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The collision cross sections for excitation energy transfer in $Rb^*(5P_{3/2})+K(4S_{1/2}) \rightarrow Rb(5S_{1/2})+K^*(4P_J)$ processes

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Abstract. The collisional excitation transfer for the processes $Rb^*(5P_{3/2})+K(4S_{1/2}) \rightarrow Rb(5S_{1/2})+K^*(4P_J)$, $J=1/2$, 3/2, was investigated using two-photon laser excitation technique with a thermionic heat-pipe diode as a detector. The population densities of the K $4P_J$ levels induced by collisions with excited Rb atoms as well as those produced by direct laser excitation of the potassium atoms were probed through the measurement of the thermionic signals generated due to the ionization of the potassium atoms emerging from the $K(4P_J) \rightarrow K(7S_{1/2})$ excitation channel. The measurements of the thermionic signals in addition to the spectroscopic determination of the potassium number density yield the following values for the excitation transfer cross sections: $\sigma_1(Rb\ 5P_{3/2} \rightarrow K\ 4P_{1/2}) = 8$ Å^2 and $\sigma_2(Rb\ 5P_{3/2} \rightarrow K\ 4P_{3/2}) = 11$ Å^2. The accuracy of the presented results is $\mp 15\%$. The obtained results are compared to those for the opposite processes $K^*(4P_J)+Rb(5S_{1/2}) \rightarrow K(4S_{1/2})+Rb^*(5P_{3/2})$.

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1. Introduction

Alkali-atom systems are very convenient for experimental and theoretical investigations of low-energy collisional excitation energy transfer processes. Among the most investigated processes are the collisions involving atoms excited in the first resonance state. In the case of heteronuclear alkali mixtures the K–Rb system is especially instructive due to energetically close lying first excited states. Recently it has been reported on rubidium 5^2P fine-structure transitions induced by collisions with potassium atoms [1]. The mixing between the 4^2P states of a potassium atom induced in a collision with a rubidium atom in the ground state has been studied experimentally by Hrycyshyn and Krause [2]. The excitation transfer from potassium 4^2P resonance states to rubidium 5^2P resonance states has been investigated by several authors [3–6]. The experimental and theoretical results [7, 8] for this particular process differ considerably. Moreover, this can be regarded to be the usual feature of the data in this field [9]. In order to complete the set of the data concerning the energy excitation transfer in K–Rb systems, here we report the results for the processes $Rb^*(5P_{3/2})+K(4S_{1/2}) \rightarrow Rb(5S_{1/2})+K^*(4P_J)$. Since these processes are just reversed to those investigated in [4, 6], our results may enlighten the existing disagreement. In order to determine the collisional transfer rates for the process $Rb^*(5P_{3/2})+K(4S_{1/2}) \rightarrow Rb(5S_{1/2})+K^*(4P_J)$, the population densities of the K $4P_J$ levels generated through two different excitation channels, were compared. The first channel is defined by the excitation of the Rb, followed by the collisional transfer to the K, while the second one is direct excitation of the potassium. In both cases the population densities of the excited potassium levels were probed by second excitation step $K(4P_J) \rightarrow K(7S_{1/2})$, and detected using a thermionic-diode technique [10].

Regarding the particular excitation channel that we used for obtaining the thermionic signals, as well as the sensitivity of the applied method, the specific conditions in the experiment had to be attained. This concerns particularly the number densities of Rb and K as well as their ratio. The magnitude of the first plays in favour of the transfer signals, while the latter is important for the initialization of the thermionic process itself. It was found that accurate measurement of the signals was possible under the conditions of $N_K \cdot N_{Rb}$ being not less than 10^{23} cm^{-6}. The requirements on the optical thickness of the Rb D2 line allowed Rb number density to be not more than $\simeq 10^{10}$ cm^{-3}. This evidently restricted the range for variation of K number density. With typical value of $8 \cdot 10^{13}$ cm^{-3} for N_K, potassium resonance lines happened to be optically thick. Fortunately, the radiation trapping under such conditions was still reasonable enough not to produce unavoidable difficulties.

2. The excitation transfer between rubidium and potassium

Figure 1 shows the partial term diagrams of the rubidium and potassium atoms together with the radiative

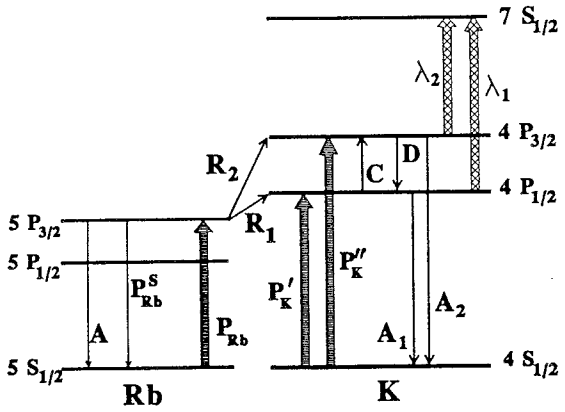

Fig. 1. Partial term diagrams of the rubidium and potassium atoms (the explanation of the rates shown is given in Sect. 2). Note that each pumping rate indicated in the figure participates in one particular section of the experiment solely

and collisional rates relevant for the investigation that is going to be presented in this paper. The rest of the rates not shown, can be neglected in the following presentation of the rate equations due to the particular experimental conditions. As for the rubidium intermultiplet mixing, this is justified due to typical values of the number densities of the rubidium, potassium and buffer gas and the corresponding cross sections [1, 9]. The argument for disregarding the excitation transfer from K to Rb can be found in the small value of the ratio of the rubidium and potassium number densities.

