

## Rapid Communications

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### Experimental evidence for negative-ion formation by the collisional reaction $\text{Rb}(6d) + \text{Rb}(5s) \rightarrow \text{Rb}^+ + \text{Rb}^-$

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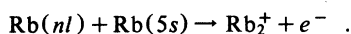
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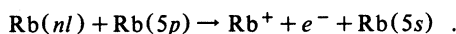
Negative ions are observed in a rubidium vapor when atoms are excited to the  $6d$  level. Analysis shows that they correspond to the collision  $\text{Rb}(6d^2D_{5/2}) + \text{Rb}(5s) + \Delta E \rightarrow \text{Rb}^+ + \text{Rb}^-$ . The rate coefficient of the process is found to be  $(1.1 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and the corresponding cross section  $1.3 \times 10^{-16} \text{ cm}^2$ .

When highly excited atoms are created in a rubidium vapor, atomic and molecular ions ( $\text{Rb}^+$  and  $\text{Rb}_2^+$ ) are observed. Under our experimental conditions<sup>1,2</sup> the following collisional reactions are predominant.

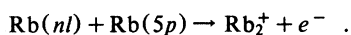
(a) Hornbeck-Molnar associative ionization:



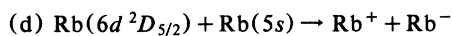
(b) Penning atomic ionization:



(c) Penning molecular ionization:



By exciting the  $\text{Rb}(6d^2D_{5/2})$  state we also observe  $\text{Rb}^-$  ions. The present paper describes the systematic search undertaken to explain the origin of these ions. Ion pair formation by collision between a highly excited atom and a ground-state atom, according to



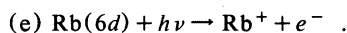
appears to be the only reaction consistent with the different experimental observations. A cross section  $\sigma^-$  for this mechanism is then deduced from the measurements.

The experimental arrangement has already been described.<sup>1</sup> Two multimode low-power cw dye laser beams cross in the center of a cylindrical cell ( $T_{\text{pot}} = 355 \text{ K}$ ,  $T_{\text{cell}} = 450 \text{ K}$ ,  $\text{Rb density} = 10^{12} \text{ cm}^{-3}$ ). The first laser beam (ir  $\lambda = 780 \text{ nm}$ ,  $P = 230 \text{ mW}$ ) pumps the resonant state  $\text{Rb}(5p^2P_{3/2})$  (density:  $10^{10} \text{ cm}^{-3}$ ) and the second one (visible,  $\lambda = 630 \text{ nm}$ ,  $P = 210 \text{ mW}$ ) completes the two step excitation to the  $6d^2D_{5/2}$  state (density  $10^8 \text{ cm}^{-3} \text{ s}^{-1}$ ).

The total ion current is measured by two plates one on each side of the interaction volume and the ions are mass analyzed using a quadrupole spectrometer system located above the reaction cell in a differentially pumped chamber. In order to observe negative ions the voltages on the ion optic electrodes are inverted. The electron multiplier is wired up to operate under both polarities without any

change in its gain. With such a device, the short time required to change the electrodes polarities allows positive and negative ions to be analyzed alternately under the same experimental conditions. The ion current at the output of the electron multiplier varies with the voltage on the first dynode. It is assumed that the efficiency is the same for both ion species when the ion current is saturated at constant gain.<sup>3</sup> This occurs at approximately 2400 eV for positive ions and 1800 eV for negative ions.

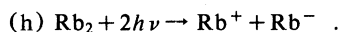
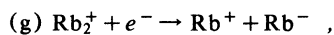
A multichannel analyzer integrates the signal over a large number of mass scanning cycles. A mass spectrum of positive ions [Fig. 1(a)] reveals  $\text{Rb}^+$  and  $\text{Rb}_2^+$  ions formed by reactions (a) and (b) [reaction (c) is negligible for  $\text{Rb}(6d)$ ] and by photoionization of  $\text{Rb}(6d)$  with the exciting lasers:



The same mass scanning performed after inverting the electrode polarities clearly shows the presence of  $\text{Rb}^-$  ions [Fig. 1(b)].

