Non-dipole excitation transfer between the 6^2S and 4^2D states in potassium.

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Abstract

We report an experimental study of collisional excitation transfer between the 6^2S and 4^2D states in potassium. The experiment was performed in potassium vapour, using two-step laser excitation of the 6^2S state. The cross-sections of excitation transfer from the 6^2S to the 4^2D state and of the 4^2D state quenching in collisions with ground state atoms were determined as $\sigma_{6S\rightarrow 4D} = (1.8\pm0.6)\times10^{15}\mathrm{cm}^2$ and $\sigma_{4D}^{q} = (2.7\pm1.2)\times10^{14}\mathrm{cm}^2$, respectively.

PACS: 34.50.Fa, 32.50.+d

1. Introduction

Among the large variety of collisional excitation transfer (ET) processes the most detailed studied, both experimentally and theoretically, are the so-called energy pooling (EP) collisions of two excited alkali atoms resulting in population of high-lying states:

$$M^*(^2P) + M^*(^2P) \rightarrow M^{**}(^2S \text{ or } ^2D) + M(^2S) + \Delta E. \qquad (1)$$

For details concerning experimental studies of these processes we refer the interested reader to publications [1-4] and references therein. A theoretical approach to the EP processes has been developed in [5] for EP in caesium, and later elaborated and applied to other alkalis by various authors [6-10]. A common feature of the processes of type (1) is that they proceed efficiently owing to the strong dipole-dipole interaction between the intital (^2P+^2P) and the final (^2S+^2D or ^2D+^2S) configurations of atoms.

Already in early studies of ET processes, it had been noticed that the cross-sections (i.e., rate constants) of different reactions possess a common dependence on the energy defect ΔE [11]. The data existing at present on the EP allow one to establish an empirical relation between the reaction rate constant k and the energy defect ΔE [12]:

$$k = A \times \exp\left(-\frac{\Delta E}{k_{\mathrm{B}} T} \right), \tag{2}$$

where $A = (5.0 \pm 0.6) \times 10^{-9}\,\mathrm{cm^3 s^{-1}}$. This relation is valid for the processes with positive ΔE. Moreover, if one compares the rates of other ET processes, they also seem to obey relation (2), no matter whether or not the dipole-dipole interaction between the initial and final configurations is present.

One may expect that the ET processes between the atomic ^{2}S and ^{2}D states (hereafter referred to as *SD-transfer*),

$$\mathrm{M}^{**}(^2\mathrm{S}) + \mathrm{M}(^2\mathrm{S}) \rightarrow \mathrm{M}^{**}(^2\mathrm{D}) + \mathrm{M}(^2\mathrm{S}),$$

will be inefficient because of the lack of interactions that would couple the (^{2}S+^{2}S) and (^{2}D+^{2}S) configurations. However, the existing studies [13-15] on the SD-transfer processes show that they also obey, within uncertainty limits, relation (2). Theoretical studies [16,17] of the process

$$\mathrm{Rb}^{**}(7^2\mathrm{S}) + \mathrm{Rb}(5^2\mathrm{S}) \rightarrow \mathrm{Rb}^{**}(5^2\mathrm{D}) + \mathrm{Rb}(5^2\mathrm{S}), \tag{3}$$

for which an experimental cross-section of $8 \times 10^{-15}\,\mathrm{cm}^2$ has been reported [14], attributed the efficient ET in this case to the proximity of the (5^2P+5^2P) configuration, which introduces a strong dipole coupling between the initial (7^2S+5^2S) and the final (5^2D+5^2S) configurations. In order to clarify the role of interaction in the ET, we are interested in pairs of close lying ^{2}S and ^{2}D states which are energetically well isolated from the ^{2}P states. Such isolation would eventually allow one to exclude effects like that of the perturbing (5^2P+5^2P) configuration in the case of SD-transfer process (3), and, hence, the dipole-dipole interaction. The pair of the 6^2S and 4^2D states in potassium (see Fig. 1) seems to be appropriate. The energy defect between these two states is only 53 $\mathrm{cm^{-1}}$. The 6^2P state lies 1548 $\mathrm{cm^{-1}}$ above 6^2S, and 4^2P+4^2P energy is 1311 $\mathrm{cm^{-1}}$ below 4^2D. In the present work we are concerned with the ET process