The excitation of the rubidium atoms by laser radiation was done in Doppler kernel of the one of the optically thin hyperfine components of the $Rb(5S_{1/2}) \rightarrow Rb(5P_{3/2})$ transition. The corresponding pumping rate is given by:

$$P_{Rb}(\Delta\nu) = \rho_{Rb}\, B_{Rb}(\Delta\nu)\, N_{Rb}(5S_{1/2}), \tag{1}$$

where ρ_{Rb} is the spectral power density of the radiation field of the diode laser, B_{Rb} is the corresponding Einstein coefficient, $N_{Rb}(5S_{1/2})$ is the number density of the rubidium atoms in the ground state, $\Delta\nu = \nu^0_{Rb} - \nu_L$ is the detuning from the line centre and ν_L is the frequency of the laser radiation. In order to obtain the reliable signals due to rubidium-potassium collisional excitation transfer, high number density of the excited rubidium atoms was needed. Therefore the $Rb(5S_{1/2}) \rightarrow Rb(5P_{3/2})$ transition was optically saturated. Taking into account the stimulated emission rate P^S_{Rb} (equal to $(g_0/g_2) \cdot P_{Rb}(\Delta\nu)$), the steady-state population density of the Rb $5P_{3/2}$ level is described by:

$$\dot{N}_{Rb}(5P_{3/2}) = 0 = \rho_{Rb}\, B_{Rb}(\Delta\nu)\left(N_{Rb}(5S_{1/2}) - \frac{g_0}{g_2} N_{Rb}(5P_{3/2})\right) - A\, N_{Rb}(5P_{3/2}), \tag{2}$$

where A is the spontaneous emission coefficient of the Rb $5P_{3/2}$ state, and g_0 and g_2 are the statistical weights of the ground and excited state, respectively.

In this case the corresponding absorption coefficient is given by:

$$k^S_{Rb}(\Delta\nu) = (h\nu^0_{Rb}/c)\, B_{Rb}(\Delta\nu)\left(N_{Rb}(5S_{1/2}) - \frac{g_0}{g_2} N_{Rb}(5P_{3/2})\right). \tag{3}$$

The steady-state equations for the population densities of the K $4P_J$ levels generated due to excitation energy transfer in collisions with the excited rubidium atoms are:

$$\dot{N}_K(4P_{1/2}) = 0 = R_1\, N_{Rb}(5P_{3/2}) + D\, N_K(4P_{3/2}) - (C + A_1)\, N_K(4P_{1/2}), \tag{4}$$

$$\dot{N}_K(4P_{3/2}) = 0 = R_2\, N_{Rb}(5P_{3/2}) + C\, N_K(4P_{1/2}) - (D + A_2)\, N_K(4P_{3/2}), \tag{5}$$

where A_1 and A_2 are the effective (comprising the radiation trapping effects) spontaneous emission coefficients for the K $4P_{1/2}$ and K $4P_{3/2}$ states, respectively, while C and D denote the intermultiplet collisional mixing rates of the K $4P_J$ levels due to collisions with the ground state K and Ar atoms.

The following rate equations correspond to the second excitation channel. The K $4P_{1/2}$ and K $4P_{3/2}$ levels were excited in the line wings at detunings for which they can be considered to be optically thin. In such a case one can be sure that the signals for both excitation channels were obtained in analogous conditions and therefore their comparison is correct.

If the K $4P_J$ ($J = 1/2, 3/2$) levels are optically excited the corresponding pumping rates are:

$$P'_K(\Delta\nu') = \rho'_K\, B'_K(\Delta\nu')\, N_K, \qquad \Delta\nu' = \nu^{0\prime}_K - \nu_L, \tag{6}$$

$$P''_K(\Delta\nu'') = \rho''_K\, B''_K(\Delta\nu'')\, N_K, \qquad \Delta\nu'' = \nu^{0\prime\prime}_K - \nu_L, \tag{7}$$

where ρ_K is the spectral power density of the radiation field of the diode laser, B_K is the Einstein coefficient for the absorption transition $K(4S_{1/2}) \rightarrow K(4P_J)$ ($J = 1/2, 3/2$), N_K is the number density of the potassium atoms in the ground state, $\Delta\nu$ is the detuning from the line centre and ν_L is the frequency of the laser radiation. Here, the quantities appearing in the expressions related to the excitation of K $4P_{1/2}$ state are labeled with prime, while the analogous ones for the case when the K $4P_{3/2}$ state is involved are labeled with double prime. This notation will be used throughout the paper.

The steady-state population densities of the K $4P_J$ levels when K $4P_{1/2}$ is optically excited by laser radiation are described by:

$$\dot{N}'_K(4P_{1/2}) = 0 = \rho'_K\, B'_K(\Delta\nu')\, N_K + D\, N'_K(4P_{3/2}) - (C + A_1)\, N'_K(4P_{1/2}), \tag{8}$$

$$\dot{N}'_K(4P_{3/2}) = 0 = C\, N'_K(4P_{1/2}) - (D + A_2)\, N'_K(4P_{3/2}). \tag{9}$$

If the K $4P_{3/2}$ state is excited the corresponding rate equations for the steady-state population densities of the K $4P_J$ levels are:

$$\dot{N}''_K(4P_{3/2}) = 0 = \rho''_K B''_K(\Delta\nu'') N_K + C N''_K(4P_{1/2}) - (D + A_2) N''_K(4P_{3/2}), \quad (10)$$

$$\dot{N}''_K(4P_{1/2}) = 0 = D N''_K(4P_{3/2}) - (C + A_1) N''_K(4P_{1/2}). \quad (11)$$

