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Deactivation of krypton atoms in the metastable $5s\,(^3P_2)$ state in collisions with krypton and argon atoms

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***Abstract*. The collision deactivation of the metastable $5s[3/2]_2^o(^3P_2)$ state of krypton atoms is studied by the absorption probe method in electron-beam-excited high-pressure Ar – Kr mixtures with a low krypton content. The rate constants of plasma-chemical reactions $Kr^* + Kr + Ar \rightarrow Kr_2^* + Ar$ [$(4.1 \pm 0.4) \times 10^{-33}$ cm^6 s^{-1}] and $Kr^* + 2Ar \rightarrow ArKr^* + Ar$ (less than 10^{-35} cm^6 s^{-1}) are measured for the first time and the rate constant of the reaction $Kr^* + Ar \rightarrow$ products + Ar [$(3.8 \pm 0.4) \times 10^{-15}$ cm^3 s^{-1}] is refined.**

Keywords: *inert gases, krypton, argon, deactivation, absorption spectroscopy*.

1. Introduction

The work is devoted to the experimental study of poorly investigated deactivation processes of excited krypton atoms in the lower metastable $5s[3/2]_2^o\,(^3P_2)$ state in collisions with argon and krypton atoms. These processes play an important role in the formation of the population inversion in high-pressure lasers on atomic transitions in inert gases [1], high-power excimer krypton-fluorine lasers [2], and krypton dimer lasers [3]. The knowledge of the rate constants of plasma-chemical reactions studied in the work is also necessary for other applications, in particular, for increasing the efficiency of compact UV excimer lasers [4] and TV plasma displays [5], which are being extensively developed at present.

We studied practically important high-pressure Ar – Kr mixtures with a low content of krypton, which were excited by a fast electron beam. The deactivation of the lower excited states of Kr atoms in such mixtures occurs in two- and three-particle collision reactions

$$Kr^*\left(5s[3/2]_2^o\right) + Kr + Ar \rightarrow Kr_2^* + Ar, \quad (1)$$

$$Kr^*\left(5s[3/2]_2^o\right) + 2Ar \rightarrow ArKr^* + Ar, \quad (2)$$

$$Kr^*\left(5s[3/2]_2^o\right) + Ar \rightarrow \text{products} + Ar. \quad (3)$$

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By determining the rate constant of reaction (3), we should keep in mind that the rate constant measured in experiments is the upper bound because reactions

$$Kr^*\left(5s[3/2]_2^o\right) + M \rightarrow \text{products} \quad (4)$$

of the excited krypton with impurity atoms and molecules M in argon should be also taken into account. The concentrations of various impurities in purified argon are low (see below). However, due to large cross sections, the contribution of these reactions can be considerable.

The rate constants of reactions were measured by the absorption probe method [6, 7] from the dependences of the decay time of the $5s\,[3/2]_2^o$ state on pressure and the concentration ratio of working and buffer gases. The measurements were performed by studying the absorption dynamics of a 'transmitting' light pulse at a wavelength of 0.8929 μm corresponding to the high-oscillator strength optical transition between the metastable $5s\,[3/2]_2^o$ level and the upper $5p[1/2]_1$ level (Fig. 1).

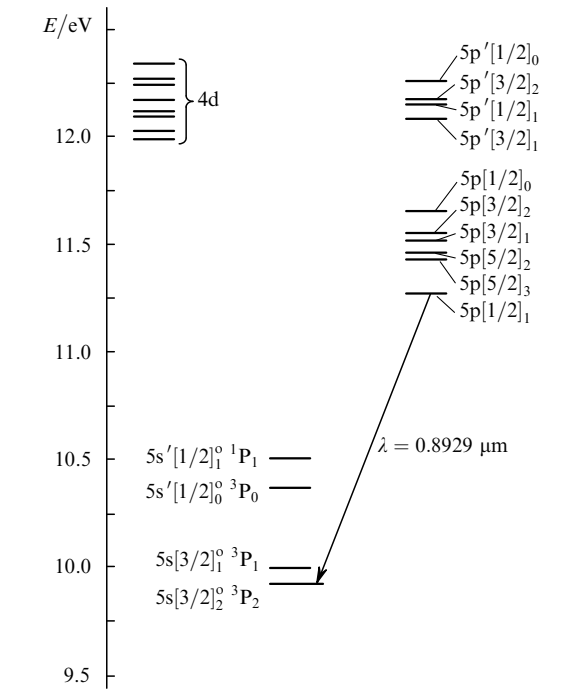

Figure 1. Diagram of the excited levels of a krypton atom.

