Ion formation in collisions of Rb(8s) with Rb(5p) and Rb(5s)

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ION FORMATION IN COLLISIONS OF Rb(8s) WITH Rb(5p) AND Rb(5s)

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A mass analysis of ions formed in a Rb cell where 5p and 8s states are created has shown that besides associative ionization [Rb(8s) + Rb(5s)], Penning ionization by collision between these two excited atomic species plays a very important role.

1. Introduction

Very few studies exist on collisional ionization reactions between two excited atomic species, and these mainly concern collisions involving inert-gas metastable levels [1,2] or alkali resonant states [3–6]. Little is known about collisions involving more highly excited states, although they may be suspected to play an important role under many circumstances [4–7].

A first estimate of the associative ionization rate for reactions between Rb($9s\,^2S_{1/2}$) and Rb($5p\,^2P_{3/2}$) has been obtained by Chéret et al. [8], and some hypotheses on the possible processes creating atomic ions have been proposed. Owing to the lack of experimental data, however, our hypotheses could not be corroborated; furthermore, the densities, deduced from the laser powers, had certainly been overestimated.

Here we have chosen the Rb(8s) state because of the unambiguity of the ionic products of the reactions under study. In contrast to the Rb(9s)–Rb(5s) reaction where $Rb^+ + Rb^-$ ion-pair formation is possible, this product channel is energetically excluded for Rb(8s) reacting with Rb(5s)

Our investigation has been performed over a wide range of parameters such as rubidium pressure, laser powers and, consequently, densities of excited states The densities are measured and the reaction can then be determined unambiguously.

The important mechanisms are found to be

(i) Penning ionization

$$Rb(nl) + Rb(5p) \rightarrow Rb^+ + Rb(5s) + e\,, \qquad (1)$$

(ii) associative ionization

$$Rb(nl) + Rb(5s) \rightarrow Rb_2^+ + e\,, \qquad (2)$$

(iii) photoionization

$$Rb(nl) + h\nu \rightarrow Rb^+ + e\,. \qquad (3)$$

2. Experimental

The apparatus used in this experiment has been described [8]. In a cell at a constant temperature of 450 K, containing Rb vapor at pressures varying from 10^{-5} to 10^{-3} Torr, two cw multimode dye lasers produce the 8s level by a two-step excitation (fig 1).

According to reactions (1) and (2), together with photoionization by the two laser beams, atomic and molecular ions are formed and are analyzed with a quadrupole mass spectrometer.

N_0, N^*, N^{**} are the 5s, 5p and 8s densities, V the interaction volume, k_1 and k_2 the rate coefficients of the Penning and associative ionization reactions, σ_1 and σ_2 the photoionization cross sections at 780 2 and 616.1 nm. The atomic ion current I_1 is the sum

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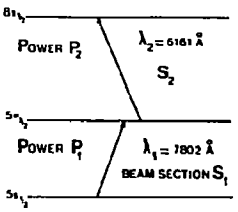

Fig. 1. Two-step excitation of Rb(8s).

of the Penning ionization current

$$I_1' = eVk_1N^*N^{**} \tag{4}$$

and of the photoionization current

$$I_\nu = eV\left[\frac{P_1}{S_1}\frac{\lambda_1}{hc}\sigma_1 + \frac{P_2}{S_2}\frac{\lambda_2}{hc}\sigma_2\right]N^{**}. \tag{5}$$

The molecular ion current I_2 is

$$I_2 = eVk_2N_0N^{**}. \tag{6}$$

An essential addition to the earlier experiment [8] is the determination of the excited-state densities by photoionization. For this purpose we used a third laser beam produced by an argon ion laser working at 4765 Å to photoionize the 5p level and at 5145 Å for the (nl) level.

Although selective excitation of rubidium atoms is achieved, cascading radiative de-excitation of the pumped level yields an appreciable population of the lower levels 7p, 7s, 5d, 6p, 6s, 4d proportional to the 8s density according to radiative transition coefficients [9]. The relative densities were determined optically and agreed with calculations

Under these conditions the reaction coefficient in formulae (4), (5) and (6) are effective coefficients correlated to the real coefficients by:

$$k_1 = \sum_i k_1(i)\,[i]/N^{**}, \tag{7}$$

where i represents any of the excited levels for which Penning ionization is energetically possible, $[i]$ is the corresponding density and $k_1(i)$ the individual rate coefficient.

Similar formulae exist for σ_1 and σ_2. Penning ionization is possible for 8s, 7p, 7s, 5d and 6p levels. If the reaction rates for all these levels are assumed to be equal, the individual value of k_1 for the 8s level is the experimental value divided by a factor 1.7. This correction is applied to the present experimental results.

