Observation and study of two-electron multiphoton ionization of atoms

I. S. Aleksakhin, N. B. Delone, I. P. Zapesochnyĭ, and V. V. Suran

Uzhgorod State University

(Submitted 2 November 1978)
Zh. Eksp. Teor. Fiz. 76, 887–895 (March 1979)

Experiments have been conducted in which doubly charged ions of a number of atoms having two optical electrons were produced by a multiphoton ionization process under the action of intense laser light. The results of the experiments are presented and analyzed, and it is shown that the doubly charged ions were produced by a two-electron process of multiphoton ionization of the atoms.

PACS numbers: 32.80.Kf, 32.80.Fb

INTRODUCTION

Multiphoton ionization of atoms has been fairly well studied in recent years.[1] However, all the results, both experimental and theoretical, pertain to the detachment of a single electron from a neutral atom. While one-electron ionization should obvioulsy predominate in the case of atoms having a single optical electron, one might expect a multielectron process to take place and multiply charged ions to be produced in the case of atoms having several equivalent electrons in the outer shell. In principle, such a phenomenon might take place, for example, in the ionization of noble-gas atoms in a strong light field. This process has been thoroughly investigated experimentally, but in all cases only singly charged ions were observed.[1,2] This, however, cannot be regarded as proof that the probability for multielectron processes is low. In the first place, the first and second ionization potentials of a noble gas atom differ widely (only for xenon is this difference only ≈ 10 eV; for the other noble gas atoms it amounts to ≈ 20 eV). And second, in the absence of resonances the simultaneous detachment of two electrons would be a process having a very low probability as compared with the one-electron ionization process since the former is to a considerably greater extent a multiphoton process. Resonances cannot change the situation significantly in the case of noble gas atoms since their first excited levels lie very high.

Starting from the simple considerations presented above, we turned our attention to the alkaline earth atoms and to a number of other atoms having two electrons in the outer shell—the lanthanides and lead. The atoms that we investigated differ considerably from the noble gas atoms—their ionization potentials are below 8 eV and their first excited states lie comparatively low.

The most important circumstance is the well known tight binding of the two optical electrons in the alkaline earths and the lanthanides. This coupling manifests itself in the existence of two-electron excited bound states lying both below (mixed terms) and above (autoionization states) the first ionization potential.[3] The probability for the excitation of these atoms to two-electron states is very high. For example, the probability for the excitation of two-electron states of the strontium and barium atoms by electron impact is comparable with the probability for excitation of one-electron states.[4] In principle, one should expect the two-electron bound states to appear along with the one-electron states in multiphoton resonance ionization of the atoms and to lead, in particular, to the production of doubly charged ions. In some of our previous studies we detected the production of doubly charged ions in the multiphoton ionization of a number of atoms—strontium,[5] barium,[6] and samarium.[7]

Here we present new experimental data on the field-strength dependence of the probability for the production of doubly charged ions. From an analysis of these new data we can conclude that the doubly charged ions are produced in multiphoton resonance ionization of these atoms.

EXPERIMENTAL SETUP

In setting up an experiment to observe the production of doubly charged ions in the multiphoton ionization of atoms we bore in mind that the mere fact that doubly charged ions are observed cannot be regarded as definite proof that the following two-electron multiphoton ionization process has taken place:

$$A+K_0^{2+}\hbar\omega\to A^{2+}+2e, \tag{1}$$

where $K_0^{2+}=\langle E_2/\hbar\omega+1\rangle$ is the number of photons that must be absorbed to conserve energy in the detachment of two electrons from the atom (E_2 is the two-electron detachment energy). Actually, doubly charged ions can also be produced in the following stepwise process:

$$A+K_0^{+}\hbar\omega\to A^{+}+e,\quad A^{+}+K_{\rm res}^{2+}\hbar\omega\to A^{2+}+e. \tag{2}$$

Although the total energy that must be transferred to the atom in order to detach two electrons is the same in both of the processes (1) and (2), the two processes are essentially different. First, they differ in the bound-state spectra of the systems being ionized; and second, they differ in the degree of nonlinearity (photon multiplicity) of the transitions taking place. We note that in the case of the stepwise process (2) it is assumed that the entire process takes place during a single laser pulse.

