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Electron–Cs^+-ion recombination in the presence of neutral helium atoms

G. Gousset, B. Sayer, and J. Berlande
Service de Physique Atomique, Centre d'Etudes Nucléaires de Saclay, B. P. No. 2-91190 Gif-Sur-Yvette, France
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Three-body neutral stabilized recombination has been studied in a pulsed discharge afterglow apparatus. The rate coefficient of the He stabilized recombination reaction $Cs^+ + e + He \rightarrow Cs + He$ at 625°K is deduced to be less than 10^{-28} $cm^6 sec^{-1}$, with the most probable value being 4×10^{-29} $cm^6 sec^{-1}$. Since this value is much lower than that obtained for the recombination of He_2^+ by the same mechanism, it suggests that the efficiency of the three-body neutral stabilized recombination process depends sensitively upon the atomic or molecular nature of the recombining ion.

I. INTRODUCTION

The three-body (electron-ion-atom) recombination mechanism,

$$A^+ + e + B \rightarrow A + B\,, \tag{1}$$

has been presumed for a long time to play an important role in the recombination of weakly ionized gases. Several calculations of an expression for the three-body rate coefficient k_N characteristic of reaction (1) have been proposed. The analytical formula of Massey and Burhop,[1] which is an extension of a simple calculation of the ion-ion recombination coefficient by Thompson,[2] and that of Pitaevski,[3] differs only by a numerical factor $[(k_N)_{Pit} \sim 6(k_N)_{Th}]$, and predicts that

$$k_N \sim \sigma / M\, T^{5/2}\,, \tag{2}$$

where M is the mass of atom B, σ is the momentum-transfer cross section for e-B collisions, and T is the temperature. Note that in this equation k_N is independent of the nature of the positive ion.

Considering process (1) in more detail for the case of He^+-e-He, Bates and Khare[4] have carried out numerical calculations of k_N which are in good agreement with the Pitaevski formula at low temperatures (100 °K), but which decrease faster with T than predicted by (2). For H^+-e-H, Drawin[5] has derived k_N coefficients that are larger than those of Bates and Khare for He^+-e-He by one to several orders of magnitude. Thus, the many discrepancies that exist among the theoretical determinations of k_N indicate that it is necessary to experimentally measure these constants. Note that all the theoretical investigations have been performed assuming that the gas temperature T_g is equal to the electron temperature T_e. Although it is certain that k_N is dependent on both T_e and T_g, this dependence is not precisely known.[6]

For an experimental study of process (1), however, a careful choice of the experimental conditions must be made in order to reduce as much as possible the effects of other ionic loss channels. On the one hand, a ratio of the concentration of atoms B to that of the electrons is desired for which the contribution of the mechanism $A^+ + e + e$ to the global electron-ion recombination is not predominant in comparison to process (1). On the other hand, the absolute values of the electron and atom densities are important. If the electron density n_e is too low, diffusion to the walls becomes the major loss process of the charged particles. A concentration of atoms B, N_B, that is too high, however, would generally result in molecular ion formation, and if these ions recombine by a very efficient dissociative mechanism, this could become the dominant loss channel.

These types of difficulties contribute to the sparcity of experimental results relating to reaction (1). To our knowledge, the only published data concern $He_2^+ + e + He$ recombination in an afterglow,[7-9] and we shall discuss later the relatively high value of the rate constant ($k_N = 5.10^{-27}$ $cm^6 sec^{-1}$ for $T = 300$ °K) that was obtained.[9] In this paper we present the results of our afterglow investigations of the three-body recombination process in a cesium-helium mixture:

$$Cs^+ + e + He \rightarrow Cs + He\,. \tag{3}$$

We chose these particular reactants for the following reasons:

(a) Cs has an ionization potential (3.9 eV) much lower than the first excitation potential of He (19.8 eV); it is thus possible to create a plasma in which only cesium atoms are excited or ionized, while the helium atoms remain in their ground state, even when the ratio of the densities N_{Cs}/N_{He} is small.

(b) According to Eq. (2), the coefficient k_N is larger when the third body is a light atom.

(c) The molecular ion He-Cs^+ is most likely weakly bound (Mason and Schamp[10] estimate 0.014 eV); so the concentration of such ions would remain small.

The coefficient k_N for reaction (3) was obtained by fitting the measured electron-density decay frequencies with calculated curves representing the contribution of the various processes that contribute to this decay.