$$\mathrm{K}^{**}(6^2\mathrm{S}) + \mathrm{K}(4^2\mathrm{S}) \rightarrow \mathrm{K}^{**}(4^2\mathrm{D}) + \mathrm{K}(4^2\mathrm{S}) + 53\ \mathrm{cm}^{-1}. \tag{4}$$

The empirical relation (2) predicts for this process a cross-section of $5.6 \times 10^{-14}\,\mathrm{cm}^2$ for the mean $k_{\mathrm{B}}T$ of the present experiment.

2. Experiment and method

The experiment was performed in a potassium vapour cell, at temperatures $520\mathrm{K} \le T \le 600\mathrm{K}$. The cell was made of alkali-resistant glass cell and placed in a two-chamber oven. The temperature of the side arm of the cell containing metallic potassium was kept 10 degrees below that of the main oven body. The potassium number densities were calculated from the temperature-vapour pressure relation [18]. The atoms were excited to the 6^2S state using two-step laser excitation (cf Fig. 1). The frequency of the first step laser (Kr^+ pumped CR-590 dye laser with Oxazine 1 dye, $\Delta\nu_{\mathrm{L1}} \approx 30\mathrm{GHz}$) was detuned from the $4^2\mathrm{S}_{1/2}\rightarrow4^2\mathrm{P}_{1/2}$ resonance by several Doppler widths in order to ensure homogeneous excitation of atoms along the beam axis. The second step laser (Ar^+ pumped CR-699 ring dye laser with DCM dye, $\Delta\nu_{\mathrm{L2}} \approx 1\mathrm{MHz}$) was set on resonance with the $4^2\mathrm{P}_{1/2}\rightarrow6^2\mathrm{S}_{1/2}$ transition. The fluorescence was detected on the modulation frequency of the first step laser with a monochromator and a photomultiplier (RCA, model C31034-05) using the lock-in technique.

The fluorescence was registered on the $6^2\mathrm{S}_{1/2}\rightarrow4^2\mathrm{P}_{3/2}$ (6938.8 Å) and $4^2\mathrm{D}_{3/2,5/2}\rightarrow4^2\mathrm{P}_{3/2}$ (6964.7 Å) transitions at various potassium number densities ($8.5\times10^{14}\mathrm{cm}^{-3} \le N_0 \le 1\times10^{16}\mathrm{cm}^{-3}$). The fluorescence intensities provide information about the relative populations in the 6^2S and 4^2D states. The $4^2\mathrm{D}_{3/2}\rightarrow4^2\mathrm{P}_{1/2}$ spectral line (6936.3 Å) was not resolved from the comparatively strong $6^2\mathrm{S}_{1/2}\rightarrow4^2\mathrm{P}_{3/2}$ fluorescence. It is important to note that the strongly edothermic EP process [3]

$$\mathrm{K}^*(4^2\mathrm{P}) + \mathrm{K}^*(4^2\mathrm{P}) \rightarrow \mathrm{K}^{**}(4^2\mathrm{D}) + \mathrm{K}(4^2\mathrm{S})$$

did not contribute to the 4^2D fluorescence signal: with the second step laser blocked, no fluorescence from the 4^2D state was observable even at highest temperatures of the experiment.

