ENERGY TRANSFER REACTION K(4S) + K(7S) → K(4S) + K(5F) THEORY AND EXPERIMENT

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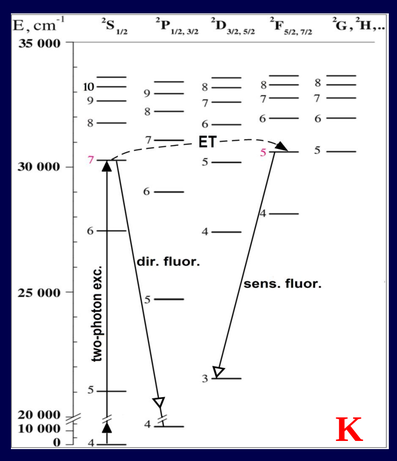
A comparison of theoretical and experimental results regarding the excitation energy transfer (ET) reaction K(4s) + K(7s) → K(4s) + K(5f)-332 cm^{-1} in thermal collisions is presented. Calculations are based on theoretical adiabatic K_2 potential energy curves (PECs) and on the use of the semi-classical multicrossing Landau-Zener model. Contributions due to various molecular symmetries are calculated for temperatures of 310 ÷ 1000 K. Experiment was carried out in pure potassium vapor by means of time-resolved laser-induced fluorescence. Pulsed laser excitation and photon counting technique was applied. For the temperature range 428 ÷ 451 K used in the experiment, the calculated cross-section varies in the range of (2.09÷2.04) x10^{-14} cm^2 and agrees well with the average of experimental values 1.8(8) x10^{-14} cm^2.

THEORY



PECs involved in the ET calculations were determined within the pseudo-potential method, in a similar way as in Ref. [1].-A satisfying agreement with experimental molecular data listed in Ref . [1] was obtained. Theoretical ET cross sections were determined by using a semi-classical multicrossing Landau-Zener (LZ) model previously applied *e. g.*, in energy pooling between sodium and potassium atoms [2,3]. Calculations were based on the estimation of the population transfer from one PEC to another in the vicinity of each avoided crossing. PECs for $^{1,3}\Sigma^{+}_{g,u}$ molecular states correlated with K(4*s*)+K(6*p*) and up to K(4*s*)+K(5*f*) were considered (see **Figs. 1, 2** and **K-atom levels**). LZ parameters (position R_n, diabatic energy U_n, splitting V_n between the two PECs, difference of the slopes ΔF_n) were extracted for each avoided crossing. They are listed in **Table I**, and the value P_n of LZ probability of transition at the avoided crossing *n* is given for one value of impact parameter (*b*=0) and one collision energy (E=400 K).The probabilities are estimated to be ≈ 0.900 for several impact parameters and collision energies, which leads to a nearly full population transfer from one PEC to the other at the corresponding avoided crossing.

Total cross sections σ(*υ*) for each molecular symmetry were determined by integrating the final population of each possible exit channel correlated with 4*s*+5*f* over different impact parameters. These values are still dependent on the collision energy (the relative velocity *υ* of the colliding partners). Bearing in mind the vapour-cell experiment , in which thermally averaged collisional transfer rates $R(T)$ are measured at various temperatures T (see below), the relevant thermally averaged cross sections were calculated defined as: $\overline{\sigma}(T) = \langle \sigma(\upsilon)\upsilon \rangle / \overline{\upsilon}$, where $\overline{\upsilon} = \sqrt{8k_B T/\pi\mu}$ is the mean relative velocity of atoms at T, with μ - their reduced mass, and k_B - the Boltzmann constant . $\langle \sigma(\upsilon)\upsilon \rangle = k(T)$ is the thermally averaged rate constant at T, related to $R(T)$ as: $k(T)=R(T)/N$, where N is atomic number density. Sum and contributions of each molecular symmetry are displayed in **Fig. 3** for the thermally averaged cross sections. The major contribution comes from avoided crossings of $^{3}\Sigma^{+}_{g}$ and $^{3}\Sigma^{+}_{u}$ molecular states.

