Resonance multiphoton ionization of alkaline Earth Ca, Ba, Sr atoms

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Abstract. In this work, we study the process of three-photon resonant ionization of alkaline earth atoms Ca, Sr, and Ba. To carry out the experiments, a frequency-tunable laser setup was created. An effusive beam of alkali atoms served as an atomic target.

1 Introduction

Discovered and identified resonances due to singlet-singlet and singlet-triplet transitions. An unambiguous relationship between the change in the quantum defect from the main quantitative indicators and the severity of the resonances of the singlet-singlet and singlet-triplet transitions was revealed.

Based on the foregoing, it can be argued that during multiphoton ionization of alkaline earth atoms, the observation of anomalously high probabilities of resonances caused by transitions through triplet states forbidden by the dipole selection rules are due to the mixing of electronic configurations.

To carry out experiments to study the processes of three-photon resonant ionization of alkaline-earth atoms, a frequency-tunable laser setup was created. Two dye lasers were pumped, respectively, by the third and second harmonics of the yttrium aluminum garnet laser radiation. Structurally, the grenade laser consisted of three modules: a master oscillator emitting in the fundamental transverse mode emitted by a diaphragm placed in the resonator, and two amplification stages. The emitters of a serial LTIFC5 laser (generator) and LTIFC8 (two amplification stages) were used as working modules. The output parameters of the garnet laser radiation after two amplification stages were as follows: pulse energy Q ~ 0.15 J, pulse duration at half-maximum τ ~ 15 ns, which corresponds to a power P ~ 10 MW. The fundamental frequency radiation was converted into the second and third harmonics in nonlinear KDP crystals with phase-matching angles of 45° (phase-matching) and 57° (phase-matching).

Tuning in the yellow-green region of the spectrum (570-540 nm) on the dye unsubstituted rhodamine was carried out with an LZHi-504 laser with pumping of the second harmonic of the YAG laser. The pulse power of the radiation was 50 kW, the duration of the radiation pulse at half maximum was 12 ns, and the spectral width of the generation line was 0.08 nm. For tuning in the green-blue region of the spectrum (540-4-20 nm) on coumarin 7,30, 47, 120

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dyes, a self-made laser was used, the prototype of which was the scheme proposed in [1]. In our scheme, a replica of a diffraction grating 50 mm wide with 1800 gratings / mm was taken. The diffraction efficiency of this grating in the wavelength range 440-520 nm is close to the maximum and amounted to 40-45%. Wavelength scanning was carried out by rotating the mirror around the vertical axis.

The atomic target in our experiments was an effusion beam of atoms. The advantage of an effusion beam is the possibility of calculating the beam intensity from the known geometry of the source [2,4]. The ions formed in the region of intersection of the atomic and laser beams were separated by mass and charge in a transit mass spectrometer (TFMS) and detected by a VEU-2B secondary electron multiplier.

To study the spectrum of the Ca atom in the intermediate energy range of 38500–47100 sm⁻¹, four different Coumarin dyes with index numbers 7, 30, 47, and 120 were used. Thus, the wavelength range from 520 to 425 nm was overlapped, which corresponds to frequency interval 8600 sm⁻¹. The dyes were chosen so that their luminescence spectral regions overlapped. This made it possible to pass the indicated energy range without “windows” and to correct the results obtained on the dye luminescence wings.

**2 Results and discussion**

The direct result of the experiment was the dependence of the Ca⁺ ion signal on the laser radiation wavelength. On Figures 1 and 2 show the obtained ionization spectra of the Ca atom in the case of linear polarization of laser radiation. The wavelength reduced to vacuum is plotted horizontally, and the logarithm of the ion signal amplitude is plotted vertically. The widths of the resonances were determined by the reduced width of the laser radiation spectrum. The strength of the electric field produced by laser radiation did not exceed 3 10⁴ V cm⁻¹. In such a field, the perturbation of the atomic spectrum in the energy range under study is negligibly small. This makes it possible to use known values of the energies of unperturbed levels to identify resonances [5].

![Fig. 1. Part of the spectrum of the Ca atom obtained by multiphoton ionization spectroscopy; O - single-photon quadrupole transition 4s²2S₀ - 4s3d²2D₂, a – one-photon transition 4s4p ¹P₁ - 4s8s¹S₀](image-url)
The designations of the levels with which two-photon resonances were observed are given in Fig. 1 and 2 in the classification of the L-S bond. Letters a, b, c, d, e denote single-photon resonances corresponding to transitions from an excited state $4s4p^1P^0_1$ into a state $4s8s^1S_0$ (a), $4s7d^1D^2_2$ (b), $4s7d^3D^2_2$ (c), $4s9s^1S_0$ (d) and $4s8d^1D^2_2$ (e). State $4s4p^1P^0_1$ was populated by dye super luminescence. This made it possible to observe single-photon resonances along with two-photon resonances. On the dependence shown in Fig. 2, the zero level is raised, which, naturally, is associated with the excitation of the level $4s4p^1P^0_1$ super luminescence.