Since the fluorescence from the 4^2D J=3/2 and J=5/2 components was not spectrally resolved, we do not distinguish the fine structure and assume that both J sublevels are populated according to statistical weights g_J. This assumption is justified because at the high K number densities of the present experiment collisional J-mixing is faster than radiative decay. The solution of the rate equation for the 4^2D state allows one to extract the cross-section for the SD-transfer process (4) from the intensity ratio of the $4^2\mathrm{D}\rightarrow4^2\mathrm{P}$ and $6^2\mathrm{S}\rightarrow4^2\mathrm{P}$ fluorescence lines. Under steady state conditions

$$\frac{\mathrm{d}N_{\mathrm{4D}}}{\mathrm{d}t} = 0 = \sigma_{\mathrm{6S}\rightarrow\mathrm{4D}} N_0 v N_{\mathrm{6S}} - \frac{1}{\tau_{\mathrm{4D}}} N_{\mathrm{4D}} - \sigma^{\mathrm{q}}_{\mathrm{4D}} N_0 v N_{\mathrm{4D}}\,, \qquad (5)$$

where $\sigma_{\mathrm{6S}\rightarrow\mathrm{4D}}$ is the cross-section for process (4), $\sigma^{\mathrm{q}}_{\mathrm{4D}}$ is the 4^2D state quenching cross-section in collisions with ground state K atoms, τ_{4D} is the lifetime of the 4^2D state, $v = \sqrt{8k_{\mathrm{B}}T/\pi\mu}$ is the mean relative velocity of colliding atoms, and N_{6S}, N_{4D} and N_0 are the number densities of the 6^2S, 4^2D and ground state atoms, respectively. From (5) we obtain for the ratio of number densities of excited atoms:

$$\frac{N_{4\mathrm{D}}}{N_{6\mathrm{S}}}=\frac{\sigma_{6\mathrm{S}\to 4\mathrm{D}}}{\sigma^{\mathrm{q}}_{4\mathrm{D}}+1/(\tau_{4\mathrm{D}}N_0 v)}. \qquad (6)$$

In order to relate this density ratio to the ratio of fluorescence intensities $I(4^2\mathrm{D}_{5/2,3/2}\to 4^2\mathrm{P}_{3/2})$ and $I(6^2\mathrm{S}_{1/2}\to 4^2\mathrm{P}_{3/2})$ measured in the experiment, a proportionality coefficient must be introduced to account for different transition probabilities of different transitions:

$$\alpha=\frac{g_{5/2}A(4^2\mathrm{D}_{5/2}\to 4^2\mathrm{P}_{3/2})+g_{3/2}A(4^2\mathrm{D}_{3/2}\to 4^2\mathrm{P}_{3/2})}{(g_{5/2}+g_{3/2})\times A(6^2\mathrm{S}_{1/2}\to 4^2\mathrm{P}_{3/2})}. \qquad (7)$$

Here A denote Einstein coefficients of the respective transitions, and $g_{5/2}$ and $g_{3/2}$ are the statistical weights of the $4^2\mathrm{D}_{5/2}$ and $4^2\mathrm{D}_{3/2}$, respectively. Using (6) and (7), we can express the ratio of the measured fluorescence intensities as

$$\eta=\frac{I(4^2\mathrm{D}_{5/2,3/2}\to 4^2\mathrm{P}_{3/2})}{I(6^2\mathrm{S}_{1/2}\to 4^2\mathrm{P}_{3/2})}=\alpha\frac{\sigma_{6\mathrm{S}\to 4\mathrm{D}}}{\sigma^{\mathrm{q}}_{4\mathrm{D}}+1/(\tau_{4\mathrm{D}}N_0 v)}. \qquad (8)$$

Thus, the SD-transfer and quenching cross-sections can be obtained from the measured intensity ratio η. In (7) and (8) we are using the values for the Einstein coefficients from [19], and lifetime $\tau_{4\mathrm{D}}$ given in [20].