Table I: Landau-Zener parameters ($R_n, U_n, V_n, \Delta F_n$) of each avoided crossing n present in the $^{1,3}\Sigma^{+}_{g,u}$ potential energy curves involved in the energy transfer reaction

$K(4s)+K(7s) \rightarrow K(4s)+K(5f)$. Probability value ($P_n(b,E) = \exp(-2\pi \frac{|V_n|^2}{\upsilon_{R_n}(b,E)\Delta F_n})$ with $\upsilon_{R_n}(b,E) = \sqrt{\frac{2E}{\mu}(1-\frac{b^2}{R_n^2}-\frac{U_n}{E})}$) is indicated for $b=0$ and $E=400K$. Parameter values are given in atomic units.

n	States	R_n	U_n	V_n	ΔF_n	$P_n(0, 400K)$
$^1\Sigma^+_g$						
1	$4s5d-4s7s$	06.66	-7.10x10^{-3}	7.14x10^{-4}	1.64x10^{-2}	0.942
2	$4s5d-4s7s$	13.44	-1.16x10^{-2}	7.82x10^{-5}	2.54x10^{-3}	0.995
3	$4s7s-4s5f$	20.82	-2.47x10^{-3}	2.17x10^{-4}	6.06x10^{-4}	0.859
$^1\Sigma^+_u$						
1	$4s6p-4s5d$	09.65	-2.25x10^{-2}	5.74x10^{-4}	4.15x10^{-3}	0.863
2	$4s6p-4s5d$	15.69	-1.31x10^{-2}	5.87x10^{-4}	1.15x10^{-3}	0.565
3	$4s5d-4s7s$	08.15	-1.87x10^{-2}	1.23x10^{-4}	3.03x10^{-3}	0.991
4	$4s5d-4s7s$	12.66	-1.22x10^{-2}	2.13x10^{-4}	7.27x10^{-3}	0.985
5	$4s7s-4s5f$	09.93	-1.55x10^{-2}	7.00x10^{-4}	9.09x10^{-3}	0.903
6	$4s7s-4s5f$	14.48	-6.34x10^{-3}	1.73x10^{-3}	3.62x10^{-3}	0.200
7	$4s7s-4s5f$	21.44	-1.68x10^{-3}	1.23x10^{-3}	5.68x10^{-4}	0.005
$^3\Sigma^+_g$						
1	$4s6p-4s5d$	10.67	-2.25x10^{-2}	2.23x10^{-4}	3.00x10^{-3}	0.969
2	$4s5d-4s7s$	13.52	-1.11x10^{-2}	8.79x10^{-4}	2.57x10^{-2}	0.944
3	$4s7s-4s5f$	09.88	-1.50x10^{-2}	3.99x10^{-4}	3.00x10^{-3}	0.903
4	$4s7s-4s5f$	15.48	-5.78x10^{-2}	2.43x10^{-4}	1.58x10^{-3}	0.929
$^3\Sigma^+_u$						
1	$4s6p-4s5d$	10.81	-1.32x10^{-2}	9.32x10^{-5}	2.81x10^{-3}	0.994
2	$4s6p-4s5d$	12.09	-1.21x10^{-2}	1.90x10^{-4}	2.31x10^{-3}	0.971
3	$4s5d-4s7s$	11.57	-1.06x10^{-2}	3.96x10^{-4}	2.84x10^{-3}	0.900
4	$4s5d-4s7s$	13.79	-7.66x10^{-3}	9.18x10^{-5}	1.78x10^{-3}	0.991
5	$4s5d-4s7s$	15.74	-5.49x10^{-3}	4.56x10^{-5}	7.43x10^{-3}	0.995
6	$4s7s-4s5f$	11.06	-8.53x10^{-3}	1.00x10^{-4}	1.18x10^{-3}	0.984

