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Investigation of collisions between electrons and excited atoms of potassium, rubidium and caesium

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Results of measurements of the rate constants for electron impact induced transitions between selected levels of potassium ($4P \rightarrow 6P$), rubidium ($5P \rightarrow 7P$) and caesium ($6P \rightarrow 8P$ and $6P \rightarrow 9P$) are presented. The experiment was done in helium plasma produced by electric discharge. The plasma was doped with the atoms of interest at a concentration of about 10^{11} cm^{-3}. The alkali atoms were excited to resonance level by a laser pulse. The rate constants for the investigated transitions were determined by the analysis of atomic fluorescence. The electron temperature was measured using a double probe method.

Keywords: electron–atom collisions, excited atoms, plasma.

1. Introduction

The knowledge of rate constants or cross-sections for collisions between atoms and electrons is crucial for understanding and modeling of a large number of phenomena in plasma physics, astrophysics, as well as for physics and engineering of various light sources. Due to strong technical problems, the data for these impacts with the excited atoms (excluding the atoms in metastable levels) are not available. These data can be calculated, using theoretical models based on classical or Born approaches [1–4]. However, the results are very often doubtful, especially for small electron energies, *i.e.*, near the transition threshold. The precise calculations using close coupling method are available for very few elements only [5]. Here we present results of experimental investigations of rate constants for electron impact induced transitions between excited levels of alkali atoms.

2. Experiment

The detailed description of the method was published in our previous papers concerning sodium and lithium [6–9]. Briefly, it consists in observation of atomic

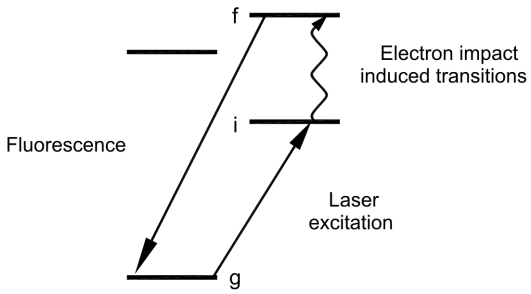

Fig. 1. Scheme of transitions observed in the experiments.

transitions in the plasma that is doped by investigated atoms. The atoms are excited to the initial level i by strong laser pulse (Fig. 1). Due to the electron impact, the transition between i and f level occurs. The fluorescence from the f-level serves to determine the efficiency of $i \rightarrow f$ excitation.

The experimental setup is presented in Fig. 2. Contrary to our previous works [6–9] where the plasma generated by the laser pulse was applied as the electron source, the measurements in potassium, rubidium and cesium were done in plasma achieved due to dc-electric discharge (~ 2 mA) in helium at a pressure of several torrs. The gas was contained in a pyrex-glass cell of 1 cm diameter ended by an anode and a cathode. The electron temperature was retrieved from voltage–current characteristic of double Langmuir probes located in the cell.

The cell containing a droplet of investigated alkali element was located in an oven which temperature was regulated within the range of 380–410 K. It corresponds to the concentration of investigated atoms about 10^{11}–10^{12} cm^{-1} [10]. The atoms were excited to the resonant levels by a pulse of Ti : Sapphire laser. The laser was tuned to the resonant lines: 766.5 nm in the case of potassium, 780 nm in the case of rubidium and 852.1 nm in the case of cesium. Fluorescence from higher excited atoms, which

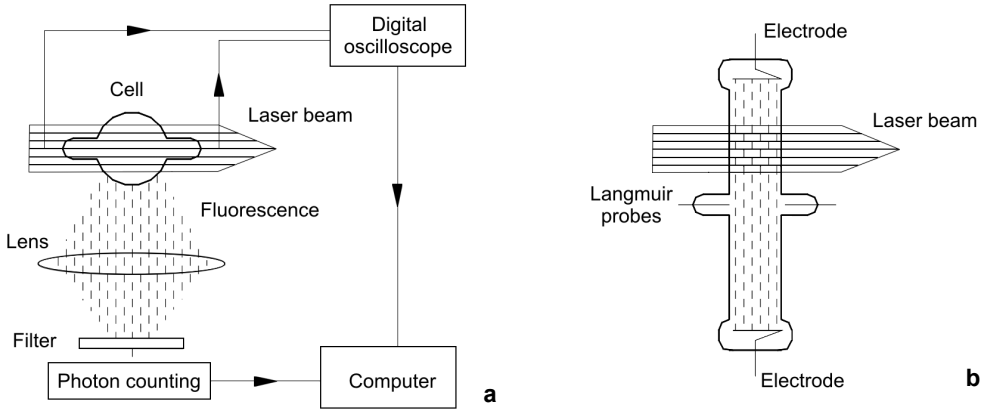

Fig. 2. Scheme of the experimental setup (**a**) and side view of the cell (**b**).

