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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

(30 January - 24 February 1989)

ENERGY TRANSER COLLISIONS IN HETERONUCLEAR ALKAKI VAPORS

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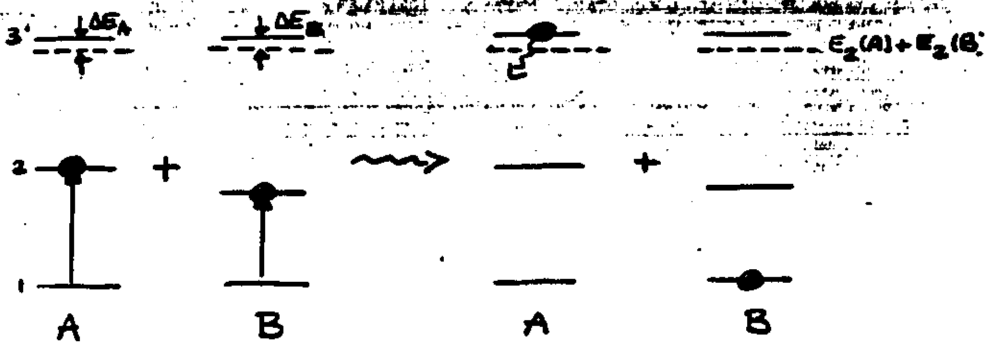
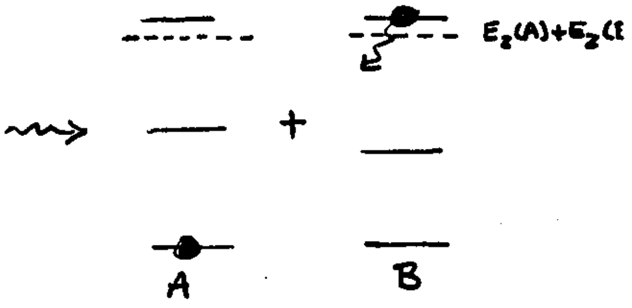
LECTURE II

- ENERGY TRANSFER COLLISIONS IN HETERONUCLEAR ALKALI VAPORS

COLLISIONS BETWEEN EXCITED ATOMS OF DIFFERENT SPECIES

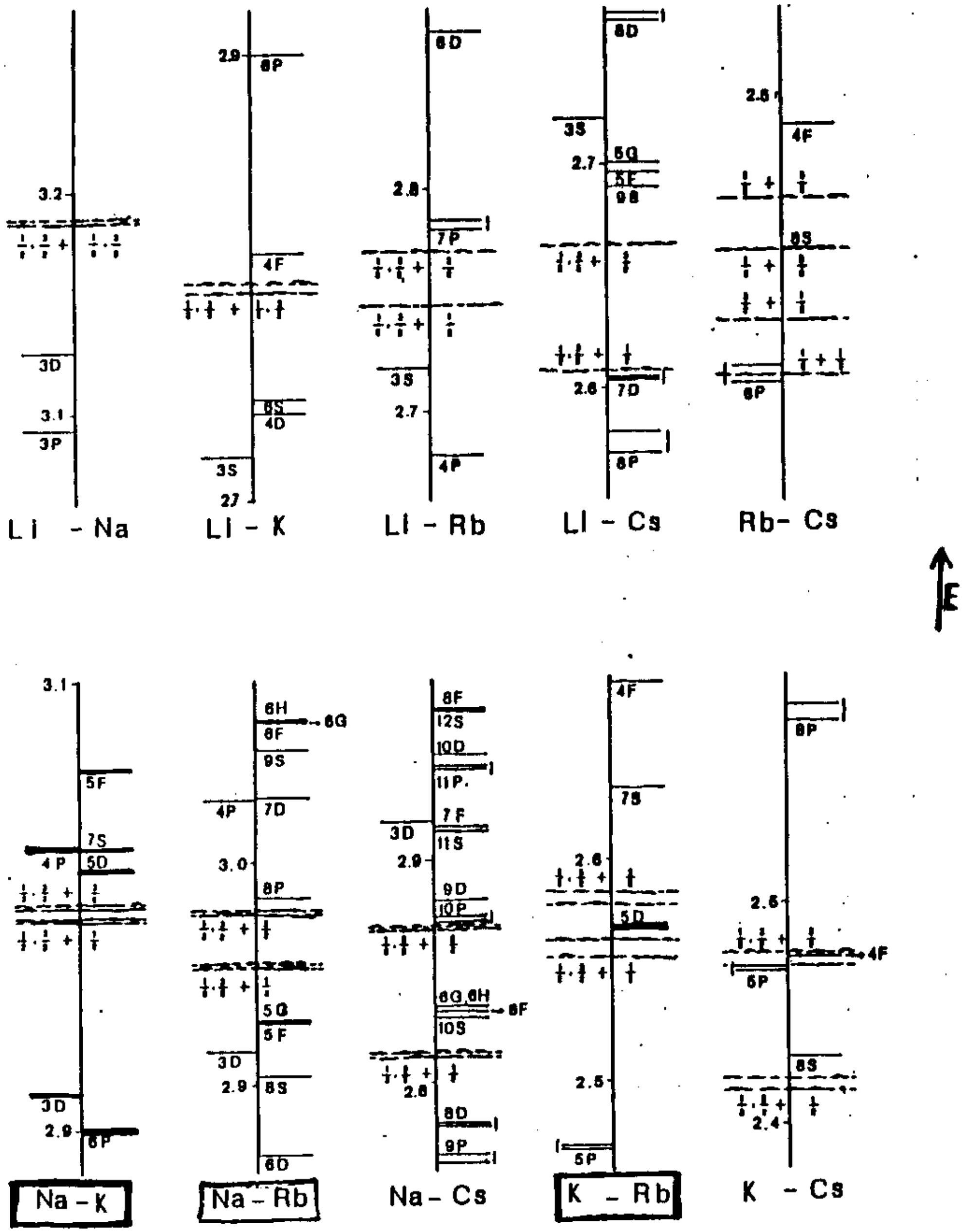




$$A^* + B^* \longrightarrow A^{**} + B$$
$$\longrightarrow A + B^{**}$$

TABLE 1. List of alkali levels with energy within 3kT to the sum energy of any possible $A(nP_I) + B(n'P_J)$. In each line first entry identifies the alkali species and level, second entry is the minimum energy difference ΔE in cm^{-1} between the four energy sums $A(nP_I) + B(n'P_J)$ and the level, third entry is ΔE expressed in unit of kT. kT is 363 cm^{-1} for row 1, 329 cm^{-1} for row 2, 294 cm^{-1} for row 3 and 259 cm^{-1} for row 4. This choice corresponds to T = 250°, 200°, 150° and 100° C respectively, an indicative temperature for which energy transfer in collisions between two excited alkali atoms in the first P level may be observable.

	Na	K	Rb	Cs
Li	Li(3D)/+577/+1.6 Li(3P)/+934/+2.6	Li(3S)/683/+1.9 K(6S)/+438/+1.2 K(4D/+491/+1.4 K(4F)/-181/-0.5 K(6P)/-1052/-2.9	Li(3S)/+277/+0.8 Rb(4F)/+691/+1.9 Rb(7P)/-114/-0.3 Rb(6D)/-967/-2.7	Li(3S)/ - 570/-1.6 Cs(8P)/+ 290/+0.8 Cs(7D)/+ 13/+0.04 Cs(9S)/- 274/-0.8 Cs(5F)/- 335/-0.9 Cs(5D)/-374/-1.0 Cs(9P)/-1001/-2.8
Na		Na(3D)/+768/+2.3 Na(4P)/-251/-0.8 K(6P)/+934/+2.8 K(6D)/-169/-0.5 K(7S)/-258/-0.8 K(5F)/-590/-1.8	Na(3D)/+362/+1.1 Na(4P)/-477/-1.4 Rb(6D)/+846/+2.6 Rb(8S)/+488/+1.5 Rb(5F)/+258/+0.8 Rb(5D)/+238/+0.7 Rb(8P)/-45/-0.1 Rb(7D)/-490/-1.5 Rb(9S)/-709/-2.2 Rb(6F)/-834/-2.6 Rb(6D)/-845/-2.6 Rb(6H)/-854/-2.6	Na(3D)/-467/-1.4 Cs(9P)/+452/+1.4 Cs(8D)/+311/+0.9 Cs(10S)/-149/-0.5 Cs(6F)/-178/-0.5 Cs(6D)/-195/-0.6 Cs(6H)/-204/-0.6 Cs(10P)/-21/-0.06 Cs(9D)/-123/-0.4 Cs(11S)/-424/-1.3 Cs(7F)/-442/-1.3 Cs(11P)/-698/-2.1 Cs(10D)/-763/-2.3 Cs(12S)/-960/-2.9
K			K(5P)/844/+2.9 Rb(5D)/- 79/-0.3 Rb(7S)/-452/-1.5	K(5P)/- 3/-0.01 Cs(8S)/-96/-0.3 Cs(4F)/+ 3/+0.01
Rb				Rb(6P)/- 35/-0.1 Cs(8S)/- 6/-0.02 Cs(4F)/-223/-0.9



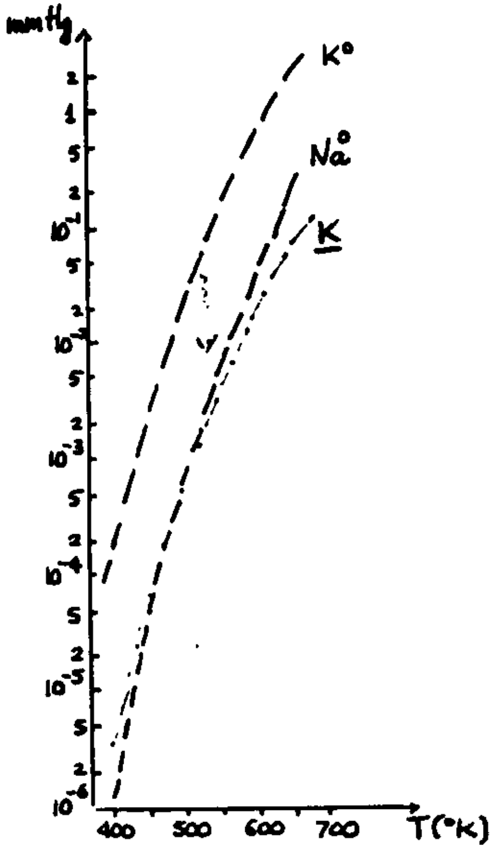
[redacted] – Energy configuration of alkali pairs of atoms A and B in proximity of

DIFFICULTIES :

1. MAKE ATOM DENSITY COMPARABLE FOR THE TWO ALKALI SPECIES
2. DISCRIMINATE CONTRIBUTIONS FROM PURE VAPOR COLLISIONS

   (Allegrini, Bicchi, Gozzini, Savino Opt. Comm. 36 443 (1981))
3. MEASURE EXCITED ATOM DENSITIES
4. MEASURE EFFECTIVE LIFETIMES

1. ATOM DENSITY in a MIXTURE of ALKALIS . Example Na - K 2.



P_A° , P_B° pressure of pure alkali

x_A , x_B molar fraction:

$P_A = x_A P_A^\circ$

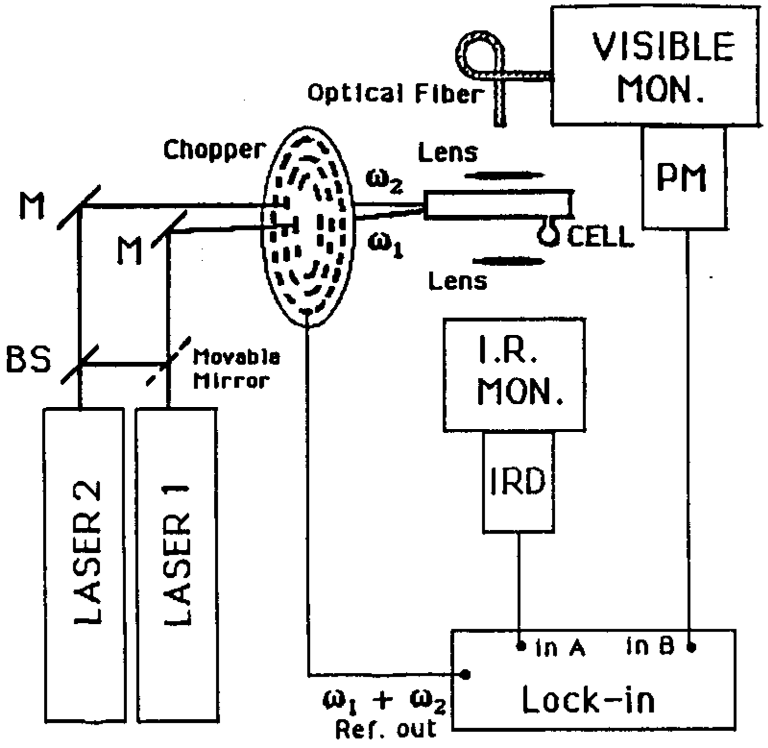
$P_B = x_B P_B^\circ$

$$x_A = \frac{\left(W(A)/M(A)\right)}{\frac{W(A)}{M(A)} + \frac{N(B)}{M(B)}} = \frac{x(A)}{x(A)+x(}$$

$$x_B = \frac{W(B)/M(B)}{\frac{W(A)}{M(A)} + \frac{W(B)}{M(B)}} = \frac{x(B)}{x(A)+x(}$$

W(A,B) alkali weigth in the cell

M(A,B) atomic weigth



For Na+K mixture :

$$\frac{[Na]}{[K]} = \frac{[Na]^\circ x_{Na}}{[K]^\circ x_K} = \frac{[Na]^\circ x(Na)}{[K]^\circ x(K)} \approx 1 \quad \Rightarrow$$

$W(Na) \approx 18\, W(K)$ at $T \simeq 500$ °K $[Na]^\circ \approx 6.6 \times 10^{-4}$ mmH

$[K]^\circ \approx 2.1 \times 10^{-2}$ mmH

MEASUREMENT of σ RELATIVE to ABSOLUTE σ of HOMONUCLEAR COLLISIONS

Example Na-K mixture

$$Na^*(3P) + K^*(4P) \longrightarrow Na(3S) + K^{**}$$
$$\longrightarrow Na^{**} + K(4S)$$

Rate equations $\dot{N}_j = -N_j \sum_{i \neq j} A_{ji} + k_j \left[Na(3P)\right]_{\omega_1} \left[K(4P)\right]_{\omega_2}$

$$Na^*(3P) + Na^*(3P) \xrightarrow{k_{5S},\, \sigma_{5S}} Na(3S) + Na(5S)$$

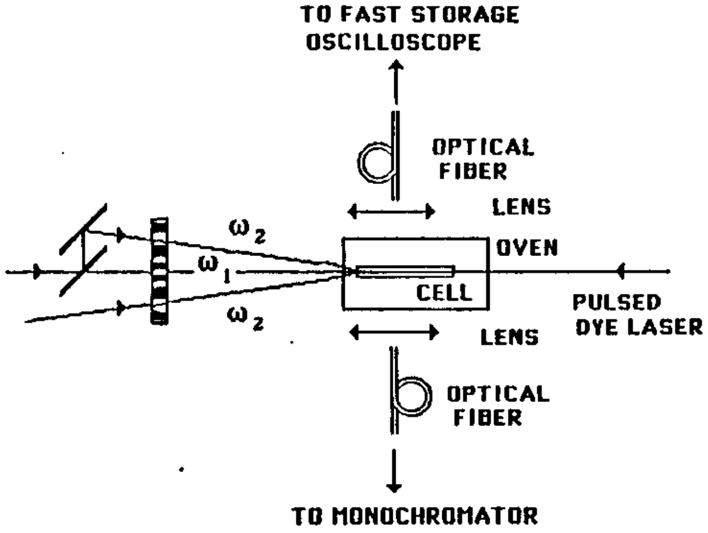
Rate equation $\dot{N}_{5S} = -N_{5S} \sum_{i \neq 5S} A_{5S,i} + k_{5S} \left[Na(3P)\right]_{\omega_1} \left[Na(3P)\right]_{\omega_1}$

Steady-state solution :

$$\frac{k_j}{k_{5S}} = \frac{\sum A_{ij}}{\sum A_{5S,i}} \cdot \frac{N_j}{N_{5S}} \frac{\left[Na(3P)\right]_{\omega_1}}{\left[K(4P)\right]_{\omega_2}}$$

$$I_{jk} = \alpha_{jk} h\nu_{jk} A_{jk} N_j \frac{V}{4\pi} \qquad \gamma_{jk} = \frac{A_{jk}}{\sum_{i \neq j} A_{ji}}$$

$$\frac{k_j}{k_{5S}} = \frac{\alpha_{5S-3P}}{\alpha_{jk}} \frac{\alpha_{4P-4S}}{\alpha_{3P-3S}} \frac{\nu_{5S-3P}}{\nu_{jk}} \frac{\nu_{4P-4S}}{\nu_{3P-3S}} \frac{\gamma_{5S-3P}}{\gamma_{jk}} \underbrace{\boxed{\frac{\tau_{3P}}{\tau_{4P}}}}_{\text{effective lifetimes}} \underbrace{\frac{I_{ij}}{I_{5S-3P}} \left[\frac{I_{3P-3S}}{I_{4P-4S}}\right]_{\omega_1}}_{\text{fluorescence intens. ratios}}$$



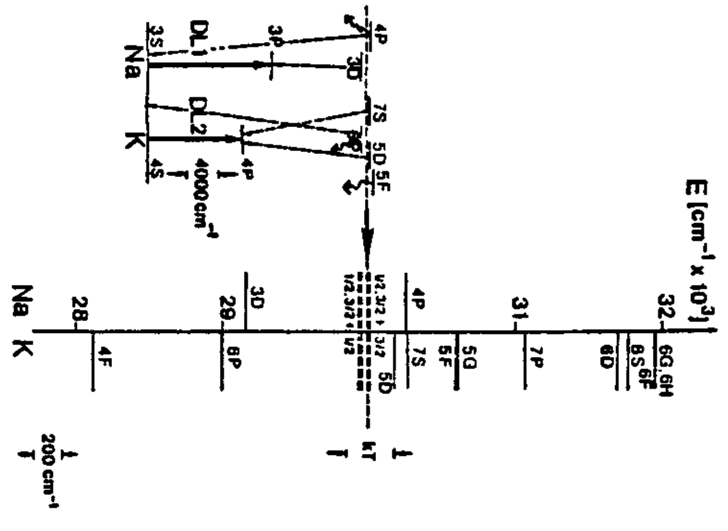


Fig. 1. Partial electronic energy level schemes of Na and K. Full arrows indicate laser excitations and broken arrows the observed transition lines. On the right side the levels of Na and K with energy close to E_T are reported in an expanded scale.

Table 1
List of levels populated by Na(3P)/K(4P) collisions with the main parameters. In the last column the measured cross sections at $T=240°C$ are reported

Atom	Level	ΔE (cm⁻¹)	Detected transition	Transition wavelength λ(Å)	γ	α	$\sigma\times10^{15}$ (cm²)
Na	3D	+768	$3D–3P_{1/2,3/2}$	8183–8195	0.83–1	0.017–0.014	1.4±0.7
	4P	−251	$4P_{1/2,3/2}–3S$	3302	0.60	0.39	
K	6P	+934	$6P_{1/2,3/2}–4S$	3446–3447	0.25	0.41	
	5D	−169	$5D_{3/2,5/2}–4P_{1/2,3/2}$	5812–5832	0.19	0.165	1.9±1.0
	7S	−258	$7S–4P_{1/2,3/2}$	5782–5802	0.18–0.36	0.165	0.9±0.5
	5F [a]	−590					

→ see ⑰

[a] No transitions have been detected from the 5F level because they are in the infrared where our apparatus is not sensitive.