The Einstein coefficients $B'_K(\Delta\nu')$ and $B''_K(\Delta\nu')$ appearing in the above equations can be, according to (3), replaced by:

$$B^J_K(\Delta\nu) = k^J_K(\Delta\nu) \frac{c}{h\nu^{0J}_K} \frac{1}{N_K}. \quad (12)$$

The equations (2), (4), and (8) taking into account (3) and (12) yield the relation for the collision transfer rate R_1:

$$R_1 = A \frac{\rho'_K}{\rho_{Rb}} \frac{\nu^0_{Rb}}{\nu^{0\prime}_K} \frac{k^{(1/2)}_K(\Delta\nu')}{k^S_{Rb}(\Delta\nu)} \frac{N_K(4P_{1/2})}{N'_K(4P_{1/2})} \cdot \frac{\left(1 - \frac{D}{C + A_1} \frac{N_K(4P_{3/2})}{N_K(4P_{1/2})}\right)}{\left(1 - \frac{D}{C + A_1} \frac{C}{D + A_2}\right)}. \quad (13)$$

Similarly, by combining (2), (5), and (10), and using (3) and (12) one obtains the expression for the collision transfer rate R_2:

$$R_2 = A \frac{\rho''_K}{\rho_{Rb}} \frac{\nu^0_{Rb}}{\nu^{0\prime\prime}_K} \frac{k^{(3/2)}_K(\Delta\nu'')}{k^S_{Rb}(\Delta\nu)} \frac{N_K(4P_{3/2})}{N''_K(4P_{3/2})} \cdot \frac{\left(1 - \frac{C}{D + A_2} \frac{N_K(4P_{1/2})}{N_K(4P_{3/2})}\right)}{\left(1 - \frac{C}{D + A_2} \frac{D}{C + A_1}\right)}. \quad (14)$$

If one takes a closer look to the denominators of the above expressions for the rates R_1 and R_2, a remark made in the introduction concerning the allowed number density for the potassium becomes evident. Namely, if A_1 and A_2 would become so small that they could be neglected compared to C and D, respectively, the denominators will tend to zero. In such a situation the determination of the rates R_1 and R_2 would be impossible. Therefore the upper limit for the potassium number density in our experiment was restricted to the one for which the trapping of the potassium resonance radiation could not affect the numerical stability of the evaluation of the above expressions. Taking into account (9) and (11) which relate $C/(D + A_1)$ and $D/(C + A_2)$ to the measurable quantities $N'_K(4P_{3/2})/N'_K(4P_{1/2})$ and $N''_K(4P_{1/2})/N''_K(4P_{3/2})$, respectively, one finally obtains the following expressions for the collision transfer rates R_1 and R_2:

$$R_1 = A \frac{\rho'_K}{\rho_{Rb}} \frac{\nu^0_{Rb}}{\nu^{0\prime}_K} \frac{k^{(1/2)}_K(\Delta\nu')}{k^S_{Rb}(\Delta\nu)} \frac{N_K(4P_{1/2})}{N'_K(4P_{1/2})} \cdot \frac{\left(1 - \frac{N''_K(4P_{1/2})}{N''_K(4P_{3/2})} \frac{N_K(4P_{3/2})}{N_K(4P_{1/2})}\right)}{\left(1 - \frac{N''_K(4P_{1/2})}{N''_K(4P_{3/2})} \frac{N'_K(4P_{3/2})}{N'_K(4P_{1/2})}\right)}, \quad (15)$$

$$R_2 = A \frac{\rho''_K}{\rho_{Rb}} \frac{\nu^0_{Rb}}{\nu^{0\prime\prime}_K} \frac{k^{(3/2)}_K(\Delta\nu'')}{k^S_{Rb}(\Delta\nu)} \frac{N_K(4P_{3/2})}{N''_K(4P_{3/2})} \cdot \frac{\left(1 - \frac{N'_K(4P_{3/2})}{N'_K(4P_{1/2})} \frac{N_K(4P_{1/2})}{N_K(4P_{3/2})}\right)}{\left(1 - \frac{N''_K(4P_{1/2})}{N''_K(4P_{3/2})} \frac{N'_K(4P_{3/2})}{N'_K(4P_{1/2})}\right)}. \quad (16)$$

In the evaluation of the results we have used the value for the spontaneous emission coefficient $A = 3.8 \cdot 10^7\ s^{-1}$ [11].

The collision cross sections for the excitation energy transfer in the $Rb^*(5P_{3/2}) + K(4S_{1/2}) \rightarrow Rb(5S_{1/2}) + K^*(4P_J)$ processes have been determined according to the relation:

$$\sigma_i = \frac{R_i}{\bar{v}_{Rb-K} \cdot N_K}, \quad i = 1, 2, \quad (17)$$

where

$$\bar{v}_{Rb-K} = (8kT/\pi M)^{1/2} \quad (18)$$

is the Maxwellian mean relative velocity of the colliding rubidium and potassium atoms, with M being the reduced mass of Rb–K quasimolecule and T is the absolute temperature. The values for N_K and T have been determined spectroscopically from the experiment.