To clarify the relative parts played by the direct (1) and stepwise (2) processes in the production of doubly charged ions in the multiphoton ionization of atoms, one must not only observe the doubly charged ions A^{2+}, but must also obtain experimental data on the probabilities for the production of the A^+ and A^{2+} ions as functions of the field strength, frequency, and polarization of the laser light. In the present work we completed only part of this research program: we obtained the field-strength dependence of the probability for fixed frequency and polarization of the laser light. As will be evident below, even these data allow us to draw definite conclusions concerning the mechanism responsible for the production of the A^{2+} ions.

For the experimental study of the production of doubly charged ions we used an intersecting-beam method involving the intersection of an atomic beam and a beam of laser light. The general scheme of the experimental apparatus is shown in Fig. 1. The atomic density in the beam was 10^{10}–10^{11} atoms/cm^3. The ions produced in the beam-intersection zone were extracted by a weak (~100 V/cm) steady field, were analyzed by a time-of-flight mass spectrometer, and were recorded by an electron multiplier. The mass spectrometer had a receiving power of ~10, which was adequate for reliable separation of the singly- and doubly-charged ions of the investigated atoms. The ions were registered by a type VÉU-1A secondary-electron multiplier, whose sensitivity to doubly charged ions was about twice its sensitivity to singly charged ones. The ratio of the sensitivities was verified by special control experiments. The threshold sensitivity of the recording apparatus corresponded to the production of ~10^2 ions in a single laser pulse.

To produce the strong light field we used the radiation from a Q-switched neodymium glass laser giving a light pulse of the order of 30 nsec long. The laser operated in a single transverse mode and many longitudinal modes at the frequency ω=9450 ±7 cm^{-1}. The laser light was plane polarized to a high degree of accuracy. Careful stabilization of the laser made it possible to obtain a constant energy in the pulse and a constant space-time distribution of the radiation within a few percent for hundreds of successive pulses. The laser light was linearly attenuated at the entrance to the interaction chamber and was focused on the center of the atomic beam. The circle of focus was ~100 μm in diameter, so that interaction of the intense light with atoms took place in a volume of the order of 10^{-6} cm^3, and up to 10^5 ions were produced in a single laser pulse. The field strength of the radiation in the ion-production zone was determined in accordance with a standard technique[2] by measuring both the energy of the radiation in a pulse passing through the interaction chamber, and the time and space distribution of the radiation. By attenuating the radiation we could vary the field strength in the ion-production region from ~10^6 to ~10^7 V/cm.

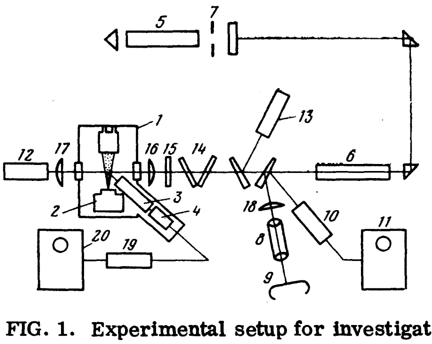

FIG. 1. Experimental setup for investigating the multiphoton ionization of atoms: 1—vacuum chamber, 2—atomic-beam source, 3—time-of-flight mass spectrometer, 4—ion detector, 5—neodymium laser, 6—amplifier, 7—diaphhragm for selecting transverse modes, 8, 9—microscope and camera for monitoring the space distribution of the radiation, 10, 11—type FEK-09 photoelement and type 12-7 oscillograph for monitoring the time distribution, 12, 13—devices for measuring the energy of the radiation, 14, 15—attenuators, 16, 17, 18—lenses, 19—broad band amplifier, 20—type S8-2 recording oscillograph.

The measuring procedure consisted in producing a series of consecutive laser pulses, varying the attenuation, and, for each laser pulse, recording the amplitudes A^+ and A^{2+} of the ion signals and the energy Q that passed through the chamber. Measurements of the space-time distribution of the radiation in the beam-intersection zone made it possible to derive the dependence of A on the field strength $\mathscr{E}$ in the light field from the measured dependence of A on Q. In the plots of A vs Q one can, as always, distinguish a range of values of Q in which the power law $A \sim Q^K$ (a straight line on a log-log plot) is well satisfied. As a rule, moreover, one can also find a region of large values of A in which the ion signal becomes saturated (see Fig. 2), owing to the large ionization probability when the relation

$$\int_0^T W\,dt \ll 1$$

is no longer satisfied (W is the ionization probability and T is the duration of the laser pulse).