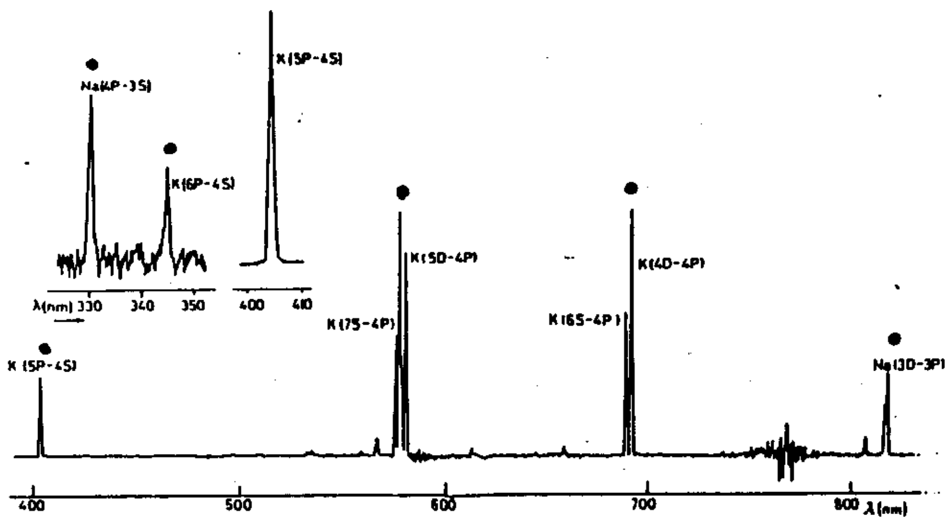
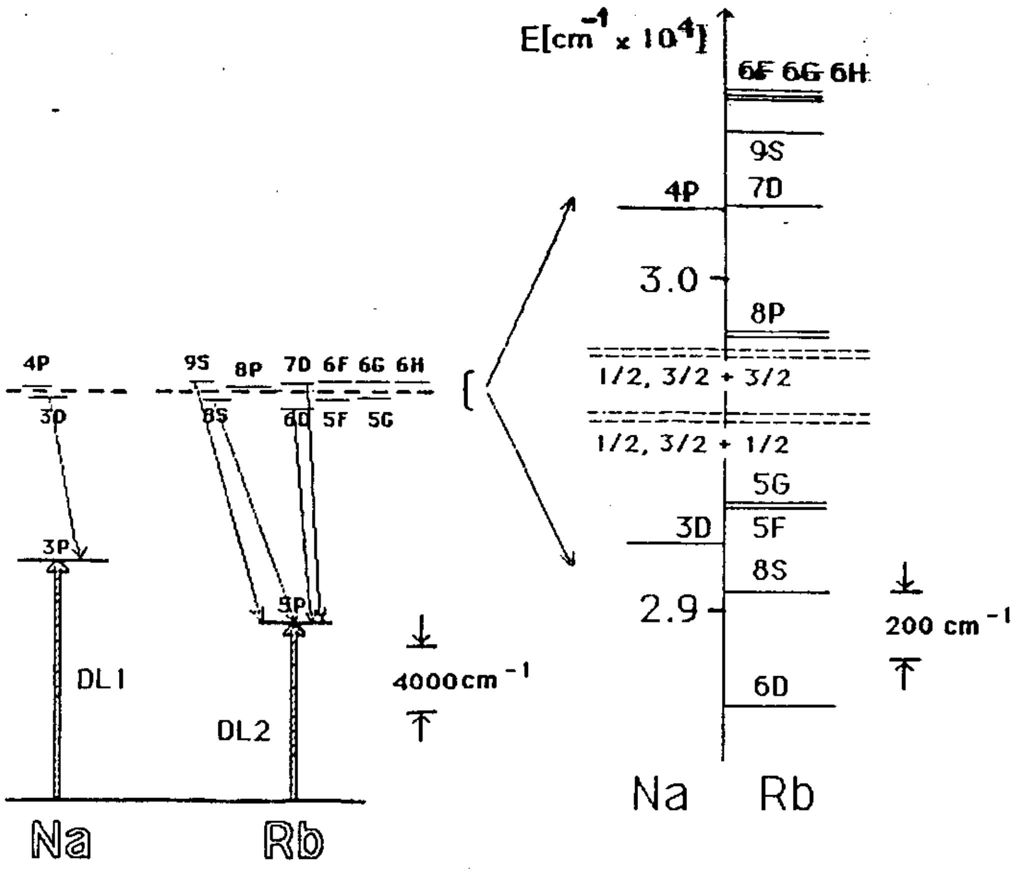


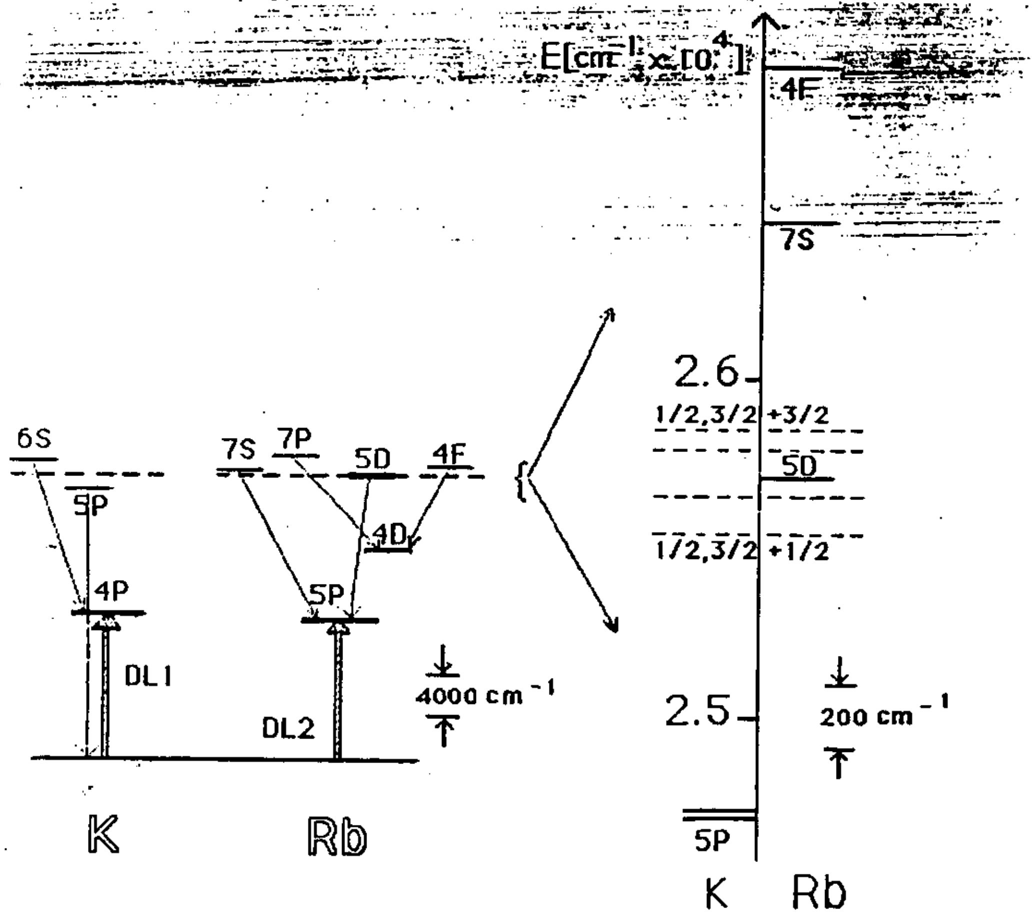
Fig.4 - Fluorescence spectrum obtained with intermodulated laser spectroscopy. The intensities of the lines are not corrected for the monochromator grating and photomultiplier efficiencies. The u.v. lines are partially absorbed by the cell glass and strongly affected by self trapping.

TABLE 2 . Relative rate constants evaluated according to eq. 11. The values of the used parameters are reported

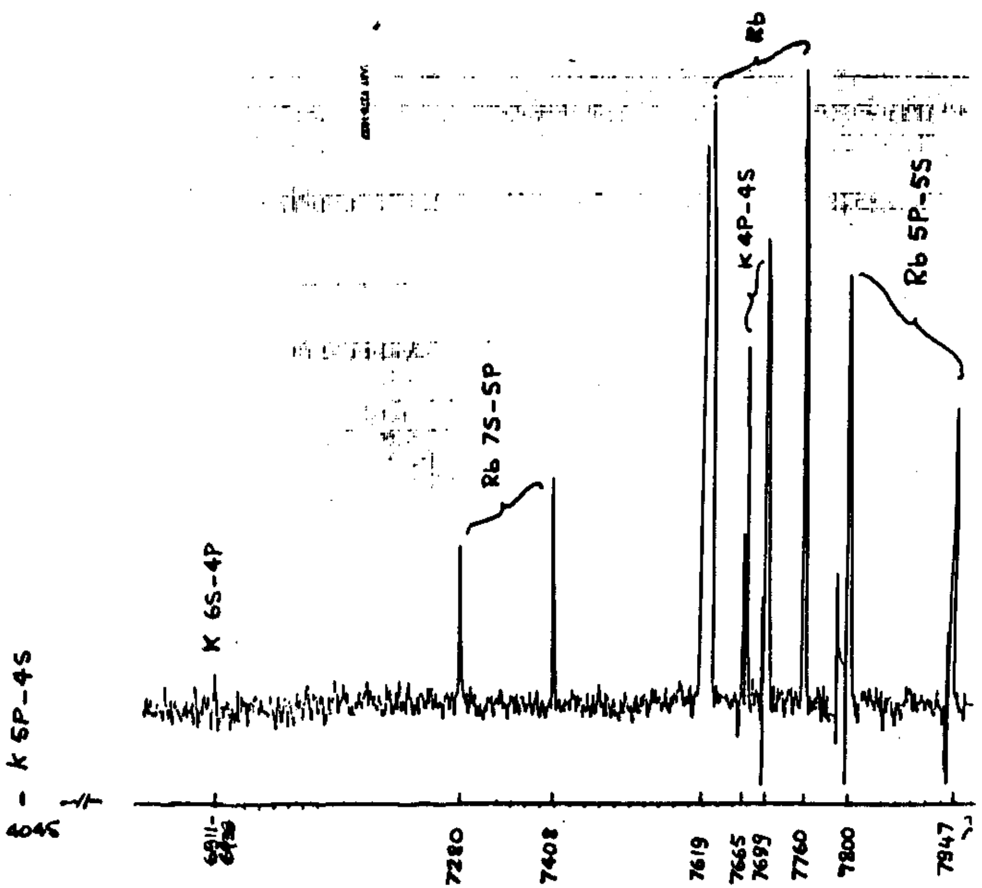
Atom	Level	Transition	$\lambda_{nL\to n'L'}$ (Å)	$\gamma^{-1}_{nL\to n'L'}$	$\alpha^{-1}_{nL\to n'L'}$ *	K/K_{7S}
K	7S	7S - $4P_{1/2}$	5782	.18	.165	1
		7S - $4P_{3/2}$	5802	.36	.165	1
	5D	5D - 4P	5822	.19	.168	2.1
	6P	6P - 3S	3446	.28	.41	~10-2 **
Na	3D	3D - $3P_{1/2}$	8131	.83	.017	1.6
		3D - $3P_{3/2}$	8195	1	.014	1.6
	4P	4P - 3S	3302	.60	.39	~10-2 **

* The coefficients are calculated for a Hamamatsu R 955 photomultiplier





K-Rb DOPPIA ECCITAZIONE IN INTERMODULAZIONE



K-Rb

DOPPIA ECCITAZIONE
IN INTERMODULAZIONE

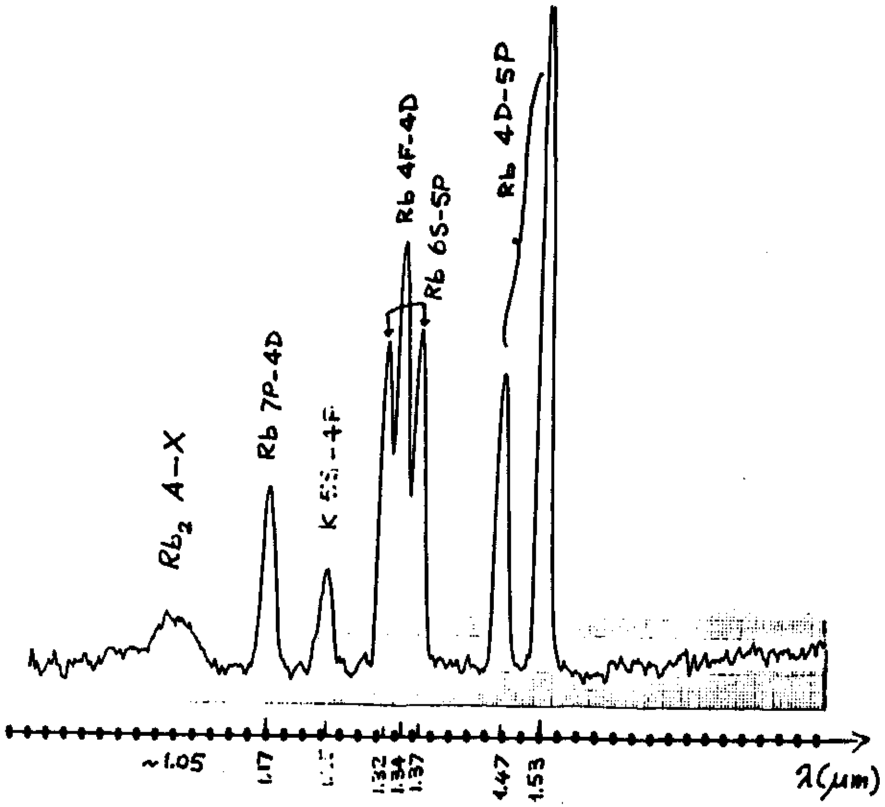


TABLE I. Characteristic parameters of the observed energy pooling transitions.

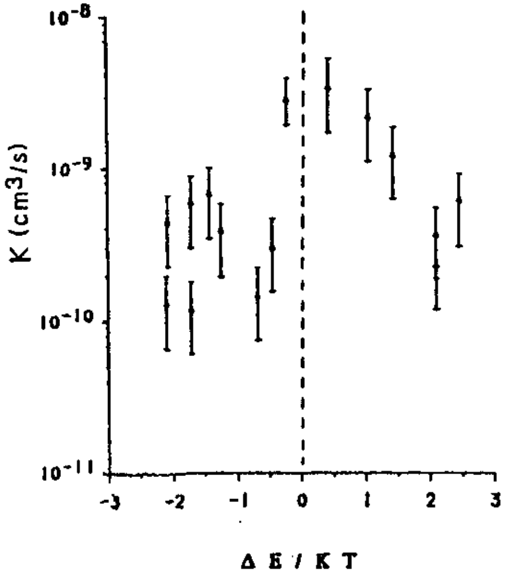
ATOM	LEVEL	ΔE (cm^{-1})	TRANSITION	λ (Å)	γ	τ (ns)
K	*5P	+1130	5P-4S	4045	0.26	
	*6S	-1591	$6S\text{-}4P_{1/2,3/2}$	6911-6940	0.59	
Rb	5D	+ 156	$5D\text{-}5P_{1/2,3/2}$	7619-7760	0.61	
	7S	- 452	$7S\text{-}5P_{1/2,3/2}$	7280-7408	0.59	
	*4F	- 910	4F-4D	13446	0.98	
	*7P	-2011	7P-4D	11744	0.15	
			Resonance Fluorescence			
K			$4P_{3/2}\text{-}4S$	7665		250±35
Rb			$5P_{3/2}\text{-}5S$	7801		300±45
Na	3D	+ 362	$3D\text{-}3P_{1/2,3/2}$	8183-8195	1	
Rb	8S	+ 488	8S-5P	6161	0.51	
	7D	- 490	7D-5P	5726	0.7	
	6D	+ 846	6D-5P	6300	0.75	
	9S	- 709	9S-5P	5655	0.47	
			Resonance Fluorescence			
Na			$3P_{3/2}\text{-}3S$	5890		200±30
Rb			$5P_{3/2}\text{-}5S$	7801		450±65

(*) The transitions marked by an asterisk have been observed only at higher temperature (T=240°C) and are not taken in consideration for the corresponding k calculations.

TABLE II. Available rate coefficients k and cross sections σ for energy transfer collisions in alkali systems.

SYSTEM	LEVEL	ΔE (cm^{-1})	T (^0C)	$k \times 10^{10}$ (cm^3s^{-1})	$\sigma \times 10^{15}$ (cm^2)	Ref.
Na-Na	5S	+716	210	3.8±1.3	4.0±1.4	[16]
	5S	+716	324	3.3±1.1	3.2±1.1	[17]
	4D	-602	210	6.0±2.1	6.4±2.1	[16]
	4D	-602	324	4.9±1.7	4.6±1.6	[17]
	4F	-642	250	1.2±0.6	1.2±0.6	[18]
Rb-Rb	5D	- 69	180	30±12	64 ±26	[14]
	7S	-678	180	1.3±0.6	2.8±1.4	this work
Na-K	3D(Na)	+768	240	2.4±1.2	2.8±1.4	[12]
	5D(K)	-169	240	3.2±1.6	3.8±1.9	[12]
	7S(K)	-258	240	1.5±0.7	1.8±0.9	[12]
K-Rb	5D(Rb)	+156	220	36±18	58±29	this work
	7S(Rb)	-452	220	4.0±2.0	6.4±3.2	this work
Na-Rb	3D(Na)	+362	200	23±12	31±16	this work
	8S(Rb)	+488	200	13±0.7	17±9	this work
	7D(Rb)	-490	200	7±4	9.4±4.7	this work
	6D(Rb)	+846	200	6.4±3.2	8.5±4.3	this work
	9S(Rb)	-709	200	4.5±2.3	6±3	this work

K and σ values corrected by a factor 2, according to the analysis of Bezuglov, Klucharev and Sheverev (19 about the difference between $<\begin{matrix}\text{CELL}\\ \text{BEAM}\end{matrix}$ experiments



THERMAL COLLISIONS $\Delta E \approx$ few kT

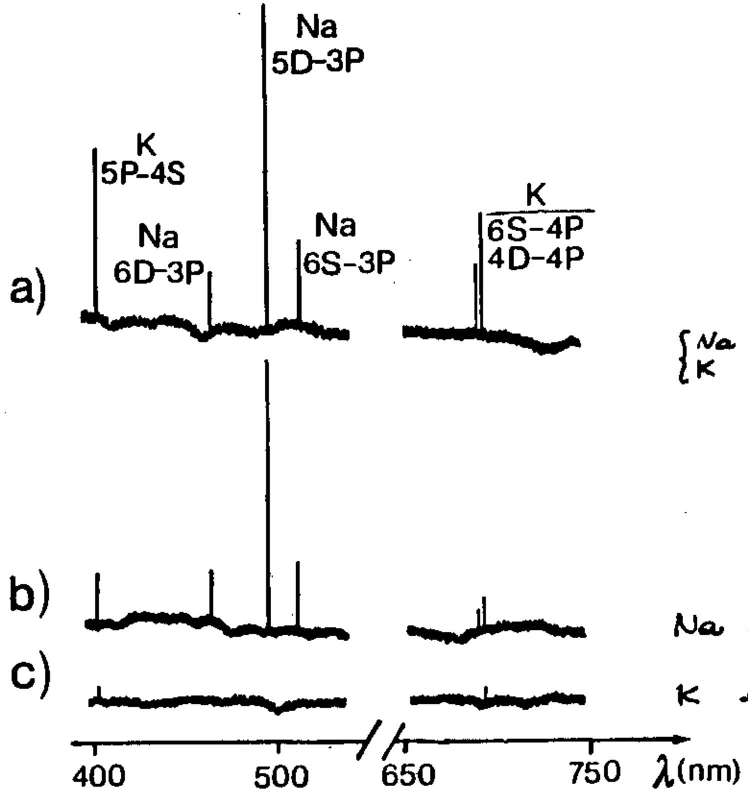
COLLISION TIME $\approx \dfrac{\text{ATOM DIMENSION}}{\text{THERMAL VELOCITY}} \approx 10^{-13}$ sec ⇝

CROSS SECTION σ FROM RATE EQUATION APPROACH

EXAMPLE SODIUM

$$\begin{cases} \sigma_{kin}(3P/3P) \approx 10^{-14}\ cm^2 \\ \sigma_{ET}(3P/3P) \approx 10^{-15}\ cm^2 \\ \sigma_{AI}(3P/3P) \approx 10^{-17}\ cm^2 \\ \sigma(3P/3P) \approx\ ? \end{cases}$$

Na-K BUFFER GAS EFFECTS



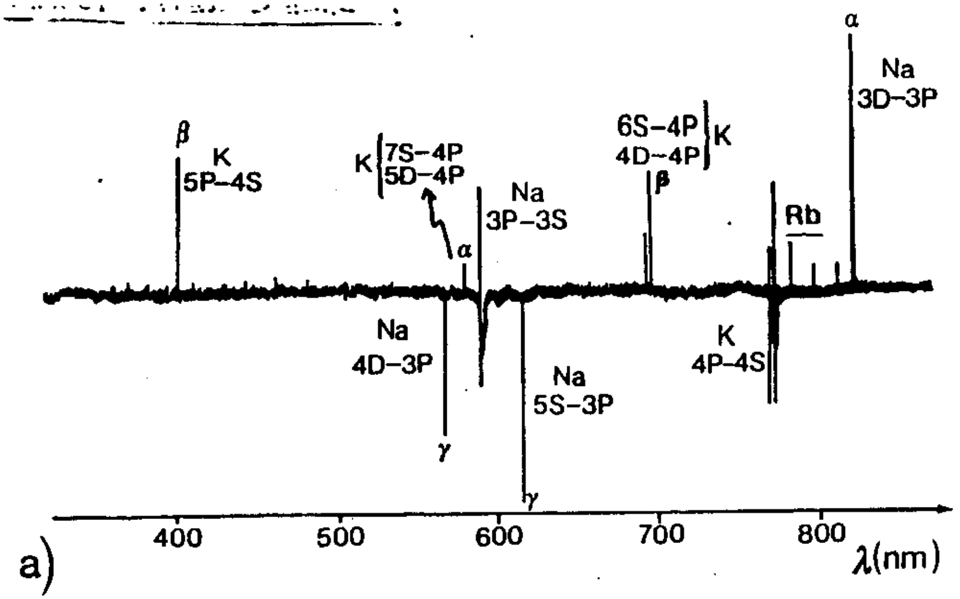
{ Na excitation +
K excitation

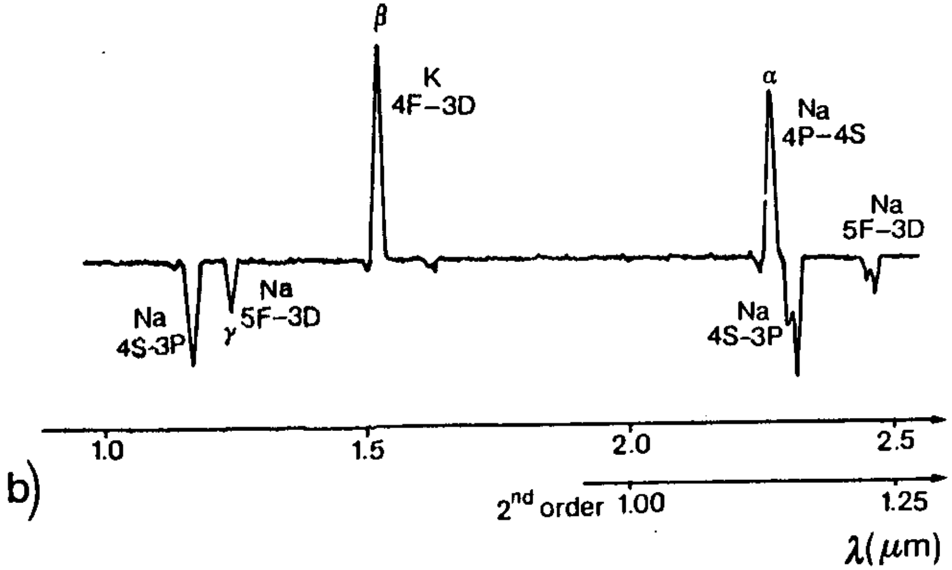
Na excitation only

K excitation only

K-lines more intense (~ 3 times) than the sum of the intensiti upon separate excitations
Na-lines do not change significantly
→ heteronuclear collisions responsible ⇝ detection through intermodulation technique.

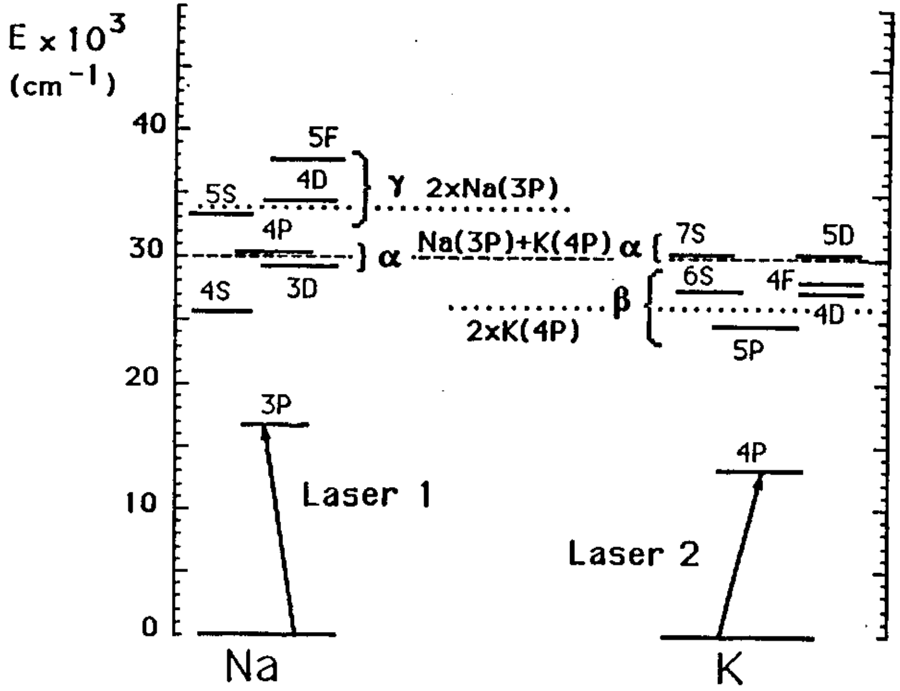
[illegible]





LEVELS α : $Na(3P) + K(4P) \longrightarrow Na^{**} + K(4S)$
$\longrightarrow Na(3S) + K^{**}$

LEVELS β : $K(4P) + K(4P) \longrightarrow K^{**} + K(4S)$



Two-body collisions (alkali/buffer gas) increase energy transfer among close levels of the same alkali ⇝ <u>do not</u> modify frequency modulation of the fluorescence ⇝ <u>do not</u> explain intermodulation spectrum.

