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COLLISIONAL IONISATION OF EXCITED RUBIDIUM ATOMS

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Résumé - Dans une vapeur de rubidium, la mesure des courants d’ions Rb⁺, Rb⁺ et Rb⁻ a permis de caractériser les processus collisionnels de formation d’ions à partir d’atomes excités et de déterminer les coefficients de taux d’ionisation associés à ces réactions.

Abstract - Ion current measurements for Rb⁺, Rb⁻ and Rb⁻ ions allowed to characterize ionizing collisional processes involving excited atoms in a Rb vapour. Rate coefficients for these reactions are determined.

When an alkali vapor is irradiated with high power laser beams a complex medium is created and it is not very easy to separate laser fields effects from purely collisional mechanisms. It is thus important to understand first the involved collisional reactions.

Low power lasers allow to study this processes in a simple medium. Two C.W. multimode dye lasers crossing at the centre of a cylindrical cell are used to pump, in a first step rubidium atoms in a resonant level Rb(5p) and in a second step in a highly excited level Rb(nl) (l=s or d). The experimental set up has been described previously /1/. Typical experimental conditions correspond to: p=10⁻⁴ Torr, Rb(5s)=10¹² cm⁻³, Rb(5d) = 10¹⁰ cm⁻³, Rb(nl)= 10⁸ cm⁻³.

The main processes are:

Hornbeck-Holnar associative ionization

\[ \text{Rb}(nl) + \text{Rb}(5s) \rightarrow \text{Rb}⁺ + \text{e}⁻ \]

Penning atomic ionization:

\[ \text{Rb}(nl) + \text{Rb}(5p) \rightarrow \text{Rb}⁺ + \text{e}⁻ + \text{Rb}(5s) \]

Beside these reactions the following processes have also been observed:

Energy pooling reaction:

\[ \text{Rb}(5p ^2P_{3/2}) + \text{Rb}(5p ^2P_{3/2}) \rightarrow \text{Rb}(5d) + \text{Rb}(5s) \]

Penning associative ionization:

\[ \text{Rb}(nl) + \text{Rb}(5p) \rightarrow \text{Rb}⁺ + \text{e}⁻ \]

Ion pair formation

\[ \text{Rb}(nl) + \text{Rb}(5s) \rightarrow \text{Rb}⁺ + \text{Rb}⁻ \]

Results concerning energy pooling reaction have been published for the Rb case /2/ and M. Allegrini presents a review on this subject at the present conference.

The other reactions correspond to ionizing mechanisms involving highly excited Rb atoms. Ions are analyzed with a mass spectrometer wired to alternately detected positive or negative ions. A typical result of mass scanning is presented in fig.1. The Rb⁺ current is 5000 times lower than the Rb⁻ current and consequently ion pair formation does not contribute significantly to the Rb⁺ current. Photoionization by the laser beams: \( \text{Rb}(nl) + h\nu \rightarrow \text{Rb}⁺ + \text{e}⁻ \) is an important mechanism contributing to the Rb⁺ current. The cross sections for this process are well known /3/ and the photoionisation contribution is used to determined the excited state densities /1/.

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The present paper only reports on Penning atomic ionisation and ion pair formation. The Penning ionization occurs via collision between a highly excited atom and a resonant state atom. In fact when a highly excited state is pumped the radiative cascading deexcitation populates the neighbouring levels. s and d levels essentially decay to p levels and consequently the studied medium is composed of the excited s or d level and of the various lower p levels. The total density of these p levels represents 80% of the density of the pumped s level and 20% of the pumped d level. The measured quantities correspond to the contribution of the pumped state and of the radiatively populated p levels. When a s state is populated the p level densities alone can explain the experimental observations /1/ - the dependency of the rate coefficients will be known only if the p contribution is correctly deduced.

Measured rate coefficients lie in the range $10^{-8}$ cm$^3$ s$^{-1}$. Theoretically two mechanisms are usually considered. The first one is the dipole-dipole interaction which give rate coefficients in the range $10^{-9}$ ads$^{-1}$ for d or p levels and in the range $10^{-1}$ cm$^3$ s$^{-1}$ for s level. The second one is the exchange theory; Kimura for Rb atoms found rate coefficients independent lying in the range $10^{-8}$ cm$^3$ s$^{-1}$ /4/. It is then important to determine the l dependency of the Penning rate coefficient.

This has been done by populating the excited states with pulsed lasers. As an example if the 7s level is excited its concentration decays exponentially and populates the 6p level. 200 ns after the laser shot the 6p density becomes higher than the 7s density (fig.2). If one of the Penning rate coefficient for 7s or 6d level is strongly predominant the Rb$^+$ current will vary as the 7s or as the 6p density. If the two levels have equal rate coefficients the Rb$^+$ current will then decay as the sum of the 7s and 6d densities. Experimental variation (points fig.2) accounts for this last hypothesis. The same results have been obtained when the 5d, 6d or 8s level is excited : experimental results clearly show that the Penning rate coefficient is independent. The rate coefficients obtained with the C.N. system then can be corrected from cascading radiative mechanisms. The results are presented in fig. 3 together with the dipole-dipole calculations for s(x), p(0), d(+) levels and Kimura's calculations (○) for levels 6d, 8s and 7d.