Theoretical calculations [10] of the Rb_2^+ potential curves show that associative ionization is only possible for the 8s level.

3. Results

The rate coefficients k_1 and k_2 are deduced from the measurements of N^*, N^{**}, I_1 and I_2 and from the calculated photoionization cross sections [11,12].

The spectral densities used are always low and the total absorption is weak, so that the density N^{**} is proportional to N^*, as shown in fig 2 A check on the dependence of N^* versus P_1 showed the expected pure linear proportionality in the range $20 \leqslant P_1 \leqslant 230$ mW. With P_2 = 236 mW the ratio R of the concentrations N^{**}/N^* is 1 : 78, independent of Rb pressure.

Once the densities are measured the photoionization current I corresponding to 780.2 and 616.6 nm is deduced from the total atomic ion current I_1.

Under these conditions the Penning ion current I_1' shows the expected quadratic dependence on P_1 and the associative ion current is linear (fig. 3). Eqs. (4) and (6) allow the determination of k_1 and k_2.

Experimental data at different pressures yield values lying within the ranges

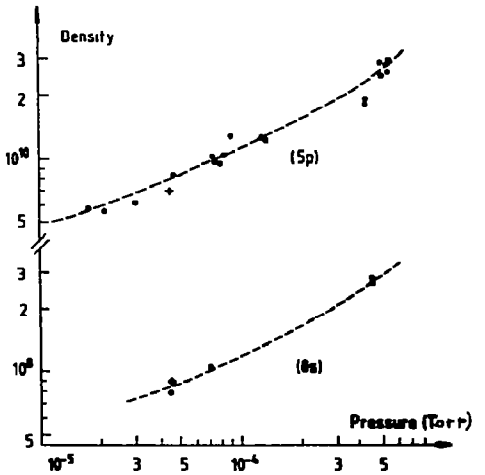

Fig. 2. ($5P_{3/2}$) and (8s) densities versus pressure for P_1 = 164 mW and P_2 = 216 mW

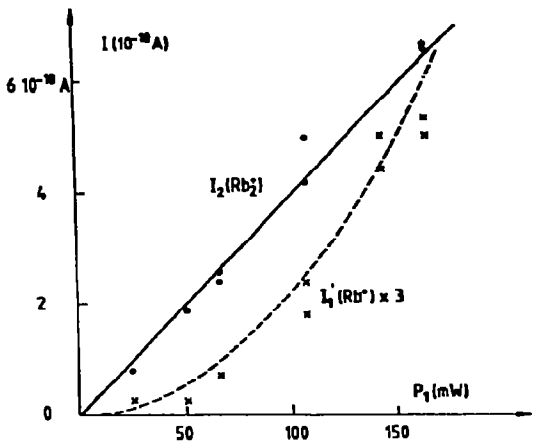

Fig. 3 Penning and associative ion currents versus infrared laser power P_2, at $p = 4.5 \times 10^{-4}$ Torr.

$$1.0 \times 10^{-8} \leqslant k_1 \leqslant 1.8 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$$

and

$$1.3 \times 10^{-10} \leqslant k_2 \leqslant 2.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} .$$

Excellent agreement of the rate coefficient value is obtained at Rb pressures as far as one order of magnitude apart. Fig. 4 gives experimental data for I_1', I_2 and total current I_{tot} versus pressure, and calculated

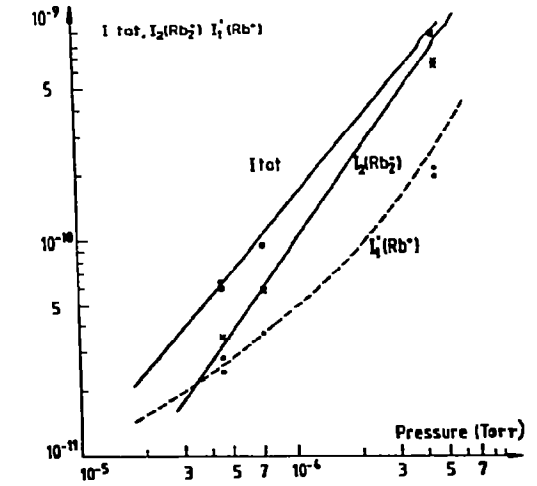

Fig. 4. Ion currents versus pressure. Full and broken curves as calculated with $k_1 = 2.0 \times 10^{-10}$ cm^3 s^{-1} and $k_2 = 1.3 \times 10^{-8}$ cm^3 s^{-1} (• and × experimental points).

curves, with $k_1 = 1.3 \times 10^{-8}$ cm^3 s^{-1}, $k_2 = 2.0 \times 10^{-10}$ cm^3 s^{-1} and the experimental densities (fig 2). Changing k_1 and k_2 will cause a parallel shift of the curves.