3. Experiment and data analysis

A schematic diagram of the experimental arrangement is shown in Fig. 2. The rubidium-potassium vapour mixture was produced in the central, 7 cm long heated zone of a stainless-steel heat-pipe having Pyrex-glass windows. The temperature was measured by calibrated Fe-constantan thermocouple glued beneath the heater to the steel wall with high thermal conductivity cement (Astroceram). The temperature stability was ∓ 0.2 K. In order to utilize the heat-pipe as the thermionic diode detector for collisionally produced ions [10], the molybdenum

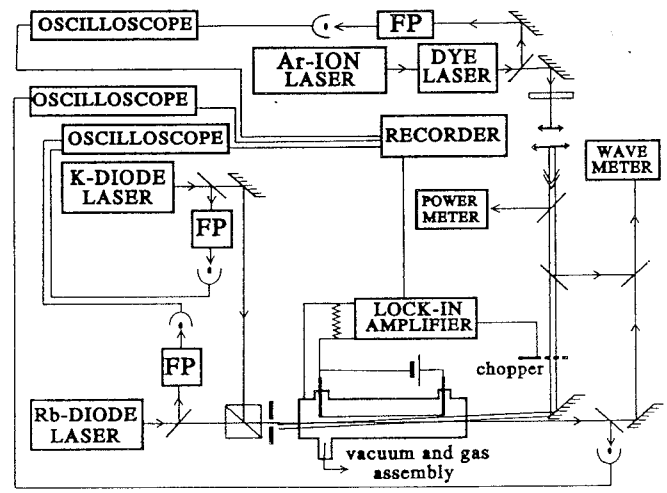

Fig. 2. Experimental set-up

cathode filament (0.3 mm in diameter) was built in. The molybdenum has been chosen because it sustained the particular experimental conditions (K vapour atmosphere) with no need for the replacement far better than tungsten. We have used argon as the buffer gas. Its pressure (measured with the MKS Baratron manometer) was kept constant at 200 mTorr. Since the typical number densities of the rubidium and potassium in the metal vapours, obtained when the central zone was heated up to 470 K were 10^{10} and $8 \cdot 10^{13}$ cm^{-3}, respectively, the partial metal vapour pressure did not exceed 6 mTorr, what means that the heat-pipe was not running in the heat-pipe mode.

Here it has to be mentioned that the preparing of the adequate alkali mixture was a tedious job itself. The first attempt to carry on the measurements in pure potassium gave no satisfactory result. The small fraction of inevitable rubidium present, happened to be insufficient to provide the measurable transfer signals at the temperatures for which potassium resonance radiation trapping still caused no problems. The enriching of the mixture with any appreciable amount of the rubidium made the mixture useless regarding the optical thickness of the rubidium D2 line. We have found experimentally that, even being the weaker component of the mixture, the rubidium, which has a higher vapour pressure than the potassium, rather quickly (regarding its fraction in the mixture) equalizes its pressure with that of the potassium over the alkali mixture. Finally, the satisfactory mixture happened to be the one in which the fraction of the rubidium was almost but not quite that characteristic for pure potassium [1].

The metal-vapour mixture was optically excited by two counter-propagating laser beams aligned along the heat-pipe cylindrical axis. The rubidium atoms were excited to the $5P_{3/2}$ state by a single-mode, frequency stabilized diode laser (SHARP LT027MDO, wavelength 784.0 nm at 25 °C, linewidth less than 100 MHz, maximal power 7 mW), which we call Rb-laser-diode for convenience.

The excitation of the potassium atoms to the $4P_{1/2}$ or $4P_{3/2}$ state was done by one and the same single-mode frequency stabilized diode laser (SHARP LT022MDO, wavelength 776.5 nm at 25 °C, linewidth less than 100 MHz, maximal power 3 mW), with both components of the resonance doublet within reach. In the text to follow this diode laser will be denoted as K-diode-laser.

The population densities of the K $4P_J$ levels produced by direct optical excitation or in collisions with the excited rubidium atoms were probed by a laser beam (counter-propagating with respect to either of the two diode laser beams) supplied by cw single-mode, frequency stabilized ring dye-laser (SPECTRA PHYSICS model 380D, dye: Rh 6G) pumped by an argon-ion laser (SPECTRA PHYSICS model 2020). The dye-laser was utilized for the $K(4P_J) \rightarrow K(7S_{1/2})$ excitation ($\lambda_{DYE} = 578.4$ nm and $\lambda_{DYE} = 580.3$ nm for $K(4P_{1/2}) \rightarrow K(7S_{1/2})$ and $K(4P_{3/2}) \rightarrow K(7S_{1/2})$ transitions, respectively). The thermionic signals generated due to the ionization of the potassium atoms emerging from the $K(4P_J) \rightarrow K(7S_{1/2})$ excitation channel, which reflect the population densities of the K $4P_J$ levels were fed to the lock-in amplifier (EG & G PAR model 5210) operated at reference frequency of 17 Hz, supplied by a chopper (SR 540) used for chopping of the dye-laser beam. The output was recorded by the three channel LINSEIS (LS 52-4) strip-chart recorder.

The dye-laser beam was expanded and attenuated, using neutral density filters, down to 2.5 mW. It has been proven that no optical saturation of the measured signals was present due to that particular laser beam. The diameter of the dye-laser beam was 5 mm.

The power of the diode-laser beam used for the optical excitation of the potassium atoms was 0.1–0.2 mW after expanding and passing through the circular aperture (2 mm in diameter). No optical saturation was produced by this laser beam either.

In order to obtain reliable signals due to the excitation transfer, it was not possible to maintain the power of the third laser, that used for the excitation of the Rb $5P_{3/2}$ state, below the limit of the optical saturation as well. The typical power used in the experiment was 1 mW, subsequent to the expanding and passing through 2 mm wide circular aperture.