2. Experimental

Experiments were performed by using a cold-cathode laser from an electron gun of a Tandem pulsed laser setup [1, 6, 7]. The 250-keV pulsed electron beam of cross section 5×100 cm with a bell-shaped current pulse of base duration 2.5 μs was directed into a measuring chamber perpendicular to its optical axis through a 20-μm-thick titanium foil. The electron current density j was 1.5 A cm^{-2}. The measuring chamber with an active volume of 5 L was made of stainless steel. Before filling with gases under study, the chamber was evacuated via a nitrogen trap down to a pressure of $\sim 10^{-5}$ Torr; the gas leaking into the chamber did not exceed 10^{-3} Torr h^{-1}. The mixtures of high-purity argon (purity 99.998 %) and high-purity krypton (purity 99.9992%) with component ratios Ar:Kr = 200:1, 100:1, and 50:1 at pressures 1.75–4 atm were investigated.

The optical scheme of absorption measurements is presented in Fig. 2. A probe signal was produced by a broadband ISI-1 pulsed light source (*1*) emitting 30-μs pulses. The probe radiation was collimated into a beam of diameter 5 cm, passed through the measuring chamber (*5*) with a mixture under study, and was focused on the entrance slit of a high-aperture ratio, 600-lines mm^{-1} grating MDR-2 monochromator (*8*). The radiation transmitted through the monochromator set to a wavelength of 0.8929 μm was focused on a photodetector (*10*) consisting of a fast BPW34 pin photodiode (Infinion) and a broadband AD8055 operational amplifier (Analog Devices) placed inside a doubly screened metal housing. Radiation in the second diffraction order was suppressed with a KS-10 optical filter (*3*) mounted at the output of the ISI-1 radiation source. A part of radiation reflected from a plane-parallel plate (*4*) mounted in front of the measuring chamber was directed on the entrance slit of an DMR-4 (*9*) monochromator and then to a second photodetector (*11*). The output signals of photodetectors were recorded with a two-channel digital DSO-2010 oscilloscope (Link Instruments) connected with a computer.

Thus, the measuring scheme allowed us to record the shape and amplitude of the probe pulse simultaneously in front and behind an absorbing medium with the time resolution no worse than 100 ns.

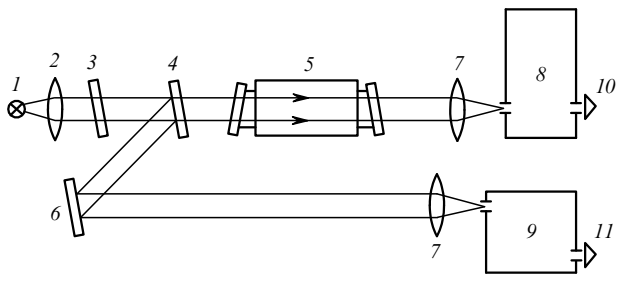

Figure 2. Optical scheme of absorption measurements: (*1*) ISI-1 pulsed light source; (*2*) collimating lens; (*3*) KS-10 optical filter; (*4*) beam-splitter; (*5*) measuring chamber; (*6*) fold mirror; (*7*) focusing lenses; (*8*) high-aperture ratio MDR-2 monochromator; (*9*) DMR-4 monochromator; (*10*, *11*) photodetectors.