served to determine $i \to f$ transition efficiency, was registered by photon counting method [11]. The respective lines were selected by means of a prism monochromator and a set of colour filters. A special diaphragm located on the cell ensured that the fluorescence light was collected only from the region (the so-called experimental volume) where the helium–alkali atoms mixture was irradiated by the laser beam.

The evolution of higher excited atoms distribution, $N_f(\mathbf{r}, t)$, is given by the differential equation:

$$\frac{\mathrm{d}N_f(\mathbf{r}, t)}{\mathrm{d}t} = -A_f N_f(\mathbf{r}, t) + k_{i \to f}(T_e) N_e N_i(\mathbf{r}, t) \tag{1}$$

where: N_e denotes the spatial distribution of electrons, $N_i(\mathbf{r}, t)$ is the spatial distribution of laser excited atoms, $k_{i \to f}(T_e)$ is the collisional rate constant for the respective transition at given electron temperature T_e and A_f is the Einstein coefficient of the f-level. We neglect the radiative and collisionally induced transitions (populating the nl-level) from other states than those excited by the laser. We also neglect the collisions depopulating the nl-level[1].

The solution of Eq. (1) provides opportunity to describe the experimental signal: the number of the fluorescence photons registered by the detector at the respective wavelength. Since in our experiment the cw discharge was used, the electron concentration N_e is time independent. We also assume that the electron concentration is uniformly distributed within the tube section. As far as the $N_i(r, t)$ is concerned, the spectral density of the laser pulse reached about 10^{-5} W/(cm^{2}Hz), so it was strong enough to saturate the resonant transition. The analysis based on the radiation diffusion allows to assume that the concentration of N_i atoms is also uniform [9]. Temporal evolution of N_i can be expressed by the formula:

$$N_i(t) = N \frac{g_i}{g_g + g_i} c_i(t) \tag{2}$$

where N denotes the total concentration of alkali atoms, while g_i and g_g are the statistic weights of ground and initial state, respectively. Function $c_i(t)$ reaches the unity during the laser pulse (full saturation of the resonant transition) and then decreases. The value of $c_i(t)$ was found due to monitoring of the vapour fluorescence [12].

The solution of Eq. (1) is given by:

$$N_i(t) = k_{i \to f}(T_e) N N_e \frac{g_i}{g_g + g_i} \exp(-A_f t) \int_{t_0}^{t} \mathrm{d}t' c_i(t') \exp(A_f t') \tag{3}$$

[1]This assumption is based on an analysis of respective rate contants which were evaluated using the theoretically calculated cross-sections [4]. More detailed discussion of the influence of other collisions on the experimental signal is done in the next chapter.

where t_0 denotes the time of the beginning of the laser shot. The number of fluorescence photons which were registered per unit of time by the detector localized at distance **R'** is:

$$n_f^F(t) = \Phi_f A_{f\to g} N_f(t) \int_{V_{0l}} \frac{\mathrm{d}^3 r}{4\pi |\mathbf{R}' - r|^2} \tag{4}$$

Here the integration is done over the experimental volume V_{0l}. Because of a small diameter of the cell (1 cm) and relatively high distance to the detector (R = 20 cm), the number of photons could be rewritten in the following form:

$$n_f^F(t) \approx \Phi_f A_{f\to g} \frac{N_f(t) V_{0l}}{4\pi R^2} \tag{5}$$

The final form of the expression describing the number of registered photons is given by:

$$N_{nl}^F(t) = \int_{t_0}^{t_0+T_R} \mathrm{d}t\, n_{nl}^F(t) =$$

$$= \frac{\Phi_f A_{f\to g} N k_{i\to f}(T_e) N_e V_{0l}}{4\pi R^2} \frac{g_{nPJ}}{g_{nS} + g_{nPJ}} \int_{t_0}^{t_0+T_R} \mathrm{d}t \exp(A_f t') \int_{t_0}^{t} \mathrm{d}t' c_i(t') \exp(A_f t') \tag{6}$$

where T_R denotes the time of photons integration.