3. Results and discussion

The experimental dependence of the intensity ratio η on the product of number density N_0 and collision velocity v, $N_0 v$, is shown in Fig. 2. By fitting equation (8) to the experimental points (solid line, Fig. 2), the cross-section for process (4), $\sigma_{6\mathrm{S}\to 4\mathrm{D}}=(1.8\pm0.6)\times10^{-15}\mathrm{cm}^2$, and the 4^2D state quenching cross-section, $\sigma^{\mathrm{q}}_{4\mathrm{D}}=(2.7\pm1.1)\times10^{-14}\mathrm{cm}^2$, were determined. If one compares the available cross-sections of different SD-transfer processes (table I), it is evident that the process in potassium is the least efficient despite the smallest energy defect. Also note that the experimental cross-section for the SD-transfer process (4) is more than 30 times smaller than predicted by the empirical relation (2). The relatively small value of this cross-section may be explained by the lack of strong interactions taht would couple the initial (6^2S+4^2S) and the final (4^2D+4^2S) configurations. The dipole-dipole interaction mediated by the (4^2P+4^2P) configuration can be eventually excluded because of its large energy separation from the 6^2S+4^2S and 4^2D+4^2S states of separated K atoms. This would explain why the cross section of process (4) is smaller than expected from relation (2). The latter was obtained for EP processes dominated by the dipole-dipole interaction, which is absent in the present case. Possibly, the process (4) is governed by interaction of K(6^2S)+K(4^2S) and K(4^2D)+K(4^2S) quasi-molecular states with the ionic $\mathrm{K}^+ + \mathrm{K}^-$ state at large internuclear distances $R > 60$ a.u. (see the potential curves calculated in [21]).

As about the quenching of the 4^2D state, we can mention few possible processes which could be responsible for it. The quenching with the ground state K_2 molecules can be excluded because of the following considerations. Assuming that the excited atoms are being quenched in collisions with the molecules, we obtain for the 4^2D quenching cross section a value of 4.3×10^{-12}cm^2, which is unrealistically large. Moreover, with the molecules as the quenching actors we could not reproduce the experimental $\eta(N_0 v)$-dependence as good as in the case of quenching with atoms. Therefore we conclude that the 4^2D state is quenched in collisions with ground state K atoms. One of the possible processes is the associative ionisation leading to formation of K_2^+. Another possibility is ET to the 4^2F state. To best of our knowledge, there are no data available in the existing literature about these processes. It should be noted, however, that both above mentioned processes are strongly endoergic (by $-923\mathrm{cm}^{-1}$ and $-730\mathrm{cm}^{-1}$, respectively), and therefore they are not expected to be particularly efficient. A more likely explanation of the quenching is capture of the colliding K(4^2D) and K(4^2S) atoms on the attractive molecular terms at small internuclear distances [17].

In conclusion, we have experimentally determined the cross sections for ET between the 6^2S and the 4^2S states of potassium, and the 4^2D state quenching cross section in collisions with the ground state atoms. The former is more than 30 times smaller than predicted by the empirical relation of the cross-section with energy defect (2). A theoretical work on these processes is in progress, and will be reported elsewhere.

Acknowledgements

This work was partially supported by the Latvian Science Council. We are grateful to Prof. K. Bergmann, who provided the necessary experimental facilities. One of us (A.E.) thanks the Deutscher Akademischer Austauschdienst (DAAD) for support.

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Table 1. Energy defects and cross-sections for SD-transfer processes in Rb and K.

Process	ΔE, cm^{-1}	Cross section, cm^{-15}	
		Experimental	Theoretical
$Rb(7^2S)+Rb(5^2S)\rightarrow Rb(5^2D)+Rb(5^2S)$	607	8±4[a]	7.0[b]
$Rb(8^2S)+Rb(5^2S)\rightarrow Rb(6^2D)+Rb(5^2S)$	358	34±12[c]	
$K(6^2S)+K(4^2S)\rightarrow K(4^2D)+K(4^2S)$	53	1.8±0.6[d]	

[a] Luo Caiyan et al., Ref. [14]
[b] Orlovsky et al., Ref. [17]
[c] Ekers et al., Ref. [15]
[d] This work