Fig. 1

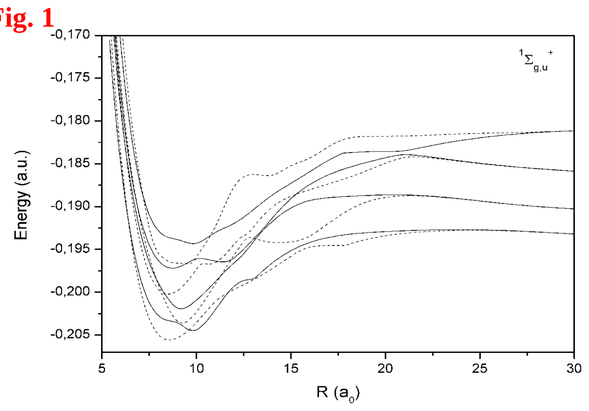


Fig. 2

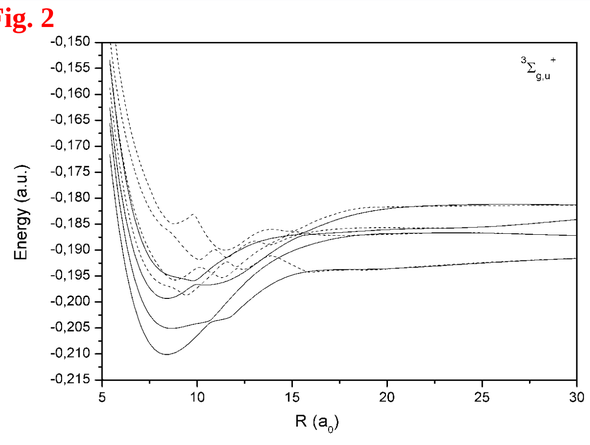
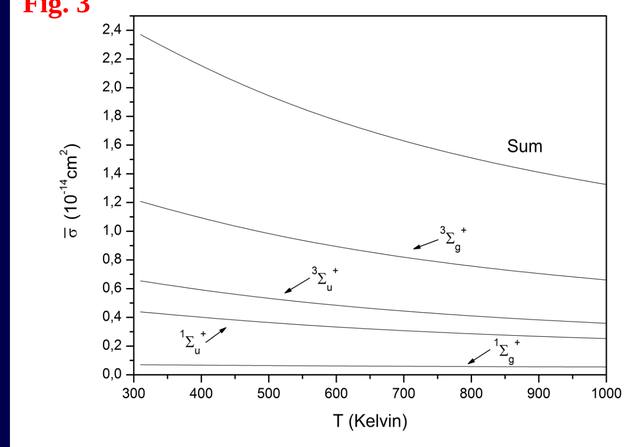


Fig. 3



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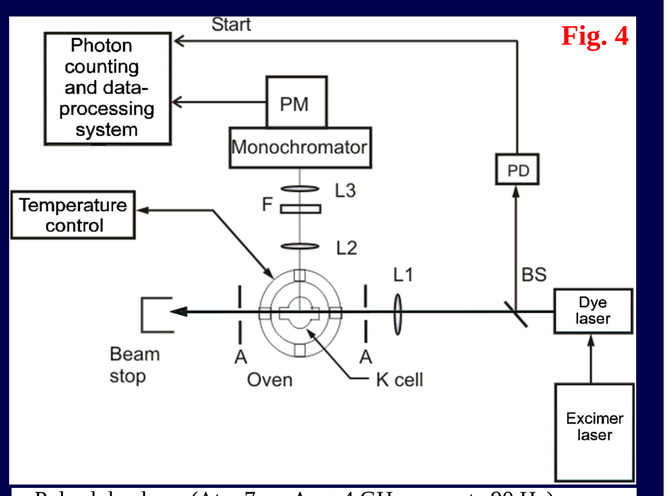
[2] Guldberg-Kjaer S, De Filipo G, Milosevic S, Magnier S, Pedersen JOP, Allegrini M. Reverse energy-pooling collisions: K(5D)+Na(3S) → K(4P)+Na(3P). Phys Rev A 1997; 55: R2515-8.
[3] Yurova IYu, Dulieu O, Magnier S, Masnou-Seeuws F, Ostrovskii VN. Structures in the long-range potential curves of Na2. II. Application to the semiclassical study of the energy pooling process between two excited sodium atoms. J Phys B 1994; 27: 3659-75.

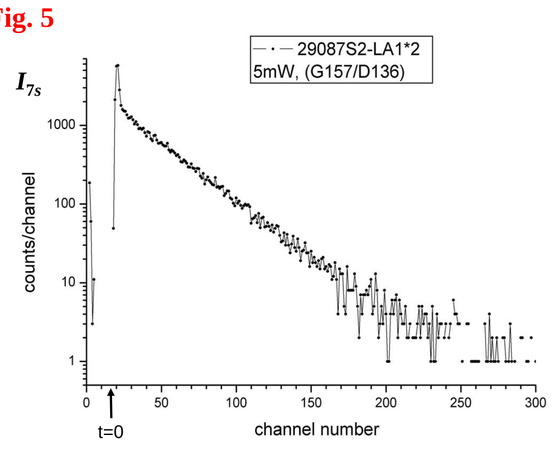
EXPERIMENT

Fig. 4



- Pulsed dye laser (Δ*t* = 7 ns, Δν = 4 GHz, rep rate 90 Hz)
- Cell made of alkali resistant Corning 1720 glass, filled with droplet of pure metal, two-fold magnetic shields, 5 thermocouples attached to the cell surface
- Oven: two-chambers with separately controlled temperatures
- Monochromator: horizontal slits, 1.5 mm wide, 6 nm resolution
- IR sensitive (S1) photomultiplier, QE = 0.3% (0.02%) for direct (sensitized) fluorescence, cooled down to 220 K; fast preamplifier
- Photon counters:
  (i) EG&G PAR 914P multichannel scaler (5 ns resolution)
  (ii) Stanford Research SR400 for auxiliary measurements
- PD fast photodiode, F filters, A apertures, L lenses, BS beam splitter
- Relative spectral sensitivity determined with callibrated tungsten-ribbon lamp

