Three-body collisions involving Na(3P), Rb(5S) and buffer gas atoms*

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Abstract Energy pooling in the Na-Rb vapor mixture has been investigated. While some kind of buffer gas is introduced into the cell the peculiar features appear. The buffer gas enhances the energy transfer between Na(3P) and Rb(5S), which can be detected through the effects induced on the highly excited states populated by the Na(3P)/Rb(5P) and Rb(5P)/Rb(5P) collisions.

Keywords Three body collision, Population transfer, Energy pooling

1 Introduction

Resonant excitation of alkali-metal vapors makes the study of processes involving excited atoms relatively easy.[1−4] The purpose of these experiments is to measure the rate constants of the induced reactions and to compare them with the corresponding calculated parameters. Information on the atom-atom and atom-molecule intermediate-range interaction potentials can be obtained.

In the experiments[1,2] performed with a Na-Rb mixture, the heteronuclear energy pooling collisions have been observed, they are represented by the following reactions:

$$\begin{aligned} \mathrm{Na(3P)} + \mathrm{Rb(5P)} &\rightarrow \mathrm{Na(3D)} + \mathrm{Rb(5S)} + \Delta E \\ &\rightarrow \mathrm{Na(3S)} + \mathrm{Rb(mL)} \pm \Delta E \end{aligned} \tag{1}$$

where mL=8S, 9S, 6D, 7D and ΔE is the energy defect or excess. The two excited atoms exchange their internal energy in such a way that one goes back to the ground state, whereas the other transits to a higher excited state. The condition to be fulfilled is

$$\Delta E = \mid E(\mathrm{3D, mL}) - [E(\mathrm{3P}) + E(\mathrm{5P})] \mid \approx KT \tag{2}$$

In the present paper an experimental analysis of the modification of the population distributions among excited levels induced by the presence of a noble gas is reported. The strong coupling between Na(3P) and Rb(5S) established by the three-body collisions including the noble gas atoms is detected through the energy pooling collisions populating the Rb(mL) levels. The processes are detected by analysing the emitted atomic fluorescence and adopting an intermodulation detection technique to isolate the heteronuclear contribution to the spectrum. In this technique the two beams of light are modulated at two different frequencies, while the signal is detected at the sum frequency. In fact, the signals due to collision between Na and Rb 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.[3]

2 Experimental

The experimental apparatus is shown in Fig.1. The cylindrical cell, 2 cm in diameter and 6 cm long, is made of glass (GG-17) and it is filled with a Na-Rb alloy and a few Torr of neon as buffer gas, the alloy containing about 0.10 mass fraction of rubidium and 0.90 mass fraction of sodium. The oven allows to maintain T=473 K. The two beams of light are su-

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perimposed into the cell after passing through

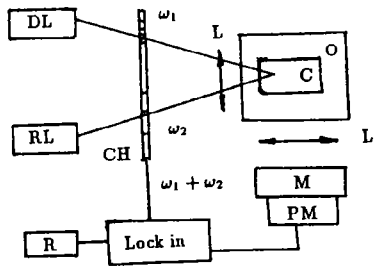

Fig.1 Sketch of the experimental apparatus
DL: Na resonant dye laser, RL: Rb lamp, C: Cell, O: Oven, CH: Chopper, L: Lens; M: Monochromator, PM: Photomultiplier, R: Recorder.

a chopper which modulates the two beams of light at the two frequencies ω_1 and ω_2. The lock-in amplifier is tuned to the sum frequency. The laser pumped by an Ar^+ laser, is tuned to the D_2 line of sodium (λ=589.0 nm). The rubidium vapor in the cell is irradiated with the light from a rubidium gas discharge lamp. The first excited 5^2P states of the atom are populated when the resonance lines 780.0~794.8 nm are absorbed. (The other wavelength portion was cut off by filters). The fluorescence is collected at right angle. A monochromator with 0.66 m focal length and a 1200 lines/mm grating, coupled to a photomultiplier, is used. The signal coming from the detector is amplified and phase detected by a lock-in amplifier tuned to the frequency $\omega = \omega_1 + \omega_2$.

The population transfers from the excited sodium to the ground state rubidium can be expressed as follows:

$$[\mathrm{Na(3P)}]_{\omega_1} + \mathrm{Rb(5S)} + M \rightarrow [\mathrm{Rb(5P)}]_{\omega_1} + \mathrm{Na(3S)} + M + \Delta E \quad (3)$$

where M is a buffer gas atom, ΔE = 4140cm^{-1} $\approx$12 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. The excited sodium atoms transfer their energy to rubidium atoms at a rate that is modulated at frequency ω_1. These excited rubidium atoms may collide with the other ones excited by the rubidium lamp. The Rb(5D) state is populated by the following process:

$$[\mathrm{Rb(5P)}]_{\omega_1} + [\mathrm{Rb(5P)}]_{\omega_2} \rightarrow \mathrm{Rb(5D)} + \mathrm{Rb(5S)} \quad (4)$$

The energy pooling process in a rubidium vapor was experimentally investigated by Barbier.[4]

The three-body collisions become important at gas pressure larger than 133Pa.[5] In order to have a quantitative understanding of the excitation transfer processes, we need to consider the following simplified rate equations. Each of the following rate equations is obtained by the production rate of each excited state equaling its destruction rate at steady state.

