of Ba atoms [4].

The radiative decay of high-lying states can lead to the cascade population of the low-lying autoionizing states. An enhancement of the cross-section caused by this process was earlier observed in the ejected-electron excitation functions of the lowest autoionizing states $4p^5 4d5s^2$ in strontium atoms [14]. In barium, the following reaction describes the cascade population of the $5p^5 5d6s^2$ states:

$$Ba^*(5p^5 n_1 l_1 n_2 l_2 n_3 l_3) \rightarrow Ba^*(5p^5 5d6s^2) + h\nu. \qquad (1)$$

Analyzing the measured excitation cross-sections in Fig. 2 shows that none of them reveals some clear signs of the presence of process (1). As was shown by our present and former [4] calculations of the decay probabilities for the $5p^5 n_1 l_1 n_2 l_2 n_3 l_3$ states with excitation thresholds above 21 eV, the reason for this is their dominant radiationless decay, including the two-step autoionization with the formation of Ba^{2+} ions. An indirect confirmation of this is the absence of the atomic lines in the VUV-photoemission spectrum of Ba atoms [15].

4. Conclusions

The excitation cross-sections of the $5p^5 5d6s^2$ autoionizing states in Ba atoms are obtained for the first time experimentally and theoretically in the electron-impact energy range from the excitation thresholds of the states up to 600 eV. The comparative analysis of these data has shown that the correlation interactions (spin-exchange and the formation of negative ions) determine the behavior of all cross-sections at low impact energies. At high impact energies, the configuration and state mixing effects influence the shape and value of the cross sections.

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ЕЛЕКТРОННЕ ЗБУДЖЕННЯ
АВТОІОНІЗАЦІЙНИХ СТАНІВ
$5p^55d6s^2$ АТОМА Ba

Р е з ю м е

Перерізи електронного збудження автоіонізаційних станів $5p^55d6s^2$ в атомах Ba досліджено експериментально і теоретично для енергій зіткнень від порогів збудження до 600 еВ. Експериментальні дані одержані шляхом визначення інтенсивностей ліній в спектрах ежектованих електронів, виміряних при куті спостереження 54,7° з енергетичною роздільною здатністю для первинних і ежектованих електронів 0,2 еВ і 0,07 еВ, відповідно. Розрахунки проведено у наближенні спотворених хвиль з використанням релятивістських радіальних хвильових функцій, отриманих у стандартному методі Дірака–Фока–Слейтера. Експериментальні перерізи приймають максимальні значення при низьких енергіях зіткнень, виявляючи тим самим спін-обмінний характер збудження автоіонізаційних станів. Наявність структури припорогових максимумів вказує на ефективне утворення резонансів негативних іонів. При великих енергіях зіткнень форма і абсолютне значення перерізів визначаються ефектами змішування як різних конфігурацій, так і станів в рамках однієї конфігурації.