3. Experimental results

The excitation of Ar–Kr mixtures by a fast electron beam leads to the ionisation and excitation of atoms (mainly buffer gas Ar atoms). At high pressures in the chains of plasma-chemical reactions of the type

$$\mathrm{Ar}^+ + 2\mathrm{Ar} \rightarrow \mathrm{Ar}_2^+ + \mathrm{Ar}, \tag{5}$$

$$\mathrm{Ar}_2^+ + \mathrm{Kr} \rightarrow \mathrm{Kr}^+ + 2\mathrm{Ar}, \tag{6}$$

$$\mathrm{Kr}^+ + \mathrm{Kr} + \mathrm{Ar} \rightarrow \mathrm{Kr}_2^+ + \mathrm{Ar} \tag{7}$$

excitation is transferred to molecular krypton ions. The dissociative recombination of these ions with electrons

$$\mathrm{Kr}_2^+ + \mathrm{e} \rightarrow \mathrm{Kr}^{**} + \mathrm{Kr} \tag{8}$$

results in the formation of krypton atoms in different highly excited states, which then rapidly relax in collisions with heavy particles and electrons and due to radiative decay to the lower excited 5s states of Kr atoms.

In the afterglow of the electron beam pulse, during the completion of recombination and relaxation, the concentration of the metastable $5s[3/2]_2^o$ state studied in our work should be mainly determined by its decay processes in reactions (1)–(4):

$$\frac{\mathrm{d}[\mathrm{Kr}^*]}{\mathrm{d}t} = -k_1[\mathrm{Kr}][\mathrm{Ar}][\mathrm{Kr}^*] - k_2[\mathrm{Ar}]^2[\mathrm{Kr}^*] - (k_3 + k_4 m)[\mathrm{Ar}][\mathrm{Kr}^*], \tag{9}$$

where k_1 and k_2 are the rate constants of excimer formation in reactions (1) and (2), respectively; k_3 is the rate constant of two-particle relaxation (3); k_4 is the rate constant of the reaction of quenching by impurities in reaction (4); and m is the relative impurity content in the mixture under study.

The time dependence of the population of this state can be described by the exponential

$$[\mathrm{Kr}^*](t) = N_0 \exp(-t/\tau_\mathrm{d}) \tag{10}$$

with the deactivation rate

$$\tau_\mathrm{d}^{-1} = k_1[\mathrm{Kr}][\mathrm{Ar}] + k_2[\mathrm{Ar}]^2 + (k_3 + k_4 m)[\mathrm{Ar}]. \tag{11}$$

When the excited medium is probed by monochromatic radiation at the wavelength of transition from the excited state to the state under study, the absorption coefficient should be proportional to the concentration of atoms in this state:

$$k(t) \sim [\mathrm{Kr}^*](t). \tag{12}$$

The widths (~ 0.2 mm) of the entrance and exit slits of the MDR-2 monochromator providing a satisfactory signal-to-noise ratio in the pressure range from 1.75 to 4.0 atm considerably exceeded the linewidth of the transition studied in our experiments. In this case, the Bouguer-Lambert-Beer law is not valid and it is necessary to use its empirical or the so-called modified form [8, 9] relating the transmission coefficient T with the absorption coefficient by the expression

$$\ln(1/T) = (kL)^{\gamma}. \quad (13)$$

Here, L is the length of the absorbing medium excited by an electron beam and γ is the dimensionless factor depending on the relation between the widths of the absorption line and the instrumental function of the monochromator. The study of experimental dependences

$$\ln \ln(1/T) = \text{const} + \gamma \ln L \quad (14)$$

confirmed the applicability of the modified Bouguer–Lambert–Beer law under our conditions with the dimensionless factor $\gamma = 0.5$ (see details in [10]).

By taking the logarithm of expression (13) taking into account (12) and expected time dependence (10) of $[Kr^*(5s[3/2]_2^o)](t)$, we obtain the time dependence of the transmission coefficient in afterglow:

$$\ln \ln[1/T(t)] = \text{const} - \gamma t/\tau_d. \quad (15)$$

Figure 3 presents an oscillogram of a probe radiation pulse. By comparing the signal amplitudes at the input [curve (*2*) in Fig. 3] and output [curve (*1*)] of the excited active medium, we can determine the transmission coefficient T of the medium at each instant at the selected wavelength. Figure 4 presents the time dependence of $\ln \ln(1/T)$ for the trailing edge of the absorption pulse corresponding to the oscillogram in Fig. 3.