Three-body collisions (important for gas pressure > 1 Torr

$$Na(3P) + K(4S) + \underbrace{\boxed{M}}_{\text{buffer gas}} \longrightarrow K(4P) + Na(3S) + \underbrace{\boxed{\Delta E}}_{\simeq 10kT}$$

Na(3P)/K(4S) coupling does modify modulation frequency ⇝ explain intermodulation spectrum.

Sodium modulated at ω_1
Potassium " " ω_2

$[Na(3P)] \propto A(1+\cos\omega_1 t)$
$[K(4S)] \propto B(1-r\cos\omega_2 t)$

A, B, r parameters depending on experimental conditions.

The collisions modify Na(3P) modulation ⇝

$$\underbrace{[Na(3P)]}_{\text{i.e. contains terms at the frequency } \omega_1 \text{ and } \omega_2 \text{ in opposition of phase.}} \propto AB(1\underbrace{\oplus}\cos\omega_1 t)(1\underbrace{\ominus}r\cos\omega_2 t)$$

$\Downarrow$

$[Na^{**}] \propto ([Na^*])^2$ has a term

$\propto (-\cos\omega_1 t \cdot \cos\omega_2 t)$ ⇝

gives signal at frequency $\omega_1 + \omega_2$ with the proper phase.

Z number of 3-body events per unit volume and unit time

n_1, n_2, n_3 densities of colliders

k_3 rate coefficient $[L^6 t^{-1}]$ dimensions

$\boxed{k_3 = \sigma_3 v_3}$ σ_3 three-body collision hyper-cross sect

$$v_3 = \frac{15\pi}{8}\sqrt{\frac{kT}{2\pi\mu_3}} \qquad \mu_3 = \sqrt{\frac{m_1 m_2 m_3}{m_1+m_2+m_3}}$$

$$\frac{dZ}{dt} = -k_3 n_1 n_2 n_3 = -k_3 [N][Na^*][K]$$

Ratio between the number of three-body and two-body collisions

$$R = \frac{k_3 N}{k_2}$$

N buffer gas density $\simeq 10^{17}\ cm^{-3}$

k_2 already measured $\approx 10^{-11}\ cm^3 s^{-1}$

Since in the experiment without buffer gas there is not evidence of γ-levels and relative intensity of β-levels is increased by a factor $\gtrsim 10$, we assume a lower value for

$R \approx 10 \div 100$ $\Longrightarrow$ lower limit for

$$k_3(Ne, Na, K^*) \approx 10^{-27}\ cm^6 s^{-1}$$

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OBSERVATION OF FLUORESCENCE FROM HIGH-LYING STATES OF POTASSIUM IN A SODIUM-POTASSIUM MIXTURE UPON RESONANT LASER EXCITATION

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Received 26 November 1980

Fluorescence from three of the highly excited states of K (6S, 5P, and 4D) has been observed in a mixed vapour of sodium and potassium upon irradiation of two cw dye lasers tuned to the D resonance lines of sodium and potassium. Processes that may populate these levels via $K^*(4P) + Na^*(3P)$ collisions are discussed.

1. Introduction

In the last few years interesting effects such as fluorescence from levels higher than the excited one [1–6] and partial or complete ionization [6–13] have been observed in the alkali vapours excited by cw or pulsed dye lasers to the first resonance P-levels [1, 3–8, 10–12] or to one of the higher levels [2,9,13]. The experiments have been performed in very different conditions, in a cell [1–9,13] or in a beam [10–12], with an atomic density varying between 10^{12} atoms/cm^3 and 10^{17} atoms/cm^3 and with a laser power density ranging from 10 W/cm^2 up to 10^8 W/cm^2. These extremely different cases are difficult to compare because many processes [8] are possible and compete with one another. Considerable efforts have also been made from a theoretical point of view [14–17], but an unified view of all the processes has not yet been reached.

In the aim of giving an useful contribution to a better understanding of these phenomena, we performed an experiment in a mixture of sodium and potassium whose results are reported in this letter.

2. Experimental results

The experiment was carried out with the experimental set up sketched in fig. 1. A cell containing sodium and potassium in two different bulbs and ~5 Torr of Ne was irradiated with two laser beams tuned to one of the resonance D-lines of K and Na respectively. The dye laser I, working with the dye Oxazine 1 Perchlorate, gave a maximum power of 200 mW on the D_2 or D_1 resonance lines of potassium (7665 Å and 7699 Å) over a spectral width of ~0.5 Å, corresponding, in the geometry of our experiment, to a maximum power density of ~10^2 W/cm^2. The dye laser II (spectral width ~0.2 Å and power ~40 mW),

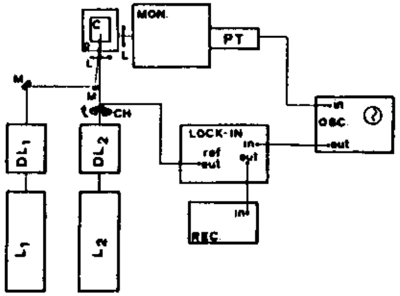

Fig. 1. Sketch of the experimental apparatus.

resonant with the sodium 3S → 3P transition, was modulated with a mechanical chopper driven by and locked to the lock-in amplifier used for the phase-sensitive detection, whilst the dye laser I was acting in cw regime. Since the effects observed were critically dependent upon the tuning over the resonance lines, it was suitable to use the standard etalons provided by the manufacturer that did not affect the laser power outputs. Moreover the experiment was very touchy and the two laser beams had to be very well aligned on the same spot of the cell.

The fluorescence spectra were obtained with the sample cell between 150°C and 200°C corresponding to 1.2×10^{13}–1.4×10^{14} K atoms/cm^3 and 1.8×10^{11}–3.6×10^{12} Na atoms/cm^3 [18]. We monitored the fluorescence emission of the alkali vapours at the modulation frequency of the beam exciting the sodium. Therefore with this kind of detection we picked-up only the levels populated through a process which involved Na excited atoms.

Besides the resonance D_2 and D_1 lines of both sodium and potassium we have observed fluorescence transitions of potassium from higher excited states, namely the 5P → 4S, the 6S → 4P and the 4D → 4P as shown in fig. 2a.

In fig. 3 the energy levels of both sodium and potassium are reported on the same scale and the transitions observed are indicated. The energy values 4P(K) + 4P(K) and 4P(K) + 3P(Na) are also shown. The experimental observations are listed below:

a) We observed only the three transitions indicated above, whilst the monochromator was scanned in the region of sensitivity of our apparatus (3400–8200 Å). In table 1 the observed potassium transitions are listed together with the energy differences, in units of kT at $T = 200°C$, between the upper level and twice the energy of the 4P potassium level or the upper level and the sum of the energies of the sodium 3P level and the potassium 4P level.

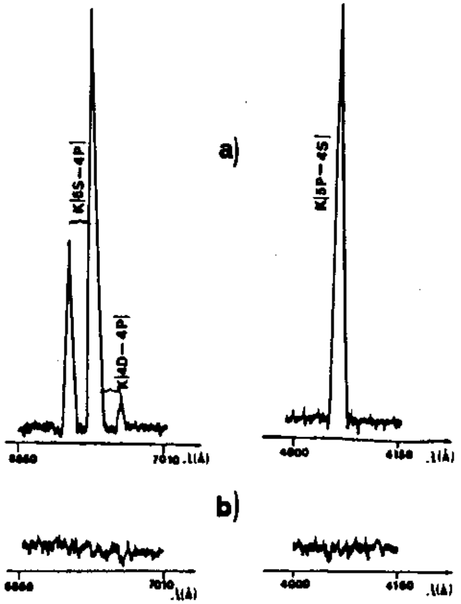

Fig. 2. a) Observed transitions of potassium by means of phase-sensitive detection upon cw excitation of the K-resonance D lines and modulated excitation of the Na resonance D lines. b) The same spectrum region as in a) with laser I off, or laser II detuned.

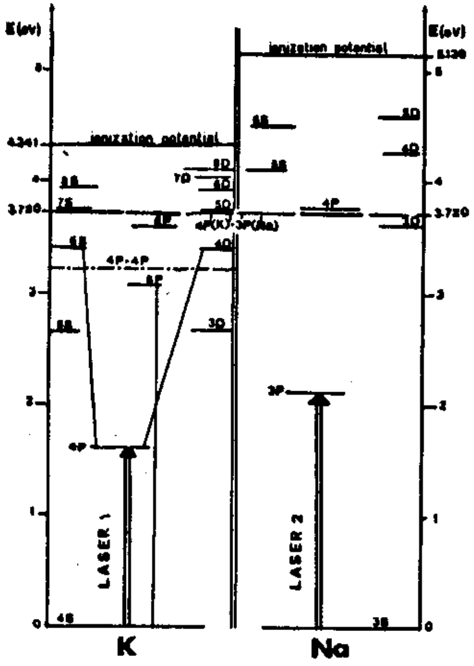

Fig. 3. Energy levels diagrams of sodium and potassium. The transitions of potassium observed at the modulation frequency of laser II are shown. The dashed curve indicates the electronic energy sum of the K(4P) and the Na(3P) atoms, whilst the dotted-dashed line indicates the electronic energy sum of two K(4P) atoms.

Table 1
Atomic transitions of potassium observed upon excitation of the D_2 resonant line of potassium and the D_2 resonance line of sodium. $T = 200°C$, $kT = 329$ cm^{-1}

Transition	Wavelength	Upper level	ΔE a)	ΔE' b)
5P–4S	4044–4047	$5P_{1/2;3/2}$	+4.2	+16.1
6S–4P	6911–6939	$6S_{1/2}$	−4.1	+ 7.8
4D–4P	6936–6965	$4D_{5/2;3/2}$	−4	+ 8

a) ΔE is the difference between twice the energy of a potassium 4P level and the upper level involved in the transition, expressed in units of kT.

b) ΔE' is the difference between the energy sum of a potassium 4P level and a sodium 3P level and the upper potassium level involved in the transition, expressed in units of kT.

b) If laser II was slightly tuned off the resonance sodium D_2 or D_1 lines or if laser I was off, the signal due to the 5P → 4S, 6S → 4P and 4D → 4P transitions disappeared (fig. 2b).

c) No fluorescence from the higher excited Na states was observed.

d) Resonance fluorescence of potassium was observed even in presence of the Na resonance excitation alone. If the K resonance excitation was added, the K resonance fluorescence signal, as observed through the lock-in amplifier, increased.

e) If the modulation was moved from the laser II to the laser I, Na resonance fluorescence was observed, surprisingly enough, even when only the D_K excitation was present. When the Na excitation was added, a more intense Na resonance fluorescence signal, of different sign, appeared. It showed that the result of an Na*(3P) and K*(4P) collision is a depopulation of the Na(3P) level.

3. Comments and conclusions

We discuss, first, what we observe in presence of both Na and K excitations. The experimental observations demonstrate that the process leading to the fluorescence from the higher levels of potassium is due to collisions that necessarily involve K atoms in the 4P state and Na atoms in the 3P state, eventually assisted by buffer gas atoms or alkali atoms in the ground state. The processes starting with a collision between the two excited atoms are several; those which may be thought of in our case are:

1) Direct electronic energy transfer in the form:

$$\mathrm{Na^*(3P) + K^*(4P) \rightarrow Na(3S) + K^{**}(5P, 6S, 4D)} + \Delta E\,.$$

2) Associative ionization followed by dissociative recombination:

$$\mathrm{Na^*(3P) + K^*(4P) \rightarrow NaK^+ + e^-}$$

$$\mathrm{\rightarrow Na(3S) + K^{**}(5P, 6S, 4D)}\,.$$

3) Laser induced ionization followed by recombination in the form:

$$\mathrm{Na^*(3P) + K^*(4P)} + h\nu \rightarrow \mathrm{Na(3S) + K^+ + e^-}$$

4) Associative ionization followed by dissociation:

$$\mathrm{Na^*(3P) + K^*(4P) \rightarrow NaK^+ + e^- \rightarrow Na(3S) + K^+ + e^-}\,.$$

We expected that in the process 1) the levels almost resonant with the sum energy of the colliding atoms Na*(3P) and K*(4P) should be the most populated whilst we have observed fluorescence from the 5P, 6S and 4D levels that have a large energy excess. For this reason we tend to exclude it. The second one is energetically possible being the bottom of the ground potential curve of the NaK$^+$ almost resonant with the sum energy Na*(3P) + K*(4P) [19]. It would explain the experimental results except for the increase in the K(4P) fluorescence when both D_{Na} and D_K excitations are present, compared with the K(4P) fluorescence when the D_K excitation is off. If this were the process, the result should be just the opposite. Moreover, it could be argued that the final result is the presence of potassium atoms in levels which lie well below the ground potential energy of the NaK$^+$ ion.

As to the two processes leading to the atomic ionization, it has been demonstrated that process (3) may be neglected for laser power densities $\leq 10^6$ W/cm^2 [12]. Process (4) could be responsible for the presence of the K$^+$ ion which would explain the main characteristics of our experimental results, except for the limited number of fluorescence transitions observed. Anyhow we would like to underline that some years ago Bearman and Leventhal [6], in a cell containing Na and K, observed K^+ as well as NaK^+ ions under the only excitation of one of the D lines of sodium. They didnot observe any KI radiation whilst we always observe the 4P → 4S potassium transition.

From this brief discussion it follows that none of the known processes can explain, by itself alone, all what we observed; there can be a combined contribution to the reported phenomena or a new process may be responsible for them. As to this, we suggest that during the collision between $Na^*(3P)$ and $K^*(4P)$ atoms, assisted by a K(4S) atom, a very highly excited quasi-molecular state of the K_2 dimer is formed and an almost immediate collisional dissociation follows; the latter should have two difference channels, namely:

$$\mathrm{Na}^*(3\mathrm{P}) + \mathrm{K}^*(4\mathrm{P}) + \mathrm{K}(4\mathrm{S}) \to \mathrm{K}_2^{**}$$

$$+\,\mathrm{Na}(3\mathrm{S})\ \begin{array}{l}\nearrow \mathrm{Na}(3\mathrm{S}) + \mathrm{K}^{**}(6\mathrm{S}, 5\mathrm{P}, 4\mathrm{D}) + \mathrm{K}(4\mathrm{S}) \\ \searrow \mathrm{Na}(3\mathrm{S}) + 2\mathrm{K}^*(4\mathrm{P})\end{array}$$

This process would indeed explain all our experimental results, the only point against it is that we have not any certain evidence of the K_2^{**} molecular fluorescence which should be expected. We may add that the formation of a quasi-molecular complex in a collision among excited atoms was already proposed by Hellfeld et al. [10].

To conclude, few words are to be said about what we observed when only one alkali species was excited. The K(4P) fluorescence monitored when only the D_{Na} excitation is present is to be ascribed to the well known "sensitized fluorescence" mechanism [20]:

$$\mathrm{Na}^*(3\mathrm{P}) + \mathrm{K}(4\mathrm{S}) \to \mathrm{Na}(3\mathrm{S}) + \mathrm{K}^*(4\mathrm{P}) + \Delta E$$

whilst the presence of Na fluorescence when only the K atoms are excited is quite surprising. It does not seem possible to appeal to the "sensitized fluorescence" in this case, as there is a too large lack of energy.

Acknowledgement

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ENERGY POOLING PROCESSES IN HETERONUCLEAR ATOM COLLISIONS

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ABSTRACT The energy pooling processes in heteronuclear alkali atom collisions are considered. They consist in the transfer of internal energy of one of the two excited colliding atoms to the other, thus resulting in a higher excitation of one species. All the atomic level configurations which may be favorable are listed with the involved energy defects. These are reported with their absolute values and in kT units. Finally the preliminary experimental results obtained for the sodium-potassium mixture are presented.

Introduction

Several collisional and radiative processes occur in vapors resonantly excited by laser radiation. Among these, great attention in the last decade has been devoted to excitation transfer in collisions between two alkali atoms excited to the first P resonance level, also called energy pooling collisions, namely:

$$A^* (nP_j) + A^* (nP_{j'}) \longrightarrow A^{**} (mL_{j''}) + A(nS_{1/2}) + \Delta E \tag{1}$$

A^* indicates an alkali atom in the first excited level with j and j' equal to 1/2 or 3/2, $A^{**} (mL_{j''})$ is a very excited atom in a level close to the sum energy of levels $nP_j + nP_{j'}$, $A(nS_{1/2})$ is the atom in the ground state and ΔE is the energy defect or excess involved in the collision. There are other exit channels to reaction (1) which are not considered here, but that have been extensively studied(1).

Since the collisions in process (1) are thermal, a proper way to describe the interaction between the excited A^* atoms is through the adiabatic potentials of the molecular complex $(A_2)^*$, connected to the $(nP_j + nP_{j'})$ dissociation limit. These molecular states are coupled by some terms of the total Hamiltonian to the other states connected to the limit dissociating into one very excited and one ground state atom. Transitions among these different electronic states occur at large interatomic distances and their positions are identified by the crossing points in the diabatic terms or by the avoided crossings in the adiabatic terms. Subsequent dissociation of the diatomic complex $(A_2)^*$ gives the atomic fragments of the exit channel of process (1). The highly excited state $A^{**} (mL_{j''})$ is then easily identified through fluorescence emission to lower states.

Observation of this phenomenon was first reported in sodium vapor(2) in which binary collisions between two 3P excited atoms produce atoms in the 5S, 4D and 4F levels. Similar results have been obtained in cesium(2), potassium(3) and rubidium(4), however the major experimental work has been done in sodium. For this vapor the rate coefficients K_{mL} (or the cross section σ_{mL}) for the process (1) have been measured in several laboratories. The common base to these experiments is the detection of the fluorescence from the collisional populated $mL_{j''}$ levels and the comparison to the resonance fluorescence nP-nS.

A rate equation approach to the problem is valid and the solution is relatively simple when the experimental conditions are chosen in such a way that energy transfer process (1) dominates over the other processes. In this case it is easy to find

$$K_{mL} = \langle \sigma_{mL} v \rangle = N_{mL} \frac{A_{mL \to m'L'}}{N_{nP}^2} \nu_{mL \to m'L'} \tag{2}$$

where v is the atomic velocity, N_{mL} is the population of level mL, N_{nP} is the population of the laser excited nP level, $A_{mL \to m'L'}$ is the transition probability from level mL to the m'L' lower level. $\nu_{mL \to m'L'}$ represents the inverse of the branching ratio of the considered transition.

$\gamma_{mL \rightarrow m'L'}$ is written as

$$\gamma_{mL \rightarrow m'L'} = 1 + \sum_{m''L'' \neq m'L'} \frac{A_{mL \rightarrow m''L''}}{A_{mL \rightarrow m'L'}} \tag{3}$$

It is worth noting that K_{mL} depends upon the square of the excited atom density N_{np} which therefore must be determined with great accuracy. In terms of the fluorescence intensities measured in the experiments eq.(2) may be written as

$$K_{mL} = \alpha_{mL \rightarrow m'L'} \; \gamma_{mL \rightarrow m'L'} \; \frac{\omega_{nP \rightarrow nS}}{\omega_{mL \rightarrow m'L'}} \; \frac{1}{N_{nP} \; \tau_{nP}} \; \frac{I_{mL \rightarrow m'L'}}{I_{nP \rightarrow nS}} \tag{4}$$

where $\alpha_{mL \rightarrow m'L'}$ is a factor which takes into account the efficiency and calibration of the detection apparatus and τ_{nP} is the effective lifetime of the nP level in presence of radiation trapping.

Different experimental approaches have been used to measure both N_{nP} and τ_{nP} (6-9), and K_{mL} values have been reported for all the expected levels in sodium. Reasonable good agreement exists between experimental and theoretical cross sections (10), so that a check of the potential energy curves at long interatomic distances has been made possible.

Even if the measurements concerning the alkali homonuclear collisions are not completed, we are now considering an extension of studies to energy pooling collisions in alkali mixtures for which there are no available informations and for which very interesting level configurations exist. In the next paragraph the minor modifications of the given rate equations necessary to describe the new process will be introduced.

Collisions between two different excited alkali atoms - Heteronuclear collisions

A mixture of two alkali vapors of species A and B is resonantly excited to the first P level of each species by two lasers (see fig.1).

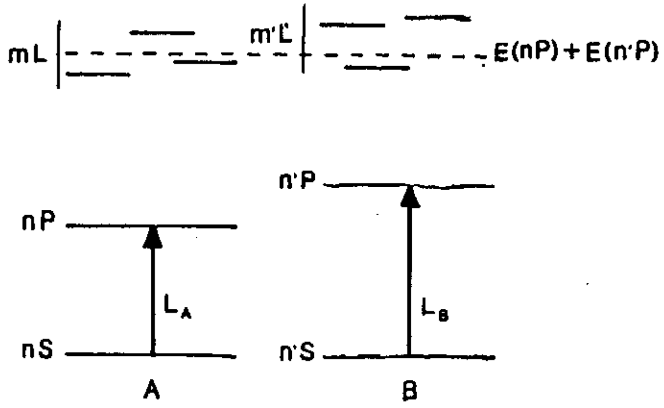

Fig.1 - Sketch of the level schemes for A and B atoms.
L_A and L_B = lasers resonant with A and B atoms respectively.

The excited atoms undergo many collisional processes: the aim of the experiment is to detect the fluorescence from the atomic levels of both atoms A and B populated by the collision

$$A^{*}(nP_j) + B^{*}(n'P_{j'}) \begin{cases} A^{**}(mL) + B(n'S_{1/2}) + \Delta E' \\ A(nS_{1/2}) + B^{**}(m'L') + \Delta E'' \end{cases} \tag{5}$$

where $\Delta E'$, $\Delta E''$ are the energy defects or excesses. In reaction (5) the total energy can be stored by one atomic species or by the other one originating, with respect to the homonuclear collisions, a more complex and rich situation.

We have considered all the ten possible alkali pair combinations $A^{*} + B^{*}$ with A,B ≡ Li, Na, K, Rb and Cs. Table 1 identifies the candidate levels for energy pooling; a convenient way to consider these levels is according to their energy defect or excess ΔE expressed in unit of kT. The reason for this is that the temperature for which vapor density is high enough to allow observation of energy pooling collisions is different for each alkali species. We have then chosen an indicative vapor density ($\simeq 10^{12}$ cm^{-3}) which determines the temperature for each alkali mixture by considering the "hardest" of the two metals. In the table we restricted the analysis to the levels lying within ± 3kT, that is an energy easily supplied during the collision.

TABLE 1. List of alkali levels with energy within 3kT to the sum energy of any possible $A(nP_j) + B(n'P_j)$. In each line first entry identifies the alkali species and level, second entry is the minimum energy difference ΔE in cm^{-1} between the four energy sums $A(nP_j) + B(n'P_j)$ and the level, third entry is ΔE expressed in unit of kT. kT is 363 cm^{-1} for row 1, 329 cm^{-1} for row 2, 294 cm^{-1} for row 3 and 259 cm^{-1} for row 4. This choice corresponds to T = 250°, 200°, 150° and 100° C respectively, an indicative temperature for which energy transfer in collisions between two excited alkali atoms in the first P level may be observable.