The parameters like the total density number of the investigated atoms N and concentration of electrons N_e, as well as the experimental volume V_{0l}, are hard to measure and they are affected by large uncertainity. This inconvenience was eliminatd using the reference signal. For this pourpose, the fluorescence from Rb($5P$), K($4P$) or Cs($6P$) levels, respectively, was applied. The fluorescence was excited by the electron impact. Durng the registration of the reference signal the laser was switched off while the discharge was switched on. In this case, the density number of resonantly excited atoms for each fine structure sublevel J (1/2 or 3/2) can be expressed by:

$$\frac{\mathrm{d}N_{iJ}^R(t)}{\mathrm{d}t} = 0 = -A_i N_{iJ}^R(t) + k_{g\to i}^J(T_e) N_e N \tag{7}$$

where $k_{g\to i}^J(T_e)$ is the collisional rate constant for electron impact excitation of J – resonant sublevel from ground state. It can be related to the rate constant for excitation of the resonant level $k_{g\to i}(T_e)$ using the formula:

$$k^{J}_{g\to i}(T_e) = k_{g\to i}(T_e)\frac{g_{iJ}}{g_{i1/2}+g_{i3/2}}N_e N \tag{8}$$

Values of $k_{g\to i}(T_e)$ rate (or respective cross-section) for all alkali metals were measured by many authors and they are easily available in [13–19].

Following the formulas (7) and (8), the reference signal registered within a certain time T_R of the photon number integration for each resonant sub-component is described by:

$$n^{FRJ}_{\mathrm{ref}} = \frac{\Phi_{\mathrm{ref}}A_i}{4\pi R^2}N^R_{iJ}V_{0l}T = \frac{\Phi_{\mathrm{ref}}k^J_{g\to i}(T_e)NN_eV_{0l}}{4\pi R^2}T_R \tag{9}$$

where Φ_{ref} denotes the quantum efficiency of the detection system at the wavelength of the reference signal.

In order to register a sufficiently large photonic signal, we used a broad slit of the monochromator so the spectral resolution of the detecting system was about 20 nm. It is worth to note that in the fine structure splitting of the first resonant level in potassium is about 3.4 nm while in rubidium – 14.7 nm. Then for these two elements the reference signal consisted of photons emitted on both resonance sublines:

$$n^{FR}_{\mathrm{ref}} = n^{FR1/2}_{\mathrm{ref}} + n^{FR3/2}_{\mathrm{ref}} = \frac{\Phi_{\mathrm{ref}}k_{g\to i}(T_e)NN_eV_{0l}}{4\pi R^2}T_R \tag{10}$$

For caesium the fine-structure splitting is about 42.2 nm. Since it is much larger than the monochromator linewidth, the reference signal was registered at $6P_{3/2}\to 6S_{1/2}$ transition only (852.9 nm). Therefore, according to formula (8) and (9), it is expressed by:

$$n^{FR}_{\mathrm{ref}} = \frac{2}{3}\frac{\Phi_{\mathrm{ref}}k_{g\to i}(T_e)NN_eV_{0l}}{4\pi R^2}T_R \tag{11}$$

Comparing and transforming Eqs. (11) and (7) one can find the expression describing the rate of electron impact excited transition:

$$k_{i\to f}(T_e) = \frac{k_{g\to i}(T_e)}{A_f}\frac{N^F_f\Phi_{\mathrm{ref}}}{N^{FR}_{\mathrm{ref}}\Phi_f}\frac{g_g+g_{iJ}}{g_{iJ}}\frac{T_RY}{\int_{t_0}^{t_0+T_R}\mathrm{d}t\exp(-A_ft)\int_{t_0}^{t}\mathrm{d}t'c_i(t')\exp(A_ft')} \tag{12}$$

where $Y = 1$ for potassium and rubidium and $Y = 2/3$ for caesium. The number of photons from higher excited levels and the number of photons of the reference signal

were measured in the experiment. Function $c_i(t)$ was found experimentally using the method described in [12].