II. EXPERIMENT AND MEASUREMENT TECHNIQUES

The experimental setup is quite similar to ones previously used.[11,12] The experimental cell consists of a cylindrical glass discharge tube 8 cm in diameter. A pulsed discharge (25 msec long with a repetition frequency between 3 and 20 Hz) is applied between two heated electrodes. The cell is placed in an oven, and the cesium pressure is controlled by regulating the temperature of the coolest point of the cell. An excellent agreement has been observed between the saturated vapor pressure corresponding to the temperature of the coolest point of the cell and that deduced from the cesium density as measured by absorption of the 8521-Å resonance line.

The electron density, averaged over the tube diameter, is deduced from the phase shift of a free-space electromagnetic wave (4-mm wavelength). The radial distribution of n_e, and consequently the electron density along the tube axis (n_{e0}), is obtained from optical measurements.[12] The actual electron temperature T_e is deduced by observing the intensity of the continuous spectrum emitted during recombination to the $6P$ level.[10,12]

Typical experimental conditions are $N_{Cs} = 10^{15}$ cm^3, initial electron density $(1-2) \times 10^{13}$ cm^{-3}, and $T_{oven} = 625\,^{\circ}K$. The working pressure of helium (p_{He}) was limited to less than 60 torr, since at higher helium pressures we have observed that during the discharge period cataphoresis effects tend to make the plasma unstable.

III. EXPERIMENTAL RESULTS AND INTERPRETATION

Because of its influence on the recombination coefficient k_N [see Eq. (2)], we shall consider first the electron temperature and its decay in the afterglow. Then, we shall look at the late afterglow and the useful information we can obtain concerning various loss processes for the electrons. Finally, we shall consider the early afterglow ($n_e > 10^{11}$ cm^{-3}) and the various recombination mechanisms involved there.

The evolution of the electron temperature during the afterglow is shown in Fig. 1. After decaying quickly during the first 100 μsec, T_e then decreases very slowly (from 1100 to 800 °K in 9 msec). The shape of the T_e decay curve is very similar to that observed in pure cesium afterglows and may be interpreted in the same way.[11] The initial fast decay of T_e corresponds to the

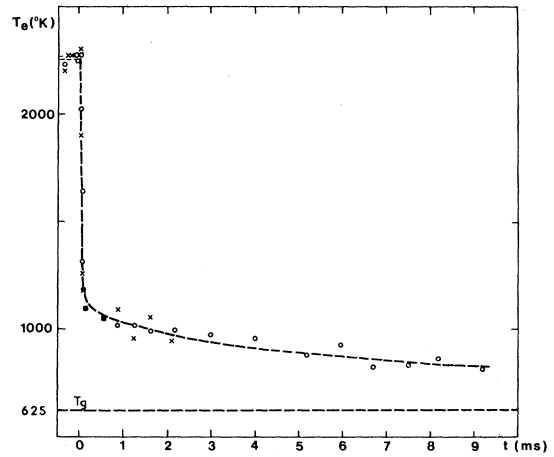

FIG. 1. Electron temperature as a function of time. $p_{He} = 60$ torr. Repetition rate of the discharge: 16.7 Hz (×), 6.7 Hz (○).

cooling of the electrons by collisions with heavy particles (ions and neutral atoms) which are at a lower temperature T_g. A quasiequilibrium situation is then reached where the electron density and electron temperature decays are coupled together. In this situation, the three-body electron-stabilized recombination supplies the free electrons with energy and compensates for the inelastic losses with heavy particles.[13] This quasiequilibrium holds as long as recombination is the main loss process.

In Fig. 1 we have plotted the electron-temperature decay for two repetition rates of the discharge pulses. From the equality of the quasiequilibrium temperature measured under both conditions, we can infer that no noticeable heating effect of the heavy particles is induced during the discharge pulse.

Figure 2 presents the time decay of the electron density on the axis of the tube (n_{e0}). For the later afterglow, the decay becomes exponential. This behavior might seem to be characteristic of a decay controlled by diffusion, but if we compare the measured time constant to the diffusion time constant calculated from the reduced mobilities of Cs^+ in helium[14,15] and in cesium,[16] we find that the experimental value (18 msec) is much smaller than the calculated one (68 msec). This large difference cannot be explained either by the uncertainties related to the values of the reduced mobilities, or by the presence of a molecular ion created by the attachment of a Cs^+ ion with one or several neutral atoms, since such a heavy ion would not diffuse sufficiently fast to explain the measured decay time constant of the electron density. An explanation of the above can be found, however. It is known (see, for example, Ref. 14) that an expo-

