Two-photon polarization spectroscopy of autoionizing states

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A method for experimental determination of the total angular momentum of autoionizing states by two-photon polarization spectroscopy has been developed. These states were excited in two stages using two laser beams with different combinations of the polarizations of the beams. This method was used to study the autoionizing states of Ba atoms in the $6p7p$ configuration.

1. INTRODUCTION

Tunable dye lasers can be used to investigate in detail the excitation spectra of atoms, including autoionizing states lying above the ionization threshold. In the specific case of atoms of alkaline earth elements there is special interest in even autoionizing states which cannot be excited by one-photon processes. Knowledge of the spectrum of autoionizing states is needed in various mass-spectrometric applications, such as the task of detection of microimpurities. This is the reason for the many recent investigations of autoionizing states.[1–5]

The main problem in spectroscopy is the identification of autoionizing states, i.e., determination of the total angular momentum of the states. This information makes it possible to predict uniquely the excitation channels for a specific resonance and to identify the processes which may be involved. Autoionizing states manifested in the photoabsorption spectra of atoms have been investigated for over a decade and have been identified using a variety of theoretical concepts such as the Hund rule, analogy with lines in a discrete spectrum, and most recently by direct comparison with the results of various calculations.[5] However, calculations cannot yet provide the precision necessary for the identification of autoionizing states. The methods used in experimental identification, acceptable for a discrete spectrum and based on the use of the Zeeman and Stark effects, are unsuitable for autoionizing states since the resonance width can be much greater than the splitting in fields available in the laboratory. There is therefore much interest in the development of various experimental methods for identification of these states.

Bekov, Vidolova-Angelova, Ivanov, *et al.*[1] used various intermediate resonances in three-stage excitation with three dye lasers to identify the autoionizing states of the $6p7s$ configuration of Yb atoms. Depending on the total angular momenta of the intermediate states, which are known in advance, the excitation spectrum should be missing specific autoionizing states because of the selection rules. A similar method was used by Camus *et al.*[5]

Another possible method for the identification of autoionizing states by multistage processes involves using various combinations of the polarization of the radiation at each of the stages. This polarization spectroscopy method was used[6] to investigate the Rydberg series of autoionizing exciting states, but it had not been carried any further. We shall use the example of Ba atoms to show that polarization spectroscopy can be employed successfully in the identification of autoionizing states.

2. DESCRIPTION OF THE IDENTIFICATION METHOD

We consider two-stage excitation, via an intermediate resonance, of an atom with zero total angular momentum in its initial state. The probability of absorption of each photon is proportional to the square of the modulus of the dipole matrix element:

$$W_{nl\to n_1l_1} \propto |\langle n_1l_1J_1M_1|d_\lambda|nlJM\rangle|^2, \tag{1}$$

where J and M are the total angular momentum of an atom and its projection;

$$d_\lambda=\left(\frac{4\pi}{3}\right)^{1/2}\sum_{i=1}^{N} r_iY_{1\lambda}(\theta_i,\varphi_i); \tag{2}$$

the summation in the above expression is carried out over all the electrons of the atom; $\lambda = 0$ applies to linearly polarized light and $\lambda = \pm 1$ to circularly polarized light. We recall that in the case of linearly polarized light the angles θ_i and φ_i are measured from the z axis, directed parallel to the polarization vector of the light, whereas in the case of circularly polarized light the z axis coincides with the direction of propagation.