	Na	K	Rb	Cs
Li	Li(3D)/+577/+1.6 Li(3P)/+934/+2.6	Li(3S)/683/+1.9 K(6S)/+438/+1.2 K(4D/+491/+1.4 K(4F)/-181/-0.5 K(6P)/-1062/-2.9	Li(3S)/+277/+0.8 Rb(4F)/+691/+1.9 Rb(7P)/-114/-0.3 Rb(6D)/-967/-2.7	Li(3S)/-570/-1.6 Cs(8P)/+290/+0.8 Cs(7D)/+13/+0.04 Cs(9S)/-274/-0.8 Cs(5F)/-335/-0.9 Cs(6G)/-374/-1.0 Cs(9P)/-1001/-2.8
Na		Na(3D)/+760/+2.3 Na(4P)/-251/-0.8 K(6P)/+934/+2.8 K(6D)/-169/-0.5 K(7S)/-258/-0.8 K(6F)/-590/-1.8	Na(3D)/+362/+1.1 Na(4P)/-477/-1.4 Rb(6D)/+846/+2.6 Rb(8S)/+488/+1.5 Rb(5F)/+258/+0.8 Rb(5G)/+238/+0.7 Rb(8P)/-45/-0.1 Rb(7D)/-490/-1.5 Rb(9S)/-709/-2.2 Rb(6F)/-834/-2.6 Rb(6G)/-845/-2.6 Rb(6H)/-854/-2.6	Na(3D)/-467/-1.4 Cs(9P)/+452/+1.4 Cs(8D)/+311/+0.9 Cs(10S)/-149/-0.5 Cs(6F)/-178/-0.5 Cs(6G)/-195/-0.6 Cs(6H)/-204/-0.6 Cs(10P)/-21/-0.06 Cs(9D)/-123/-0.4 Cs(11S)/-424/-1.3 Cs(7F)/-442/-1.3 Cs(11P)/-698/-2.1 Cs(10D)/-763/-2.3 Cs(12S)/-960/-2.9
K			K(5P)/844/+2.9 Rb(5D)/-79/-0.3 Rb(7S)/-452/-1.5	K(5P)/-3/-0.01 Cs(8S)/-96/-0.3 Cs(4F)/+3/+0.01
Rb				Rb(6P)/-35/-0.1 Cs(8S)/-6/-0.02 Cs(4F)/-223/-0.9

In fig.2 we report for each pair the levels A^{**}/B^{**} which are expected to be populated by process (5).

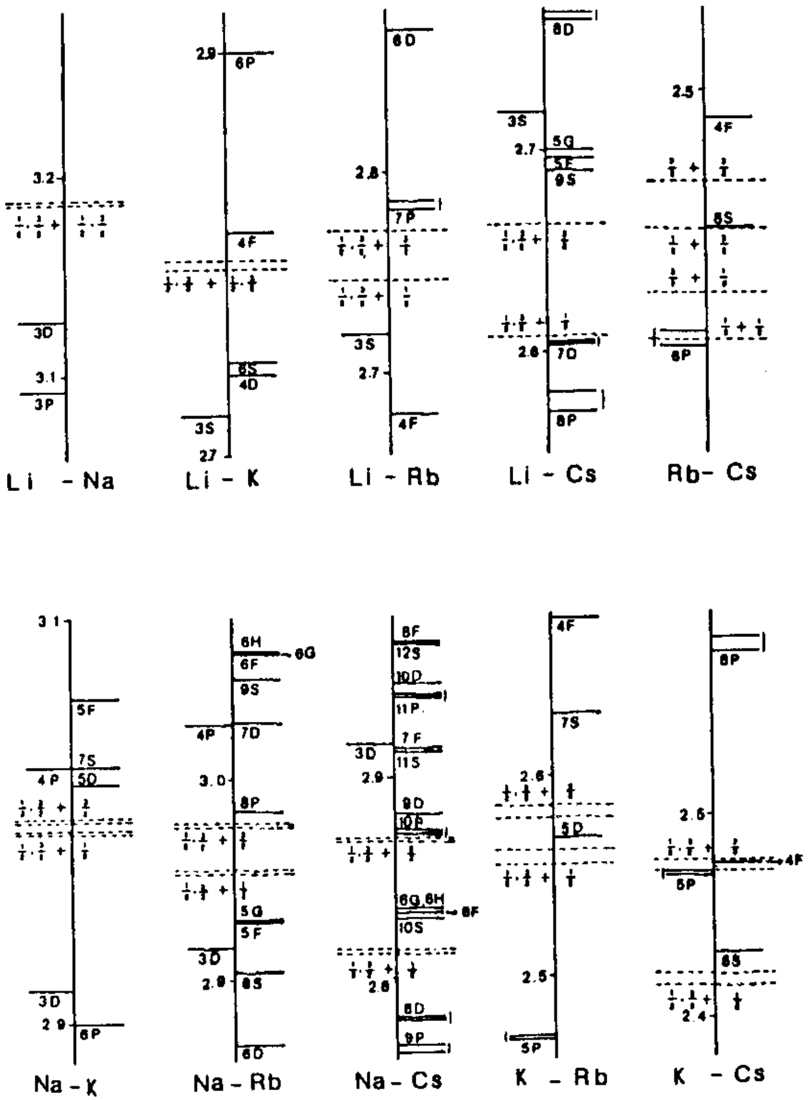

Fig.2 - Energy configuration of alkali pairs of atoms A and B in proximity of $E(A^*) + E(B^*)$.
The vertical scale represents the energy expressed in $cm^{-1} \times 10^{-4}$.

The dashed lines in each graph of fig.2 represent the energy positions of $A^*(nP_j) + B^*(n'P_{j'})$ for j, j' = 1/2, 3/2; levels A^{**} and B^{**} are restricted to those of table 1.

Among all the possible pairs considered there are about sixty highly excited states which are candidate to be populated by process (5) and from which fluorescence emission could be detected in different regions of the electromagnetic spectrum. We believe of particular interest some levels (as for example Cs(10S) in Na-Cs mixture or K(5P) in K-Cs mixture) which lie between the energy positions of $A^*(nP_j) + B^*(n'P_{j'})$ combinations. Behaviour of the fluorescence from these levels may give complete informations on the collisional transfer processes.

A set of rate equations can be written for each alkali couple in order to derive the rate constants of the levels populated through reaction (5). For a given nL level the population evolution is given by

$$N_{mL} = \langle \sigma_{mL} v \rangle \; N^A_{nP} \, N^B_{n'P'} - N_{mL} \sum A_{mL \to m'L'} \tag{6}$$

where N^A_{nP} and $N^B_{n'P'}$ represent the densities of the A and B excited atoms. In steady state regime $N_{mL} = 0$ and therefore

$$K_{mL} = \langle \sigma_{mL} v \rangle = \frac{N_{mL}}{N^A_{nP} \, N^B_{n'P'}} \sum A_{mL \to m'L'} \tag{7}$$

By introducing the fluorescence intensities of the detected lines and the corresponding ν_{mL} we have

$$K_{mL} = \langle \sigma_{mL} v \rangle = C \, \frac{\alpha_{mL \to m'L'} \; \nu_{mL \to m'L'}}{\tau^A_{nP} \; \tau^B_{n'P}} \; \frac{\omega^A_{nP \to nS} \, \omega^B_{n'P \to n'S} \; I_{mL \to m'L'}}{\omega_{mL \to m'L'} \; I^A_{nP \to nS} \; I^B_{n'P \to n'S}} \tag{8}$$

where $\alpha_{mL \to m'L'}$ is a factor taking into account the instrumental response and efficiency. C is a normalizing factor which contains the volume of emission.

As regards experiments dealing with pure alkali vapors there are immediately two problems: to discriminate the population of levels A^{**} and B^{**} coming from energy transfer collisions between atoms of the same species $A^* + A^*$ and $B^* + B^*$ and to detect weak signals hidden among the very intense fluorescence produced by the two resonant lasers. We will present in the next paragraph an experimental method which has solved these problems in a specific experiment on sodium plus potassium. Finally in order to measure the cross section of (5) both densities N_A and N_B of the excited atoms have to be measured, a serious experimental difficulty in a vapor mixture where any simple relation temperature/vapor density is cancelled out.

Preliminary results on Na-K energy pooling collisions

The Na-K mixture has been chosen to get the first results in the heteronuclear energy pooling collisions because the corresponding homonuclear reactions have been already studied and the mixture properties as function of the temperature and of the relative concentration have been analyzed in previous experiments(11). The experimental apparatus is shown in fig.3. Two c.w. lasers, respectively tuned to the D lines of sodium and potassium (the Na resonant laser is a single mode one) are superimposed on the entrance window of a pyrex cell containing a 90% Na and 10% K amalgam. This particular mixture has been chosen to have the two densities very close to each other by assuming the Raoult law

$$P_{A,B} = \frac{n_{A,B}}{n_A + n_B} \; P^0_{A,B} \tag{9}$$

where $n_{A,B}$ is the molar concentration of the two alkalis and P^0 is the pressure of the pure vapor. This expedient is always necessary in the alkali mixtures because of the large difference between the vapor pressures of the two species at a given temperature. For example pure potassium has typically a vapor pressure 100 times higher than that of pure sodium.

The collision cell is placed in an oven in which the temperature is varied between 200 and 240 °C. The atomic fluorescence is collected at right angle, analyzed by a monochromator and detected by a photomultiplier Hamamatsu R955. The fluorescence coming from the laser excited P levels is order of magnitude higher than that originated by the collisions. This scattered light produces a very high background which may hide the signals, especially if the sensitized fluorescence has a wavelenght close to the D lines, that is the case for the 7S-4P and 5D-4P transitions of potassium (see tab.2). To reduce this effect a sodium disk-shaped cell has been placed in the oven between the collision cell and the monochromator.

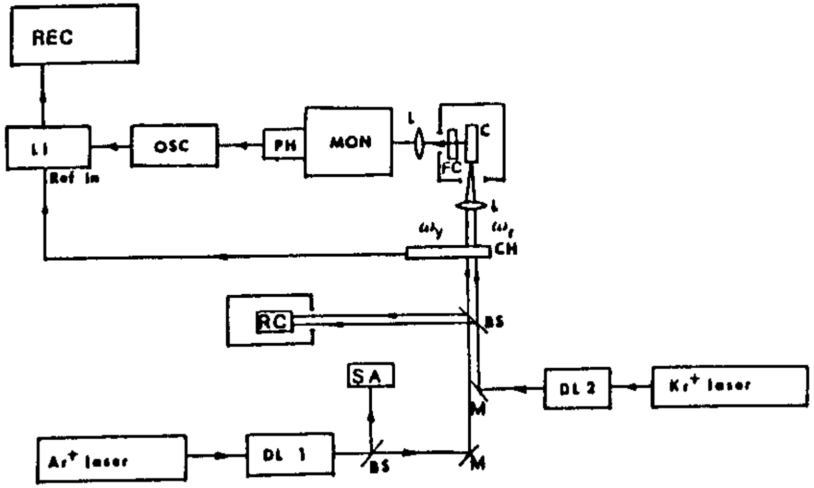

Fig.3 - Sketch of the experimental apparatus.
DL 1, DL 2= dye lasers; M = mirror; BS = beam splitter; L = lens;
C = cell; RC = reference cell; FC = filter cell; CH = chopper;
SA = spectrum analyzer; MON = monochromator; PH = photomultiplier;
OSC = oscilloscope; LI = lock-in; REC = recorder.

To discriminate the fluorescence produced by reaction (5) from that coming from other processes the intermodulated spectroscopy method has been used. The two lasers are modulated at two different frequencies ω_y and ω_r and the detection is made at the sum frequency $\omega_s = \omega_y + \omega_r$, so that the signals detected by the lock-in amplifier are only those generated simoultaneously by the two lasers. Besides that, a capillary cell with a 2 mm internal diameter is used to reduce the self trapping of the radiation. A reference cell is used to continuously check the resonance frequencies of the two lasers.

In fig.4 is shown the fluorescence spectrum obtained. In addition to the lines coming from the energy pooling populated levels the 5P-4S and 6S-4P lines of potassium are present in the spectrum; these had been already observed in a previous similar experiment[12]. The corresponding levels are probably populated by the second order processes

$$\mathrm{Na}_{\omega_y}(3P) + K(4S) \longrightarrow \mathrm{Na}(3S) + K_{\omega_y}(4P)$$
$$K_{\omega_y}(4P) + K_{\omega_r}(4P) \longrightarrow K^{**}_{\omega_s}(5P,6S) + K(4S) \qquad (10)$$

All the lines of the spectrum disappear when any one of the two lasers is off and they show a linear dependence on the intensity of each laser as expected. Incidentally, we want to stress that the fluorescence of the level 5F is out of the sensitivity of our apparatus and it has not been detected.

At the present we do not have obtained the collision cross sections of the processes populating the 7S, 5D, 6P, 4P and 3D levels yet, but we may give their relative values according to

$$\frac{K_{mL}}{K_{m'L'}} = \frac{\alpha_{mL\to m"L"}\ \gamma_{mL\to m"L"}}{\alpha_{m'L'\to m"'L"'}\ \gamma_{m'L'\to m"'L"'}}\ \frac{\omega_{m'L'\to m"'L"'}}{\omega_{mL\to m"L"}}\ \frac{I_{mL\to m"L"}}{I_{m'L'\to m"'L"'}} \qquad (11)$$

In tab.2 a very rough evaluation of the K_{mL}/K_{7S} values is reported. The rate constants corresponding to the 6P and 4P levels have not been corrected for the self trapping and glass absorption.

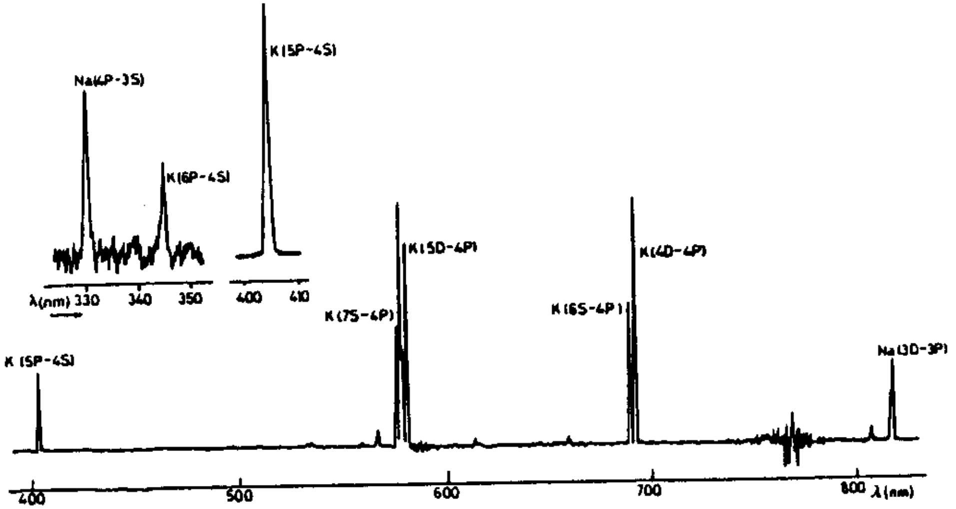

Fig.4 - Fluorescence spectrum obtained with intermodulated laser spectroscopy. The intensities of the lines are not corrected for the monochromator grating and photomultiplier efficiencies. The u.v. lines are partially absorbed by the cell glass and strongly affected by self trapping.

TABLE 2. Relative rate constants evaluated according to eq. 11. The values of the used parameters are reported

Atom	Level	Transition	$\lambda_{mL\to m'L'}$ (A)	$\gamma^{-1}_{mL\to m'L'}$	$\alpha^{-1}_{mL\to m'L'}$ *	K/K_{7S}
K	7S	7S - 4P$_{1/2}$	5782	.18	.165	1
		7S - 4P$_{3/2}$	5802	.36	.165	1
	5D	5D - 4P	5822	.19	.165	2.1
	6P	6P - 3S	3446	26	.41	~10-2 **
Na	3D	3D - 3P$_{1/2}$	8131	83	.017	1.6
		3D - 3P$_{3/2}$	8196	1	.014	1.6
	4P	4P - 3S	3302	.60	.39	~10-2 **

* The coefficients are calculated for a Hamamatsu R 955 photomultiplier

** Values not corrected for glass absorption and radiation trapping

Conclusions

We have shown the existence of a large number of possible configurations for which the energy pooling collisions are possible. A complete study would permit a more detailed knowledge of the long range interatomic potentials and a more detailed check of the different theoretical approaches. The first experimental results obtained for sodium and potassium show that this kind of processes is easily observed after some care is used in the fluorescence detection, but that the hardest part is still the absolute measurements of the collision cross sections, that directly derive from a precise determination of the excited atomic densities and of the effective lifetimes of the P levels.

As a concluding remark we like to emphasize that the energy pooling collisions can be easily extended to other atomic species with the interesting result of a deeper knowledge of their long range atomic interactions.

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Energy Transfer Collisions in Laser-Excited Mixtures of Alkali Vapors

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ABSTRACT Experiment on energy transfer in collisions between two laser excited alkali atoms of different species are reported and rate coefficients have been measured in a sodium-potassium mixture for the Na(3D) and K(7S,5D) levels. These values are of same order of magnitude as rate coefficients for sodium 3P/3P collisions.

1. Introduction

Since the discovery of electronic energy transfer in collisions between two excited atoms [1] numerous experiments on pure alkali vapors have been reported and some absolute rate coefficients have been measured [2]. The common method of determining these rate coefficients is to optically excite the alkali atoms to one of the first P-resonance states and detect the fluorescence emitted by the highly excited nL levels populated in the collisional transfer process. Results from different laboratories show that, as expected, in these thermal collisions only nL states close in energy (within a few kT) to the sum energy of the collision reactants are significantly populated.

To our knowledge no experiments have been performed with alkali atom mixtures, except for those performed in our laboratory [3,4] on sodium and potassium. The aim of those experiments was to observe and possibly to measure rate coefficients for the process

$$\begin{aligned} Na^*(3P) + K^*(4P) &\rightarrow Na^{**}(nL) + K(4S) \\ &\rightarrow Na(3S) + K^{**}(nL) \end{aligned} \qquad (1)$$

where $Na^{**}(nL)$ and $K^{**}(nL)$ indicate highly excited states, lying close to the sum energy of $N^*(3P) + K^*(4P)$ (see fig.1). However in [3] fluorescence was observed only from potassium 5P, 6S and 4D states which have an energy close to twice $E[K^*(4P)]$, therefore direct proof of reaction (1) was not possible. Despite this negative result it was clear that in a mixture of alkali atoms there should be more exit channels than for pure vapor experiments [4]. Little data are available for heteronuclear diatomic alkali molecules and very little is known about long-range interactions in these systems, therefore studies of process (1) and similar processes for all alkali pair combinations and measurements of their rate coefficients should provide knowledge about quasi-molecular potentials at internuclear distances for which other experimental methods are insensitive.

A list of levels which are expected to be populated by energy transfer collisions between two different atoms excited to the first P-resonance level has been made [4] and experiments are under way in our laboratory. Considering all possible combinations of alkali pairs there are about sixty high-lying levels in which the atoms may be excited through collisions. We have first investigated a mixture of sodium and potassium. The experimental method we used (essentially intermodulated spectroscopy) allowed the observation of reaction (1) for all expected $Na^{**}(nL)$ and $K^{**}(nL)$ levels but one. Here we briefly describe our experiment and report our measurements of the relative cross-section for levels 3D of sodium, 7S and 5D of potassium.

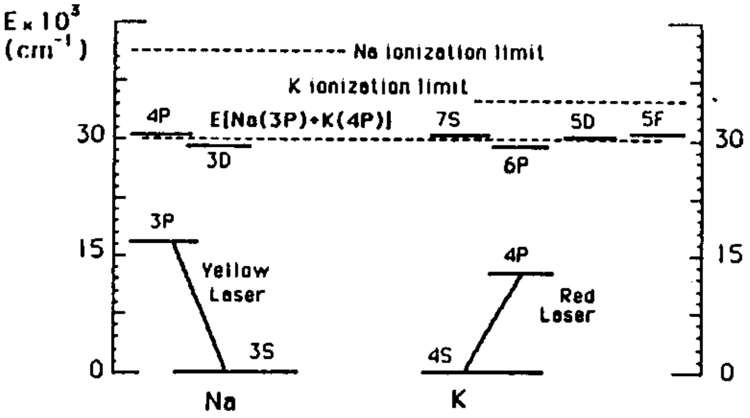

Fig. 1 Diagram of the Na and K levels of interest in the experiment.

2. Sodium-Potassium Experiment

Figure 1 shows the levels of interest in this experiment which is intended to observe reaction (1) by looking at the fluorescence emitted by levels 5D,5F,6P,7S of potassium and 3D, 4P of sodium.

The experiment was carried in a pyrex capillary cell of cylindrical shape (0.15cm internal diameter and 5 cm long). Preparation procedure of this kind of cell has already been described [5]. The cell was sealed under vacuum with an amalgam of approximately 90% pure sodium and 10% pure potassium and placed in a temperature-controlled oven. Confident in the validity of the empirical Raoult law, this particular amalgam has been chosen in order to make Na and K atom densities nearly equal. This assumption has been indeed verified in the experiment, as we will describe later on. Measurements have been made over a wide temperature range, however cross-sections have been evaluated for T = 240°C. Sodium and potassium atoms were excited to the first $P_{1/2}$ or $P_{3/2}$ resonance states by a Rhodamine 6G and an Oxazine 750 cw dye laser respectively. The two lasers were carefully superimposed on the entrance window of the cell; alignment in this experiment is very critical because of the small radial dimensions of the cell. Fluorescence emission was detected and analyzed in the visible and infrared regions with the usual apparatus for intermodulated spectroscopy. Although we tested the i.r. apparatus for proper operation, emission from 5F ⟶ 3D at 1.1μm or 5F ⟶ 4D at 3.1 μm was not observed, probably because of the poor sensitivity of the i.r. detection apparatus. Therefore, the cross-section for the 5F level has not been measured and in the following this aspect of the experiment will not be considered any more.

Under combined laser excitation of both sodium and potassium pure sodium 3P/3P and potassium 4P/4P collisions are present and produce very excited atoms; moreover, these pure collisions, either directly or by decay from higher states, also populate the levels produced by process (1). In order to measure cross-sections for process (1) we must discriminate it against these unwanted contributions. With this aim we introduce in our experimental apparatus (see figure 2) the intermodulation technique. The two laser beams exciting Na and K atoms respectively were modulated at two different frequencies ω_1 and ω_2. Fluorescence was detected at the sum frequency $\omega = \omega_1 + \omega_2$. This assured that signals from the lock-in amplifier were due only to levels produced by Na(3P)/K(4P) collisions.