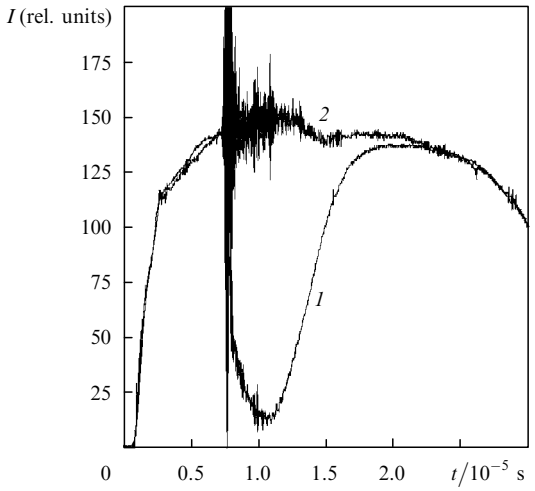

Figure 3. Time dependences of the 0.8929-μm radiation intensity propagated through the excited medium (*1*) and propagated outside it (*2*) for the Ar:Kr = 100:1 mixture at a pressure of 3.5 atm.

Note first of all that the characteristic lifetimes of the metastable krypton level under study proved to be several times larger than the lifetimes of the metastable $Xe^*(6s[3/2]_2^o)$ level measured earlier under similar conditions in Ar–Xe mixtures [7]. This shows that it is necessary to take into account that the population of the level under study depends even on 'weak' recombination fluxes, which continue to populate the level during afterglow as well, after the end of the electron pump pulse.

The influence of recombination is clearly demonstrated by the nonlinear time dependence of $\ln \ln(1/T)$, which differs from (15). For this reason we determined numerically deactivation rates by approximating dependences of type in

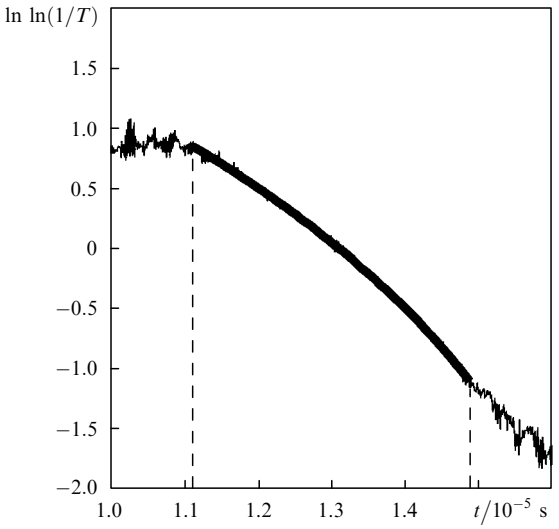

Figure 4. Time dependence of $\ln \ln(1/T)$ corresponding to signals in Fig. 3. The heavy curve is the approximation by the second-order curve.

Fig. 4 by a quadratic polynomial in which a small quadratic correction is related to recombination and relaxation processes involved in the population of the level, while the linear part determines the required quantity γ/τ_d. The coefficients were calculated by the method of least squares by using the Levenberg–Markwardt algorithm. A set of experimental data for the Ar:Kr = 50:1, 100:1, and 200:1 mixtures was processed at pressures from 1.75 to 4 atm with a step of 0.25 atm.