Using the Wigner–Eckart theorem, we can separate out the dependence of the dipole matrix element on the projection of the angular momenta:[7]

$$\langle n_1l_1J_1M_1|d_\lambda|nlJM\rangle=(-1)^{J_1-M_1}\begin{pmatrix} J_1 & 1 & J \\ -M_1 & \lambda & M\end{pmatrix}\langle n_1l_1J_1\|d\|nlJ\rangle. \tag{3}$$

The dipole matrix element describing the absorption of a second photon can be represented similarly:.

$$\langle n_2l_2J_2M_2|d_{\lambda'}|n_1l_1J_1M_1\rangle = (-1)^{J_2-M_2}\begin{pmatrix} J_2 & 1 & J_1 \\ -M_2 & \lambda' & M_1\end{pmatrix}\langle n_2l_2J_2\|d\|n_1l_1J_1\rangle. \tag{3a}$$

The selection rules for the two-stage process follow from the conditions that the two $3j$ symbols occurring in Eqs. (3) and (3a) not vanish. All three states of the atom should be described in the same coordinate system. We shall consider possible combinations of the polarizations of laser radiation on the assumption that the laser beams are parallel to one another.

1. The radiation in each stage is linearly polarized in the same direction. In this case the coordinate systems needed to describe the photons are identical so that the probability of two-stage excitation of the investigated atom is proportional

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to the square of the product of the following $3j$ symbols:

$$\begin{pmatrix} J_2 & 1 & J_1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} J_1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

where use is made of the fact that initially the momentum is zero. It follows from the conditions ensuring nonzero values of these $3j$ symbols that we must have $J_2 = 0$ or $J_2 = 2$. Therefore, the autoionizing states with total angular momentum $J_2 = 1$ are not excited by this process.

2. The radiation in the two stages is linearly polarized in mutually perpendicular directions. The systems of coordinates needed for the description of such photons with the aid of Eq. (2) are different. Therefore, when describing, for example, the second photon it is necessary to transform to the coordinate system corresponding to the first photon. Rotation of the coordinate system is performed by the Wigner D functions[8]:

$$Y_{lm'}(\theta', \varphi') = \sum_{m=-l}^{l} Y_{lm}(\theta, \varphi) D^{l}_{mm'}(\alpha, \beta, \gamma), \qquad (4)$$

where α, β, and γ are the Euler angles describing the rotation. In the specific case of rotation by 90°, we obtain

$$Y_{10}(\theta', \varphi') = \frac{1}{2^{1/2}} [Y_{1,-1}(\theta, \varphi) - Y_{11}(\theta, \varphi)], \qquad (5)$$

where the angles identified by a prime refer to the system of coordinates of the second photon, whereas those without a prime refer to the coordinate system of the first photon. Substituting the expansion of Eq. (5) into Eq. (3), we find that the probability of the two-stage process is proportional to the square of the product of the following $3j$ symbols:

$$\begin{pmatrix} J_2 & 1 & J_1 \\ \mp 1 & \pm 1 & 0 \end{pmatrix}\begin{pmatrix} J_1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The condition that these symbols have nonzero values implies $J_2 = 1$ or $J_2 = 2$. The autoionizing states with the total angular momentum $J_2 = 0$ is not excited by this process.

3. The laser radiation in both stages is circularly polarized in the same direction, for example, both beams have right-handed polarization. The coordinate systems used in the description of such photons are identical and the probability of the two-stage process is proportional to the square of the product of the $3j$ symbols

$$\begin{pmatrix} J_2 & 1 & J_1 \\ -2 & 1 & 1 \end{pmatrix}\begin{pmatrix} J_1 & 1 & 0 \\ -1 & 1 & 0 \end{pmatrix}.$$

We see that J_2 can only have one value, namely, $J_2 = 2$, and the autoionizing states with the total momenta $J_2 = 0$ and $J_2 = 1$ are not excited.

Other combinations of the polarizations of the two laser radiations do not provide any new information. We can easily show that the two variants using linearly polarized photons are sufficient for unique determination of the total angular momenta of the autoionizing states in a two-stage process. By using certain combinations of polarizations which do not excite a given autoionizing state we can thus determine uniquely the total angular momentum J. The same method can be used also to find the total angular momenta of discrete excited states.