Fig. 5



Experimental I_{7s} *signal*

The potassium atoms in a glass vapour-cell were excited to the 7*s* state by short laser pulses (λ=660.4 nm) in the two-photon 4*s* →7*s* transition. The development in time of the direct-fluorescence I_{7s} and of the collisionally sensitized fluorescence I_{5f} was registered perpendicular to the laser beam, on the respective transitions: 7*s*→4*p* (λ_{7s}=579.2 nm) and 5*f*→3*d* (λ_{5f}=1102.1 nm), see **Fig. 4** and the **K energy level diagram**. The measurements were carried out for vapour temperature varied in the range of 428-451 K, which corresponded to the range of 9.2x10^{12}-3.5x10^{13} cm^{-3} of the number density N of potassium atoms. The upper limit for the acceptable laser-beam intensity was established as a value above which processes "interfering" with the 7*s*→5*f* transfer were evidenced. Under the assumption that 5*f* state is populated only by the direct 7*s*→5*f* collisional transfer (with the rate $R_{7s\rightarrow 5f}$), and that the 7*s* and 5*f* states' populations N_i decay with their respective effective rates Γ_{7s} and Γ_{5f} (each consisting of the decay rates due to: spontaneous decay, the total collisional quenching and the BBR induced transitions), the simple two rate-equation model (Eqs (1), (2)) represents the evolution in time of these populations (with no back-stream), see *e.g.*, [4]. Solutions of (2) with (1), under the initial conditions: $N_{7s}(t=0)= N_{7s}^0$, $N_{5f}(t=0)=0$, are a single- and a double-exponential functions for N_{7s} and N_{5f}, respectively. With these solutions for N_i and with the relation $I_i = A_{i\text{-}k} N_i$, where $A_{i\text{-}k}$ are Einstein coefficients (ECs), one obtains functions (1a) and (2a) for time dependence of intensities I_{7s} and I_{5f} to be fitted to the corresponding registered signals. The calibration factor ξ, for the spectral sensitivity of the system, is also introduced into (2a).

$$\frac{dN_{7s}}{dt} = -\Gamma_{7s} N_{7s} \quad (1) \qquad | \qquad I_{7s} = I_{7s}^0 e^{-\Gamma_{7s} t} \quad (1a)$$

$$\frac{dN_{5f}}{dt} = R_{7s\rightarrow 5f} N_{7s} - \Gamma_{5f} N_{5f} \quad (2) \qquad | \qquad I_{5f} = \xi \frac{A_{5f-3d}}{A_{7s-4p}} I_{7s}^0 \frac{R_{7s\rightarrow 5f}}{\Gamma_{5f}-\Gamma_{7s}} \left(e^{-\Gamma_{7s} t} - e^{-\Gamma_{5f} t} \right) \quad (2a)$$

In the framework of this model, the experimental values for $\sigma_{7s\rightarrow 5f}$ could be determined from the rates $R_{7s\rightarrow 5f}$ obtained by fitting (2a) to fluorescence signals from 5*f* state (**Fig. (6)**, blue curve) and by using the relation $\sigma_{7s\rightarrow 5f} = R_{7s\rightarrow 5f} / N\overline{\upsilon}$. ECs were taken from NIST data, values for I_{7s}^0 and for Γ_{7s} were obtained by fitting (1a) to experimental I_{7s} signals , like this in **Fig. 5** (in fitting a number of initial channels, in which a short "peak" was observed passed t=0, were skipped); values for Γ_{5f} were taken from our other experiment [6]. $R_{7s\rightarrow 5f}$ was the only free parameter of the fit.