By approximating the linear part of the relation between log$A$ and log$Q$ by the method of least squares we were able to evaluate one of the basic characteristics of nonlinear processes—the exponent K_{exp} in the power-law relationship $A \sim Q^{K_{\text{exp}}}$. Observation of the linear part together with the saturation region makes it possible to determine the multiphoton cross sections $\alpha_{K_0} = WF^{-K_0}$ for the direct ionization process by a relative method.[8]

The apparatus and measuring technique were tested

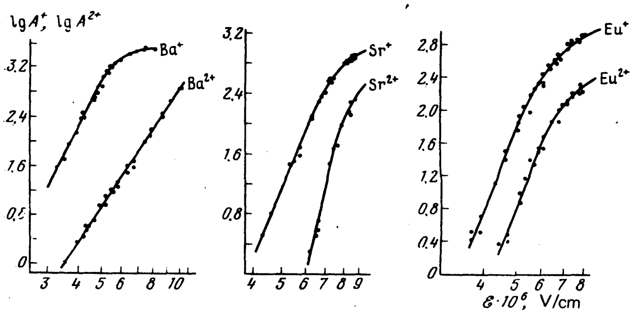

FIG. 2. Amplitudes of the ion signals from singly- and doubly-charged ions of barium, strontium, and europium vs the field strength $\mathscr{E}$.

together by observing the five-photon ionization of the sodium atom and measuring the cross section for that process. The relation $W=\alpha_5 F^K$ was obtained with the values $K=4.8\pm0.2=5$ and $\log\alpha_5=-(140^{+2.0}_{-1.6})$. These values are in good quantitative agreement with earlier measurements.[9]

EXPERIMENTAL RESULTS

We observed the multiphoton ionization of the alkaline earths magnesium, calcium, strontium, and barium, which have two *s* electrons in the outer shell, of the lanthanides europium and samarium, which also have two outer *s* electrons, and, finally, of lead, which has two outer *p* electrons.

We shall first present the results of the experiments in which we observed the production of singly charged ions. The principal data are given in Table I. As is evident from the table, in the ionization of strontium, calcium, and europium, the Q dependence of A is of power-law type with the exponent K^+_{exp} equal to K_0, i.e. to the number of quanta that must be absorbed to conserve energy. In these cases the multiphoton ionization process is accordingly of direct type involving no intermediate resonances. The multiphoton cross sections for the direct ionization of strontium, calcium, and europium were determined by the relative method. These cross sections are listed in Table II together with the results of calculations[10] performed in the one-electron approximation using standard methods of time-dependent perturbation theory. In Table II the calculated results, which were obtained for strictly monochromatic radiation, have been increased by a factor of $K_0!$ since a nonmonochromatic field was used in the experiments.[11] For calcium the calculated cross section is close to the measured one, while for strontium the calculated value is appreciably lower than the observed cross section. In our opinion, this difference may be due to competition from two-electron multiphoton ionization of this atom (see below).

In the other cases $K^+_{\text{exp}} < K_0$; and the multiphoton ionization process is of resonance type. Analysis of the spectra of the magnesium, barium, and lead atoms reveals a number of bound electron states with which resonance might take place, in view of the frequency of the radiation, the width of the spectrum, the selection rules for multiphoton transitions, and the shifts of the levels in a 10^6–10^7 V/cm field. A six-photon resonance is possible in magnesium via the $5d$ state, and a four-photon resonance in barium via a number of levels of the $8d$ multiplet. By analogy with known data on the alkali atoms[2] it must be supposed that the deviations of the values of K^+_{exp} from the corresponding values of K_0 may be due both to shifting of the resonance levels and to broadening of the levels by the action of the external field. We note that since the transitions from these states to the continuum are of one-photon type, they should obviously exhibit saturation.

On the whole, the present experimental data on multiphoton ionization of atoms having two optical electrons (see Tables I and II) leading to the production of singly charged ions are in qualitative and quantitative agreement with results obtained earlier on multiphoton ionization of atoms having one outer electron.[2] Because of the inadequacy of the quantitative data on multiphoton cross sections for direct ionization processes and the considerable errors in measuring the cross sections, it is impossible to draw any definite conclusion at present concerning the accuracy of the one-electron approximation in calculating multiphoton cross sections. The problem of the accuracy of the one-electron approximation as applied to the ionization of atoms having many electrons in the outer shell is very important and timely, and in our opinion its solution will require careful research and the united efforts of experimentalists and theoretricians.