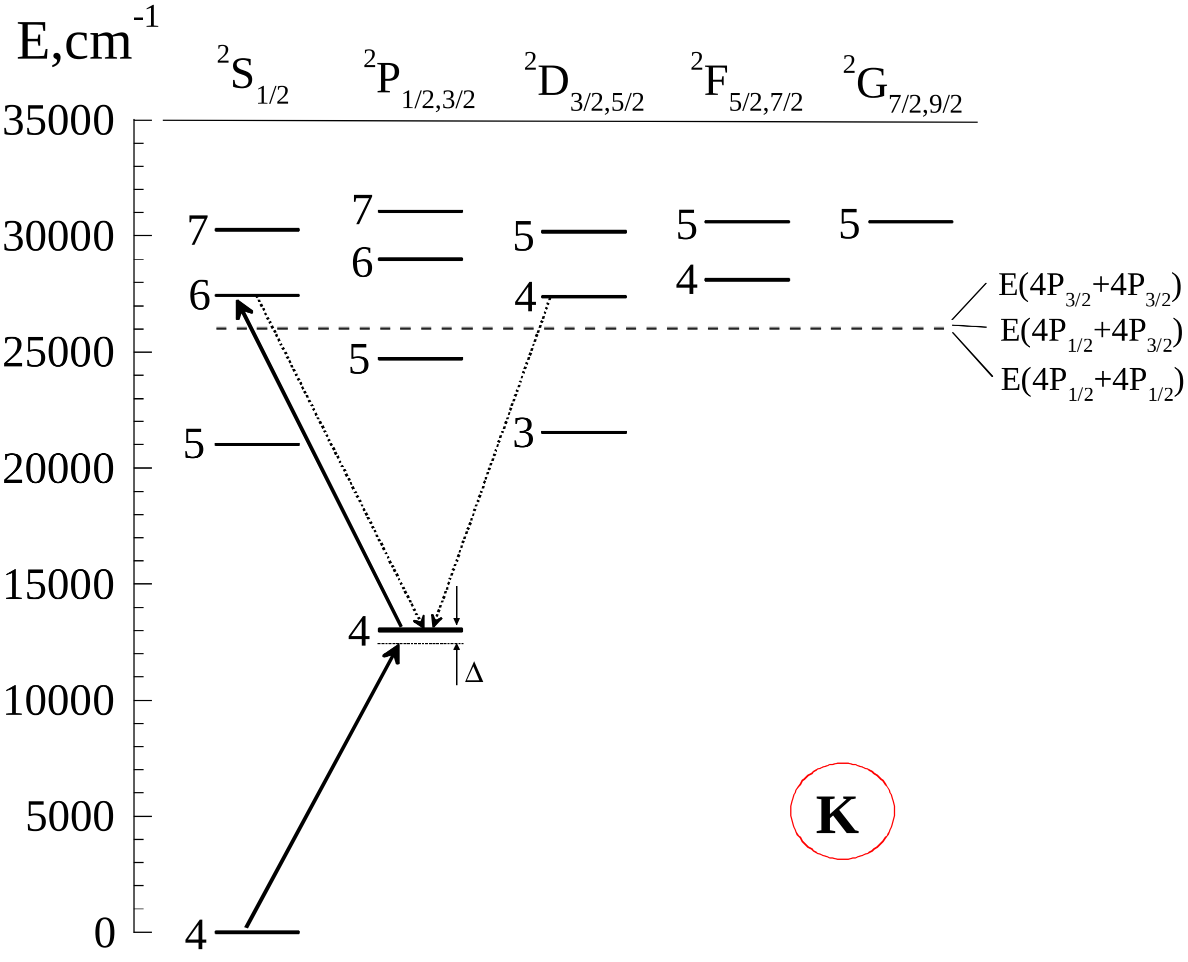

Fig. 1. Energy level diagram for the lowest and intermediate excited states of potassium. Solid arrowlines depict two steps of the laser excitation. Detuning of the first step laser Δ is exaggerated on this picture. Dotted arrowlines mark the observed fluorescence transitions.