Reactions producing negative ions have been experimentally investigated.

The medium is basically composed of ground-state atoms, molecules in a low-density ratio ( $[\text{Rb}_2]/[\text{Rb}] = 4 \times 10^{-6}$ ), and excited atoms. Charged particles  $\text{Rb}^+$ ,  $\text{Rb}_2^+$ , and  $e^-$  are created by reactions (a), (b), and (e); laser photons are permanently present. The studies of Massey<sup>4</sup> and Smirnov<sup>5</sup> indicate that many processes leading to the formation of negative ions have to be examined in such a medium; they involve neutral or ionized molecules reacting with electrons or photons:



This last reaction was used by Klewer, Beerlage, Los, and Van der Wiel<sup>6</sup> to explain  $\text{Cs}^+$  observation after  $\text{Cs}_2$  excitation. Under our experimental conditions we have verified

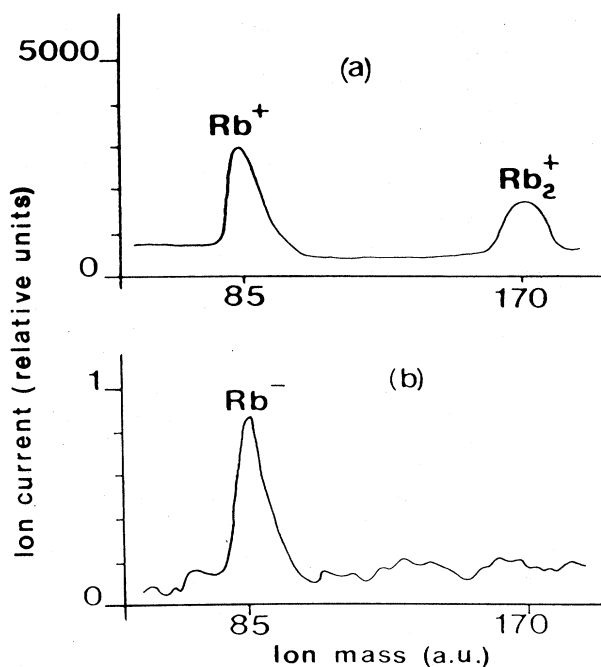


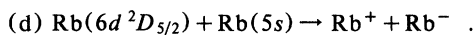
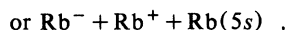
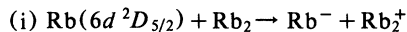
FIG. 1. Mass spectra of positive (a) and negative (b) ions. (a) 500 mass scanning, (b) 50 000 mass scanning and amplification factor 46.

that both lasers need to be tuned to the atomic transitions to produce negative ions. This eliminates reaction (h) and indicates that the  $\text{Rb}(6d^2D_{5/2})$  level must be populated.

The intensity of the  $\text{Rb}^-$  signal varies linearly with the different laser powers (Fig. 2) as well as  $\text{Rb}(6d^2D_{5/2})$  concentration and  $\text{Rb}_2$  current. This observation is a second correlation between the excited level and the  $\text{Rb}^-$  signal. According to reactions (a), (b), and (e), the production rate of electrons contains a linear and a quadratic part in terms of the different laser powers.<sup>1</sup> This consideration eliminates any reaction involving electrons and particularly reactions (f) and (g).

It is also possible to photoionize the  $\text{Rb}(5p^2P_{3/2})$  atom with one line of the  $\text{Ar}^+$  laser (476 nm). This very efficient process produces an electron current ten times higher than the total collisional current. With this high electron density no  $\text{Rb}^-$  ions were detected. This definitely eliminates reactions between atoms or molecules and electrons.  $\text{Rb}^-$  ions are not produced by electrons or photons.

At least two reactions have to be considered:



Decreasing the cell temperature from 453 to 383 K with a constant reservoir temperature of 353 K increases the  $\text{Rb}_2$  concentration by a factor of 10 at approximately constant  $\text{Rb}$  density.<sup>7</sup> The  $\text{Rb}^-$  current remains at the same level: reactions with  $\text{Rb}_2$  molecules are then invalidated.