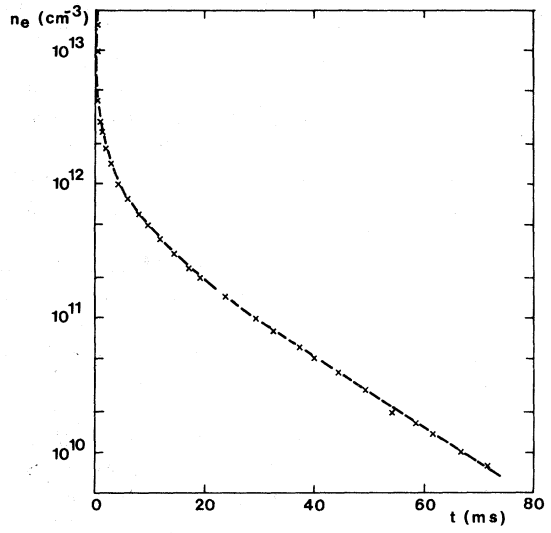

FIG. 2. Decay of electron density along the axis of the discharge tube. $p_{He} = 60$ torr. Repetition rate: 6.7 Hz.

nential decay of the electron density is observed in an afterglow when, besides being lost by ambipolar diffusion, electrons recombine rapidly with molecular ions that have been created by a slow three-body conversion process from atomic ions. Under these circumstances, the atomic ions remain the majority ions and the decay rate $(1/\tau_{exp})$ of the electron density is equal to the sum of the ambipolar diffusion and the three-body ion conversion frequencies, ν_D and ν_C, respectively.

If we adopt this interpretation for our work, the three-body ion conversion process being either

$$Cs^+ + Cs + He \rightarrow Cs_2^+ + He \tag{4}$$

or

$$Cs^+ + He + He \rightarrow HeCs^+ + He\,, \tag{5}$$

with Cs_2^+ or $HeCs^+$ recombining rapidly, we obtain at $p_{He} = 60$ torr for ν_c a value of 40 sec^{-1}, since $1/\tau_{exp} = 55$ sec^{-1} and $\nu_D = 15$ sec^{-1} for Cs^+ ions and electrons. At $p_{He} = 30$ torr, uncertainties in the measured τ_{exp} and the computed ν_D prevent us from precisely determining the value of ν_c. From the comparison of ν_c at 60 and 30 torr, the dependence of ν_c on helium pressure cannot be accurately obtained, so that the exact nature of the conversion process, (4) or (5), cannot be elucidated. We suggest, however, that it is process (4) (see Ref. 16), since analogous processes have been evoked to explain the late afterglow decay of discharges in mercury mixed with helium,[17] or in pure cesium at high pressures.[18]

We will now try to interpret the behavior of the first part of the afterglow at $p_{He} = 60$ torr ($n_{e0} \geq 10^{11}$ cm^{-3}, $t < 25$ msec). The experimental decay rate of the electron density along the axis of the tube,

$$\nu_{exp} = \frac{1}{\tau_{exp}} = -\frac{1}{n_{e0}}\frac{dn_{e0}}{dt}\,, \tag{6}$$

can be reasonably assumed to contain contributions from (i) the two processes which have been already found responsible for the decay of n_{e0} in the later afterglow, i.e., ambipolar diffusion (frequency ν_D) and three-body ion conversion (frequency ν_c), (ii) three-body electron stabilized recombination

$$Cs^+ + e + e \rightarrow Cs + e \tag{7}$$

(frequency ν_R), and finally, (iii) a recombination process corresponding to reaction (3) with a frequency ν_N. In order to calculate these four frequencies from the measured parameters (p_{He}, n_{Cs}, n_{e0}, T_e), we need to make the following assumptions:

(a) The diffusion frequency can be expressed as

$$\nu_D = -\left(\frac{1}{n_{e0}}\frac{dn_{e0}}{dr}\right)_{diff} = \frac{D_a \nabla^2 n_{e0}}{n_{e0}} \simeq \frac{D_i}{\Lambda^2}\left(1 + \frac{T_e}{T_i}\right), \tag{8}$$

where D_a and D_i are the ambipolar and Cs^+ ion diffusion coefficients, respectively, and T_i is the ionic temperature (assumed equal to the oven temperature). Relation (8) is strictly true only if diffusion is the dominant loss process. In that case Λ is the diffusion length characterizing the spatial distribution of charged particles in the cell according to the fundamental mode. If diffusion is not the major loss process, the spatial distribution is different and the last equality of (8) is no longer valid. A good approximation can be obtained, however, if Λ is written as $\Lambda_0 \xi$, where Λ_0 is the classical diffusion length and where ξ takes into account the modification of the spatial distribution (see Ref. 19).