By assuming that other processes, like multiphoton excitation and atomic ionization, are negligible (the experimental conditions are chosen to minimize them), the rate Eq.(1) becomes

$$N_j \sum_{i \neq j} A_{ji} = k_j \cdot [\mathrm{Na(3P)}]_{\omega_1} \cdot [\mathrm{Rb(5P)}]_{\omega_2} \quad (5)$$

where N_j is the population density of the excited level, j=3D, mL; $\sum A_{ji}$ is the sum of the spontaneous transition probabilities of the level j; k_j is the rate constant of the process. The subscripts ω_1 and ω_2 mean that the populations of the excited levels are modulated at two different frequencies. The density of atoms in each of the excited levels is denoted by square brackets.

The rate equation for process (3) is given by

$$[\mathrm{Rb(5P)}]_{\omega_1} = \tau_{5P} k_3 [\mathrm{Na(3P)}]_{\omega_1} [\mathrm{Rb(5S)}] N \quad (6)$$

where τ_{5P} is the effective lifetime of the Rb(5P) level, N the buffer gas density and its value in our experiment is $N = 10^{17}\mathrm{cm}^{-3}$, k_3 is a three-body rate coefficient and it is expressed in $\mathrm{L}^6\mathrm{T}^{-1}$ unities.

The rate equation of reaction (4) is

$$[\mathrm{Rb(5D)}]\Sigma A_{5\mathrm{D},l} = k_{5\mathrm{D}}[\mathrm{Rb(5P)}]_{\omega_1}[\mathrm{Rb(5P)}]_{\omega_2} \tag{7}$$

where $k_{5\mathrm{D}}$ has been already measured[4] and $k_{5\mathrm{D}} = 3.0 \times 10^{-9}\mathrm{cm^3 s^{-1}}$.

From Eqs.(5-7) and under stationary conditions, we derive

$$k_3 = \frac{k_j \Sigma A_{5\mathrm{D},l}[\mathrm{Rb(5D)}]}{k_{5\mathrm{D}}\Sigma A_{ji}\tau_{5\mathrm{P}}N_j[\mathrm{Rb(5S)}]N} \tag{8}$$

By introducing the experimental fluorescence line intensities

$$I_{mn} = \alpha_{mn} h\nu_{mn} A_{mn} N_m \tag{9}$$

and the branching ratios

$$\gamma_{mn} = A_{mn}/\Sigma A_{mn}$$

where α_{mn} is a factor taking into account the detection efficiency of the apparatus, ν_{mn} is the transition frequency, Eq.(8) becomes

$$k_3 = \frac{k_j}{k_{5\mathrm{D}}} \cdot \frac{\alpha_{ji}\nu_{ji}\gamma_{ji}}{\alpha_{5\mathrm{D}\to 5\mathrm{P}}\nu_{5\mathrm{D}\to 5\mathrm{P}}\gamma_{5\mathrm{D}\to 5\mathrm{P}}} \cdot \frac{I_{5\mathrm{D}\to 5\mathrm{P}}}{I_{ji}} \cdot \frac{1}{\tau_{5\mathrm{P}}[\mathrm{Rb(5S)}]N} \tag{10}$$

3 Results

The resonant excitation of an alkali vapor produces an almost continuum fluorescence spectrum due to the energy transfer between the atoms and between the atoms and the dimers. 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 resolved. In Fig.2 the lines marked with a star are those excited by the heteronuclear energy pooling collisions. The rest lines in the spectrum are originated by the processes (3) and (4).

In our experiment the effective lifetime of Rb determined at T=473 K, $\tau_{5\mathrm{P}}$=450 ns.[1] The rubidium density is measured using the absorption-equivalent-width technique on the 5S→ 5P transitions to be $[\mathrm{Rb(5S)}]=8.6\times10^{13}\mathrm{cm^{-3}}$.

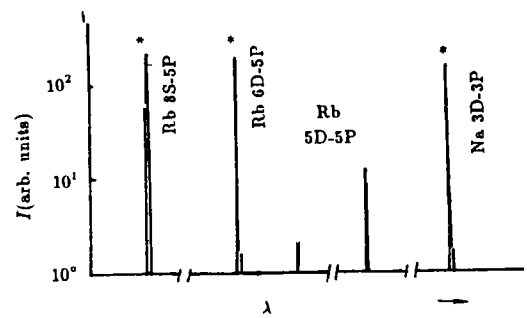

Fig.2 Fluorescence spectrum obtained with the intermodulation technique

By applying the procedures described above the three-body rate coefficients have been measured. (see Table 1)

Table 1 Determination results of k_3

System	Level	$k_j^{[1]}/k_{5\mathrm{D}}$	Transition	γ	$\alpha_{ji}/\alpha_{5\mathrm{D}\to 5\mathrm{P}}$	$k_3/10^{-27}\mathrm{cm^6 s^{-1}}$
Na-Rb	3D(Na)	0.77	3D-3P	1	0.32	6.5
	8S(Rb)	0.43	8S-5P$_{1/2}$	0.26	1.9	5.4
	6D(Rb)	0.21	6D-5P	0.75	2.1	8.9
Rb-Rb	5D	–	5D-5P	0.61	–	–

From Table 1 one can obtain the average value for the rate coefficient k_3 = $6.9\times10^{-27}\mathrm{cm^6 s^{-1}}$.

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