To determine the contribution from one or another plasma-chemical reaction to the deactivation rate for each of the Ar–Kr mixtures, it is convenient to represent the experimental values of τ_d^{-1} in the form of the dependence of the so-called reduced deactivation rate $\tau_d^{-1}[Ar]^{-1}$ on the buffer gas concentration (Fig. 5). According to the linear dependences

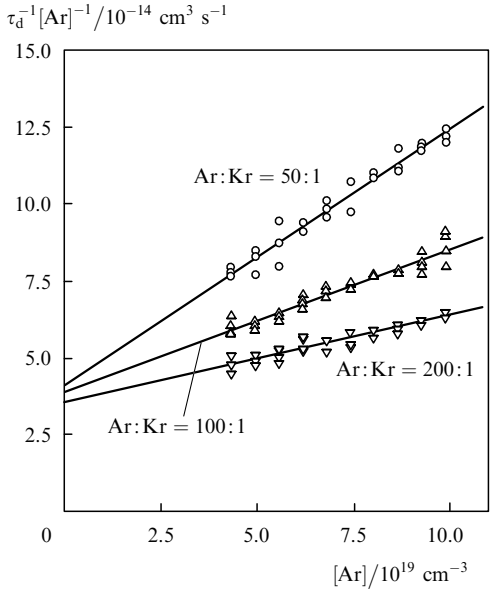

Figure 5. Dependences of the reduced deactivation rates $\tau_d^{-1}[Ar]^{-1}$ on the argon concentration in different Ar–Kr mixtures.

Table 1. Rate constants of the collision deactivation of the $5s[3/2]_2^o$ state of the Kr atom in the Ar – Kr mixture.

$k_1/cm^6\ s^{-1}$	$k_2/cm^6\ s^{-1}$	$k_3/cm^3\ s^{-1}$	References
$(4.1 \pm 0.4) \times 10^{-33}$	less than 10^{-35}	$(3.8 \pm 0.4) \times 10^{-15}$	this paper
	$(1.0 \pm 0.04) \times 10^{-33}$	$(0.69 \pm 0.06) \times 10^{-15}$	[11]
		$(1.1 \pm 0.1) \times 10^{-15}$	[12]

$$\tau_d^{-1}[Ar]^{-1} = (\delta k_1 + k_2)[Ar] + (k_3 + k_4 m), \quad (16)$$

which follow from (11) ($\delta = [Kr]/[Ar]$ is the relative krypton content in a mixture), experimental points lie on straight lines, demonstrating the correctness of experimental data processing.

The rate constants k_1, k_2, and k_3 presented in Table 1 were calculated by the method of least squares with the use of the Levenberg – Markwardt algorithm by varying the required constants in relations

$$\tau_d^{-1} = k_1[Kr][Ar] + k_2[Ar]^2 + k_3[Ar] \quad (17)$$

simultaneously for all the set of experimental values of τ_d^{-1}.

The results obtained in our study show that the metastable $Kr^*(5s[3/2]_2^o)$ state decays under our experimental conditions in three-particle process (1) with formation of the homonuclear dimer Kr_2^* and in two-particle reactions (3) and (4). At the same time, three-particle reaction (2) with formation of the heteronuclear dimer $ArKr^*$ is not involved in the collision quenching of Kr^*. This can be explained by the fact that the heteronuclear dimer produced in reaction (2) is unstable because of its low binding energy (0.106 ± 0.02 eV) [13] and rapidly decays into the initial components. In this case, the effective rate constant of the $ArKr^*$ dimer formation measured in experiments proves to be close to zero.

Note that the high value of the rate constant of reaction (2) obtained at low gas pressures [11] is not confirmed in our experiments at least because for $k_2 \approx 10^{-33}\ cm^6\ s^{-1}$ the 'tails' of absorption pulses with the characteristic time of a few microseconds recorded in our experiments (Fig. 3) should not by observed at all.

4. Conclusions

We have studied the deactivation of the metastable $Kr^*(5s[3/2]_2^o)$ state in mixtures close in the composition and pressure to the mixtures used in excimer lasers and high-pressure lasers on atomic transitions in inert gases. It has been shown that this state decays mainly due to the formation of Kr_2^* dimers with the rate constant of $4.1 \times 10^{-33}\ cm^6\ s^{-1}$, which is almost five times lower than the rate constant of deactivation of the similar $Xe^*(6s[3/2]_2^o)$ level. At the same time, as for Xe^*, reactions with formation of heteronuclear dimers do not play any noticeable role in deactivation.

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