(b) As already mentioned, the exact nature of the conversion process of Cs^+ ions into molecular ions which then induce an electron loss is not known, but whatever it is, it will be dependent on neither n_e nor T_e. Consequently, the same value of ν_c deduced from the late afterglow decay (40 sec^{-1} at $p_{He} = 60$ torr) has been assumed to be present during the whole afterglow.

(c) The decay frequency ν_R characterizing three-body electron-stabilized recombination (7) can be calculated according to the relation deduced from results obtained in pure cesium for the same range of n_e and T_e[11]:

$$\nu_R \equiv \alpha n_{e0} = 2.4 \times 10^{-10} n_{e0}^2 T_e^{-4.2}\,,$$

where α is the recombination coefficient. Note that the variation of ν_R with n_{e0} will appear less

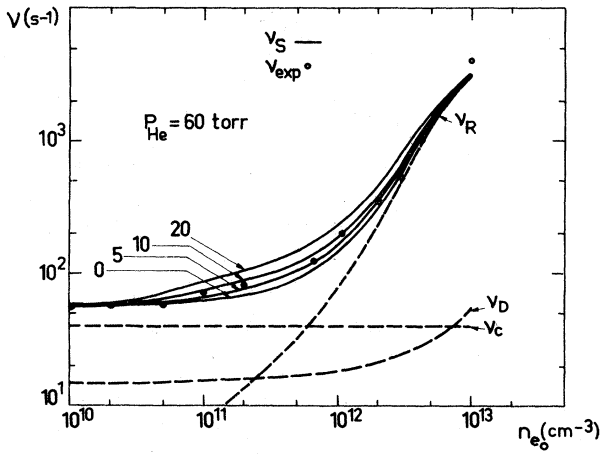

FIG. 3. Comparison of the inverse of the measured decay time constant of n_{e0} with the calculated sum $\nu_S = \nu_R + \nu_D + \nu_C + \nu_N$ for the values of $k_N^{(0)} = 0$, 5, 10, and 20×10^{-29} $cm^6 sec^{-1}$. For electron densities lower than 5×10^{11} cm^{-3}, the electron temperatures are extrapolated.

than quadratic because T_e also increases with n_{e0} (see Figs. 1 and 2).

(d) Process (3) is characterized by a frequency $\nu_N = k_N(T_e, T_g) n_{e0} N_{He}$. The variation of k_N as a function of T_e for $T_e \neq T_g$ is not known, as already mentioned. We have chosen to write

$$k_N(T_e, T_g) = k_N^{(0)}(T_g) \times \left(\frac{T_e}{T_g}\right)^{-2.5}, \qquad (9)$$

where $k_N^{(0)}(T_g)$ is the three-body recombination coefficient when $T_e = T_g$. By taking this form of k_N, we certainly overestimate its dependence upon T_e.[6]

The frequencies ν_D, ν_C, and ν_R are plotted in Fig. 3 as a function of n_{e0}. Also plotted is the sum $\nu_S = \nu_D + \nu_C + \nu_R + \nu_N$ as calculated for four values of $k_N^{(0)}$ (with $k_N^{(0)} = 0$, 5, 10, and 20×10^{-29} $cm^6 sec^{-1}$). These values of ν_S are compared with the measured ν_{exp} in Fig. 3. It appears that ν_D and ν_C are the major terms contributing to the sum ν_S for $n_{e0} < 2 \times 10^{11}$ cm^{-3}, while ν_R becomes preponderant for $n_{e0} > 2 \times 10^{12}$ cm^{-3}. Between these limits is the region where the decay of n_{e0} is the most sensitive to the value of ν_N. In this region the best agreement between experimental results and calculated curves is obtained for $k_N^{(0)}(625\,°K) = 5 \times 10^{-29}$ $cm^6 sec^{-1}$.

Note that if a weaker dependence of $k_N(T_e, T_g)$ as a function of T_e had been chosen in Eq. (9), it would lead to a smaller value of $k_N^{(0)}$. For example, if we take the exponent in Eq. (9) to be -1.5 (which appears to be an upper limit as suggested by Ref. 6), we obtain $k_N^{(0)}(625\,°K) = 3.5 \times 10^{-29}$ $cm^6 sec^{-1}$. Therefore, taking into account the dispersion of the experimental values of ν_{exp} and the uncertainties introduced in the calculation of ν_S, we think it reasonable to attribute to $k_N^{(0)}$ an upper limit of 10^{-28} and a probable value around 4×10^{-29} $cm^6 sec^{-1}$.