All the experimental observations back up reaction (d) and indicate that the collision between a  $6d^2D_{5/2}$   $\text{Rb}$  atom and a ground-state atom is responsible for the  $\text{Rb}^-$  formation. In this reaction the energy necessary to create the pos-

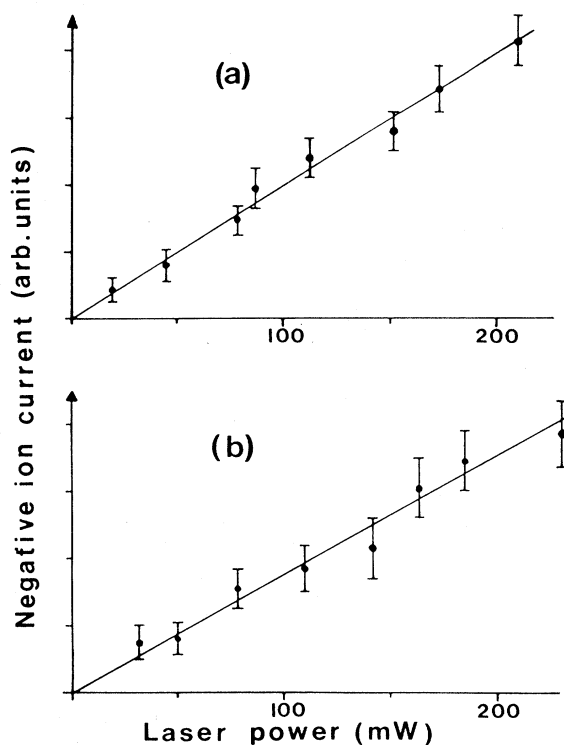


FIG. 2.  $\text{Rb}^-$  current (arbitrary unit) against laser power (mW) visible 630 nm (a) ir 780 nm (b).

itive  $\text{Rb}^+$  ion ( $33\,691.0\text{ cm}^{-1}$ ) is approximately balanced by the electron affinity of  $\text{Rb}(5s)$  ( $3919.2\text{ cm}^{-1}$ , Ref. 8) and by the electronic excitation of  $\text{Rb}(6d^2D_{5/2})$  ( $28\,698.4\text{ cm}^{-1}$ ). The reaction is endoergic with an energy defect of  $1082.4\text{ cm}^{-1}$ . This value can be compared to the thermal energy  $kT = 315\text{ cm}^{-1}$  at 453 K.

A rate coefficient  $k^-$  for ion pair formation can be obtained from the measurements. As  $\text{Rb}^-$  and  $\text{Rb}_2^+$  ions are produced by collisions between the same partners,  $k^-$  is deduced from the Hornbeck-Molnar rate coefficient  $k_2$  using

$$k^- = k_2 \frac{I(\text{Rb}^-)}{I(\text{Rb}_2^+)} = k_2 R \text{ .}$$

The ratio  $R$  between the ion currents  $I(\text{Rb}^-)$  and  $I(\text{Rb}_2^+)$  represents the relative production rate for the two ion species. An additional laser beam was used to check that photodissociation of the  $\text{Rb}^-$  ion does not play a significant role. At 453 K  $k_2 = (1.6 \pm 4) \times 10^{-10}\text{ cm}^3\text{ s}^{-1}$ ,  $R = (6.7 \pm 2) \times 10^{-3}$ , and  $k^-$  is  $(1.1 \pm 0.6) \times 10^{-12}\text{ cm}^3\text{ s}^{-1}$ .

The cell temperature was reduced from 453 to 383 K. At various temperatures  $k^-$  can be determined as previously.  $\text{Rb}_2^+$  ion current measurements show that  $k_2$  is consistent within 20% throughout the whole temperature range. The  $k^-(T)$  values are reported in Fig. 3. The experimental points can be fitted with a cross section  $\sigma^-$  equal to  $1.3 \times 10^{-16}\text{ cm}^2$  above the threshold and equal to zero below this limit and with a Maxwellian velocity distribution  $f(v)$  according to

$$k^- = \int_0^\infty \sigma^-(v) f(v) v dv \text{ .}$$

Ion pair formation in such collisions has been calculated in the framework of the Landau-Zener theory applied at the