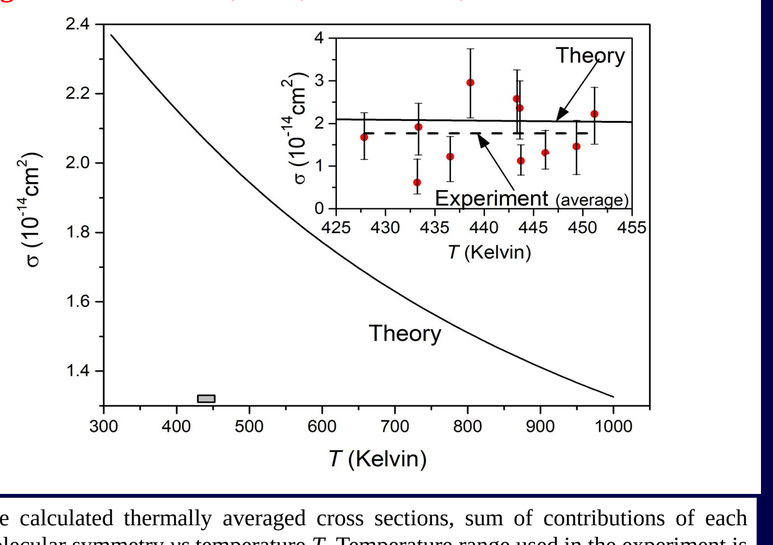
It turned out, that to get a more accurate reconstruction of the registered I_{5f} signals, additional processes should be considered Thus, additional population of the 5*f* state by ET from a short living state *X*, and by spontaneous emission from a long living state *Y* was assumed. (The latter was probably the 6*d* state; both were excited about t=0). In the revised model, two following double-exponential expressions were added to (2b)

$$I_{5f}^{(X)} = \alpha^{(X)} \left(e^{-\Gamma_X t} - e^{-\Gamma_{5f} t} \right) \Big/ \left(\Gamma_{5f} - \Gamma_X \right) \quad \text{and} \quad I_{5f}^{(6d)} = \alpha^{6d} \left(e^{-\Gamma_{6d} t} - e^{-\Gamma_{5f} t} \right) \Big/ \left(\Gamma_{5f} - \Gamma_{6d} \right).$$

Analysing the data, also those from various suplemental measurements, we found that, strong bursts of photons were generated along the laser beam just after 7s excitation at various wavelength (*e.g.*, due to observed in the literature, superradiant cascading and/or ASE. The 6*d* state could be then populated *e.g.*, *via* excitation of fast dissociating molecular states correlated with the asymptote 4s+6d. To identify the *X* state we refer to the earlier neglected short peak (**Fig. 5**). We attribute it to the abrupt depleting of 7*s* population due to the development of the first step of the cascade , and we assume the hypothetic fast (exponentially) decaying state *X*, which along with 7*s* contributes to collisional ET to 5*f* . Red curve in **Fig. 6** is the fitting result of this new revised model.

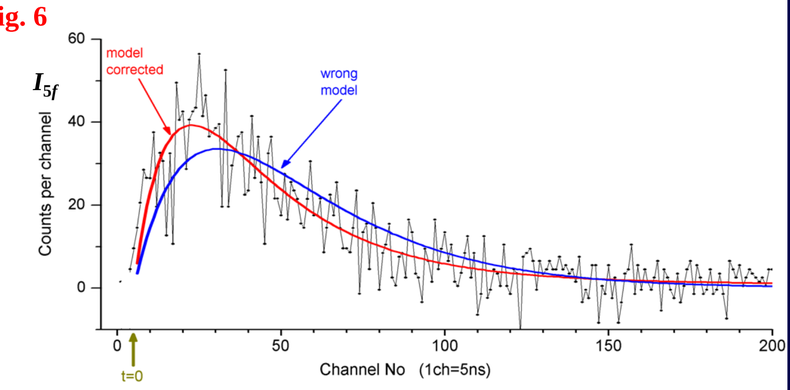
For more details see [6]

Fig. 7 Theory compared with experiment



The calculated thermally averaged cross sections, sum of contributions of each molecular symmetry *vs* temperature *T*. Temperature range used in the experiment is marked with gray bar over the *T*-axis.
Inset: The theoretical predictions in this range (full line) compared with the experimental values (red dots) with the dashed line marking their average.

Fig. 6



Comparison of curve fitting to experimental I_{5f} data, for a two-level (blue curve) and four-level (red curve) model

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[5] Głódź M, Huzandrov A, Safronova MS, Sydoryk I, Szonert J, Klavins J. Experimental and theoretical study of the *nf*-level lifetimes of potassium. Phys Rev A 2008; 77: 022503 pp. 8.
[6] Głódź M, Huzandrov A, Magnier S, Petrov L, Sydoryk I, Szonert J, Klavins J, Kowalski K. Energy transfer reaction K(4s) + K(7s) → K(4s) + K(5f), theory compared with experiment. arXiv:1801.00147v1 [physics.atom-ph] pp.1-16.