The method discussed above can be used when there are more than two stages. If an atom in the ground state has a nonzero total angular momentum, then before this method is applied we need to prepare the initial states so that only the level with a specific projection of the total momentum is populated. This can be done using, for example, the optical pumping method. Another possibility is the selection of a sequence of stages in which atoms are in a state with a specific value of the projection of the total momentum in one of the intermediate states.

3. DESCRIPTION OF THE APPARATUS

We investigated experimentally the autoionizing states of Ba atoms corresponding to the $6p7p$ configuration and lying in the energy range 49 000–54 500 cm^{-1}. We used the apparatus shown schematically in Fig. 1. Two dye lasers were pumped synchronously by one YAG:Nd^{3+} laser. The output power of each laser was $\leqslant$0.5 mJ, the duration of the pulses was 20 ns, and their repetition rate was 12.5 Hz. The laser emission line was 3 cm^{-1} wide and the tuning range was 550–680 nm. The radiation emitted by one of the lasers was frequency-doubled in a KDP crystal with a conversion efficiency of 10%, making it possible to cover the wavelength range 270–340 nm. The radiation from both lasers was focused by a lens with a focal length 61.4 cm at the ion source of a time-of-flight mass spectrometer. The diameter of the focal spot was 0.8 mm. The linear polarization was done with a Glan–Thompson prism placed at the entry to the

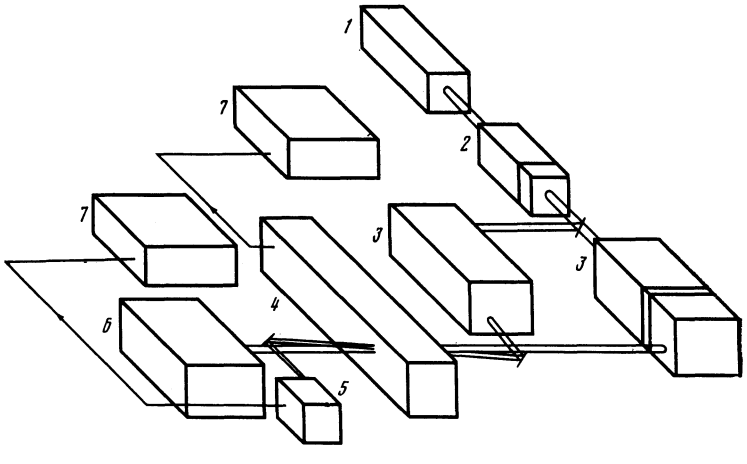

FIG. 1. Schematic diagram of the apparatus: 1) YAG:Nd^{3+} laser; 2) amplifier; 3) dye lasers; 4) time-of-flight mass spectrometer; 5) IT-28 Fabry–Perot etalon; 6) MDR-3 monochromator; 7) recording system.

TABLE I. Results of investigations of autoionizing states in the $6p7p$ configuration reported in Refs. 5 and 12.

Term		Energy, cm^{-1}		
LS coupling	*jj* coupling	calc., Ref. 12	calc., Ref. 5	experiments, Ref. 5
$^1P_1$	$(^1/_2, ^1/_2)_1$	50 176	50 382.63	50 383
$^3D_1$	$(^1/_2, ^3/_2)_1$	51 017	51 102.41	51 113
$^3D_2$	$(^1/_2, ^3/_2)_2$	51 046	51 201.9	–
$^3P_0$	$(^1/_2, ^1/_2)_0$	51 995	51 511.08	51 491.51
$^3P_1$	$(^3/_2, ^1/_2)_1$	52 429	52 126.73	52 158
$^3D_3$	$(^3/_2, ^3/_2)_3$	52 340	52 325.32	52 301
$^3P_2$	$(^3/_2, ^1/_2)_2$	53 346	52 589.47	52 583
$^3S_1$	$(^3/_2, ^3/_2)_1$	53 732	53 332.4	53 336
$^1D_2$	$(^3/_2, ^3/_2)_2$	54 815	53 427.62	–
$^1S_0$	$(^3/_2, ^3/_2)_0$	53 224	54 799.2	54 803

dye lasers. The polarization vector was rotated by 90° by two Fresnel rhombs inclined at 45°.