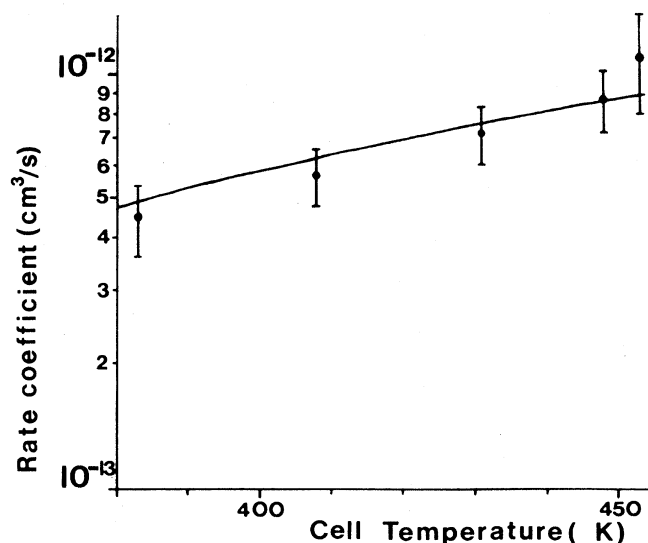


FIG. 3. Rate coefficient for negative-ion production,  $k^-$  ( $\text{cm}^3 \text{s}^{-1}$ ) against cell temperature  $T(\text{K})$ : crosses, experimental points, full line, fitted curve with  $\sigma^- = 1.3 \times 10^{-16} \text{ cm}^2$ .

crossing point between the unperturbed atomic curve and the Coulombic  $\text{Rb}^+$ ,  $\text{Rb}^-$  ion pair curve.<sup>6,9</sup> For  $\text{Rb}(6d^2D_{5/2})$  this crossing point occurs at 203 a.u. At this large internuclear distance it is not surprising that the scaling law of Olson<sup>10</sup> gives a very low value for the Landau-

Zener coupling factor and consequently a negligible contribution to the rate coefficient: the crossing point is passed diabatically.  $H_{12}$  is larger for  $5d$  and  $7s$  levels (crossing points at 53 and 70 a.u.). These levels are weakly populated by radiative cascading mechanisms.<sup>1</sup> It has been checked by a direct excitation that they do not contribute to the measured  $\text{Rb}^-$  current.

In order to interpret the experimental results, crossing points at shorter distances could be considered, these points corresponding to another crossing of the covalent curve  $\text{Rb}(6d) + \text{Rb}(5s)$  or to a transfer to another potential curve dissociating in a lower excited state.<sup>6</sup> It is also worth citing the calculation of Sidis, Kubach, and Fussen<sup>11</sup> on the system  $\text{H}^+ + \text{H}^- \rightarrow \text{H}^*(n) + \text{H}$ . They used both curve crossing (Landau-Zener) and curve noncrossing (Demkov-Nikitin<sup>12</sup>) models. The  $n=2$  and 3 levels (crossing points with the unperturbed atomic curve, respectively, at 10.3 and 30.5 a.u.) explain the results of neutralization experiments above 200 eV and the authors suggest that below 200 eV the  $n=4$  level (crossing point at 270 a.u.) could explain the discrepancy between experiment and theory.

For the first time  $\text{Rb}^-$  ions have been observed in an excited vapor. The complete set of experimental tests leads us to the conclusion that these ions originate from collisions between excited atoms and ground-state atoms. A theoretical explanation appears to require the determination of the molecular  $\text{Rb}_2$  potential curves. The present study was performed for a level close to the ionic curve limit. Studies are presently underway on different excited levels above and below the ionic limit.

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<sup>6</sup>M. Klewer, M. J. M. Beerlage, J. Los, and M. J. Van der Wiel, *J. Phys. B* **10**, 2809 (1977).

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<sup>8</sup>P. Frey, F. Breyer, and H. Hotop, *J. Phys. B* **11**, L589 (1978).

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<sup>11</sup>V. Sidis, C. Kubach, and D. Fussen, *Phys. Rev. A* **27**, 2431 (1983).

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