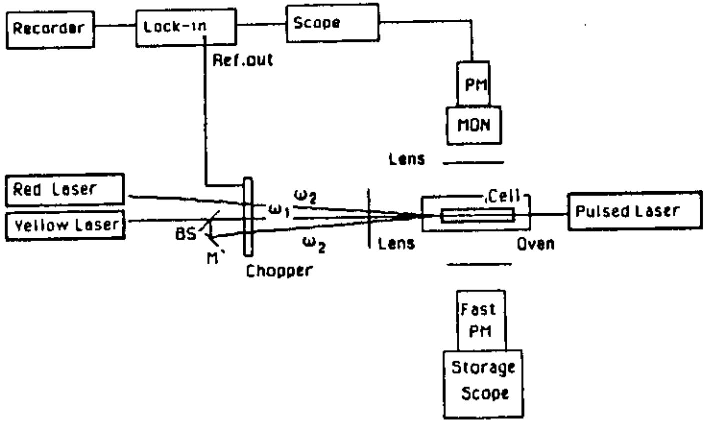

Fig. 2 Sketch of the experimental apparatus
BS beam splitter; M mirror. The lasers are shown as acting simultaneously. In fact, only one of the two ω_1-modulated laser beams was present at a time.

With this apparatus we have observed fluorescence from all expected levels except 5F, namely the following transitions:

Table 1. Transitions observed from levels populated by process(1).

Atom	Level	Transition	Wavelength (nm)
Na	4P	4P-3S	330
	3D	3D-3P	819
K	5D	5D-4P	582
	7S	7S-4P	579
	6P	6P-3S	345

Instead of measuring absolute cross-sections of process (1) we took advantage of the fact that absolute cross-sections for energy transfer have been already measured in different laboratories [5,6] for the following process in pure sodium vapor.

$$Na^{*}(3P) + Na^{*}(3P) \longrightarrow Na^{**}(5S,4D) + Na(3S) \qquad (2)$$

In our case we chose the 5S-3P transition at 616nm and thus our cross-sections for reaction (1) are relative to σ_{5S} of process(2). In order to measure I(5S-3P) we replaced the red laser with a second yellow beam, still at the frequency ω_1. In this way we could then measure 5S-3P fluorescence intensity with the same density of Na ω_1-excited atoms: as we will see later, this will permit simplification of the formulas. It was convenient to choose the 3D level of sodium as the one for which we measure cross-section relative to the 5S state. Other level cross-sections are then simply deduced from intensity ratios relative to 3D. In the experiment we have also measured the intensity ratio between the fundamental resonances in sodium and potassium, $I(3P-3S)/I(4P-4S)$ excited by the ω_1-modulated laser beams; we will see that we need this ratio for the final evaluation of cross-sections, unless absolute atom densities for both sodium and potassium were known.

A second part of the experiment involved measurement of the effective lifetime of sodium 3P and potassium 4P levels that again enter the cross-section determination. In this case pulsed dye lasers, pumped by a nitrogen laser (see figure 2), were used for excitation to first $P_{1/2}$ or $P_{2/3}$ states of sodium and potassium; fluorescence was detected by a fast photomultiplier and a storage oscilloscope. Measured lifetimes were roughly ten times natural lifetimes for both sodium and potassium, which indirectly proved that our empirical choice of the amalgam to produce comparable atom densities of sodium and potassium at a given temperature, was correct.

3. Data Analysis for Cross-Section Determination

Let us work first with the 3D level of sodium Upon combined excitation of sodium and potassium atoms, solution of rate equations at steady-state gives its population - $[Na_{3D}]$ as a function of $[Na_{3P}]_1$ and $[K_{4P}]_2$ where subscripts 1 and 2 indicate that 3P atoms are excited by laser modulated at frequency ω_1 and 4P atoms are excited by laser modulated at frequency ω_1

$$[Na_{3D}] = \frac{k_{3D}\,[Na_{3P}]_1\,[K_{4P}]_2}{A_{3D-3P}} \qquad (3)$$

where k_{3D} is the rate coefficient for production of 3D atoms by (1) and A_{3D-3P} is the transition probability from 3D to 3P, which is the only one because the 3D level decays 100% to 3P. Dealing with thermal collisions, rate coefficients and cross-sections are related simply by the mean interatomic velocity $k_{nL} = v\sigma_{nL}$ with $v = (8kT/\pi\mu)^{\frac{1}{2}}$. Since in the experiment we measure fluorescence intensities it is convenient to express relation (3) as

$$I_{3D-3P} = K_{3D}\,\alpha_{3D-3P}\,\hbar\omega_{3D-3P}\,(V/4\pi)\,[Na_{3P}]_1\,[K_{4P}]_2 \qquad (4)$$

where I_{3D-3P} is the intensity of 3D-3P transition, α_{3D-3P} is a correction factor for the response of the apparatus, ω_{3D-3P} is the transition frequency and V the fluorescence volume.

We consider now the case when only sodium excitation is present at two different modulation frequencies with the second laser beam replacing geometrically the potassium laser beam of the previous case. The population of collision-produced levels $[N_{nL}]$ is then

$$[N_{nL}] = \frac{k_{nL}\,[Na_{3P}]_1\,[Na_{3P}]_2}{\Sigma_{n'L'}\,A_{nL,n'L'}} \qquad (5)$$

where $[Na_{3P}]$ is modulated at frequency ω_1 from one beam and at ω_1 from the other beam. Writing explicitly expression (5) for level 5S, our reference level, we get

$$[N_{5S}] = \frac{k_{5S}\,[Na_{3P}]_1\,[Na_{3P}]_2}{A_{5S-4P} + A_{5S-3P}} \qquad (6)$$

where k_{5S} is known /5,6/. I_{5S-3P} has been measured, then

$$I_{5S-3P} = k_{5S}\ \gamma_{5S-3P}\ \alpha_{5S-3P}\ \hbar\omega_{5S-3P}\ (V/4\pi)\ [Na_{3P}]_1\ [Na_{3P}]_2 \qquad (7)$$

where γ_{5S-3P} is the branching ratio of the transition.

Assuming that fluorescence is coming from the same volume (a good approximation with the geometry of our cell) and making the ratio we get

$$\frac{I_{3D-3P}}{I_{5S-3P}} = \frac{k_{3D}}{k_{5S}}\ \frac{\alpha_{3D-3P}}{\alpha_{5S-3P}}\ \frac{1}{\gamma_{5S-3P}}\ \frac{\omega_{3D-3P}}{\omega_{5S-3P}}\ \frac{[K_{4P}]_2}{[Na_{3P}]_2} \qquad (8)$$

Densities of sodium and potassium are unknown, however we have determined their ratio by measuring the intensity of resonance fluorescence lines and the effective lifetimes of sodium 3P (τ_{3P}) and potassium 4P (τ_{4P}) levels as shown in (9).

$$\frac{[K_{4P}]}{[Na_{3P}]} = \frac{\alpha_{3P-3S}}{\alpha_{4P-4S}}\ \frac{\tau_{4P}}{\tau_{3P}}\ \frac{\omega_{3P-3S}}{\omega_{4P-4S}}\ \frac{I_{4P-4S}}{I_{3P-3S}} \qquad (9)$$

We have assumed that correction factors are essentially due to monochromator and photomultiplier spectral response. Making all substitutions with quantities measured at T = 240°C, where effective lifetimes were roughly ten times longer than natural lifetimes, we obtain $k_{3D} \cong 0.6 k_{5S}$. k_{5S} was determined in refs.[5,6] with an uncertainty of 35%.
k_{3D} as derived quantity has higher uncertainty, especially as related to measurements of effective lifetimes. A resonable estimate of overall uncertainty may rise to 50%, giving $\sigma_{3D} = (1.4 \pm 0.7) \times 10^{-15}\ cm^{-2}$.

Cross-sections for others levels can be determined in a similar way, or, more simply by using rate coefficient ratios already determined in [4]. However, for the two transitions in the u.v., 4P-3S in sodium and 6P-3S in potassium, we could not correct fluorescence intensity for glass absorption precisely enough to give their cross-sections with meaningful uncertainty. Therefore final results of the present work are k_{7S}, k_{5D} for potassium and k_{3D} for sodium; they are summarized in table 2.

Table 2. $Na^*(3P) + K^*(4P) \rightarrow Na^{**}(nL) + K(4S)$ cross-sections.
$ \rightarrow Na(3S) + K^{**}(nL)$

ΔE is the difference between the energy of $Na^*(3P) + K^*(4P)$ and the energy of highly excited level nL.

Atom	Level	$\Delta E(cm^{-1})$	$\sigma(cm^{-2})$
Na	3D	+ 768	$(1.4 \pm 0.7) \times 10^{-15}$
K	5D	- 169	$(1.9 \pm 1.0) \times 10^{-15}$
	7S	- 258	$(0.9 \pm 0.5) \times 10^{-15}$

4. Conclusions

We have started a series of experiments to investigate production of highly excited states by energy transfer in collisions between two alkali atoms of different species, laser excited to the first P-resonance states. The experiment is based on an intermodulation technique, which distinguishes between the desired signals and those from collisions between atoms of the same species. First results have been obtained for a sodium-potassium mixture. Fluorescence has been observed only from expected levels (except for one which emits only in the infrared), proving once again that only levels with energy defects (positive or negative) within a few kT are significantly produced. Cross-section values have been estimated for three such levels; D-levels seems to be favourite compared with S-levels. These values are comparable to those for energy transfer in sodium/sodium collisions, suggesting the same exchange mechanism in pure as well as mixed alkali vapors. However, calculation of the corresponding molecular adiabatic potentials and nonadiabatic energy transfer at the avoided crossing would provide a check on our cross-section measurements. Experiments are now in progress in our laboratory on a potassium/rubidium mixture for which only three levels are expected to be populated by energy transfer collisions.

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INELASTIC COLLISIONS IN LASER EXCITED ALKALI ATOMS

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ABSTRACT

This paper will briefly outline inelastic collisions between two laser excited alkali atoms. Special emphasis will be on recent progress made in our laboratory for heteronuclear systems.

INTRODUCTION

Resonant laser excitation of alkali atomic vapors generally produces several different phenomena. Among these we have studied the collisions between two alkali atoms, both laser-excited to the first P-resonance level. Products of these collisions are highly excited atoms[1] (sometimes highly excited molecules as well[2]) and molecular ions[3] plus electrons:

$$A^*(nP) + A^*(nP) \longrightarrow A^{**}(n'L) + A(nS) \quad \text{energy transfer}$$

$$\longrightarrow A_2^+ + e \quad \text{associative ionization}$$

Energy balance between entrance and exit channels is provided by kinetic energy and is of the order of few kT. Electrons produced in the associative ionization are therefore "slow" electrons and do not cause any secondary effect, unless they gain energy through superelastic collisions with the excited atoms.

Excited atoms A^{**} are detected by their fluorescence emission, while ions can be identified and counted by well established and efficient techniques such as mass spectrometry. More recently, electron spectrometry suitable for these very low energy electrons has been developed[4]. Final goal of these investigations is to provide rate coefficients or cross sections for energy transfer and associative ionization, which, when compared to calculated values, give information on long range interactions.

In our laboratory we have extensively investigated the energy transfer collisions in alkali vapors. To discriminate this particular phenomenon from all others processes, there are some constraints on the main parameters of the experiment: i) atom density has to be high enough to make the collision products observable, but not too high in order to avoid superelastic collisions; a reasonable value for experiments is 10^{12}-10^{13} cm^{-3}. ii) the laser merely serves as a tool to prepare the reactants for the collision and therefore its power can not be too high in order to avoid direct multiphoton ionization of the atoms and any laser induced or laser assisted collisional process. In our experiments we have been working with 10^{1}-10^{3} W/cm^2.

These collisions are thermal; this fact has several consequences. Rate coefficients drop rapidly with increasing energy defect/excess or, in others words, only excited levels n'L with energy within few kT of the nP+nP energy are populated by the collision. Rate coefficients K are related to cross sections σ, (K=vσ), simply through the mean interatomic velocity $v=(8kT/\pi\mu)^{1/2}$, which in our experiments is about 10^5cm/sec. Collision time duration, which very roughly is given by the ratio atom dimension/thermal velocity, is such that a rate equation approach is appropriate to evaluate σ from data measured in the experiments. From a theoretical point of view, the production of highly excited states n'L by thermal collisions between two excited atoms nP/nP may be considered as due to transitions among different electronic molecular states corresponding to the atomic dissociation limits nP+nP and nS+n'L. The nonadiabatic energy transfer usually occurs at the internuclear distances of avoided crossings. Calculations of electronic excited molecular potentials for alkali dimers have been flourishing in the last few years and some of them extend also to large internuclear distances of interest for energy transfer collisions. However specific calculations of the coupling terms and consequent evaluation of cross sections for nP+nP transfer to nS+n'L have been rather limited.

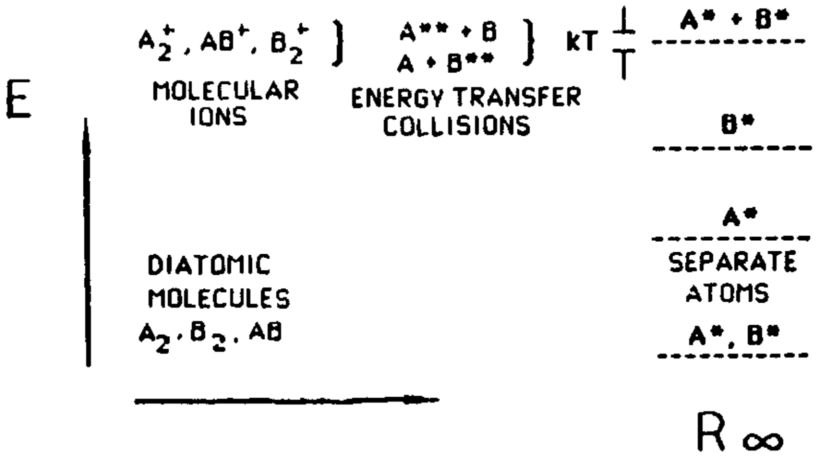

Fig. 1. Schematic representation of energy transfer collisions between two excited atoms.

Recently we have tried to complement our experimental results for energy transfer collisions 3p/3p to 4d and 4f levels in sodium with a calculated value of σ[5]. We have made some approximations because almost every pair of molecular states having the right symmetry are coupled by some terms of the total Hamiltonian. Of course approximations which are reasonable for sodium cannot immediately be extended to other systems, however the theoretical approach should be valid in the general case.

Our experiments are based on the detection of the fluorescence emitted by the highly excited states populated by np/np energy transfer collisions. The intensity of these lines may be several orders of magnitude weaker than the resonance fluorescence, i.e. the fluorescence emitted by the nP state directly excited by the laser. Therefore, even if the spectrum is usually simple because atomic alkali lines are very well known, the apparatus for spectroscopy must be rather sensitive. We have detected fluorescence lines in the visible region with intensity up to 10^{-6} compared to resonance fluorescence; however detection in the infrared is not so efficient and sometimes we have not been able to observe some expected lines. The fluorescence intensity of collision-produced high-lying states varies quadratically with both the atomic density and the laser power because the process depends upon two laser excited atoms; this characteristics may be sometimes useful to discriminate levels which are produced by other mechanisms.

Energy transfer in collisions between two excited atoms have been observed with almost all alkali vapors and measurements of cross sections have been made in several laboratories. Problems related to these measurements have been solved in various laboratories with different approaches, which can be found in the original papers. A table with all measurements up to 1984 has been reported[6] and more recent results in sodium, taking into account also the dependence on J value of the colliding 3P-atoms, have been published[7]. Here we only wish to make a brief comment about the size of the cross sections. For example, cross sections for sodium 3p/3p energy transfer collisions are of the order of 10^{-15}cm^2, which is a significant fraction of ordinary geometrical cross section for 3p atoms (≈ 10^{-14}cm^2). Collisions between two excited atoms are therefore important and cannot be disregarded whenever there is a resonant laser excitation of the vapor. In comparison associative ionization cross section in sodium from 3p/3p atoms[8,9] is of the order of 10^{-17}cm^2. Measurements of these cross sections and calculations of potential energy curves at long interatomic distances have improved understanding of long range interactions, at least in sodium. Since for heteronuclear alkali systems there are less spectroscopic data and theoretical calculations, we have started experimental studies of collisions between two excited alkali atoms of different species, which is briefly described in what follows.

COLLISIONAL EXCITATION TRANSFER IN ALKALI MIXTURES

The process we consider now is

$$A^{*} + B^{*} \dashrightarrow A^{**} + B$$
$$\dashrightarrow A + B^{**}$$

where A and B are alkali atoms of different species, A^{*} and B^{*} indicate excitation to the first P-resonance level, A^{**} and B^{**} are high-lying states produced by the collisions. Exit channels are obviously more in number than for pure alkali collisions. Altogether there are about 60 levels for the 10 possible pairs of alkali atoms. The general method to investigate these collisions in a mixture is the same as for a pure alkali vapor: two dye lasers (cw in our experiments) provides the excited reactants A^* and B^* and transfer to A^{**} and B^{**} is monitored through fluorescence emissions. Rate equations involving fluorescence intensity ratios (which are measured in the experiment) are easily written down and steady-state solutions give rate coefficients and total averaged cross sections, exactly in the same way as in pure vapor experiments.

There are however specific problems to be solved for these new experiments. Atomic densities of two different alkali atoms can be very different at the same temperature; moreover the relative densities in a mixture are not simply related to the temperature of the sealed cell containing the saturated vapors. In the presence of A^{*}/B^{*} collisions there are also A^{*}/A^{*} and B^{*}/B^{*} pure collisions which produce excited atoms; in the experiment we have to select fluorescences originated from A^{*}/B^{*} collisions from all other fluorescence, in particular the very strong resonance fluorescence of both laser excited atoms.

We have started our investigation in a sodium-potassium mixture for which the process to be investigated is

$$\begin{aligned} Na^{*}(3p) + K^{*}(4p) &\dashrightarrow Na^{**}(4p,3d) + K(4s) \\ &\dashrightarrow Na(3s) + K^{**}(7s,6p,5d,5f) \end{aligned} \tag{1}$$

An amalgam made of 90% pure Na and 10% pure potassium gives a comparable density for the two alkalis at the temperatures of our interest, according to the empirical Raoult law[10]. The amalgam is sealed in a capillary pyrex cell[11] which is heated in a temperature controlled oven. A Rhodamine cw dye laser (yellow laser) excites sodium atoms to $3P_{1/2}$ or $3P_{3/2}$ level and an Oxazine cw dye laser (red laser) excites potassium atoms to $4P_{1/2}$ or $4P_{3/2}$ level. The yellow laser is modulated at frequency ν_Y, the red laser is modulated at frequency ν_R and detection is made at the sum frequency $\nu_Y + \nu_R$. This intermodulated technique assures that only fluorescence from levels populated by Na(3P)+K(4P) collisions is observed. A schematic diagram of the apparatus is shown in figure 2.

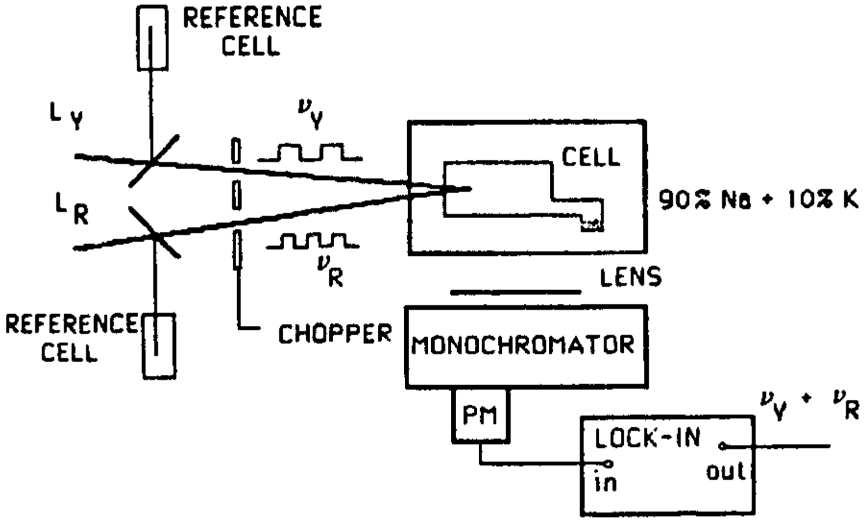

Fig. 2. Sketch of the experimental apparatus.

Fluorescence has been observed from all the expected levels of process (1), except the 5F state of potassium because it emits mainly in the infrared, where our apparatus is not very sensitive. Fluorescence from Na(4P) and K(6P) is in the u.v. and it has been observed without any problem. However, since we can not have precise corrections for glass absorption of these u.v. lines, cross sections have not been evaluated. Densities of Na(3P) and K(4P), (necessary for cross section determination), have been deduced from measurements of the effective lifetimes from time-resolved resonance fluorescence observation under pulsed laser excitation. We have found it convenient to measure the cross sections for process (1) relative to the cross section for production of Na(5S) from sodium 3P/3P collisions for which absolute measurements exist[11,12]. Typical rate equation approach gives, for example, the following relation for the 3D state production of sodium by process (1)

$$\frac{I_{3D-3P}}{I_{5S-3P}} = \frac{K_{3D}}{K_{5S}}\,\frac{\alpha_{3D-3P}}{\alpha_{5S-3P}}\,\frac{\gamma_{3D-3P}}{\gamma_{5S-3P}}\,\frac{\omega_{3D-3P}}{\omega_{5S-3P}}\,\frac{[K_{4P}]_{\nu_R}}{[Na3P]_{\nu_Y}} \tag{2}$$

Fluorescence intensities I_{i-j} are measured; α_{i-j} are correction parameters for the detection system, γ_{i-j} is the transition branching ratio, ω_{i-j} is the transition frequency and $[K_{4P}]_{\nu_R}$, $[Na_{3P}]_{\nu_Y}$ are the densities of atoms excited by the laser beams modulated at frequency ν_R and ν_Y respectively. Excited atom densities are independently measured in the pulsed experiment from intensity of resonance fluorescence lines and effective radiative lifetimes. Relation (2) gives $K_{3D} = 0.6K_{5S}$, which means $\sigma_{3D}=(1.4\pm0.6)\times10^{-15}cm^2$. In a similar way we have measured $\sigma_{5D}=(1.9\pm0.9)\times10^{-15}cm^2$ and $\sigma_{7S}=(0.9\pm0.4)\times10^{-15}cm^2$ for potassium. The size of these cross sections indicates that the energy transfer in collisions between two excited alkali atoms of different species is essentially due to the same mechanism as in pure alkalis, in spite of the different symmetries of the corresponding molecular potentials. The next alkali mixture under investigation in our laboratory is potassium plus rubidium. In this case there is one level, the 5D of rubidium, whose energy is in the midst of the four fine structure levels $K^*(4P)+Rb^*(5P)$. Cross section measurements for production of this state may turn out to be particularly interesting.

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ENERGY POOLING COLLISIONS IN Na-K AND Na-Rb VAPOR MIXTURES

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ABSTRACT We have studied the energy-pooling collisions in laser excited Na-K and Na-Rb vapor mixtures. The Na-K experiment has given quantitative results for the cross sections and also results on the influence of a foreign buffer gas. The Na-Rb experiment shows interesting molecule formation and work is in progress to determine cross section values.