The level energies measured by us coincide with the energy values in the tables [5] except for two cases. For the state $4s7d^1D_0$ we got the energy value $46199,8\pm0,5$ sm$^{-1}$, which is on $110$ sm$^{-1}$ less than the value from the tables [5], but coincides within the experimental error with the results of [6]. Two resonances at wavelengths $425,54$ and $425,09$ nm, denoted in Fig. 2 by the letters i and g, could not be correlated with any known bound state [7] or autoionization state J=1 [3]. Experimental data on autoionization states with J>1 is unknown to the author.

At a wavelength $\lambda=457,57$ nm we registered a resonance, which we identified as a single-photon transition from the ground state $4s^2S_0$ into a state $4s3d^1D_2$. This transition is a quadrupole one, and in Figure 1 the resonance corresponding to this transition is denoted by the letter Q. As can be seen, its amplitude is only 30 times smaller than the amplitude of the nearest two-photon dipole transitions. The resonance amplitude Q in circularly polarized radiation is 10 times smaller than in linearly polarized radiation of the same intensity.

We did not observe a resonance with the $4s5d^3D_2$ triplet state. The amplitude of the resonance with the $4s6d^3B$ triplet state is only an order of magnitude smaller than the amplitude of the resonance with the $486a^1D$ singlet state. And then, with increasing $n$, the relative amplitude of resonances with triplet states increases.

Investigation of the intermediate energy region $36190-44800$ sm$^{-1}$ spectrum of the Sr atom was carried out using the dyes “unsubstituted rhodamine” and “coumarins” 7, 30, 47. The spectral range from 570 to 445 nm. The generation linewidth for “unsubstituted rhodamine” was 0.08 nm, for “coumarin” - 0.03 nm. The experimentally obtained ionization spectra of the Sr atom are shown in Fig. 3, 4, 5. With a change in the wavelength, a resonant increase in the ion signal was observed in some cases by more than three orders of magnitude. The strength of the electric field created by the focused laser radiation did not exceed $3\times10^4$ Bsm$^{-1}$. This made it possible to carry out the identification of resonances according to the tables of energy levels [9], without taking into account the perturbation of the levels.
Fig. 3. Section of the ionization spectrum of the Sr atom, obtained a) with circular polarization, b) with linear polarization of radiation. Unlabeled resonances are not identified.

Fig. 4. Portion of the ionization spectrum of the Sr atom. The polarization is linear.