4. Discussion

Some other reactions could be postulated to explain the Rb^+ and Rb_2^+ ion currents but are negligible under our experimental conditions. Thus the linear variation of Rb_2^+ with P_1 (or with P_2) eliminates reactions depending quadratically on the laser power such as:

(i) Associative ionization between two excited states.

$$Rb(5p) + Rb(nl) \rightarrow Rb_2^+ + e . \quad (8)$$

Assuming that this mechanism contributed less than 10% to the Rb_2^+ current, an upper limit of 2×10^{-9} cm^3 s^{-1} is obtained for the rate coefficient.

(ii) Photodissociation of Rb_2^+.

$$Rb_2^+ + h\nu \rightarrow Rb^+ + Rb \quad (9)$$

(upper limit = 5×10^{-17} cm^2)

In the same way Penning ionization between two excited states,

$$Rb(nl) + Rb(nl) \rightarrow Rb^+ + Rb(5s) + e^- . \quad (10)$$

gives a quadratic variation versus P_1 and P_2 whereas in relation (1) the variation is quadratic versus P_1 and linear versus P_2. An upper limit of 1×10^{-7} cm^3 s^{-1} is thus determined.

Energy pooling [4] plays an important part when a quasi-resonant reaction between highly populated levels is possible and so only concerns collisions between two Rb(5p) atoms. It has been checked that the ion currents are three to four orders of magnitude lower when the 8s level is not excited. Calculations show that under our experimental conditions superelastic collisions of electrons [13] are not important.

Hence the only possible ion formation mechanisms are associative ionization with ground-state atoms for Rb_2^+ ions, and Penning ionization with Rb(5p) atoms and photoionization for Rb^+ ions.

A different way of estimating the ratio R is to use the equation

$$R = \frac{1}{2}\left[1 + 8\pi h\left(\sum_j A_{8s,j}\right)(\lambda^3 \rho(\nu) A_{8s,5p})^{-1}\right]^{-1},$$

where $\rho(\nu)$ is the radiation density per unit frequency and $A_{8s,j}$ denotes the various Einstein coefficients from the 8s to lower states. Eq. (6) gives $R = 1:60$ for the present conditions, a ratio which agrees with the experimentally obtained ratio of 1 78. This argues for the validity of the photoionization cross sections used above.

The use of other photoionization cross sections would change the densities of the 8s and $5P_{3/2}$ levels and the rate coefficients accordingly, but would not affect the photoionization current due to the dye lasers. As a matter of fact this current is determined from the photoionization current by the Ar^+ laser and from the cross-section ratios. Under these conditions there is no doubt about the creation of Rb^+ ions by collision processes

The value $k_2 = 2.0 \times 10^{-10}$ cm^3 s^{-1} is in agreement with a model of Mihajlov and Janev [14], which predicts an increase of k with the effective quantum number n^* in the vicinity of $n^* = 5$ corresponding to the 8s and 9s levels of Rb Thus the present data seem to validate the model of ref [14] based on the interaction of an excited electron with the system $Rb^+ + Rb$. It is not surprising therefore that rate coefficients for this kind of reaction are of the same order of magnitude as rate coefficients for most ion–molecule reactions with electronic transfer which also take place through charge-induced dipole interaction (k_5 from ref. [15]).

The value $k_1 = 1.3 \times 10^{-8}$ cm^3 s^{-1} for reaction (1) however is much larger than the values usually obtained for charge-induced dipole interactions, actually lying within the range of typical values observed for dissociative recombination. The transfer of momentum from the free electron, which is necessary to allow for a high recombination coefficient, occurs easily in the case of dissociative recombination, where two product particles exist, but cannot occur in the recombination of an atomic ion with an electron In the present case however the loosely bound and thus quasi-free electron of the highly excited Rb atom can interact and recombine with the ionic core of the second one, whilst the ejection of the second-excited electron allows for the balance of momentum in the reactive system. this is the so-called exchange ionization process proposed by Olson [16].

Moreover, Olson estimates the absolute values of ionization cross sections in the thermal regime to be as large as several times the geometrical cross section of the collision partners, which would correspond to rate coefficients of the order of 10^{-8} cm^3 s^{-1} for the combination of Rb(8s) and Rb(5p), in agreement with our experimental observations. Preliminary measurements on the neighbouring levels 6d and 7d give similar results, tending to support the correction factor introduced for k_1.

This shows that ionizing collisions involving a highly excited and an excited species have a very large rate coefficient. Such collisions may therefore play an important yet unexpected role in the characteristics of ionized gases when the densities of the excited states are large. Careful analysis of the properties of ionized gases should include such fast ionizing collisions

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