Introduction

In the last few years the resonant excitation of an alkali vapor has been widely studied. Depending upon the conditions of the vapor (pressure, temperature, cell size, etc.) and upon the characteristics of the laser (pulsed or c.w., single mode or broadband, weak or strong power density) different processes occur; examples of such events are multiphoton ionization, Penning ionization, superelastic collisions and other kinds of ion and molecule formation. When the laser is operating at low power density ($\approx$ 1-10 W/cm^2) and the atomic density is relatively low ($\approx 10^{11} - 10^{13}$ /cm^3), the most important processes are the energy pooling collisions and the associative ionization. In the first process two excited alkali atoms in a np state collide and the energy is transferred from one atom to the other leading the first atom to the ground state ns and the second one to a more excited state; this process is effective for levels which differ for a few kT from the sum energy 2xE(np). In the associative ionization process the collision of two excited atoms leads to the formation of a molecular ion. The overall reaction scheme may be written as

$$A(nP) + B(mP) \begin{cases} \longrightarrow A(nS) + B(m'L) \pm \Delta E \\ \longrightarrow B(mS) + A(n'L) \pm \Delta E' \\ \longrightarrow AB^+ + e^- \pm \Delta E'' \end{cases} \quad (1)$$

Since the first observation of the energy pooling effect [1], homonuclear collisions (with A=B) have been mainly studied. Only recently [2] the interest has been extended to heteronuclear collisions (with A=B). In this paper we will deal about energy pooling collisions in Na+K and Na+Rb mixtures. The levels of interest are shown in figure 1, in respect to the energy defect. The two alkali species are excited with two dye lasers. The interest about this kind of collisions comes from the information they give about the interatomic potentials at medium and large ranges; the experimental cross sections of such a process have been compared with theoretical calculations [3] and an agreement between them can be considered as a good test for the quantum calculations of the interatomic potentials. In the case of heteronuclear collisions the information about the interatomic potentials are even more interesting because these curves are less known. Besides that a large number of quasi resonant levels are involved into the heteronuclear collisions; a summary of that levels in the various alkali species has been given [2]. Moreover this kind of collisions allows the production of an appreciable population on levels which have forbidden transitions with the ground state. The influence of a buffer gas in the collision may be investigated [4]; as its presence enhances three body collisions it modifies the stationary populations of the levels. With the experimental technique used in our experiment, we are able to separate the contribution of the heteronuclear collisions from that of the homonuclear ones and, in presence of a buffer gas, it is also possible to discriminate the contribution of the three body collisions involving one buffer gas atom.

In the following sections the rate equations for the heteronuclear energy pooling collisions are applied to our experiment on a mixture of Na and K atoms. Preliminary results on a running experiment in a mixture of Na and Rb are also reported.

Rate Equations

The rate equations in the stationary case describing process (1) may be written as

$$N_i \sum_{j=i} A_{ij} = K_i N_{np}^{(A)} N_{mp}^{(B)} \qquad (2)$$

the indexes i and j are couples of quantum numbers describing the levels, A_{ij} is the spontaneous emission coefficient in the transition i-j. $K_i = < \sigma_i\ v >$ with σ_i the cross section of the process and v the mean interatomic velocity and $N_{np}^{(A)}$, $N_{mp}^{(B)}$ are the laser excited atomic densities. As the intensity of a line coming from a transition i-j can be expressed as

$$I_{ij} = \frac{V}{4\pi} \alpha_{ij} \hbar\omega_{ij} N_i A_{ij} \qquad (3)$$

where V is the fluorescence volume, α_{ij} is a factor taking into account the efficiency of the apparatus and ω_{ij} is the frequency of the transition i-j, it follows that

$$K_i = \frac{4\pi}{V} \frac{I_{ij} \sum_{j=i} A_{ij}}{\alpha_{ij} \quad A_{ij} \quad N_{np}^{(A)} N_{mp}^{(B)}} \qquad (4)$$

We want to stress out the fact that the above equations are valid if the detected signal is due only to the heteronuclear energy pooling collisions, and therefore it is of particular importance to discriminate and to eliminate any fluorescence coming from secondary processes. This can be done by adopting a special procedure described in the following section. In general it is very difficult to have the absolute values of the excited $N_{np}^{(A)}$ and $N_{mp}^{(B)}$, however we can measure the intensities of the fluorescence lines related to the atomic densities via eq.(3) where A_{ij} must be substituted by $(\tau_{np})^{-1}$, the ffective lifetime of the np-level; in fact in presence of high densities of excited atoms, he radiation trapping modifies the spontaneous decay rate of the level, which must be easured from the experiment.

Experimental apparatus and procedure

The general sketch of the experimental apparatus is shown in fig.2.
he vapor is contained in a cell heated at the temperature necessary to have typically an tomic density of $10^{11}-10^{13}$ /cm^3.

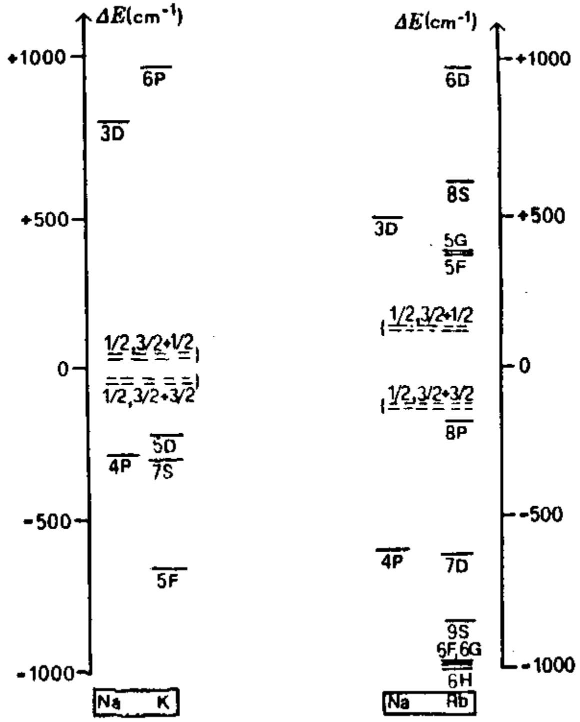

Fig. 1 Scheme of the energy levels involved in energy pooling collisions in Na-K and Na-Rb mixtures. The levels are plotted in respect to their energy defect from the center of the sum energy $A(np_i) + B(mp_j)$ with $i,j = 1/2, 3/2$.

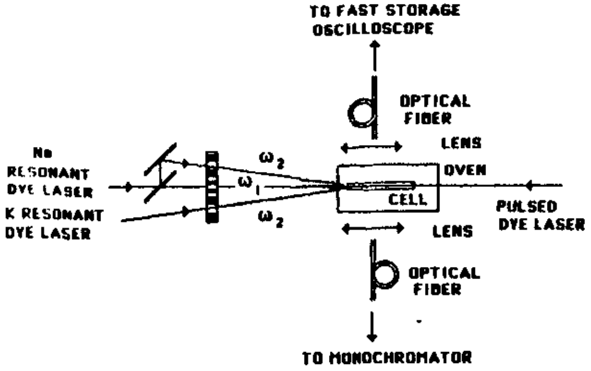

Fig. 2

Sketch of the experimental apparatus; only one of the two beams modulated at frequency Ω_2 was used at the time together with the Ω_1 modulated beam.

More care must be taken in the experiments dealing with mixtures in order to have comparable densities of the two species: assuming the Raoult law to be valid, it follows that the ratio between the vapor pressures in a mixture of two species A and B is proportional to the respective molar fractions of the two species. Following Nesmeyanov data [5] on vapor pressures of alkali atoms, the ratio $P_A/P_B = 1$ corresponds to an amalgam prepared with 5% K and 95% Na in the case of Na plus K experiment and 2% Rb and 98% Na in the case of Na plus Rb experiment.

To better control the fluorescence volume and to reduce the radiation trapping effect, the standard cylindrical cells have been substituted by capillary ones (= 2mm) prepared following a special procedure described elsewhere [6].

The two atomic species are excited by two c.w. dye lasers tuned to the D_2 resonance lines of the alkalis. We used a single mode Rodhamine 6G dye laser pumped by an Ar^+ laser for sodium (λ =589nm) and a multimode Oxazine 750 Perchlorate pumped by a Kr^+ ion laser for potassium (λ =766nm) and rubidium (λ =780nm).

The output powers are of the order of 100mW; the beams are focussed to have laser intensities of the order of 1-10 W/cm^2.

The beams are superimposed at the entrance of the cell; the fluorescence coming from the cell is collected at right angles and focussed on an optical fiber connected to the detection system. A 1m focal length Jobin-Yvon HR 1000 monochromator and a Hamamatsu R955 photomultiplier have been used for the visible region (300-850 nm). A 1/3 m focal length Jarrel-Ash monochromator and a PbS detector have been used to explore the infrared region (1-2.5μm).

As we said in the previous section, we must eliminate the contribution to the fluorescence coming from different processes, and mainly from the homonuclear energy pooling collisions always present in the experiment.

At this aim, we adopted an intermodulation technique consisting in the modulation of the two beams at different frequencies Ω_1 and Ω_2. At the same time the output of the photomultiplier is sent to a lock-in amplifier driven at the sum frequency $\Omega_1 + \Omega_2$. In this way we are able to detect signals coming only from the interaction of the species modulated at the frequency Ω_1 with the other modulated at the frequency Ω_2. This method has shown to be very sensitive as the fluorescence signal disappears when any one of the two laser is off even if a strong fluorescence is still visible in the cell.

The measure of the rate coefficients K_i for heteronuclear collisions has been made as related to the known rate coefficient K_{5S} for the homonuclear reaction

$$Na(3p) + Na(3p) \longrightarrow Na(5s) + Na(3s) \qquad (5)$$

$$K_{5S} = \frac{4p}{V} \frac{I_{5S-l} \sum_{i=j} A_{ij}}{\alpha_{5s-l}\, \hbar\omega_{5s-l}\, A_{ij}\, {N_{3P}}^2} \qquad (6)$$

where l is a level populated through the decay from the 5s level. In particular we found to be convenient to use the 5s-3p transition of sodium at 616nm.

For this reason, and to calibrate the apparatus, we need to measure the intensity of a transition from the 5s level of sodium with the same method. To this purpose we split the yellow beam into two components modulated at the frequencies Ω_1 and Ω_2 and we detected the signal from the desired level. Subsequently we replaced the Ω_2 yellow beam with the red one resonant with the second alkali species, and we detected the fluorescence from the levels populated by the heteronuclear collisions.

To measure the lifetime of the excited levels we sent two pulsed dye lasers resonant with the fixed transitions and we analyzed the exponential decay of the fluorescence on the screen of a fast storage oscilloscope.

K_i are related to K_{5S} of sodium by the volume independent expression

$$\frac{K_i}{K_{5S}} = \frac{\alpha_{5S\text{-}3P}}{\alpha_{ij}} \frac{A_{5S-3P}}{\sum_{l=5S} A_{5S-l}} \frac{\sum_{j=i} A_{ij}}{A_{ij}} \frac{\omega_{5S-3P}}{\omega_{ij}} \frac{I_{ij}}{I_{5S-3P}} \frac{{N_{3P}}^2}{N_{np}^{(A)} N_{mp}^{(B)}} \qquad (7)$$

According to the experimental procedure described previously ${N_{3p}}^2$ and $N_{np}^{(A)} N_{mp}^{(B)}$ may be better written as

$$\begin{aligned} N_{3P}^2 &= |N_{3P}|_{\Omega_1}\, |N_{3P}|_{\Omega_2} \\ N_{np}^{(A)}\, N_{mp}^{(B)} &= |N_{np}^{(A)}|_{\Omega_1}\, |N_{mp}^{(B)}|_{\Omega_2} \end{aligned} \qquad (8)$$

where the subscripts Ω_1 and Ω_2 indicate that the populations are modulated at these frequencies. In this way we can simplify the equation if we choose one of the atomic species, say A to be sodium modulated at the Ω_1 frequency. Eventually the equation results

$$\frac{K_i}{K_{5S}} = \frac{\alpha_{5S-3P}}{\alpha_{ij}} \frac{\alpha_{mp-ms}}{\alpha_{3P-3S}} \frac{A_{5S-3P}}{\sum_{l=5S} A_{5S,l}} \frac{\sum_{j=i} A_{ij}}{A_{ij}} \frac{\tau_{3P}}{\tau_{mp}} \frac{\omega_{5S-3P}}{\omega_{ij}} \frac{\omega_{mp-ms}}{\omega_{3P-3S}} \left|\frac{I_{3P-3S}}{I_{mp-ms}}\right|_{\Omega_2} \qquad (9)$$

where all the quantities are known or experimentally determinated.

Results

i) Na - K

We performed a first experiment on a mixture of sodium and potassium to study the exit channels of the reaction

$$\begin{aligned} Na(3P) + K(4P) &\longrightarrow Na(nl) + K(4S) \pm \Delta E \\ &\longrightarrow K(mj) + Na(3S) \pm \Delta E \end{aligned} \qquad (10)$$

The observed transitions are listed in table 1 along with the energy of the levels and the cross sections [7]. The measurements were performed at T=240 °C with laser intensity of about 80mW on the red laser and 50mW on the yellow laser. The effective lifetimes of the 3p level of sodium and of the 4p level of potassium resulted to be τ_{3p} =176 ± 20ns and τ_{4p} = 287 ± 30ns respectively. The obtained cross sections do not exhibit remarkable differences with those obtained for the homonuclear reactions.

An experiment was also performed in a cell containing sodium, potassium and 10 Torr of Ne as buffer gas. New features appeared in the spectra under intermodulated technique, showing some additional lines of sodium coming from more excited levels and in opposition of phase. This results from the population modification induced by the buffer gas through a three body collision of the type

$$\mathrm{Na}(3P) + \mathrm{K}(4S) + \mathrm{M} \longrightarrow \mathrm{Na}(3S) + \mathrm{K}(4P) + \mathrm{M} \pm \Delta E \qquad (11)$$

where M indicates a buffer gas atom. A pure two body collision alkali atom/buffer gas atom can not change the frequency modulation and therefore does not affect the intermodulation spectrum. The effect of process (13) on the contrary is to couple atoms modulated at two different frequencies. States populated from energy transfer collisions involving these atoms are then present in the intermodulated spectrum. The signal of the fluorescence lines also indicates if the collision is responsible for a population or depopulation process, as it is clear from the spectrum reported in figure 3.

Our model explains the differences observed in the spectra obtained without and with buffer gas. Moreover, by the comparison of relative fluorescence intensities in the two cases we have evaluate [4] the first lower limit for the three body rate coefficient of process (13) to be $\approx 10^{-27}$ $cm^6 s^{-1}$.

ii) Na - Rb

The same method is applied to study an amalgam of sodium and rubidium.

As one can see from the scheme of Na and Rb (fig.1), this combination of alkali atoms gives a larger set of quasi resonant energy-pooling levels; besides that, the larger fine structure of the excited level of rubidium can carry new interesting informations about this kind of collisions following a D_1 or a D_2 excitation. In our preliminary experiment, we used one laser line at a time, exciting first the D_2 line of sodium (laser 1) and then the D_2 line of rubidium (laser 2); phase sensitive detection was used both in the infrared and in the visible part of the spectrum as in the Na-K experiment. Four different spectra for a cell temperature of 200 °C are shown in fig.4-5; a low pass filter at 850nm was used when we recorded the infrared spectra. Fluorescence occurs from many other levels different from the first excited one; with laser 2 on, a first interesting result is that fluorescence comes not only from the more resonant homonuclear energy-pooling 5D of rubidium, as in a previous experiment with a rubidium beam [8], but also from 7S,6D and 8S levels. In the spectra it is also clear a large molecular fluorescence coming from known states of NaRb (B-X band in the visible) and Rb_2 (A-X band in the infrared); the energy-pooling processes can be effective in populating such molecular states. Using laser 1 to excite sodium, a large population also builds in the 5P levels of rubidium; that allows us to see fluorescence from the 8p level of rubidium populated by the heteronuclear process

$$\mathrm{Na}(3P) + \mathrm{Rb}(5P) \longrightarrow \mathrm{Na}(3S) + \mathrm{Rb}(8P) \pm \Delta E \qquad (12)$$

with $\Delta E = -50 cm^{-1}$. In fig.6 the 8P-5S fluorescence line of rubidium at 335nm is shown next to the 4P-3S line of sodium at 331nm. An experiment with the intermodulation technique as in the the Na-K amalgam is in progress to determine the cross section of the 8P level and also of other less resonant levels.

Conclusions

We report experiments on heteronuclear energy pooling in two different mixtures of alkali atoms. In the Na-K we have determined cross sections for several levels populated by this kind of collision between excited atoms and the influence of a buffer gas and consequently of three body collisions were studied. We also report preliminary results on a experiment in a Na-Rb mixture which is in progress.

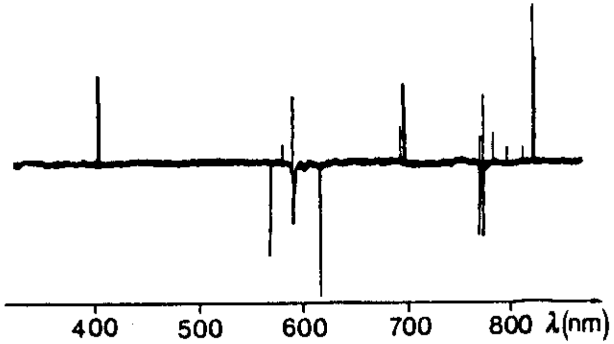

Fig. 3 Fluorescence spectrum of the Na-K mixture in presence of a buffer gas; the lines in opposition of phase come from a depopulating mechanisms.

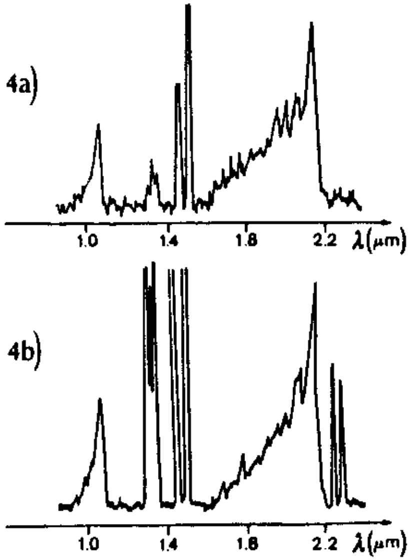

Fig. 4 Infrared spectra of the Na-Rb mixture with D_2 excitation of sodium (4a) and D_2 excitation of Rb (4b).

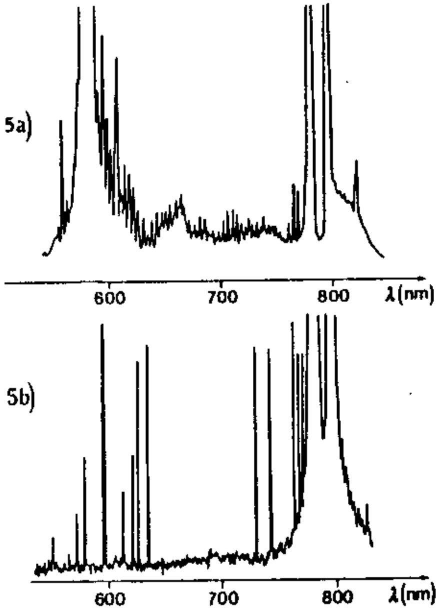

Fig. 5 Visible spectra of the Na-Rb mixture with D_2 excitation of sodium (5a) and D_2 excitation of Rb (5b).

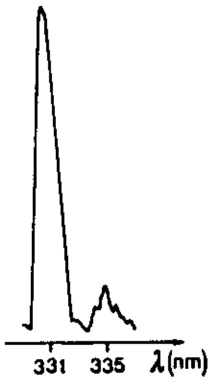

Fig. 6 Fluorescence line 8p-5s of rubidium at 335nm next to fluorescence line 4p-3s of sodium at 330nm.

TABLE 1. Heteronuclear energy pooling levels and cross sections in the Na-K mixture

Atom	Level	Energy level (cm^{-1})	Detected transition	λ(nm)	$\sigma x10^{15}$ (cm^2)
Na	3D	29172	$3D-3P_{1/2,3/2}$	818-820	1.4 ± 0.7
	4P	30266-30272	$4P_{1/2,3/2}-3S$	330	
K	6P	28999-29007	$6P_{1/2,3/2}-4S$	345	
	5D	30185	$5D_{3/2,5/2}-4P_{1/2,3/2}$	581-583	1.9 ± 1.0
	7S	30274	$7S-4P_{1/2,3/2}$	578-580	0.9 ± 0.5

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HETERONUCLEAR ENERGY POOLING COLLISIONS: THE Na(3P)+K(4P) REACTION

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An experiment has been performed in which two different atomic species – sodium and potassium – have been simultaneously excited in a cell by two resonant cw dye lasers and the fluorescence spectrum has been analysed by using an intermodulation technique to isolate the contributions due to the heteronuclear processes. The energy pooling collisions between Na(3P) and K(4P) have been observed for the first time and the relative collision cross sections have been measured.

1. Introduction

Collisions between excited atoms and/or molecules are of great interest because they give information both on the interatomic potentials in the mean and long range distances and on the laser radiation–vapor coupling. This last point is particularly important for a more deep understanding of the many and complex phenomena produced by an intense laser excitation of dense vapors and plasmas. The energy pooling collisions are those in which the electronic energy $E_T = E_i + E_j$ of the two incoming atoms is transferred to only one of them, while the other one decays to the ground state. These collisions may have many reaction products like, for example, very excited atoms, atomic or molecular ions, excited molecules, molecular dissociations etc., depending on the laser excited levels and on the peculiar properties of the involved atoms; in the following only the energy pooling collisions which populate very excited levels will be considered.

Since the paper by Allegrini et al. [1], in which the first experimental evidence of this process has been reported, many experiments have been performed mainly with alkali atoms [2]. All these experiments involve homonuclear collisions and only one laser excited atomic species.

The energy pooling collisions are effective only if the involved energy defect ΔE, calculated as the difference between E_T and the energy of the collision excited level, is comparable with kT and, for this reason, there are, in general, very few "quasi" resonances for a given atomic species. This condition limits the number of possible reactions and the amount of achievable information. The simultaneous excitation of atoms of two different species in a vapor mixture increases the number of possible "quasi" resonances and it proposes new interesting level scheme combinations. Moreover, it opens the possibility of a theoretical and experimental study of the interatomic potentials between different atoms in an important range of interatomic distances. The heteronuclear energy pooling collisions between alkali atoms present, in the $\Delta E/kT = 0$–3 range, about 60 "quasi" resonances which give an almost continuum spectrum versus the energy defect. Detailed tables are reported in ref. [3] with the preliminary results on heteronuclear Na-K energy pooling collisions.

In this paper we report the first observation of heteronuclear energy pooling collisions between Na and K and the experimental measurement of the collision cross sections σ_{ij}.