IV. DISCUSSION

The values of the $k_N^{(0)}$ coefficients associated with the three-body recombination mechanism (1) and calculated from the theoretical models[1-4] are compared in Table I with the available experimental results. The experimental conditions for the $He_2^+ + e + He$ study[8] were $10^9 \leq n_e \leq 10^{11}$ cm^{-3} and $10 \leq p_{He} \leq 100$ torr. Although the value obtained for $k_N(625\,°K)$ in the present work is lower than that calculated according to Pitaevski,[3] it is not in contradiction with those deduced by Thompson[1] or by Bates and Khare.[4] However, it is two orders of magnitude lower than the experimental value of k_N obtained for the recombination of the He_2^+ ion stabilized by an He atom.[9] Such a variation can be explained neither by the difference between the gas temperatures of the two experiments nor by the difference between the mass of the ions involved, as is suggested by Ref. 4. It is possible

TABLE I. Theoretical and experimental three-body coefficients $k_N^{(0)}$ (in $cm^6 sec^{-1}$) corresponding to recombination process (1). The notation $A(B)$ means $A \times 10^B$.

	Thompson[a]	Pitaevski[b]	Bates and Khare[c]	Experimental results	References
Cs^+-He (625 °K)	6.1(–29)	3.8(–28)	~3.5(–29)	<1.(–28) Probable value 4.(–29)	This work
He_2^+-He (300 °K)	3.9(–28)	2.4(–27)	~6(–28)	5±1(–27)	9

[a] References 1 and 2.

[b] Reference 3.

[c] The values of $k_N^{(0)}$ in this column have been extrapolated from those given in Ref. 4, assuming the ionic mass dependency suggested by Bates and Khare.

that the molecular nature of the He_2^+ ion is responsible for the large value of k_N. One can note that the results obtained in the study of a helium afterglow suggest that the three-body recombination stabilized by a helium atom would be less efficient for He^+ than for He_2^+.[20] Further experimental work is needed to compare the different behavior of atomic and molecular ions with respect to process (1).

The $Cs^+ + e + e \rightarrow Cs + e$ recombination reaction has a coefficient which nearly equals 4×10^{-22} $cm^6\,sec^{-1}$ for $T_e = 625\,°K$.[11] In view of the value found for $k_N^{(0)}$ we can see that the stabilization of the $Cs^+ + e$ recombination by an atom may compete with the stabilization by an electron only if $n_e/n_{He} \leq 10^{-7}$.

V. CONCLUSION

By using a static afterglow system, we have examined the role played by the three-body neutral stabilized recombination process [process (3)] in the recombination of Cs^+ ions. For our experimental conditions ($n_e/n_{He} \simeq 10^{-6}$), this process does not appear to play an important role by comparison to diffusion, ion conversion, or the $Cs^+ + e + e$ recombination mechanism. A value of the rate coefficient for reaction (3) is found to be approximately $k_N^{(0)} = 4 \times 10^{-29}$ $cm^6\,sec^{-1}$, at $T_e = T_g = 625\,°K$, which agrees with theoretical estimates of Thompson[1] and Bates and Khare,[4] but not with Pitaevski.[3] The value of k_N obtained here appears to be two orders of magnitude lower than the one measured for $He_2^+ + e + He$,[9] suggesting that the molecular nature of that ion plays an important role in the recombination mechanism.

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[16]Two ionic conversion processes can be envisaged: $Cs^+ + 2He \rightarrow HeCs^+ + He$ or $Cs + Cs^+ + He \rightarrow Cs_2^+ + He$, which would, respectively, have a frequency ν_C proportional to p_{He}^2 or p_{He}. Because of the probable weak binding energy of $HeCs^+$ (see Ref. 9), we think that the correct conversion process is the one leading to Cs_2^+. Using this hypothesis, the value of ν_C deduced from the experiment at $p_{He} = 60$ torr would lead to a three-body coefficient for the conversion process close to 4×10^{-32} $cm^6\,sec^{-1}$. This value is about the same order of magnitude as the one found by Biondi (Ref. 17) for $Hg^+ + Hg + He \rightarrow Hg_2^+ + He$ (1.7×10^{-31} $cm^6\,sec^{-1}$).
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[19]Λ has been taken equal to $\Lambda_0 \xi$, where $\Lambda_0 = R/2.405$, is the classical diffusion length of a long cylinder having a radius R. $\xi(t)$ is a correction factor which is introduced for taking into account the evolution of the spatial distribution of the charged particles with time. $\xi(t)$ has been taken as the ratio between the measured halfwidth of the n_e radial distribution and the Bessel distribution function J_0. During the initial discharge period, the plasma is "pinched" and thus does not fill in radially all the volume of the tube; it then diffuses during the afterglow. Consequently, ξ is smaller than 1 at the beginning of the afterglow, and then, in our experiment, approaches unity after about 2 msec.
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