Resonances denoted by spectral symbols $^{2s+1}L_J$, correspond to two-photon transitions from the ground state $5s^{2}1S_0$ into the excited states indicated by the symbols. The resonances denoted by the letters a, b, c, d, e, f are due to single-photon transitions from the excited state...
5s5p3p0 was excited by the luminescence of the dye, while the zero line on the spectrogram rose. The widths of the resonances were mainly determined by the reduced width of the laser radiation spectrum, with the exception of three resonances, which were clearly asymmetrically broadened. These are resonances with the level 5p23P0 in Figure 3 and with levels 8s1S0 and unidentified (499.63 nm) in Figure 4. The broadening profile of these resonances is similar to the Fano profile and, apparently, can be explained by the contribution of autoionization states, the energy of which is close to the energy of three-photon ionization through these states [10]. The measured energies of most levels coincided with the tabulated values [12], but some features were also found. Level Energy 5s9d1D2, measured by us was 43755.5 ± 0.5 sm⁻¹, which differs from the tabular value [8] by 25 sm⁻¹, but coincides with the result of [6]. Resonance with level 5s10d1D2 we have not observed. On the spectrogram (Figure 5), its location is indicated by an arrow. Perhaps its absence is due to the interference of various ionization channels, similarly to the situation with the level 4s13d1D2 in Ca [6]. In the studied region of the spectrum of Sr, we observed a number of resonances that could not be identified. In spectrogram (4), these are resonances at wavelengths 499.63 nm, 502.96 nm and 506.83 nm. Their amplitudes are two orders of magnitude smaller than the amplitudes of resonances with neighboring singlet states 6d1D2 and 8s1S0, but an order of magnitude higher than the zero line, so they are clearly distinguishable. In the wavelength range from 555 to 565 nm around resonance with the state 5p1P0 (Figure 3) a large group of unidentified resonances is observed. A similar group of resonances in this wavelength region was also seen by the authors of [10, 11]. In this figure, unidentified resonances are labeled A, B, C, D at wavelengths 563, 562, 559.8, and 559.2 nm respectively. We registered two more resonances. Resonance A at wavelength 563 nm in our spectrum split into two, corresponding to the wavelengths 562.95 and 562.84 nm. And there appeared one more adjacent to the resonance 5p23P2, at a wavelength 560.52 nm (Figure 3). For the remaining resonances corresponding to resonances B, C, D from [11], we obtained more accurate positions 561.90 nm, 559.95 nm, 559.33 nm. What we have been able to resolve, two additional resonances, is apparently explained by the difference in laser intensities. In our experiment, the power density of the focus region did not exceed 1 MBrrsm⁻², in the experiment [11] it was 25 GBrrsm⁻². At such high-power densities, the levels are broadened, so neighboring resonances can merge and register as one. All of the above confirms once again that in our experiments the perturbation of the levels by the laser field is not essential. We failed to attribute any of the resonances of this group to the known bound [8] or autoionization [3] states, however, as well as the authors of [11, 3]. Such a dense arrangement of narrow resonances is interesting in itself and requires a special study. At present, we can only say that they do not disappear in a circular field - (Figure 4), only their relative amplitude changes. The resonance at a wavelength of 562.84 nm in a linear field (Figure 4) has the smallest amplitude, in a circular field, on the contrary, it is the largest of all unidentified resonances of this group.
Fig. 5. Continuation of the ionization spectrum of the Sr atom towards larger n. The radiation polarization is linear. The letters a.c.d.e.f denote the resonances corresponding to single-photon transitions $5s5p^1p_1^0 - 5s9s^1S_0$, $5s8d^3D_2$, $5s8d^3D_2$, $5s10s^1S_0$, $5s9d^3D$, $5s9d^3D_2$.

At a wavelength $\lambda = 496.15$ nm we registered a resonance corresponding to a single-photon quadrupole transition $5s^2S - 5s4d^1D_2$. On Figure 4 it is denoted by the letter Q. Its amplitude is 500 times smaller than the neighboring resonances corresponding to two-photon dipole-allowed transitions. In a circular field, this resonance is not observed, possibly because of the small amplitude.

Two-photon and one-photon resonances with triplet states $5s6d^3D - 5s9d^2D$ well distinguishable. Their relative amplitude changes with the principal quantum number (Figure 5).

The study of the Ba spectrum was carried out using only two dyes “unsubstituted rhodamine” and “coumarin 30” covering the wavelength range from 580 to 540 and from 520 to 480 nm. Resonances designated by spectral symbols $2s+1L$, correspond to two-photon transitions from the ground state $6s^2S_0$ of the Ba atom into the designated excited states. It must be said that the region of intermediate energies in Ba lies lower than in Ca and Sr; therefore, only the coumarin 30 dye was sufficient to study it.

In this region, the authors of [3, 5] registered many unidentified resonances. Just as in Sr, we repeated the measurements in the region of the spectrum, where there are the most unidentified resonances. This was done with the aim of elucidating the nature of such resonances. The section of the spectrum shown in Figure 6 was obtained on the “Rhodamine unsubstituted” dye. Special measures were taken to ensure that the super luminescence of the dye did not fall into the region of interaction of radiation with Ba atoms. As a result, of the six unidentified resonances observed in [5], only two remained (Figure 6). It follows that the four missing resonances were due to the excitation of the level $6s6p^1p_1^0$ dye super luminescence. They correspond to the following transitions from the state $6s6p^1p_1^0$: single-photon - to bound states $6s6d^3D_2$ (551.17 nm), $6p^3D_2$ (578.57 nm) [8], two-photon - to autoionization states - odd with $J = 0$ $6p_{1/2}$, $8s_{1/2}$ (565.2) and odd with $J = 2$ [4]. The remaining two resonances at wavelengths 566.92 and 569.51 nm cannot be associated with any of the known coupled [8] or autoionization [9, 4] resonances.
Fig. 6. Part of the ionization spectrum of the Ba atom. All resonances are asymmetrically broadened. Unmarked resonances unidentified.