The wavelength of the particular laser radiation has been measured by BURLEIGH wavemeter, while the measurement of its power has been done by COHERENT "Fieldmaster" power meter.

As can be seen in Fig. 2 the laser-beams geometry was arranged so that the dye-laser beam comprised simultaneously both diode-laser beams. Therefore no additional alignment of the beams intercepting in the heat-pipe (except simple interchange of the shutters for the diode-laser beams) was necessary once the optimal geometry was achieved. Such an arrangement enabled the very same geometry to be maintained through the whole duration of the experiment. The absorption spectra of the rubidium and potassium were detected by photodiodes whose signals were fed to the HAMEG (HM 205-3, 20 MHz) storage oscilloscope. The real time output of the oscilloscope was recorded by the strip-chart recorder. The measured absorption spectra were used for the determination of the Rb and K number densities, using the method of curve of growth for optically thin lines in the case of the rubidium, while the number density of the potassium atoms have been obtained from the measurement of the absorption coefficient in the impact resonance wing.

The dispersion calibration of the measured spectra was done using one 50 cm (f.s.r. 150 MHz) and two 3 cm (f.s.r. 2 GHz) confocal Fabry-Perot interferometers for marking the dye-laser and diode-laser scans, respectively.

The measurements of the quantities required for the evaluation of the transfer rates R_1 and R_2 have been performed in the following way.

With the Rb-diode-laser locked at the frequency of one of the Rb $5P_{3/2}$ hyperfine components (^{85}Rb or ^{87}Rb isotope) the population densities of the K $4P_{1/2}$ and K $4P_{3/2}$ levels were probed by the dye-laser through the $K(4P_J) \rightarrow K(7S_{1/2})$ excitation channel. The peak intensities of the thermionic signals S_1 and S_2 obtained during the dye-laser scans over the $K(4P_{1/2}) \rightarrow K(7S_{1/2})$ and $K(4P_{3/2}) \rightarrow K(7S_{1/2})$ transitions are proportional to the population densities $N_K(4P_{1/2})$ and $N_K(4P_{3/2})$, respective-

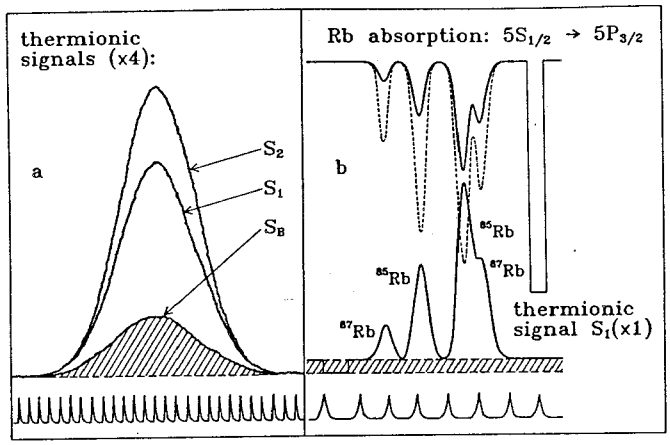

Fig. 3a, b. Direct reproduction of typical spectra obtained in the determination of the transfer signals. The part **a** shows the signals obtained in the case when the Rb-diode-laser was locked at the frequency of the weaker hyperfine component of the ^{87}Rb isotope, while the dye-laser was scanned over the $K\,4P_{1/2} \rightarrow K\,7S_{1/2}$ (S_1 signal, $\lambda_{DYE} = 578.4$ nm) and $K\,4P_{3/2} \rightarrow K\,7S_{1/2}$ (S_2 signal, $\lambda_{DYE} = 580.3$ nm), respectively. The S_B denote the thermionic signal measured in the case when Rb-diode-laser was tuned off the resonance. The thermionic signal obtained with the dye-laser locked at the frequency corresponding to the maximum of the S_1 signal displayed in the **a** part of the figure, during the Rb-diode-laser scan over the rubidium D2 line is shown in the **b** part of the figure. The corresponding absorption spectrum measured simultaneously is also displayed (*full* and *dotted line* correspond to the case with and without optical saturation, respectively). The dispersion calibration marks are separated by 150 MHz and 2 GHz in the **a** and **b** part of the figure, respectively. The number densities of the rubidium and the potassium were $9.7 \cdot 10^9\,cm^{-3}$ and $9.1 \cdot 10^{13}\,cm^{-3}$, respectively. The temperature was 463 K