An atomic beam was formed in a cylindrical molybdenum ampoule with an aperture 0.5 mm in diameter in the side wall. This ampoule was heated by a tungsten helix to a temperature of the order of 1000 °C. The distance from the aperture in the ampoule to the focused laser beams was 25 mm. The atomic beam was shaped by an aperture 3 mm in diameter located 5 mm from the ampoule. The concentration of atoms in the region of intersection of the atomic and laser beams could be varied from 10^8 to 10^{13} cm^{-3} by altering the ampoule temperature. The concentration of atoms was determined by the surface ionization method.[9]

The autoionizing states were identified on the basis of the total angular momentum by the above method, subject to the condition that the atoms excited by the absorption of the first photon not become depolarized before absorbing the second photon. Such depolarization could result from the effusion of the radiation[10] and also because of collisions with unexcited atoms.[11] Theoretical estimates and special measurements carried out in the course of multistage excitation of discrete states demonstrated that the depolarization by effusion of the radiation began to matter at atomic concentrations exceeding 10^{10} cm^{-3}, whereas collisional depolarization became important at higher concentrations. Therefore, all the measurements were carried out when the atomic concentration in the beam was of order 10^8–10^9 cm^{-3}, so that the depolarization effects were weak.

4. INVESTIGATION OF AUTOIONIZING STATES IN THE $6p7p$ CONFIGURATION OF Ba ATOMS

The autoionizing states of the $6p7p$ configuration in Ba atoms were investigated first by Camus *et al.*[5] They found experimentally eight resonances as a result of two-stage excitation from the $6s5d$ state. The autoionizing states were identified by means of calculations carried out using the Slater–Condon method. The results of these calculations and measurements are presented in Table I. Kotochigova and Tupitsyn[12] used the Hartree–Fock–Dirac method and allowed for the superposition of the configurations in finding the positions of the same autoionizing states. It is clear from Table I that the results of the calculations reported in Refs. 5 and 12 differed very significantly and even the sequence of the levels was different.

Camus *et al.*[5] checked the theoretical identification by experiments in which various intermediate resonance states were selected. They noted the excitation of the autoionizing states in cases which were in conflict with their theoretical identification. Moreover, two of the levels predicted theoretically were not observed experimentally. Note also that the system of the autoionizing states proposed in Ref. 5 did not satisfy the Hund rule or the Landé interval rule, whereas in the $6p^2$ configuration both these rules were known to be satisfied.[13] Therefore, an additional investigation of the autoionizing states in the $6p7p$ configuration would be highly desirable.

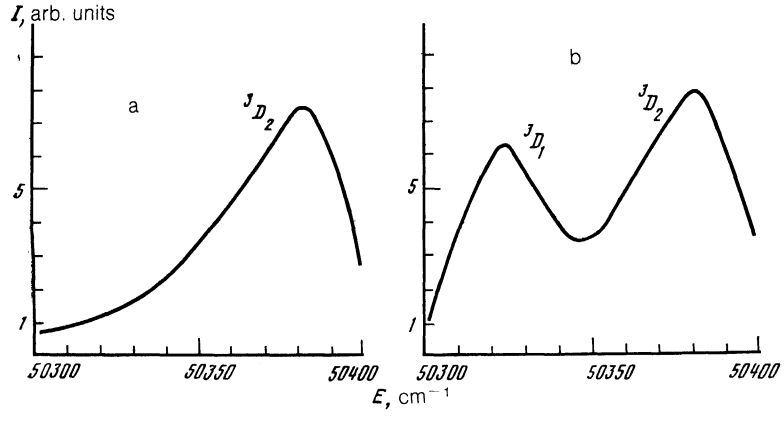

FIG. 2. Curves representing the autoionizing states $6p7p(^3D_1)$ and $6p7p(^3D_2)$ obtained when the radiations of both lasers were linearly polarized along mutually parallel (a) and mutually perpendicular (b) planes.