3. Results and discussion

The measurements were done for the following *i–f* transitions: 4*P*–6*P* in potassium, 5*P*–7*P* in rubidium and 6*P*–8*P* as well as 6*P*–9*P* in caesium. The monitoring of population of K(6*P*) atoms was performed by the observation of fluorescence at 345 nm. In the case of Rb(7*P*) the 359 nm line was used. For registration of Cs(8*P*) atoms the 388 nm line was observed while for Cs(9*P*) the 361 nm wavelength was selected.

As it was mentioned in the previous chapter, the radiative and collisionally induced transitions populating the *f*-level from the states other than *i*-level were neglected because of their small population. The population due to electron impact from the ground state is also negligible due to large energy gap between *g–f* levels. Moreover, in order to increase the precision of measurements we applied the experimental procedure that eliminated such photons from the experimental signal. We measured independently the number of photons corresponding to the situation when only the laser was switched on, and then when only the discharge was switched on. These counts were subtracted from the number of photons registered when both laser and discharge were switched on. That eliminated the counts which do not occur due to the double excitation scheme (*i.e.*, due to the laser excitation and electron collision, as it was shown in Fig. 1).

Collisions of helium atoms with the excited atoms of interest might lead to the population transfer among the excited levels. However, due to large energy distance among the investigated levels and low pressure of helium, their influence is also negligible [2, 20]. We also neglected the collisions depopulating the *f*-level, because their rates are much smaller than the fluorescence rates [4].

We avoided the measurement of the transition rates to the levels lying lower than 6*P* in potassium, 7*P* in rubidium and 8*P* in caesium since their population can be strongly affected by the energy pooling collisions [22]. Scheme of this reaction can be written as follows:

$$A_i + A_i \rightarrow A^{**} + A_g + \Delta E$$

where A_g, A_i and A^{**} denote the atom in ground, resonance and higher excited levels respectively, and ΔE is the energy balance. The cross-section for these collisions rises sharply in the case when $|\Delta E| < kT$ (k – the Boltzmann constant, T – the atomic temperature) [23]. An analysis of alkali levels shows that due to low value of $|\Delta E|$ the energy pooling collisions might populate the most efficiently the atoms like K(5*P*), K(6*S*), K(4*D*), or Rb(6*P*), Rb(7*S*), Rb(4*D*) as well as Cs(7*P*), Cs(7*D*). Then from these