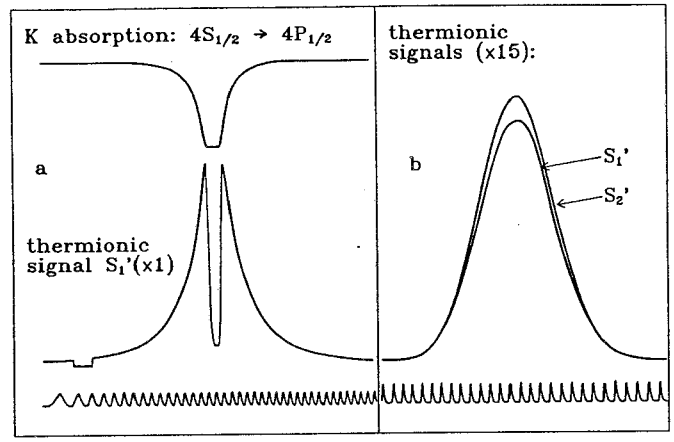

Fig. 4. The **a** part of the figure displays the thermionic signal, together with the corresponding absorption spectrum, obtained during the K-diode-laser scan over the potassium D1 line, with the dye-laser locked at the frequency corresponding to the maximum of the S_1 signal (Fig. 3a). The **b** part of the figure shows the thermionic signals measured in the case when the potassium was directly optically excited in the resonance wing of the D1 line while the dye-laser was scanned over $K\,4P_{1/2} \rightarrow K\,7S_{1/2}$ (S_1' signal, $\lambda_{DYE} = 578.4$ nm) and $K\,4P_{3/2} \rightarrow K\,7S_{1/2}$ (S_2' signal, $\lambda_{DYE} = 580.3$ nm), respectively. The dispersion calibration marks are separated by 2 GHz and 150 MHz in the **a** and **b** part of the figure, respectively. The number densities of the rubidium and the potassium were $9.7 \cdot 10^9\,cm^{-3}$ and $9.1 \cdot 10^{13}\,cm^{-3}$, respectively. The temperature was 463 K

ly. The ratio of the measured peak intensities, S_1/S_2 therefore yields the value for the quantity $N_K(4P_{1/2})/N_K(4P_{3/2})$. The typical scans obtained for S_1 and S_2 are shown in Fig. 3a. The illustration of the transfer signal obtained when the dye-laser was locked at the frequency corresponding to the maximum of the S_1 signal while the Rb-diode-laser was simultaneously scanned over the Rb D2 line, is displayed in Fig. 3b. The corresponding absorption spectrum recorded at the same time is also included.

The test of the measured thermionic signals against a presence of the possible nongenuine contributions has been done. Such a contribution was confirmed to exist by exciting the rubidium atoms slightly off resonance. The thermionic signal obtained under this conditions, S_B (background signal) is also displayed in the Fig. 3a. In the evaluation of the ratio $N_K(4P_{1/2})/N_K(4P_{3/2})$ we have deducted this (S_B) contribution from the S_1 (S_2) signal. The measurements of the S_1 and S_2 signals (each of them being followed by the determination of the S_B) were repeated several times to gain the statistics.

Once the sequence of the determination of the ratio $N_K(4P_{1/2})/N_K(4P_{3/2})$ has been completed, the dye-laser was locked at the frequency corresponding to the maximum of the S_1 signal, the Rb-diode-laser beam was shuttered and K-diode-laser beam was passed instead. The thermionic signal, S_1' proportional to the reference population density of the $K\,4P_{1/2}$ level ($N_K'(4P_{1/2})$) was recorded while scanning the K-diode-laser over the 770.1 nm line (Fig. 4a). The laser-beam absorption in the metal vapours was measured by a photo-diode simultaneously. This scan was immediately followed by the measurement of the S_1 signal, i.e. the population density $N_K(4P_{1/2})$ of the $K\,4P_{1/2}$ level in the manner described above, in order to check on a possible alteration due to change of the dynamical conditions of the experiment. The obtained set of the spectra have provided the data for the evaluation of the quantity $k_K^{(1/2)}(\Delta\nu') \cdot N_K(4P_{1/2})/N_K'(4P_{1/2})$, which is equal to $k_K^{(1/2)}(\Delta\nu') \cdot S_1/S_1'$.

The values for the absorption coefficient and the S_1' signal were taken at the same detuning $\Delta\nu'$ in the resonance wing. The care was taken to determine the absorption coefficient and the S_1' signal in the region where the well established $\Delta\nu^{-2}$ dependence of both signals was observed. Such a dependence of S_1' signal has been observed for the detunings $\Delta\nu > 20$ GHz. At the frequencies closer to the line centre the thermionic signal was apparently reduced compared to the one expected, because of the weakening of the diode-laser beam due to the increased absorption. Consequently, the value of the absorption coefficient was required at the detunings for which the measured absorption spectrum did not supply reliable information. The value of the absorption coefficient in the region $\Delta\nu > 20$ GHz was obtained by extrapolation of the data (clearly displaying $\Delta\nu^{-2}$ dependence) obtained from the part of the wing for which the absorption coefficient could be determined with satis-

factory precision. The $\Delta\nu^{-2}$ dependence of the S'_1 signal (which is proportional to the absorption coefficient) at greater detunings, justifies such an extrapolation.

Finally, the ratio of the population densities $N'_K(4P_{3/2})/N'_K(4P_{1/2})$ was measured. The K-diode-laser was locked at a detuning $\Delta\nu > 20$ GHz in the optically thin region of the resonance wing of the potassium D1 line. The ratio of the peak intensities of the thermionic signals S'_2 and S'_1, generated through the $K(4P_J) \rightarrow K(7S_{1/2})$ $(J=3/2, 1/2)$ excitation channel yields the value for the $N'_K(4P_{3/2})/N'_K(4P_{1/2})$. The typical S'_2 and S'_1 signals are shown in Fig. 4b. Here, the detuning $\Delta\nu$ at which the potassium atoms have been excited might not exactly coincide with the one for which the value of S'_1 (i.e. $k_K^{(1/2)}(\Delta\nu')\cdot S_1/S'_1$) was previously determined. This is of no importance as far as the evaluation of the latter is done in the region where the $\Delta\nu^{-2}$ dependence of both $k_K^{(1/2)}(\Delta\nu')$ and S'_1 was proven, since they enter the expression for R_1 in the form of ratio.

Subsequent to the measurements involving the D1 component of the potassium resonance doublet, exactly the same procedure was repeated for the D2 component. This part of the measurement yielded the values for $N''_K(4P_{1/2})/N''_K(4P_{3/2})$ and $k_K^{(3/2)}(\Delta\nu'')\cdot N_K(4P_{3/2})/N''_K(4P_{3/2})$ which completed the set of the quantities needed for the evaluation of the collision transfer rates R_1 and R_2.