TABLE II. Positions and identifications of autoionizing states in the $6p7p$ configuration of Ba atoms determined in the present study.

Energy, cm^{-1}	Total ang. momentum	Likely term*	Energy, cm^{-1}	Total ang. momentum	Likely term*
50 320	1	$^3D_1$	51 491.5	2	$^1D_2$
50 383	2	$^3D_2$	52 158	1	$^1P_1$
50 680 **	1	$^3P_1$	52 583	1	$^3S_1$
51 113	2	$^3P_2$			

*LS coupling

**Weak resonance

TABLE III. Values of the quantum defect ν for terms of the $6p^2$ and $6p7p$ configurations of the Ba atoms relative to the ionization threshold of the $6p_{1/2}$ levels (62 296.7 cm^{-1}).

Term	Quantum defect ν		
	$6p^2$, Ref. 13	$6p7p$	$6p7p$
$^3P_0$	1.987	–	3.187
$^3P_1$	1.999	3.074	3.290
$^3P_2$	2.028	3.132	3.361
$^1D_2$	2.150	3.187	3.517
$^1S_0$	2.504 *	–	3.827

Note. The values of ν for the $6p^2$ level are calculated using the results of Ref. 13, whereas those for the $6p7p$ level are based on the results of the present study (third column) and should be compared with the results for the same level reported in Ref. 5 (fourth column).

*This level was proposed in Ref. 5.

We excited the autoionizing states in the $6p7p$ configuration via intermediate $6s7p(^1P_1)$ and $6s8p(^1P_1)$ resonances (preliminary results of our investigation were given in Ref. 14). The autoionizing states were identified using two parallel and mutually perpendicular linear polarizations. We investigated the energy range from 48 000 to 54 000 cm^{-1}. Estimates indicated that only the $6p7p$ configurations of the autoionizing states could occur in this range of energies. The results of our measurements are presented in Table II. Out of nine autoionizing states of the $6p7p$ configuration (apart from the $^3D_3$ state, which cannot be excited by the two-photon process from the ground state), we found seven. The missing states are known to have zero total angular momenta. In addition to the results reported in Ref. 5, we found two new resonances at energies 50 320 and 50 680 cm^{-1}, the latter of which was weak. In Fig. 1, by way of illustration, we plot the results of measurements in the vicinity of the resonances at 50 320 and 50 383 cm^{-1} using two different combinations of the linear polarizations of the laser beams. Table II gives the values of the total angular momenta of the autoionizing states obtained on the basis of such polarization measurements applied to all the states. This table includes also possible terms of the autoionizing states deduced in the LS-coupling approximation, which are in agreement with the Hund rule. Since the terms of the $6p^2$ configuration are well known,[13] we can compare the quantum defects for the levels with identical terms in the $6p^2$ and $6p7p$ configurations. This is done in Table III, which demonstrates that in the case of the identification we have proposed the change in the quantum defect on transition from the $6p$ to the $7p$ state is close to unity, whereas the identification proposed in Ref. 5 results in a considerable deviation from unity.

5. CONCLUSIONS

We used two-stage excitation via an intermediate resonance and the method of polarization spectroscopy in an investigation of the autoionizing states in the $6p7p$ configuration of the Ba atoms. In contrast to the published results,[5] we found two new autoionizing states and identified experimentally all the seven states detected in the present study. The values of the total angular momenta of the autoionizing states differed from the corresponding values proposed in Ref. 5; this was true of all the levels (apart from one) which had the same energy positions in both investigations. The results of our investigation demonstrated that two-photon polarization spectroscopy can be applied successfully to determine the total angular momenta of the autoionizing states, in the same way as the momenta of excited states in a discrete spectrum.

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