TABLE I. Experimental data on the one-electron multiphoton ionization of a number of atoms with two electrons in the outer shell*

	Ba	Sr	Eu	Ca	Mg	Pb
I, eV	5.2	5.7	5.7	6.1	7.6	7.4
$K_0{+}$	5	5	5	6	7	7
K^+_{exp}	4.0	5.0	5.0	5.9	5.0	5.9
ΔK^+_{exp}	±0.1	±0.2	±0.2	±0.1	±0.3	±0.2
$K^+_0-K^+_{\text{exp}}$	1.0	0	0	0	2.0	1.0
$\mathscr{E}\cdot10^6$, V/cm	4.9	6.7	5.3	5.9	14.0	11.0

*I—ionization potential of the atom, $\mathscr{E}$—field strength of the laser light, ΔK—experimental error in determining K; the other symbols are defined in the text.

Let us now turn to the results of experiments in which the production of doubly charged ions has been observed in multiphoton ionization of atoms having two optical electrons.[5-7,12] Such production has been observed simultaneously with the production of singly charged ions for the strontium, barium, samarium, and europium atoms. The principal results on doubly charged ions are presented in Table III and Fig. 2. From these data together with the data on the production of singly charged ions (Table I) we can draw three basic conclusions concerning the nature of the process by which the doubly charged ions are produced:

1. The probability for the production of doubly charged ions is always lower, although not very much lower (in multiphoton terms), than the probability for the production of singly charged ions.

2. There is no systematic relation between the degree of nonlinearity of the process responsible for the production of doubly charged ions (K^{2+}_{exp}) and that of the process

TABLE II. Multiphoton cross sections for the direct one-electron ionization of atoms (α_{exp} and α_{theor} are the measured and calculated values, respectively)

	Sr	Eu	Ca
$K_0{+}$	5	5	6
$K_0{+}!$	$\sim 10^2$	$\sim 10^2$	$\sim 10^3$
$\lg\alpha_{\text{exp}}$	$-140.6^{+1.8}_{-1.7}$	$-140.5^{+1.8}_{-1.3}$	$-170.2^{+2.7}_{-1.3}$
$\lg\alpha_{\text{theor}}$	-137.6	—	-172.0

TABLE III. Experimental data on the production of doubly charged ions

	Ba	Sr	Eu
K^{2+}_{exp}	2.9	10,1	4.9
$\Delta K^{2+}_{\mathrm{exp}}$	±0.2	±0.3	±0,2
$\mathscr{E}\cdot 10^6$, V/cm	13.0	7,6	5,8

responsible for the production of singly charged ions (K^+_{exp}). As is evident from Tables I and III, $K^{2+}_{\mathrm{exp}} < K^+_{\mathrm{exp}}$ for barium, $K^{2+}_{\mathrm{exp}} = K^+$ for europium, and $K^{2+}_{\mathrm{exp}} > K^+_{\mathrm{exp}}$ for strontium.

3. Differences can be seen (Fig. 2) in the manner in which the ion signals corresponding to the production of doubly- and singly-charged ions become saturated. In the ionization of the barium atom, saturation sets in at a different field strength. In the ionization of the strontium atom, the yield of doubly charged ions saturates more gradually with increasing field strength than does the yield of singly charged ions.

These basic conclusions from the experimental results, together with the quantitative data presented in Tables I and III and in Fig. 2, provide a foundation for a discussion of various mechanisms for the production of doubly charged ions in the ionization of the strontium, barium, europium, and samarium atoms.