In order to obtain the data for the collision cross sections for the excitation energy transfer in the $Rb^*(5P_{3/2})+K(4S_{1/2}) \rightarrow Rb(5S_{1/2})+K^*(4P_J)$ processes, the number density N_K of the potassium atoms in the ground state is left to be determined.

We have determined the value of N_K from the measurement of the absorption coefficient $k_K^{(3/2)}(\Delta\nu)$, in the resonance wing of the D2 component of the potassium resonance doublet. The $k_K^{(3/2)}(\Delta\nu)$ could be accurately determined in the range of $\Delta\nu$ (6 GHz $< \Delta\nu <$ 12 GHz) which falls within the impact region, where $k_K^{(3/2)}(\Delta\nu)$ exhibits the usual Lorentzian form:

$$k_K^{(3/2)}(\Delta\nu) = \pi e^2 f N_K \frac{\Gamma}{2\pi(\Delta\nu)^2}, \tag{19}$$

where Γ is the half-width (FWHM) of the Lorentzian profile and f is the oscillator strength of the potassium 766.7 nm line. The half-width Γ is given by:

$$\Gamma = \Gamma_N + \Gamma_{K-Ar} + \Gamma_{K-K}, \tag{20}$$

where Γ_N is the natural half-width, while Γ_{K-Ar} and Γ_{K-K} are the half-widths due to the K–Ar and K–K broadening, respectively. As for the Γ_N we have used the value 6.05 MHz [11]. The half-widths Γ_{K-Ar} and Γ_{K-K} can be expressed in the form:

$$\Gamma_{K-Ar} = \eta_{K-Ar} N_{Ar}, \tag{21a}$$

and

$$\Gamma_{K-K} = \eta_{K-K} N_K, \tag{21b}$$

where η_{K-Ar} and η_{K-K} are the reduced half-widths for K–Ar and K–K broadening, respectively, and N_{Ar} is the number density of the argon atoms.

We have used the value $\eta_{K-Ar} = 6.30\cdot10^{-10}\ s^{-1}\ cm^3$, experimentally obtained by [12], and theoretical value $\eta_{K-K} = 1.03\cdot10^{-7}\ s^{-1}\ cm^3$ in the impact region [13, 14]. With all necessary substitutions (19) yields the quadratic equation for N_K, provided that N_{Ar} in the central heated zone of the heat-pipe is known. Since the value for the pressure measured during the experiment comprises both argon and metal-vapour contribution, the argon number density in the middle of the heat-pipe is given by:

$$N_{Ar} = (p/kT) - N_K = \alpha - N_K, \tag{22}$$

where p is the pressure measured by manometer, k is the Boltzman constant and T is the temperature in the central zone of the heat-pipe.

With the above expression for N_{Ar}, one finally obtains for $k_K^{(3/2)}(\Delta\nu)$:

$$k_K^{(3/2)}(\Delta\nu) = \frac{2.95\cdot10^{-10}}{(\Delta\nu)^2} N_K^2 + \frac{2.88\cdot10^{-3}}{(\Delta\nu)^2} \cdot(6.05\cdot10^6 + 6.30\cdot10^{-10}\alpha) N_K, \tag{23}$$

where $\Delta\nu$ is measured in s^{-1}, N_K and α are in cm^{-3}, and $k_K^{(3/2)}$ is in cm^{-1}. Bearing in mind that the measurements were done in the heat-pipe the temperature T_{TC} measured by the thermocouple at its outer wall is not correct one to be ascribed to the vapours in the interior. One should expect that the actual temperature is going to be somewhat lower than T_{TC}. The knowledge of the temperature affects the determination of N_K through the value of α. Therefore we have estimated the greatest error one can introduce by being short of knowing the exact temperature of the vapours.

The two extreme temperatures related to our experiment are those of the cold end (T_0) and the middle of the heat-pipe (T_{TC}). This two temperatures at the same time determine the highest (although not realistic) and the lowest value for α. A typical spread of α in our experimental conditions was $3.2–6.0\cdot10^{15}\ cm^{-3}$. Such an uncertainty in α introduces the error of roughly $\mp 10\%$ in the coefficient of the linear term of the quadratic equation for N_K, which consequently produces an error of $\mp 5\%$ in the determination of N_K. The overall uncertainty of N_K, taking into account the error in the determination of the metal-vapour column length is about $\mp 10\%$.

Since the knowledge of the vapour temperature is needed for the determination of $\bar{v}_{Rb-K}$, we have estimated the actual temperature in the following way. Using the measured temperature T_{TC} we have determined N_K in the way described above. Also from the absorption measurement for the 780.2 nm rubidium line we have determined N_{Rb} by the method of the curve of growth for the optically thin lines. For the temperature range covered by our experiment, we have obtained that the ratio N_{Rb}/N_K has not exceeded the value of $5\cdot10^{-4}$. Following the argumentation of Hrycyshyn and Krause [4] (and

references therein), concerning the partial vapour pressures over the binary mixture of alkali metals, one obtains that for such a value of the ratio N_{Rb}/N_K that we had, the partial pressure of the potassium could be hardly distinguished from the vapour pressure of pure potassium. Therefore considering the determined value for N_K to be the one corresponding to the vapour pressure of pure potassium and using the temperature-vapour pressure plot given by Nesmeyanov [15], we have estimated the actual temperature of the metal vapour in the heat-pipe. The error in the determination of the temperature was as much as the error of $\mp 10\%$ in the N_K produced, i.e. typically ∓ 2 K. The temperature of the metal vapour determined in such a way as 20% lower than the one measured by the thermocouple, which is not surprising taking into account the effect of heat conduction of the heat-pipe as well as temperature gradient along its central zone.