As presented in fig.1 mass scanning of negative ions indicates the presence of a low Rb$^-$ current. Molecules are commonly considered as responsible for negative ion formation /5/, the main reactions being:

$$\text{Rb}_2 + e \rightarrow \text{Rb}(5s) + \text{Rb}^-$$
$$\text{Rb}_2 + h\nu \rightarrow \text{Rb}^+ + \text{Rb}^-$$

Fig.1 - Mass scanning of positive (a) and negative ions for the excitation of the 6d $^2D_{5/2}$ level.
Under our experimental conditions (cell temperature 450°K) the ratio between the dimer density and the atom density is equal to $4 \times 10^{-6}$.

Experimental checks show that:
- negative ion formation requires both lasers to be resonant.
- negative ion current does not vary when the Rb$_2$ concentration is increased by a factor of 10 (by varying the cell temperature at constant Rb pressure).
- negative ion current varies linearly with both laser powers.

These observations rule out reactions involving any of the following particles: molecules, molecular ions, photons, electrons.

Ion pair formation by a collision between a highly excited atom and a ground state atom, namely

$$\text{Rb}(n\ell) + \text{Rb}(5s) \rightarrow \text{Rb}^+ + \text{Rb}^-$$

is a reaction that fulfills all our experimental checks. This reaction involves the same partners Rb(n\ell) and Rb(5s) than the Hornbeck-Molnar associative ionization. The rate coefficient for ion pair formation, $k^-(n\ell)$, can be deduced from the rate coefficient for associative ionization $k_{AI}(n\ell)$ by comparing the negative ion current $I(\text{Rb}^-)$ to the molecular ion current $I(\text{Rb}_2^+)$:

$$k^-(n\ell) = k_{AI}(n\ell) \frac{I(\text{Rb}^-)}{I(\text{Rb}_2^+)}$$

When the 6d $^2D_{5/2}$ level is excited, the cell temperature varying between 383°K and 453°K at constant Rb pressure, the $k^-(6d)$ values, reported on fig.4 are measured. As the electron affinity of the Rb atom is equal to 3919.2 cm$^{-1}$, the reaction is exoergic by 1082.4 cm$^{-1}$ for the 6d $^2D_{5/2}$ level. The experimental values of the rate coefficient can be fitted with a cross section $\sigma^-$ equal to $1.3 \times 10^{-16}$ cm$^2$ above the threshold and equal to zero below this limit and with a maxwellian velocity distribution $f(v)$ being assumed, leading to

$$k^- = \int_0^\infty \sigma^-(v) vf(v) \, dv.$$
This cross section value is not theoretically explained. A Landau-Zener calculation /5/ at the crossing point between the unperturbed atomic curve and the coulombic $\text{Rb}^+$, $\text{Rb}^-$ ion pair curve (fig.5) give a negligible contribution: it is not surprising as the crossing point (203 a.u) is passed diabatically.

Negative ion current measurements have been performed on levels lying energetically under ($5d$, $7s$, $6d$, $8s$) or above ($7d$, $9s$) the $\text{Rb}^+$, $\text{Rb}^-$ limit.

In fig. 6 are plotted the $k^-(n\ell)$ values against the energy defect of the reaction. The corresponding cross section are reported in fig. 7.

As for the $6d$ level the Landau-Zener calculation at the crossing point between the atomic curve and the ionic curve does not explain these results for levels under the $\text{Rb}^+$, $\text{Rb}^-$ limit. For levels above such a calculation is not possible. More sophisticated theoretical approaches are then needed. One may consider crossing points at shorter distances obtained by splitting the excited level /6/ or by manifold crossings in the molecular system (fig.8).

Another possibility is a delocalised calculation as applied by Sidis /7/ to the $\text{H}^+$, $\text{H}^-$ system (fig.9)

These various methods require first the knowledge of the molecular potential curves.

For the first time ion pair formation have been observed in an excited vapor. As the exit channel for the reaction (i.e. the Coulombic $\text{Rb}^+$, $\text{Rb}^-$ curve) is well known this process appears appealing to check the other involved molecular potential curves.
Fig. 6 - rate coefficient (fig.6) and cross section (fig.7) for ion pair formation versus the energy defect of the reaction.

Fig. 7 - Delocalised scheme in the molecular system.

Fig. 8 - (a) splitting of the atomic curve (b) crossing in the molecular system.

References