DISCUSSION OF THE EXPERIMENTAL RESULTS ON PRODUCTION OF DOUBLY CHARGED IONS

The experimental data on the production of doubly charged ions cannot be explained on the assumption of a stepwise ionization process. In that case the probability W^{2+} for the production of doubly charged ions A^{2+} would be equal to the product of the probability W^+ for the first transition and the probability W^{2+}_{step} for the second transition: $W^{2+} = W^+ W^{2+}_{\mathrm{step}}$. If both transitions are direct, K^{2+}_0 should be 13 for barium and 15 for strontium and europium. The experimental value K^{2+}_{exp} is several times smaller (see Table III). Bearing in mind the data on the degree of nonlinearity in the production of the corresponding singly charged ions (see Table I), one can assert that the observed values of K^{2+}_{exp} could arise only as a result of a resonance process for the ionization of singly charged ions. Analysis of the spectra of the Sr^+ and Ba^+ ions[13] shows that resonances cannot be involved. Indeed, the energy deviations between groups of several radiation quanta and the bound states are large—too large (several hundred reciprocal centimeters) to be compensated by perturbation of the spectrum of the ion by the radiation field. A stepwise process for the production of Eu^{2+} ions cannot be ruled out because of the lack of tabulated data on the spectrum of the Eu^+ ion.

Now let us turn to the two-electron mechanism (1) for the production of doubly charged ions. There are two possible cases. In the first case, on absorbing several radiation quanta the atom is excited by the multiphoton process to a two-electron bound state lying below the first ionization potential, and the atom is subsequently ionized from this state, both electrons passing over to the continuous spectrum. In the second case, we have multiphoton excitation of an autoionization state, from which both electrons pass over to the continuous spectrum under the action of the external field. In both cases we have a multiphoton resonance ionization process which, as is well known,[1,2] can lead to deviation of the observed K^{2+}_{exp} values from the corresponding K^{2+}_0 values as a result of the action of the external field, which may alter the transition energy (by shifting the resonance levels) and broaden the resonance state. It is known[3] that the autoionization states crowd together and even overlap one another completely on approaching the first ionization potential from above. Hence the possibility that a multiple resonance with two-electron and autoionization states may occur cannot be ignored.

The data on two-electron states in the spectrum of the barium atom show that the transition energy to the $5d6d\,^1D_2$ bound state (37 837 cm^{-1}, Ref. 13) and that to the $5d19p\,^1P^0_1$ autoionization state (47 240 cm^{-1}, Ref. 14) correspond to the energy of four and five laser-light quanta, respectively, within the limits of the effective line width. These transitions are allowed by the selection rules for multiphoton transitions.[1] (Since we are considering the two-electron character of the transition, we have in mind the selection rules on parity and on the total angular momentum of the atom.[3]) Thus, it must be assumed that the Ba^{2+} ions are produced by a multiphoton resonance ionization process, and that either the resonances take place with a two-electron bound state or an autoionization state, or there is a multiple resonance.

The data on the two-electron states of the strontium atom show that there are no resonances with two-electron bound states, since the differences between the energy of $K < K^+_0$ quanta and the energies of allowed transitions to bound electron states are large, amounting to hundreds of reciprocal centimeters. In the case of strontium, the effect may involve multiphoton excitation of an autoionization state. Indeed, the work of Hudson *et al.*[15] shows that there is a large number of autoionization states in the energy region close to the energies of five and six laser-light quanta.

We note, finally, that, as was pointed out above, two-electron states are found not only in the alkaline earth atoms, but also in the lanthanides—in europium,[16] for example; there is therefore every reason to suppose that such states may also be the reason for the production of doubly charged ions in the case of europium and samarium.

Thus, an analysis of the spectra of the barium and strontium atoms shows that the resonance ionization process associated with multiphoton excitation of two-electron and autoionization states can lead to the production of doubly charged ions. It is natural to call such a process the two-electron multiphoton ionization of the atom.

It is unfortunately impossible at present to give a quantitative description of this process that, in particular, would account for the observed values of the degree of nonlinearity, since there are no data on the perturbations of the autoionization and two-electron resonance states by the radiation field. Indeed, it is known that the shifting and broadening of the resonance states under the action of the field are responsible for the deviation of the observed degree of nonlinearity of the resonance process from the corresponding K_0^{2+} value.[1]

In concluding, we note that from our point of view the two-electron multiphoton ionization process is an entirely natural manifestation of the two-electron and autoionization states that are characteristic of the spectra of a number of complex atoms and play an essential part in the excitation and ionization of these atoms by photons and electrons. From this point of view the possibility of also observing the three-electron multiphoton ionization process cannot be ruled out in principle, since two-electron and autoionization states are known in the spectra of the doubly-charged ions of a number of lanthanides.[17]