Sodium and potassium atoms are both excited by two cw dye lasers resonant with the first electronic transitions and the collision process is monitored through the analysis of the fluorescence spectrum. The process is described by the following reactions

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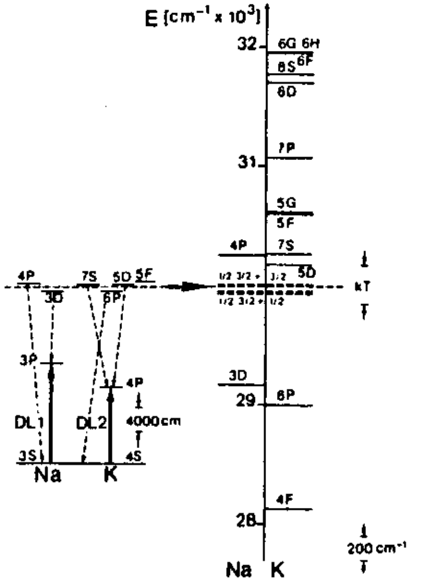

Fig. 1. Partial electronic energy level schemes of Na and K. Full arrows indicate laser excitations and broken arrows the observed transition lines. On the right side the levels of Na and K with energy close to E_T are reported in an expanded scale.

$$\mathrm{Na(3P)+K(4P)\rightarrow Na(3S)+K(}x\mathrm{L)}\pm\Delta E\,, \qquad (1a)$$

$$\rightarrow \mathrm{Na(}y\mathrm{L)+K(4S)}\pm\Delta E\,, \qquad (1b)$$

where xL = 6P, 5D, 7S, 5F and yL = 3D, 4P (see table 1). In fig. 1 the partial level schemes of Na and K are reported. The dashed horizontal line represents the sum energy of the Na(3P) and K(4P) levels, the full arrows simulate the laser excitation and the dashed ones indicate the detected transition lines. On the left the very excited states with energy close to E_T are reported in an expanded scale.

The double atomic excitation produces a very rich spectrum in which the contribution due to the homonuclear reactions overwhelms, in general, the one from the heteronuclear collisions. This has been demonstrated in a previous experiment with a sodium–potassium mixture and double laser excitation where only the potassium high excited levels were observed [4]. To eliminate this problem an intermodulation technique has been adopted: the two lasers are modulated at two different frequencies and phase sensitive detection is made at the sum frequency. The obtained signal is therefore only due to the processes related to the double laser excitation. In order to obtain the collision cross sections of reactions (1) the effective lifetimes of the laser excited levels have been measured.

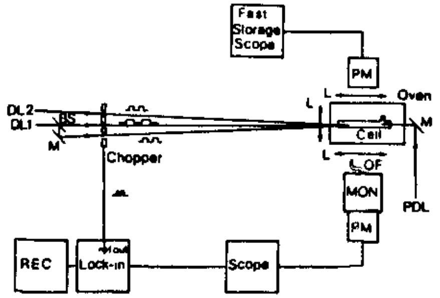

Fig. 2. Sketch of the experimental apparatus. M = mirror, BS = beam spliter, L = lens, OF = optical fiber, MON = monochromator, PM = photomultiplier, REC = recorder, DL1 and DL2 = cw dye lasers, PDL = pulsed dye laser.

2. Experimental appartus and measurement procedure

A sketch of the experimental apparatus is shown in fig. 2. The vapor mixture is confined in a capillary cell with an internal diameter d = 1.8 mm and a length L = 5 cm. A small reservoir for the metal deposit is welded on the side of the main body of the cell to which it is connected by a short capillary. Details of the special procedure adopted to build up this kind of cell can be found in ref. [5]. This particular geometry has been adopted to reduce the selftrapping of the resonance radiations and to have a constant and known excited volume that is a fundamental condition for a correct measurement of σ_{ij}.

In order to have the heteronuclear collision frequency comparable with the homonuclear ones the vapor densities of the two alkalis have to be comparable. To satisfy this condition the metal reservoir has been filled with a Na–K alloy because the vapor density of pure potassium is about two orders of magnitude higher than that of pure sodium [6]. According to the empirical Raoult law [7], the vapor pressure of each component is given, in first approximation, by

$$p(\mathrm{Na,K})=\frac{x(\mathrm{Na,K})}{x(\mathrm{Na})+x(\mathrm{K})}\,p^0(\mathrm{Na,K})\,, \qquad (2)$$

where p(Na, K) and p^0(Na, K) represent the Na/K vapor pressure of the alkali mixture and of the pure metal respectively, and x(Na, K) are the molar fractions of the two alkalis in the alloy. An alloy containing about 10% of potassium and 90% of sodium roughly satisfies this requirement.

This is a favourable condition for the observation of the heteronuclear collisions, it reduces the possibility of secondary processes due to too high density of one of the two atomic species and it makes equal the excited volumes of sodium and potassium for comparable absorbed laser powers. The cell, after it has been cleaned and evacuated down to 10^{-7} Torr for many hours, is placed in an oven at temperatures ranging between 200 and 260°C.

Two cw dye lasers are used to excite sodium (DL1) and potassium (DL2) respectively. The two laser beams cross a disk shaped chopper on which three series of holes have been drilled in order to modulate DL1 at the frequency ω_1, DL2 at frequency ω_2 and to give to the lock-in amplifier the reference signal at frequency $\omega_1+\omega_2$. A beam splitter, intercepting the DL1 laser beam, produces a second yellow laser beam which is modulated at frequency ω_3. This auxiliary yellow beam is used to monitor the homonuclear energy pooling collisions as it will be discussed here below. DL1 is a single mode dye laser actively stabilized with a maximum output power W_1 = 100 mW; DL2 is a multimode dye laser with a maximum output power W_2 = 200 mW. The wavelengths are λ_1 = 589.0 nm and λ_2 = 766.5 nm. The excited fluorescence is collected at right angles, focussed by a lens which reproduces the image of the cell. To eliminate volume effects a multimode optical fiber (λ = 0.6 mm) is used to collect only the fluorescence emitted very near to the entrance of the cell. The fluorescence is then analysed by a 1 m focal length monochromator and phase-detected by a photomultiplier connected to a lock-in amplifier.

To measure the effective lifetimes of the two laser excited levels a pulsed excitation has been used: a dye-laser, with grazing incidence grating and pumped by a nitrogen laser, is tuned alternatively to the two resonance transitions by using rhodamine 6G and Oxazine 750 to excite sodium and potassium atoms respectively. The fluorescence is analyzed with a fast transient storage oscilloscope that gives the temporal evolution of the signal.

An absolute measurement of the collision cross section of reaction (1) would be very difficult because many independent parameters have to be measured. For that reason it has been convenient to measure these cross sections relatively to that of reaction

$$\mathrm{Na(3P)+Na(3P)\rightarrow Na(3S)+Na(5S)}+\Delta E\,, \qquad (3)$$

for which absolute measurements exist [5,8].

By assuming that other processes, like for example multiphoton excitation, atomic ionization etc., are negligible (the experimental conditions are chosen to minimize them), the rate equations for reactions (1) become

$$(\mathrm{d/d}t)\,N_j=-N_j\sum_{i\neq j}A_{ji}$$

$$+k_j[\mathrm{Na(3P)}]_{\omega_1}[\mathrm{K(4P)}]_{\omega_2}\,, \qquad (4a)$$

where N_j is the population density of the excited level, $j=x$L, yL; $\sum A_{ji}$ is the sum of the spontaneous transition probabilities of the level j; $k_j=V\sigma_j$ is the rate constant of the process. The subscripts ω_1 and ω_2 put in evidence that the populations of the laser excited levels are modulated at two different frequencies.

The rate equation for process (3) is given by

$$(\mathrm{d/d}t)\,N_{5S}=-N_{5S}\sum_{i\neq 5S}A_{5S,i}$$

$$+k_{5S}[\mathrm{Na(3P)}]_{\omega_1}[\mathrm{Na(3P)}]_{\omega_3}\,. \qquad (4b)$$

The solution of these equations at the steady state provides the ratios

$$\frac{k_j}{k_{5S}}=\frac{\sum A_{ji}}{\sum A_{5S,i}}\,\frac{N_j}{N_{5S}}\,\frac{[\mathrm{Na(3P)}]_{\omega_3}}{[\mathrm{K(4P)}]_{\omega_2}}\,. \qquad (5)$$

By introducing the experimental observed fluorescence line intensities

$$I_{jk}=\alpha_{jk}h\nu_{jk}A_{jk}N_jV/4\pi\,,$$

and the branching ratios

$$\gamma_{jk} = A_{jk} \Big/ \sum_{i<j} A_{ji} ,$$

we obtain

$$\frac{k_j}{k_{5S}} = \frac{\alpha_{5S-3P}}{\alpha_{jk}} \frac{\alpha_{4P-4S}}{\alpha_{3P-3S}} \frac{\nu_{5S-3P}}{\nu_{jk}} \times \frac{\nu_{4P-4S}}{\nu_{3P-3S}} \frac{\gamma_{5S-3P}}{\gamma_{jk}} \frac{\tau_{3P}}{\tau_{4P}} \frac{I_{ij}}{I_{5S-3P}} \left[\frac{I_{3P-3S}}{I_{4P-4S}}\right]_{\omega_2} ; \qquad (6)$$

where α_{ij} are factors taking into account the efficiency of the detection apparatus, ν_{ij} are the transition frequencies, V is the emission volume and τ_{3P}, τ_{4P} are the effective lifetimes of the laser excited levels of Na and K respectively.

With this method it is not necessary to measure directly the two vapor densities and to perform an absolute calibration of the detection apparatus but it is sufficient to measure the ratios I_{jk}/I_{5S-3P} and the ratio between the two lines I_{3P-3S} and I_{4P-4S} excited by the laser beams modulated at the frequency ω_2.

The measurement procedure is as follows: at a fixed temperature the effective lifetimes of the 3P and 4P levels of sodium and potassium respectively are measured upon resonant pulsed excitation; then DL1 is switched on and split in two beams that are modulated at the two frequencies ω_1 and ω_2. This excitation activates reaction (3) and the intensity of the line due to the transition from the 5S to 3S level is measured together with the intensity of the D-lines due to the beam modulated at the ω_2 frequency. The DL1 modulated at ω_2 is then stopped and the DL2 is switched on. The intensities of the lines due to the reaction (1) are measured as well as the potassium D-line intensities and the signals are compared to the ones obtained with the previous excitation. The two series of measurements are perfectly comparable because the DL1 main beam is the same.

3. Results and discussion

The resonant excitation of an alkali vapor produces an almost continuum fluorescence spectrum due to the energy transfer between the atoms and the atoms and the dimers [9]. This fact may obscure the effect or, at least, it may induce huge errors in the line intensity evaluation. By using the intermodulation technique this problem has been eliminated and the spectrum shows only the lines excited by the heteronuclear energy pooling collisions or those connected, in any case, to the double excitation, whereas any other contribution is cancelled out. In fact in fig. 3 a spectrum obtained at 240°C shows only few atomic lines. The lines marked with a star are those excited by the heteronuclear energy pooling collisions and they originate only from the levels with an energy defect or excess lower than $3kT$, while there is no evidence of lines from higher or lower lying levels like for example the K(6D) and K(8S) which would be around 535 nm. This clearly shows the "quasi" resonant behaviour of the effect and also that higher order processes are negligible. Therefore all the expected lines are in the spectrum except the 5F–3D, which is in the infrared part of the spectrum, i.e. out of the sensitivity of our apparatus. The other lines in the spectrum are originated by a two step process in which excited sodium atoms are involved accordingly to the following reactions:

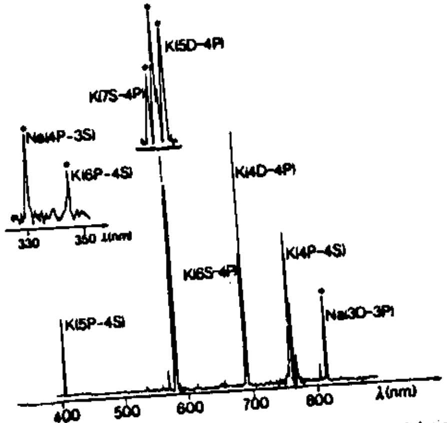

Fig. 3. Fluorescence spectrum obtained with the intermodulation technique and upon simultaneous excitation of Na and K. $T = 240$ C, $W_1 = 65$ mW and $W_2 = 190$ mW; the stars indicate the lines due to the heteronuclear energy pooling collisions.

$$[\mathrm{Na(3P)}]_{\omega_1} + \mathrm{K(4S)} \to \mathrm{Na(3S)} + [\mathrm{K(4P)}]_{\omega_1} , \qquad (7)$$

$$[\mathrm{K(4P)}]_{\omega_1} + [\mathrm{K(4P)}]_{\omega_2} \to \mathrm{K}(xL) + \mathrm{K(4S)} , \qquad (8)$$

i.e. the excited sodium atoms transfer their energy to potassium atoms with a rate that is modulated at frequency ω_1. These excited potassium atoms may collide with the other ones excited by the DL2 laser and populate the higher energy levels [10]. The intensities of these lines are comparable with the other ones supporting a previous measurement of the electronic energy transfer collision cross section between Na(3P) and K(4S), which is of the order of 10^{-14} cm² [11].

All the lines in the spectrum show a linear dependence on both laser intensities and they disappear when any one of the two lasers is switched off, even if a strong fluorescence is still visible in the cell.

In our experimental conditions the effective lifetimes of Na and K resulted, at $T = 240$°C, $\tau_{3P} = 176 \pm 20$ ns and $\tau_{4P} = 287 \pm 30$ ns respectively, which are about ten times longer than the natural ones ($\tau_{3P} \approx 16$ ns and $\tau_{4P} \approx 27$ ns).

By applying the described procedure, the collision cross sections for the reactions populating the 3D level of sodium and the 5D and 7S of potassium have been measured. The obtained values are reported in table 1. Unfortunately the same result has not been possible, for the moment, for the other levels in the table. For the 5F the reason was a lack of sensitivity of the detection apparatus in the near infrared region, whereas for the other levels, i.e. the 4P of sodium and the 5P of potassium, the main problems were originated by unresolved self trapping effects and to a very poor evalution of the cell glass absorption in the uv.

The errors have been evaluated to be of the order of 50% as a result of the uncertainty on the lifetimes, the line intensity measurements, the error on k_{5S} and possible small differences in the excited volumes of sodium and potassium.

4. Conclusions

Sodium and potassium atoms in a vapor mixture have been simultaneously excited by two resonant cw dye lasers. This double excitation originates a very bright fluorescence due to many collisional processes which distribute the absorbed energy over many electronic levels of the two atoms and of the molecules. We have adopted a special detection technique and particular experimental conditions to isolate one of those inelastic processes i.e. the energy pooling collisions between sodium and potassium atoms. This particular reaction has been observed and the relative collision cross-sections have been measured with a satisfactory accuracy.

The obtained σ_{ij} values do not exhibit remarkable differences with those obtained for the homonuclear reactions, while the experiment clearly shows the "quasi" resonant behaviour of the effect that becomes rapidly negligible for increasing ΔE.

Table 1
List of levels populated by Na(3P)/K(4P) collisions with the main parameters. In the last column the measured cross sections at $T = 240$°C are reported

Atom	Level	ΔE (cm^{-1})	Detected transition	Transition wavelength λ(Å)	γ	α	$\sigma \times 10^{15}$ (cm²)
Na	3D	+768	3D–3P$_{1/2,3/2}$	8183–8195	0.83–1	0.017–0.014	1.4±0.7
	4P	−251	4P$_{1/2,3/2}$–3S	3302	0.60	0.39	
K	6P	+934	6P$_{1/2,3/2}$–4S	3446–3447	0.25	0.41	
	5D	−169	5D$_{3/2,5/2}$–4P$_{1/2,3/2}$	5812–5832	0.19	0.165	1.9±1.0
	7S	−258	7S–4P$_{1/2,3/2}$	5782–5802	0.18–0.36	0.165	0.9±0.5
	5F [a]	−590					

[a] No transitions have been detected from the 5F level because they are in the infrared where our apparatus is not sensitive.

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Three-Body Collisions between Laser-Excited Na and K Atoms in the Presence of Buffer Gas.

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Summary. — Energy pooling in alkali vapour mixtures has been previously investigated by us in an amalgam of sodium and potassium. In this paper we describe the peculiar features appearing when some buffer gas is introduced in the cell. We demonstrate that the buffer gas enhances the energy transfer between Na($3P$) and K($4S$), which is detected through the effects induced on the highly excited states populated by the Na($3P$)/Na($3P$) and K($4P$)/K($4P$) collisions.

PACS. 34.50. – Inelastic scattering of atoms and molecules.

1. – Introduction.

The resonant laser excitation of an alkali vapour easily produces high densities of excited atoms owing to the very large dipole moment of the fundamental transition. These excited atoms, behaving during the collision like energy absorbers or sources, speed up the population transfer to other atoms or electronic levels. This can be revealed by observing the emitted complex spectrum that contains atomic lines and molecular bands which evidence the presence of different collisional processes. In particular, intense fluorescence lines coming from highly excited levels appear when the vapor density is high enough. These lines are generated by the energy-pooling process (¹), followed, under appropriate conditions, by others like, for example, molecular and atomic

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ionization (2). Many experiments have been carried out on this subject during the last few years and it is possible to affirm that almost all the population-leaking channels of the laser-excited levels have been studied in detail in the homonuclear reactions of the alkali atoms, where only one atomic species is excited by the laser. In this specific case, the electronic-energy transfer and the associative ionization have been found to be the main reaction channels.

We started a new series of experiments on alkali vapour mixtures, in which two atomic species are simultaneously excited by two resonant lasers, to study the electronic-energy transfer processes occurring in the heteronuclear collisions. A review of all the possible «quasi»-resonances with preliminary results has been reported in (3).

In a first experiment performed with a Na-K mixture (4), we have observed the heteronuclear energy-pooling collisions described by the following reactions:

$$(1)\qquad \begin{cases} \mathrm{Na}(3P) + \mathrm{K}(4P) \rightarrow \mathrm{Na}(nL) + \mathrm{K}(4S) \pm \Delta E\,, \\ \mathrm{Na}(3P) + \mathrm{K}(4P) \rightarrow \mathrm{Na}(3S) + \mathrm{K}(mL) \pm \Delta E\,, \end{cases}$$

where $nL = 3D, 4P$; $mL = 6P, 5D, 7S, 5F$ and ΔE is the energy defect or excess. The two laser-excited atoms exchange their internal energy in such a way that one of the two atoms goes down to the ground state, whereas the other one jumps to a highly excited state. The condition to be fullfilled is that

$$(2)\qquad \Delta E = |E(nL, mL) - [E(3P) + E(4P)]| \simeq KT\,,$$

where $E(x)$ is the energy of the x-state. In ref. (4) the experimental technique as well as the measurement method have been described and the collision cross-sections of these processes have been reported.

In the present paper an experimental analysis of the main collisional depopulation pathways undergone by the laser-excited atoms in the heteronuclear collisions in the presence of low-pressure buffer gas is reported. The processes are detected by analysing the emitted atomic fluorescence and by adopting an intermodulation detection technique to isolate the heteronuclear contribution to the spectrum. In this technique the two lasers are modulated at two different frequencies, while the signal is detected at the sum frequency. In fact, as will be discussed below, the signals due to collisions between Na and K or to collisions of higher order involving heteronuclear reactions, and only these ones, have components modulated at frequencies that are sum or difference of the modulation ones.

With respect to ref. (4) in the present paper the new features induced by the buffer gas are stressed and the role of three-body collisions is shown.

2. – Experimental apparatus.

The experimental apparatus is shown in fig. 1. It consists of a collision cell, placed in an oven to control the vapour densities, of two c.w. dye lasers and of a wide-window detection apparatus.

The collision cell, having cilindrical shape with (1 × 6) cm dimensions, is the bulb of a spectral lamp and it is filled with Na and few Torr of neon as buffer gas, whereas the potassium atoms are present as impurity. The oven allows us to reach temperatures up to $T = 300\,^{\circ}\mathrm{C}$ and to maintain T constant within $1\,^{\circ}\mathrm{C}$. The beams of two c.w. dye lasers are superimposed inside the cell after they

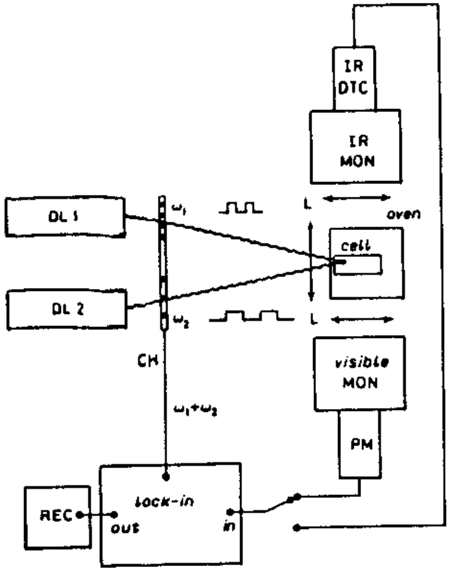

Fig. 1. – Sketch of the experimental apparatus. DL1 = Na-resonant dye laser, DL2 = K-resonant dye laser, CH = chopper, L = lens, PM = photomultiplier, IR DTC = = infrared detector, REC = recorder, MON = monochromator.

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intersected a chopper which modulates the two lasers at the two frequencies ω_1 and ω_2. Laser 1, a single mode Rhodamine 6*G* dye laser pumped by an Ar^+ laser, is tuned to the D_2 line of sodium ($\lambda = 589.0$ nm); laser 2, a multimode Oxazine dye laser pumped by a Kr^+ laser, is tuned to the D_2 line of potassium ($\lambda = 766.5$ nm). The output powers of the two lasers are of the order of 100 mW.

The detection apparatus permits to analyse the entire spectrum from 400 nm to 2.5 μm and it consists of two independent sections, one for the visible from 400 nm to 850 nm and one for the near infrared from 1 μm up to 2.5 μm. For the visible radiation we used a monochromator with 1 m focal length and a 1200 lines/mm grating, coupled to a Hamamatsu *R*955 photomultiplier, while for the near infrared we adopted a monochromator with a 35 cm focal length and a 300 lines/mm grating coupled to a PbS detector cooled to the dry-ice temperature. The signal coming from the detectors is amplified and phase detected by a lock-in amplifier tuned to the frequency $\omega = \omega_1 + \omega_2 = 900$ Hz. This frequency has been chosen to optimize the sensitivity of the near-infrared detector.

3. – Results.

The resonant laser excitation of both Na and K produces a quite bright fluorescence that covers, obviously with very different intensities, the whole visible spectrum as a consequence of the presence of collisionally excited atomic lines and molecular bands.

In addition to the fundamental *D*-lines of Na and K some other atomic lines can be detected, whose intensities increase quadratically or with faster rate as functions both of the laser intensity and of the atomic density. It is important to note here that, in our experimental conditions, *i.e.* low laser power density, the fluorescence can be generated only by collisional processes and not by multiphoton ionization. An example of such a spectrum can be found in ref. (4), where Na has been resonantly excited at relatively high temperature.