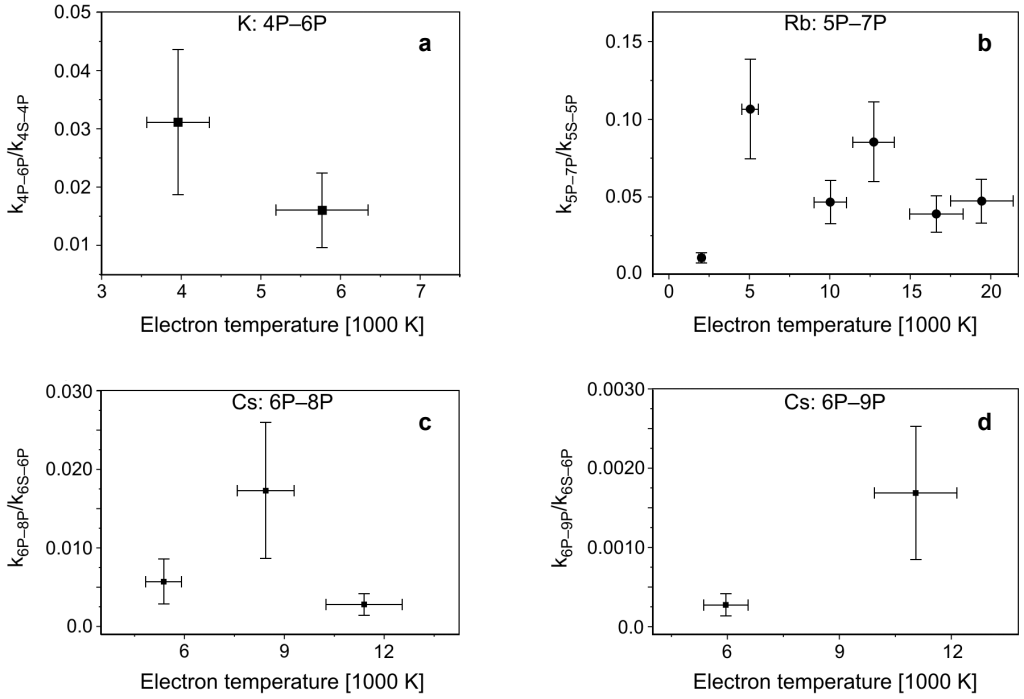

Fig. 3. Ratio of rate constants for electron impact induced transitions between excited levels of: potassium (**a**), rubidium (**b**), caesium (**c** and **d**).

levels the excited atoms of lover energy like K(5*P*), Rb(6*P*) and Cs(7*S*) or Cs(5*D*) might be populated due to cascade transitions [24].

For higher excited levels with large $|\Delta E|$ (like 6*P* levels in potassium, and 7*P* in rubidium as well as 8*P* as 9*P* in caesium) the influence of energy pooling collisions is small. The evaluation done using the cross-section provided by [25, 26] shows that in comparison with the electron collisions their influence on the population of atoms of interest does not exceed 15%.

Figure 3 presents experimentally determined rates of the electron impact induced transitions from resonant levels to selected higher levels of potassium, rubidium and caesium, respectively. The experimental values are not compared with the theoretical ones because the data for transitions between $nP \rightarrow mP$ levels for heavy alkali atoms are not available in the literature[2]. The experimental errors, which are shown in the figures, represent the statistical uncertainties of the data. They follow from

[2]For potassium and rubidium any experimental or theoretical data for this type of collisions cannot be found. The rate contants for population of 10*S*, 8*D* and 9*S* levels of ceasium due to electron collision with Cs(6*P*) atoms were measured by KLUCHAREV and SEPMAN [27].

uncertainties of the parameters that were used in the Eq. (12). The statistical error reached about 50% and it is much higher than the eventual systematic error (15%) that was evaluated within the discussion presented above.

References

[1] GRYZIŃSKI M., *Classical theory of electronic and ionic inelastic collisions*, Physical Review **115**(2), 1959, pp. 374–83.

[2] GRYZIŃSKI M., *Two particle collisions. I. General relations for collisions in the laboratory system*, Physical Review **138**(2A), 1965, pp. A305–21; GRYZIŃSKI M., *Two-particle collisions. II. Coulomb collisions in the laboratory system of coordinates*, Physical Review **138**(2A), 1965, pp. A322–35.

[3] VAJNSTEIN L.A., SOBELMAN I.I., IUKOV E.A., *Secenia vozbuzdenia atomov i ionov elektronami*, Nauka, Moskwa 1973.

[4] KRISHNAN U., STUMPF B., *Calculated electron excitation cross sections for excited state–excited state transitions in alkali atoms*, Atomic Data and Nuclear Data Tables **51**(1), 1992, pp. 151–69.

[5] SCHWEINZER J., BRANDENBURG R., BRAY I., HOEKSTRA R., AUMAYR F., JANEV R.K., WINTER H.P., *Database for inelastic collisions of lithium atoms with electrons, protons and multiply charged ions*, Atomic Data and Nuclear Data Tables **72**(2), 1999, pp. 239–73.

[6] STACEWICZ T., *Investigation of electron-impact-induced transitions between excited atomic levels*, Proceedings of SPIE **1711**, 1992, pp. 63–70

[7] STACEWICZ T., *Investigations of electron impact induced excitations from 3P to high lying levels of sodium*, Acta Physica Polonica A **84**(2), 1993, pp. 259–69.

[8] STACEWICZ T., *Method of investigation of electron impact induced transitions between excited atomic level*, Zeitschrift für Physik D: Atoms, Molecules and Clusters **27**(2), 1993, pp. 149–54.

[9] PIETRUCZUK A., STACEWICZ T., *Investigation of collisions between Li(2P) atoms and electrons: excitation of 4l levels*, Acta Physica Polonica A **103**(5), 2003, pp. 423–32.