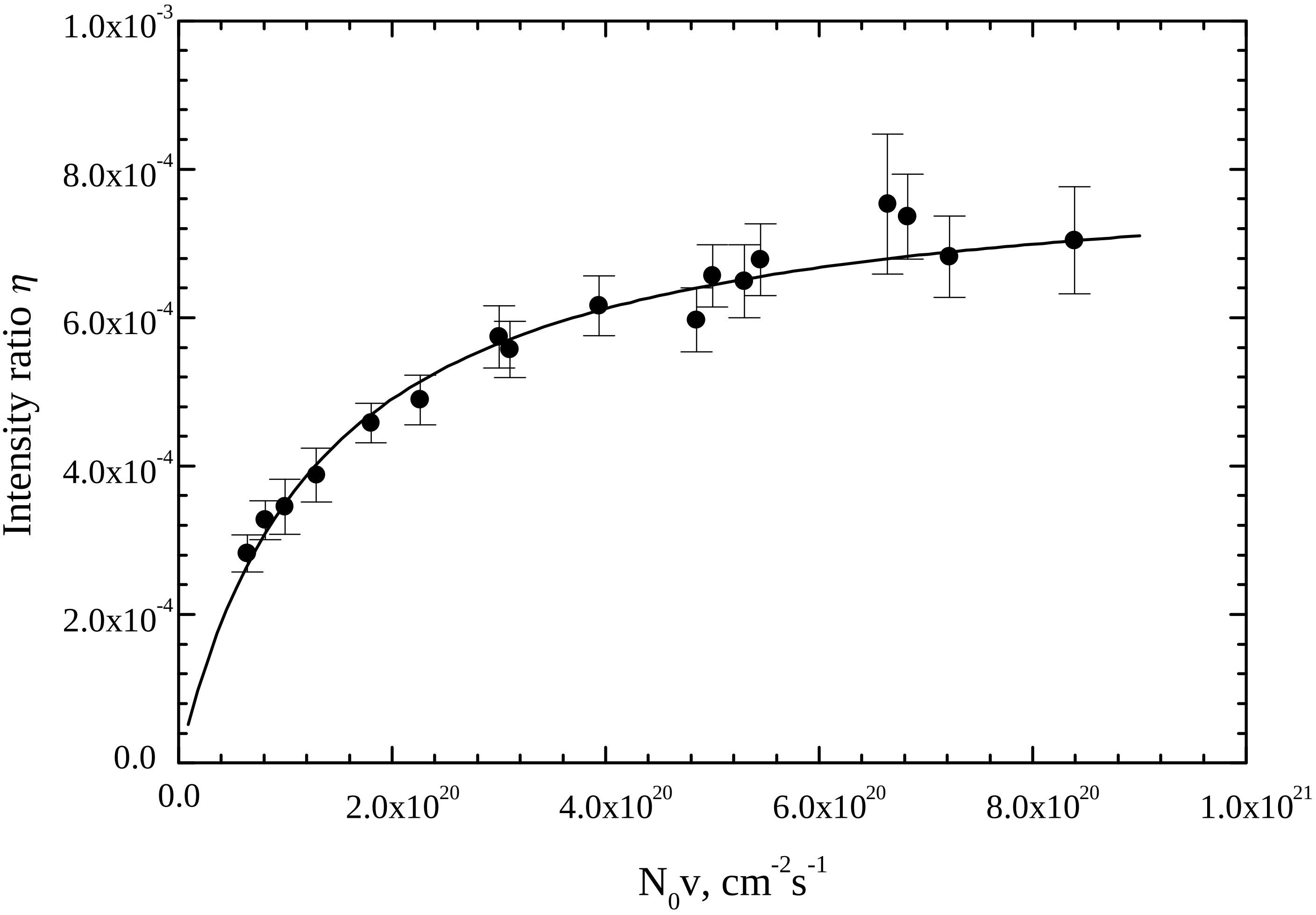

Fig. 2. Dependence of the intensity ratio $I\left(4^2\mathrm{D}_{5/2,3/2} \to 4^2\mathrm{P}_{3/2}\right)/I\left(6^2\mathrm{S}_{1/2} \to 4^2\mathrm{P}_{3/2}\right)$ on $N_0 v$; ●, experiment; solid line, least squares fit of eq. (8).