The additional check of the temperature was made by measuring the halfwidth (FWHM) of the Doppler limited signals S_1' and S_2'. The agreement was found to be within 10 K.

The temperature (determined as described above) in our experiment varied between 448 K and 468 K. The corresponding change in the potassium number density was determined to be from $4.7 \cdot 10^{13}\,\mathrm{cm}^{-3}$ to $1.1 \cdot 10^{14}\,\mathrm{cm}^{-3}$. The ^{87}Rb number density varied in the range from $5 \cdot 10^{9}\,\mathrm{cm}^{-3}$ to $1.4 \cdot 10^{10}\,\mathrm{cm}^{-3}$.

The temperature range covered in our experiment was limited from below due to the weak thermionic signals obtained in the case of atom number densities being lower than declared above. The upper limit was restricted by the increased optical trapping of the potassium resonance radiation whose influence on the evaluation of the rates R_1 and R_2 has been mentioned before (Sect. 2).

The values of the collision cross sections for excitation energy transfer in the $Rb^*(5P_{3/2}) + K(4S_{1/2}) \rightarrow Rb(5S_{1/2}) + K^*(4P_J)$ processes obtained in our experiment are as follows:

$$\sigma_1(Rb\,5P_{3/2} \rightarrow K\,4P_{1/2}) = 8\,\text{Å}^2 \mp 15\%,$$

and

$$\sigma_2(Rb\,5P_{3/2} \rightarrow K\,4P_{3/2}) = 11\,\text{Å}^2 \mp 15\%.$$

The error stated comprises the uncertainty due to the temperature, the potassium number density as well as the statistical error in determination of R_1 and R_2.

4. Discussion and conclusion

To the best of our knowledge the collision cross sections for the excitation energy transfer in the $Rb^*(5P_{3/2}) + K(4S_{1/2}) \rightarrow Rb(5S_{1/2}) + K^*(4P_J)$ processes have not been reported so far. Therefore we compare the obtained results with the existing ones for the inverse processes i.e. $K^*(4P_J) + Rb(5S_{1/2}) \rightarrow K(4S_{1/2}) + Rb^*(5P_{3/2})$. Hrycyshyn and Krause [4] have reported $\sigma_1(K\,4P_{1/2} \rightarrow Rb\,5P_{3/2}) = 40 \mp 8\,\text{Å}^2$ and $\sigma_2(K\,4P_{3/2} \rightarrow Rb\,5P_{3/2}) = 27 \mp 7\,\text{Å}^2$, while Stacey and Zare [6] have reported $\sigma_1(K\,4P_{1/2} \rightarrow Rb\,5P_{3/2}) = 5.3 \mp 0.8\,\text{Å}^2$ and $\sigma_2(K\,4P_{3/2} \rightarrow Rb\,5P_{3/2}) = 5.5 \mp 1.2\,\text{Å}^2$. Assuming detailed balancing, the cross sections for the inverse processes are $\sigma_1(Rb\,5P_{3/2} \rightarrow K\,4P_{1/2}) = 10\,\text{Å}^2$, $\sigma_2(Rb\,5P_{3/2} \rightarrow K\,4P_{3/2}) = 11\,\text{Å}^2$ for the results of Hrycyshyn and Krause. The corresponding values based on the results of Stacey and Zare are $\sigma_1(Rb\,5P_{3/2} \rightarrow K\,4P_{1/2}) = 1.4\,\text{Å}^2$, $\sigma_2(Rb\,5P_{3/2} \rightarrow K\,4P_{3/2}) = 2.3\,\text{Å}^2$.

As one can see there is a huge discrepancy, far outside the stated error bars, between the results of Hrycyshyn and Krause and the results of Stacey and Zare. The possible causes of their mutual discrepancy were already discussed by the authors themselves [6, 9] and no obvious reason to account for the discrepancy was found.

Up to now no attempt has been made to reinvestigate these processes or to study the inverse ones. Since our results are in excellent agreement with those of Hrycyshyn and Krause, although they used quite a different method and technology (fluorescence measurements with a spectral lamp as a light source instead of laser spectroscopy in thermionic diode), we have to conclude that the results of Hrycyshyn and Krause are more likely to be correct.

Regarding the theoretical predictions for the cross sections for these processes there is the result of Dashevskaya et al. [7, 8], who have reported $\sigma_1(K\,4P_{1/2} \rightarrow Rb\,5P_{3/2}) = 10\,\text{Å}^2$. Again, the principle of detailed balance yields for the process that we have investigated the value of $2.6\,\text{Å}^2$. Compared to that theoretical prediction, our result as well as that of Hrycyshyn and Krause, is too high while the result of Stacey and Zare is in excellent agreement with the theory. However it has to be mentioned that the review [9] of the cross sections for the excitation energy transfer between dissimilar alkali atoms shows that the experimentally determined cross sections are always higher than the theory predicts. The singular case of the agreement between experiment and theory is that of Stacey and Zare and Dashevskaya et al.

The results of the present investigation contribute to the completeness of the set of the data for collisional energy transfer among the first resonance states in mixed alkali systems. Also they are one more of the kind in the growing list [16, 17] of the experimentally determined cross sections which systematically overcome the theoretically predicted values. This intriguing fact might give rise to a more thorough theoretical investigation of these processes.

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