[10] NESMEYANOV A.N., *Vapour Pressure of the Elements*, Academic Press, New York 1963.

[11] STACEWICZ T., KRAIŃSKA-MISZCZAK M., *Time resolved photon counting with digital oscilloscope*, Measurement Science and Technology **8**(4), 1997, pp. 453–5.

[12] PIETRUCZUK A., STACEWICZ T., WILSKA M., P. WNUK, *Method for monitoring of excited atoms population*, Measurement Science and Technology **16**(2), 2005, pp. 535–9.

[13] WILLIAMS W., TRAJMAR S., *Electron impact excitation of potassium at 6.7, 16 and 60 eV*, Journal of Physics B: Atomic and Molecular Physics **10**(10), 1977, pp. 1955–66.

[14] BUCKMAN S.J., NOBLE C.J., TEUBNER P.J.O., *Intermediate energy electron scattering from potassium*, Journal of Physics B: Atomic and Molecular Physics **12**(18), 1979, pp. 3077–91.

[15] VUŠKOVIĆ L., TRAJMAR S., REGISTER D.F., *Electron impact cross section for the 2^2P state excitation of lithium*, Journal of Physics B: Atomic and Molecular Physics **15**(15), 1982, pp. 2516–29.

[16] VISCONTI P.J., SLEVIN J.A., RUBIN K., *Absolute total cross sections for the scattering of low-energy electrons by rubidium, cesium and potassium*, Physical Review A **3**(4), 1971, pp. 1310–7.

[17] CHEN S.T., GALLAGHER A.C., *Electron excitation of the resonance lines of the alkali-metal atoms*, Physical Review A **17**(2), 1978, pp. 551–60.

[18] NASS P., ELLER M., LUDWIG N., REICHERT E., WEBERSINKE M., *Polarization transfer in the n^2P-excitation of alkali atoms by longitudinally polarized electrons*, Zeitschrift für Physik D: Atoms, Molecules and Clusters **11**(1), 1989, pp. 71–9.

[19] WEI Z., FLYNN C., REDD A., STUMPF B., *Electron-impact excitation of the Rb $7^2S_{1/2}$, $8^2S_{1/2}$, $5^2D_{3/2}$ and $6^2D_{3/2}$ states*, Physical Review A **47**(3), 1993, pp. 1918–29.

[20] DUBREUIL B., CHALEARD C., *$4^2D \rightarrow 4^2F$ excitation transfer in Li induced by collisions with Li, He, and Ar ground-state atoms*, Physical Review A **29**(2), 1984, pp. 958–61.

[21] CHALEARD C., DUBREUIL B., CATHERINOT A., *Quenching and excitation transfers in n = 3 lithium sublevels*, Physical Review A **26**(3), 1982, pp. 1431–40.

[22] ALLEGRINI M., ALZETTA G., KOPYSTYŃSKA A., MOI L., ORRIOLS G., *Electronic energy transfer induced by collisions between two excited sodium atoms*, Optics Communications **19**(1), 1976, pp. 96–99.
[23] GABBANINI C., GOZZINI S., SQUADRITO G., ALLEGRINI M., MOI L., *Energy-pooling collisions for K(4P) + Rb(5P) and Na(3P) + Rb(5P) heteronuclear systems*, Physical Review A **39**(12), 1989, pp. 6148–53.
[24] RADCING A.A., SMIRNOV B.M., *Atoms and Ions Parameters, Handbook*, Energoatomizdat, Moscow 1986.
[25] KOWALCZYK P., *Asyptotic potentials and coupling terms of excited sodium atoms in thermal collisions*, Chemical Physics Letters **68**(1), 1979, pp. 203–6.
[26] KOWALCZYK P., *Radiative collisions of sodium atoms. Asymptotic calculations*, Chemical Physics Letters **74**(1), 1980, pp. 80–4.
[27] KLYUCHAREV A. N., SEPMAN W. I., *Filling of the upper levels in the optical excitation of cesium vapor*, Optics and Spectroscopy **34**(3), 1973, pp. 241–2 (original: Optika i Spektroskopiya **34**(3), 1973, pp. 425–7).

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