CONCLUSION

In our opinion, analysis of the experimental data presented above on the production of doubly charged ions in the multiphoton ionization of a number of alkaline earth atoms and lanthanides allows us to assert that the two-electron resonance ionization process is responsible for the appearance of the doubly charged ions. A quantitative description of the process leading to the production of the doubly charged ions, however, will require further research with more refined methods, including, in particular, frequency tuneable lasers providing radiation with various degrees of elliptic polarization. Experience in investigating resonances with one-electron states has revealed exceptional prospects for such experiments, whose results can be easily interpreted without ambiguity.[1,2] It is also necessary to develop a quantitative theoretical description of resonance with two-electron and autoionization states, which will include a description of the perturbation of these states in a strong light field.

In conclusion, we note that the results of the present work indicate the necessity of taking two-electron states into account in the resonance ionization of a number of complex atoms in connection with a wide range of problems associated with the selective excitation of laser radiation in atomic media.

[1] N. B. Delone and V. P. Kraǐnov, Atom v. sil'nom pole (The Atom in a Strong Field). Atomizdat., 1978.

[2] N. B Delone, Usp. Fiz. Nauk **115**, 361 (1975) [Sov. Phys. Usp. **18**, 169 (1975)].

[3] S. É. Frish, Opticheskie spektry atomov (Optical Spectra of Atoms), Fizmatgizdat., 1963.

[4] I. S. Aleksakhin, I. P. Garga, I. P. Zapesochnyǐ, and V. P. Starodub, Optika i Spektrosk. **34**, 1053 (1973); **35**, 1037 (1973); **37**, 20 (1974); **38**, 228 (1975) [Optics and Spectrosc. (USSR) **34**, 611 (1973); **35**, 603 (1973); **37**, 10 (1974); **38**, 126 (1975)].

[5] V. V. Suran and I. P. Zapesochnyǐ, Pis'ma v Zh. Tekh. Fiz. **1**, 973 (1975) [Sov. Tech. Phys. Lett. **1**, 420 (1975)].

[6] I. S. Aleksakhin, I. P. Zapesochnyǐ, and V. V. Suran, Ukrain. Fiz. Zh. **21**, 1383 (1976).

[7] V. V. Suran, Optika i Spektrosk. **41**, 901 (1976) [Optics and Spectrosc. (USSR) **41**, 532 (1976)].

[8] T. U. Arslanbekov, V. A. Grinchuk, G. A. Delone, and K. B. Petrosyan, Kratkie soobshcheniya po fiziki (Brief communications on physics), FIAN, **10**, 33 (1975).

[9] G. A. Delone, N. B. Delone, V. K. Zolotarev, N. L. Manakov, G. K. Piskova, and M. T. Tursunov, Zh. Eksp. Teor. Fiz. 65, 481 (1973) [Sov. Phys. JETP **38**, 236 (1974).

[10] G. A. Delone, N. L. Manakov, G. P. Piskova, and L. P. Rapport, Trudy FIAN **115**, 5 (1978).

[11] T. U. Arslanbekov, N. B. Delone, A. V. Masalov, S. S. Todirashku, and A. G. Faǐnshteǐn, Zh. Eksp. Teor. Fiz. **72**, 907 (1977) [Sov. Phys. JETP **45**, 473 (1977)].

[12] I. S. Aleksakhin, I. P. Zapesochnyi, and V. V. Suran, Pis'ma v Zh. Eksp. Teor. Fiz. **26**, 14 (1977) [JETP Lett. **26**, 11 (1977)].

[13] C. E. Moore, Atomic energy levels as derived from the analyses of optical spectra, Nat. Bur. Standards, USA, 1949, 1958, 1971.

[14] W. R. S. Garton and K. Codling, Proc. Phys. Soc. **75**, 87 (1960).

[15] Robert D. Hudson, Virginia L. Carter, and Paul A. Young, Phys. Rev. **180**, 77 (1969).

[16] N. V. Golovchak, I. I. Garga, and L. L. Shimon, Optika i Spektrosk. **44**, 23 (1978) [Optics and Spectrosc. (USSR) **44**, 1978].

[17] J. Blaise, C. Morillon, Marie-Gabrielle Schweighofer, and J. Verges, Spectrochim. Acta **24B**, 405 (1969).

Translated by E. Brunner