All resonances in Figure 6 are in homogeneously broadened, and in different directions. A characteristic asymmetry can be generated by the interference between direct photoionization, in this case, from the excited state, and stepwise photoionization through the autoionization state [12]. The reason for this asymmetry can be identified as follows. The sign of the amplitude of the probability of excitation of the autoionization state will be different for the photon energy below and above the resonance with the autoionization state. As a result, the interference contribution is positive on one side of the line center (resonance point) and negative on the other side. Therefore, in this wing of the line, where the interference contribution is positive, the total absorption will be higher than the level of the surrounding continuous spectrum, and where it is negative, lower. Ratio of the photo absorption cross section \( \sigma \) in the presence of an autoionization (AI) level to the photo absorption cross section \( \sigma_0 \), when AI level is missing, equals [12,18]

\[
\sigma / \sigma_0 = (q + \varepsilon)^2(1 + \varepsilon^2),
\]

where \( q \) - Fano parameter, \( \varepsilon = 2\Delta A G_A, \Delta A = E_A - hw \) - detuning from resonance with AI state, \( G_A \) - AI state width. The Fano parameter \( q \) is

\[
q = \sqrt{2/\Pi V_{nA} [G_A V_{nE}]}
\]

\( V_{nA} \) - transition matrix element from state \( n \) to AI state, \( V_{nE} \) - matrix element of the transition from \( n \) to the continuous spectrum. The sign of \( q \) depends on the sign of the matrix elements \( V_{nE}, V_{nA} \) and shows that it is the absorption minimum or maximum that takes place on the line wing. In Figure 6, the profiles of resonances with the states 6s7d^3D_2 and 5d6d^3D_2 asymmetrically broadened in different directions so that the wings of the resonance profiles smoothly pass into each other. This can be understood on the basis of all that has been said above, if we assume that the energies of the photons that transfer states 6s7d^3D_2 and 5d6d^3D_2 into a continuous spectrum lies on opposite sides of the energy of the same AI state. In this case, the contribution of the interference of direct photoionization channels from these states and stepwise through the autoionization state will have a different sign for the first and second states, and, therefore, the resonances should broaden asymmetrically in different directions.
In the region of intermediate energies (Fig. 7, 8), the widths of all resonances were determined by the reduced width of the laser radiation spectrum. The level energy measured by us 6s10d3D2 (39922.2 sm⁻¹) on the 28sm⁻¹ differed from the value in the tables [8], but coincided within experimental errors with the value given in [6]. It should be noted that in the tables [8] there are no values of the energies of the levels lying above 10d, and for the identification of resonances we used the results of works [6, 9, 17]. The level energies measured by us coincided with good accuracy with the energy values from [6, 9], except for the following four resonances. Three of them look like satellites to the levels: 6s15d3D2 at a wavelength 484.05, to 6s15d3D2 at a wavelength of 484.28, to 4s11d3D2 at a wavelength 494.69 nm. And one, separately separated, lies on the wavelength 491.91 nm. The listed resonances have not been identified because their positions do not correspond to the known energies of bound [8,6,9,15] or autoionization [9,4,16] states.

As can be seen from the spectrograms in Figure 6-8, two-photon resonances with triplet states in the Ba atom are more numerous and have a much higher amplitude than in the Ca and Sr atoms. If in the spectra of Ca and Sr there were relatively small regions where resonances with triplet states appeared, then in Ba, on the contrary, there were small regions where there were no resonances with triplets. For example, near the level 6s12d1D2 and above the level 6s16d1D2 (Figure 8). Resonance at a wavelength 485.87 nm consists of two merged resonances of the same amplitude - a resonance at a wavelength 485.85 nm, corresponding to the state 6s14d1D2 (41166.46 sm⁻¹) and resonance at a wavelength 485.89 nm, corresponding to the state 6s14d3D2 (41162.4 sm⁻¹) [19, 20, 21].

3 Conclusion

States 14d1D2 и 14d3D2 located abnormally close, at a distance of only two reverse centimeters. Therefore, during the first scanning of the spectrum by radiation with a linewidth 0.03 nm it can be seen that at these wavelengths the width corresponds to 1.5 sm⁻¹, we have not resolved the triplet and singlet states. To distinguish them, we had to narrow the width of the laser generation line to 0.01 nm (0.5 sm⁻¹), which significantly reduced the radiation energy and, naturally, the amplitude of the resonances. Since the relative amplitudes of the resonances are important to us, the amplitude of the resonance with level III is shown in Figure 8 for the energy and spectral width of the radiation at which the entire spectrum was measured and, therefore, the states1D2 and 3D2 not distinguishable.

References