In fig. 2 a portion of the spectrum obtained under different irradiation conditions is reported. In fig. 2*a*) the spectrum obtained under double resonant laser excitation is shown. The comparison of this spectrum to those obtained with only the yellow Na resonant laser beam (fig. 2*b*)) and with only the red K resonant laser beam (fig. 2*c*)) exibits the nonlinear increasing of some lines. In fact, when both lasers are on, the K(5*P*-4*S*), K(6*S*-4*P*) and *K*(4*D*-4*P*) lines are about three times more intense than the sum of the intensities upon separate excitations, while the sodium lines do not change significantly. It is evident that this behaviour is determined by the heteronuclear collisions between excited atoms which deeply modify the population distributions among the high-lying energy levels.

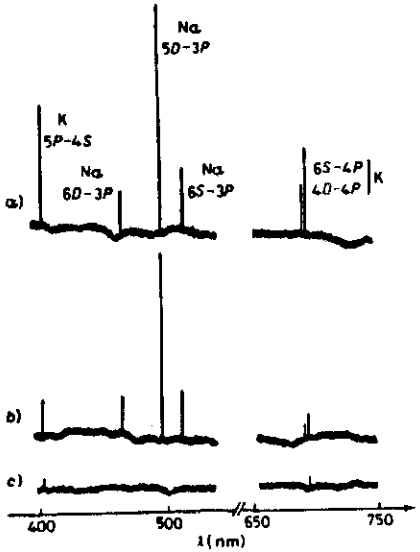

Fig. 2. – Spectra obtained with single or double laser excitations: *a*) double laser excitation; *b*) only Na-resonant laser excitation; *c*) only K-resonant laser excitation.

As the induced modification is not always so important with respect to the total intensity of each line, a detection method able to reveal only this contribution would be more useful. By adopting the intermodulation technique the heteronuclear part of the signal is separated from all the others and a more detailed picture of the effect is obtained.

In fig. 3 the fluorescence spectrum obtained under a double modulation is reported. In fig. 3*a*) the spectrum in the visible and in fig. 3*b*) the one in the near infrared are shown. Three kinds of transitions, marked with α, β and γ, can be distinguished, which correspond to three different collisional processes.

This spectrum shows some new features with respect to those reported in ref. (4): the presence of the fluorescence from levels near the energy $2 \cdot E(3P)$ of sodium (γ levels); a different relative intensity among the other lines. Moreover, the phase of the γ lines is negative, which must be interpreted as due to a depopulation mechanism. The corresponding levels are the 4*D* and 5*S*, which give origin to the two lines at 569 nm and 616 nm, respectively, and the 5*F* which fluoresces at 1.26 μm. In the infrared region also the 4*S*-3*P* transition of Na at 1.14 μm is present, but, as this level is populated by the decay from the 4*P* level in the transition 4*P*-4*S* at 2.21 μm, it has opposite phase.

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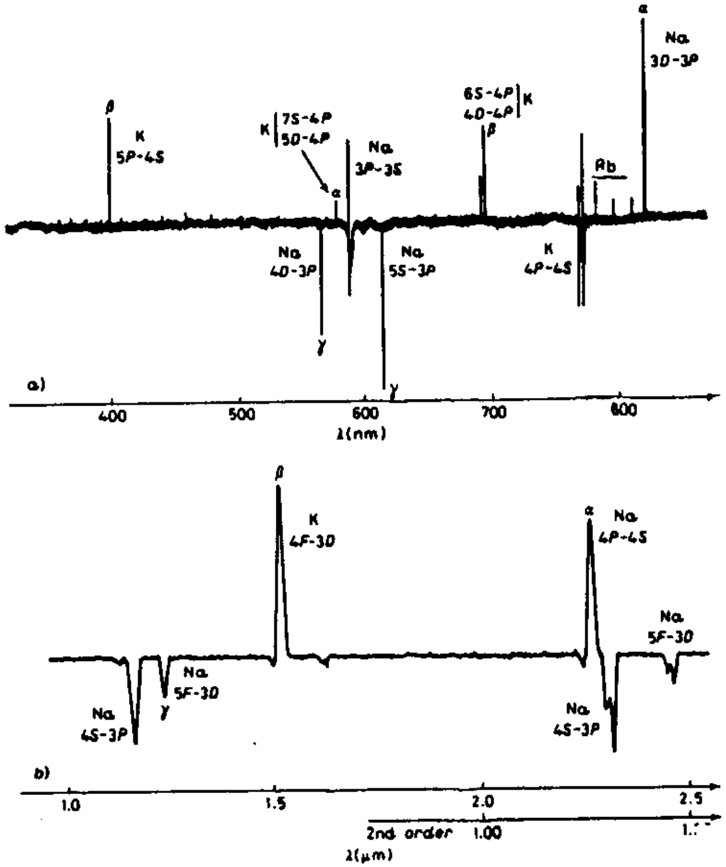

Fig. 3. – Spectra obtained with double laser excitation and with the intermodulation technique: *a*) visible spectrum; *b*) infrared spectrum.

In order to better understand the origin of these lines and to give reason of the phase reverse, two simplified energy level schemes of Na and K are reported in fig. 4. The two full arrows simulate the double laser excitations, the lower dotted line the double of the energy of the 4*P* level of K, the upper one the double of the energy of the 3*P* Na level and the broken line represents the sum of the energies of 4*P* and 3*P* levels. In this scheme only the levels contributing to the spectrum are reported. It is evident that all those levels are very close to someone of the horizontal lines, while all the others are missing.

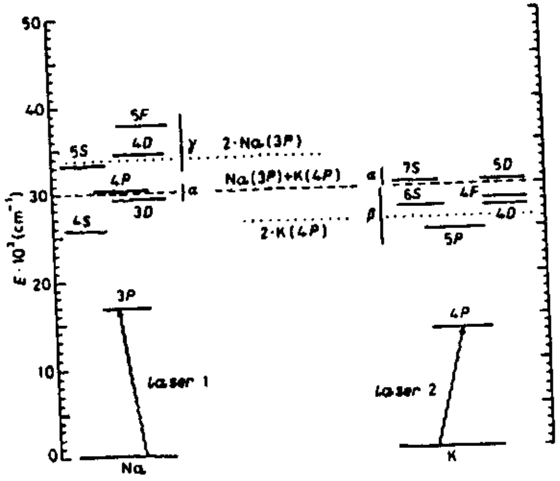

Fig. 4. – Simplified energy level schemes of Na and K atoms.

By referring to the given energy scheme and to the letters α, β and γ, the following energy-pooling processes can be introduced to explain the spectrum

$$\left\{\begin{array}{ll} \text{levels } \alpha & \\ \mathrm{Na}(3P)+\mathrm{K}(4P) & \to \mathrm{Na}(xL)+\mathrm{K}(4S)\pm\Delta E\,, \\ & \to \mathrm{Na}(3S)+\mathrm{K}(yL)\pm\Delta E\,; \\ & \\ \text{levels } \beta & \\ \mathrm{K}(4P)+\mathrm{K}(4P) & \to \mathrm{K}(y'L)+\mathrm{K}(4P)\pm\Delta E\,; \\ & \\ \text{levels } \gamma & \\ \mathrm{Na}(3P)+\mathrm{Na}(3P) & \to \mathrm{Na}(x'L)+\mathrm{Na}(3S)\pm\Delta E\,. \end{array}\right. \tag{3}$$

All the given reactions have been experimentally observed and, in the case of α and γ collisions, the cross-sections have been measured. Therefore, to a first insight the presence of all these lines can be easily justified by assuming effective the energy-pooling collisions discussed in the introduction and by considering also the homonuclear ones. Indeed, we adopted the intermodulation spectroscopy to cancel this contribution, and, therefore, their presence must be explained by assuming effective new processes that were not important in experiments without buffer gas, as is proved by the absence of some of these lines or by the very different relative intensities of some others with respect to the previous experiment.

The role played by the buffer gas is to remove or to supply the energy excess or defect in the inelastic reactions and to increase the reaction rate. The introduction of some buffer gas affects, first of all, the population distribution between close levels by inducing a fast transfer from one level to the others. But, as this effect is active on the same laser-excited atom, it does not modify the frequency modulation of the fluorescence and this is true for any two-body collision between the buffer gas and the alkalis. That means that this kind of collisions does not modify the intermodulation spectrum. Therefore, we have to consider a more complex process able to modify the population distribution and the frequency modulation of the fluorescence; this process can be a three-body collision involving a sodium, a potassium and a buffer gas atom.

The population transfer from the excited sodium to the ground-state potassium

$$\mathrm{Na}(3P) + \mathrm{K}(4S) + \mathrm{M} \rightarrow \mathrm{K}(4P) + \mathrm{Na}(3S) + \mathrm{M} + \Delta E\,, \tag{4}$$

where M is a buffer-gas atom, $\Delta E = 3931\ \mathrm{cm}^{-1} \simeq 10\,KT$, can be the process. This is a highly exothermic reaction that can be enhanced by the presence of the buffer gas which we assume to carry out the huge energy excess in a three-body collision. Moreover, if a strong Na(3P)/K(4S) coupling is realized, this may mix up the two modulation frequencies.

The three-body collisions become important at gas pressure larger than 1 Torr (6) and they can be conveniently described in terms of a three-body rate coefficient, k_3, defined, similarly to the two-body collisions, as

$$\frac{\mathrm{d}Z}{\mathrm{d}t} = -k_3 n_1 n_2 n_3\,, \tag{5}$$

where Z represents the number of three-body events in the unit time and unit volume and n_1, n_2 and n_3 are the densities of the collidents. k_3 is expressed in $L^6 t^{-1}$ unities and it can be written as $k_3 = \sigma_3 v_3$, where σ_3 is the three-body collision hyper–cross-section and

$$v_3 = \frac{15\pi}{8}\sqrt{\frac{KT}{2\pi\mu_3}} \tag{6}$$

with

$$\mu_3 = \sqrt{\frac{m_1 m_2 m_3}{m_1 + m_2 + m_3}}\,. \tag{7}$$

The ratio between the number of three-body collisions and the two-body ones is then given by

$$R = k_3 N / k_2\,, \tag{8}$$

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(6) J. B. HASTED: *Physics of Atomic Collisions* (Butterworths, London, 1972).

where $k_2 = \langle \sigma_2 v \rangle = \sigma_2 \bar{v}$ is the rate constant for two-body collisions; N is the buffer-gas density and its value in our experiment is $N \approx 10^{17}\ \mathrm{cm}^{-3}$, k_2 has been already measured (7) and its value is $k_2 \approx 10^{-11}\ \mathrm{cm}^3\,\mathrm{s}^{-1}$.

As in the experiment without buffer gas, there is no evidence of the γ levels and, as the relative intensity of the β levels is increased by more than a factor 10, we may assume that, in our conditions, R must have a lower value $R \approx 10 \div 100$, from which derives the lower-limit value for $k_3(\mathrm{Ne, Na, K^*}) \approx 10^{-27}\ \mathrm{cm}^6\,\mathrm{s}^{-1}$, that is, to our knowledge, its first experimental evaluation.

Thus the qualitative picture is the following: the Na(3P) sodium atoms modulated at the ω_1 frequency collide with the atoms which are excited to the 4P with this modulation; on the contrary, as the K(4S) density is modulated at ω_2 by the red laser, there is an ω_2-induced modulation on the Na(3P) population. The result is that the strong coupling factor $\mathrm{d}Z/\mathrm{d}t = k_3 N\,\mathrm{Na}(3P)\,\mathrm{K}(4S)$ induces a reciprocal modulation on both atoms, which can be easily verified by simple algebra.

A detailed analysis of the equations describing the processes is complicated and not fruitful: we have made an approximate treatment by assuming the laser-modulated populations to be

$$\mathrm{Na}(3P) \propto A(1 + \cos\omega_1 t) \quad \text{and} \quad \mathrm{K}(4S) \propto B(1 - r\cos\omega_2 t)\,, \tag{9}$$

where A, B and r are parameters depending on the experimental conditions, while the minus sign takes into account the fact that the 4S level is depopulated by the laser. The collision modifies the Na(3P) modulation as

$$\mathrm{Na}(3P) \propto AB(1 + \cos\omega_1 t)(1 - r\cos\omega_2 t)\,. \tag{10}$$

It comes out that Na(3P) contains terms at the ω_1 and ω_2 frequencies in opposition of phase. As Na($x'L$) is proportional to the square of the Na(3P) density, we find in Na($x'L$) one term $\propto [-\cos\omega_1 t \cos\omega_2 t]$, which gives origin to the signal at the $\omega_1 + \omega_2$ frequency with the proper phase, while the others represent components at different frequencies. The same agreement is obtained for the other observed lines.

Let us conclude with two final remarks: in the spectrum of fig. 3a) the signals due to the fundamental transition of Na and K are obscured by saturation of the photomultiplier due to the very high intensity of the fluorescence; the comparison of this spectrum with that of fig. 2 shows that the Na lines are missing here, while the ones corresponding to the 4P, 6S and 4D levels of potassium, that are the most affected by the double laser excitation, are present. This confirms that these K lines are induced by heteronuclear collisions, while is

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(7) M. ALLEGRINI, G. ALZETTA, L. MOI and D. GIULIETTI: *Nuovo Cimento B*, 28, 69 (1975).

not the same for those Na levels which are populated by higher-order homonuclear processes.

4. – Conclusions.

Many collisional processes take place when high densities of excited atoms are produced by double resonant laser excitation. In this experiment the modification of the population distributions among excited levels induced by the presence of a buffer gas is shown. The strong coupling between Na($3P$) and K($4S$) established by the three-body collisions with the buffer-gas atoms is detected through the energy-pooling collisions populating the Na (γ) levels and the K(β) levels. The fluorescence emitted by these levels has, in fact, a frequency modulation evidencing a previous heteronuclear collision between Na and K. A limiting value for the three-body collision cross-section has been derived from the experiment.

● RIASSUNTO

Abbiamo in precedenza studiato il processo di collisione di energy pooling in una miscela di sodio e potassio. In questo lavoro si analizzano i particolari effetti indotti dalla presenza di alcuni Torr di gas tampone introdotti nella cella. Viene dimostrato che il gas tampone favorisce il processo di trasferimento di energia fra Na($3P$) e K($4S$), che viene rivelato attraverso gli effetti indotti sugli stati altamente eccitati popolati dalle collisioni Na($3P$)/Na($3P$) e K($4P$)/K($4P$).

Трех-частичные соударения между атомами Na и K, возбужденными лазером, в присутствии буферного газа.

Резюме (*). — Ранее авторы в амальгаме натрия и калия исследовали распределение энергии в смесях щелочных паров. В этой статье мы описываем особенности, возникающие при введении буферного газа в ячейку. Мы показываем, что буферный газ усиливает обмен энергией между Na($3P$) и K($4S$), который детектируется через эффекты, связанные с высоко возбужденными состояниями, заселенными при Na($3P$)/Na($3P$) и K($4P$)/K($4P$) соударениях.

(*) *Переведено редакцией.*

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ENERGY TRANSFER COLLISIONS IN LASER EXCITED MIXTURES OF ALKALI VAPORS

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ABSTRACT

Energy transfer collisions between two laser excited alkali atoms of different species have been investigated in cell experiments using an intermodulation technique. Cross sections have been measured for the potassium/rubidium mixture and evidence of three-body collisions in presence of a buffer gas has been obtained in the sodium/potassium mixture.

INTRODUCTION

The collisions involving two atoms both in an excited state play an important role in different fields of atomic and molecular physics. The colliding atoms may evolve to several exit channels giving quite different products : ions plus electrons through associative ionization, very excited atoms through electronic energy transfer and excited molecules through atom/molecule energy transfer or molecule formation. At first these collisions have risen much interest as a mean to produce plasmas at very low laser power[1]. Later on they have been considered as a possible mechanism for population inversion in atomic and molecular levels with consequent opportunity for new laser sources[2,3]. More recently the associative ionization has been considered as a limiting process in the atom density achievable with cooling techniques[4]. The population transfer from the initial laser excited atoms to higher levels has been extensively studied in alkali vapors. We have pointed out the interest of extending these studies to mixtures of different alkalis[5] and designated a set of experiments to measure the relative cross sections of heteronuclear energy transfer collisions.

The processes we consider are

$$A^*(nP) + B^*(mP) \quad \text{--->} \quad A^{**}(n'L) + B(mS) \qquad (1)$$

where [$A(nS)$, $B(mS)$], [$A^*(nP)$, $B^*(mP)$] and [$A^{**}(n'L)$, $B^{**}(m'L)$] indicate two alkali atoms of different species in the ground state, in the first excited state and in highly-lying states respectively. The energy transfer is effective only to $A^{**}(n'L)$ and $B^{**}(m'L)$ levels such that the energy defect $|\Delta E|$ from initial to final energy of the reaction is comparable with kT. In order to measure the cross sections of reactions (1), atoms A and B are optically excited to the first P-level and fluorescence intensities are measured from the $A^{**}(n'L)$ and $B^{**}(m'L)$ states. Two dye lasers (cw in our experiments) are required for the selective excitation of the two alkali species. Because $A^*(nP)$ and $B^*(mP)$ atoms are simultaneously produced, the fluorescence spectrum contains emission also from levels populated through homonuclear collisions

$$\begin{aligned} &A^*(nP) + A^*(nP) \;\text{--->}\; A^{**}(n''L) + A(nS) \\ &B^*(mP) + B^*(mP) \;\text{--->}\; B^{**}(m''L) + B(mS) \end{aligned} \qquad (2)$$

This contribution may predominate over the fluorescence lines coming from highly excited atoms populated by heteronuclear collisions and must be eliminated. To this purpose we have adopted an intermodulation technique, whose details have been described in reference [6], which involves modulation of the two laser beams at two different frequencies ω_1 and ω_2 and phase sensitive detection of the fluorescence at the sum frequency $\omega_1 + \omega_2$. The alkali vapors are produced in a sealed pyrex cell containing an amalgam of the two different metals under study. The amount of the two metals in the amalgam are chosen in such a way that at a given temperature the two species have comparable densities. The determination of the cross sections requires also knowledge of the excited atoms A^* and B^* densities; these have been indipendently deduced from the effective radiative lifetimes measured in a resonance fluorescence experiment under pulsed excitation. For processes (2) absolute cross sections have been measured in several cases; cross sections for heteronuclear processes (1) are, however, more difficult to measure because many independent parameters are needed. For that reason we have found convenient to determine the cross sections of processes (1) relatively to suitable cross sections of processes (2).

RESULTS

Table I shows the results obtained for the sodium/potassium and potassium/rubidium mixture while table II lists the absolute cross sections for sodium/sodium and rubidium/rubidium collisions used as reference.

Table I. List of levels populated by the collisions of column 1. The cross sections reported in column 5 have been measured relatively to the absolute cross sections (a) and (b) reported in table II.

Collision process	Atom	Level	T(^{0}C)	$\sigma \times 10^{15} cm^2$	Reference process	Ref.
Na(3P)/K(4P)	Na	3D	240	2.8 ± 1.4	(a)	[6]
	K	5D	240	3.8 ± 1.9	(a)	[6]
		7S	240	1.8 ± 0.9	(a)	[6]
K(4P)/Rb(5P)	Rb	5D	220	58 ± 29	(b)	[7]
		7S	220	6.4 ± 3.2	(b)	[7]
Rb(5P)/Rb(5P)	Rb	7S	180	2.8 ±1.4	(b)	[7]

The values for Na/K collisions reported in reference [6] have been doubled to take into account the correction introduced by Bezuglov et al.[8], valid for experiments performed in cells rather than in beams. The preliminary results for the potassium/rubidium mixture are reported here for the first time. For the moment they are restricted to collisions involving Rb atoms excited to the $5P_{3/2}$; however, work is in progress to investigate collisions involving also the lower $5P_{1/2}$ level. The measurement of the cross section in this case may be of particular interest because one of the collisionally populated levels is in the midst of the four fine structure levels $K^*(4P) + Rb^*(5P)$. The last cross section in table I is for energy transfer in pure rubidium. In previous studies[9] of the process

$$Rb^*(5P) + Rb^*(5P) \longrightarrow Rb^{**}(n''L) + Rb(5S) \qquad (3)$$

population transfer was observed only to the 5D state. Since we use the absolute cross section $\sigma_{5D}(Rb/Rb)$ of process (3) as reference (see table II) in the measurement of the cross sections for the heteronuclear potassium/rubidium collisions, we have checked if our apparatus give a $\sigma_{5D}(Rb/Rb)$ value in agreement with that of reference [9], (which is the case). During this experiment we have observed fluorescence also from the 7S level and therefore measured $\sigma_{7S}(Rb/Rb)$ relatively to $\sigma_{5D}(Rb/Rb)$. The resulting value matches other cross sections[3] for population transfer collisions in alkali vapors involving similar energy defects (in this case about 2kT).

Table II. List of collision processes and measured absolute cross sections used as reference for measuring the cross sections of table I.

	Collision process	Atom	Level	Absolute $\sigma \times 10^{15} cm^2$	Ref.
(a)	Na(3P)/Na(3P)	Na	5S	$3.6 \pm 1.3^{(*)}$	[10]$^{(**)}$
(b)	Rb(5P)/Rb(5P)	Rb	5D	$64 \pm 26^{(*)}$	[9]

(*) The original values have been doubled according to ref. [8].

(**) We have made an average of the two values from ref. [10].

THREE-BODY COLLISIONS

Heteronuclear collisions in a sodium/potassium mixture have been investigated also in presence of a foreign buffer gas[11]. The experiment has been performed using as cell the bulb of a Na spectral lamp which, in addition to sodium, contains a few torr of neon and potassium as impurity. Fluorescence spectra have been recorded upon three different excitation : i) with a single laser tuned to one of the Na D-lines, ii) with a second single laser tuned to one of the K D-lines and iii) with both lasers. While the intensity of fluorescence lines originated by sodium levels does not change significantly in the three spectra, that due to potassium levels exibits a nonlinear increase. Assuming that heteronuclear collisions are responsible for this behaviour, we have adopted the intermodulation technique to distinguish their contribution from that of homonuclear collisions. This intermodulation spectrum exibits new lines with respect to the analogous intermodulation spectrum observed without buffer gas. Moreover some of the fluorescence lines have opposite phase, which indicate a depopulation process of the level emitting the fluorescence. It is well known that the buffer gas increases the energy transfer rate between close levels, however the binary collisions involving alkali and buffer gas atoms can not modify the frequency modulation of the fluorescence. Therefore, in order to explain the modifications observed in the intermodulation spectrum, we have to consider a process able to affect both the population distribution and the modulation frequency of the fluorescence. A process that satisfies these two requirements is the three body collision

$$Na(3P) + K(4S) + M \longrightarrow Na(3S) + K(4P) + M \qquad (4)$$

where M indicates a buffer gas atom. The ratio between the number of three-body and two-body collisions can be expressed[12] as $R = k_3 N / k_2$, where k_3 is the three-body collision rate constant, N is the buffer gas density and k_2 is the two-body rate constant, which has been measured in reference [13]. Comparison of the intermodulation spectrum in presence and absence of buffer gas, suggests a lower value of $R \approx 10-100$, from which we deduce a lower limit for k_3 of $10^{-27} cm^6 s^{-1}$.

CONCLUSIONS

The intermodulation technique has been proved to be very useful to study the energy pooling collisions in mixtures of alkali atoms. The measured cross sections confirm the fact that the efficiency of these collisions decreases rapidly with increasing energy defects. With the same technique we have also demonstrated the effects of the buffer gas on these collisional processes.

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