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Ion Conversion in Krypton Afterglow Plasmas

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Mass-identified measurements of the time dependence of the density of krypton ions in decaying plasmas are reported. The measurements show that the conversion of atomic into molecular krypton ions occurs by the three-body reaction $\mathrm{Kr}^+ + 2\,\mathrm{Kr} \rightarrow \mathrm{Kr}_2^+ + \mathrm{Kr}$ with a conversion rate of 2.3×10^{-31} cm^6 sec^{-1} at a gas temperature of 300 °K. The measured value of the mobility of atomic krypton ions in krypton is in agreement with the previously published values.

INTRODUCTION

In recent years, there has been considerable interest in the study of the rate of formation of diatomic molecular ions in rare-gas discharges. It is generally accepted that the conversion of atomic to molecular ions in rare-gas afterglow plasmas occurs by a three-body reaction of the form

$$X^+ + X + X \rightarrow X_2^+ + X \quad . \qquad (1)$$

The results of measurements of the rate of formation of molecular ions in He, Ne, and Ar are available in the literature. These rates have been also theoretically calculated by a number of workers.[1–5] However, to the knowledge of this author no such experimental studies of krypton discharge have been reported in the literature. In contrast, the mobilities of krypton ions in krypton have been accurately determined by a number of workers utilizing different techniques.[6–9]

The results of mass-identified measurements of the rate of conversion of atomic krypton ions into molecular ions and the mobility of Kr^+ ions in krypton afterglow plasmas are reported here. The well-known afterglow measurement technique has been used to study decaying krypton plasmas in the pressure range of 1–4 Torr.

APPARATUS AND METHOD OF MEASUREMENTS

A block diagram of the equipment used to measure the time dependence of the number density of the ions in the afterglow of a pulsed discharge is shown in Fig. 1. The ion-signal measuring technique was analogous to that used by Sauter *et al.*[10] The bakable quadrupole mass spectrometer had a mass-analyzing field length of 20 cm and a field radius of 0.5 cm. The mass spectrometer was of a design similar to that of Sauter *et al.* A U.S. Government surplus BC-191 transmitter was used as the rf power supply for the mass spectrometer. The dc voltage was obtained by rectifying part of the rf voltage. The mass spectrometer was operated in the constant $(m/\Delta m)$ mode. For the results reported here, it was operated at a frequency of about 0.5 MHz. The ionic mass spectrum was obtained by varying the plate voltage of the BC-191 transmitter.

Figure 2 shows schematically the mass spectrometer and the discharge-tube assembly. The plasma was produced in a 3.2-cm long cylindrical Pyrex glass tube with a 2.2-cm i.d. A 60-W 110-MHz pulse of 2–5-msec duration was applied at intervals of 60 msec to produce the discharge. The high-frequency pulse was capacitively coupled to the discharge tube. The ions from the plasma effused through a small sampling aperture (~ 50 μ) in a flange at one end of the tube and into the mass spectrometer, where their mass and relative intensities were determined. Ion signals from the quadrupole were amplified by a 14-stage RCA C7187K electron multiplier with oxidized Cu-Be dynodes.

The time-sampling technique was used to measure the time dependence of the ion densities during the plasma-decay period.[10–12] This involved sensitizing the ion multiplier for a short time (40–80 μsec) at a fixed time in the afterglow. The current signals from the ion multiplier were averaged by a *RC* network, measured by an electrometer and displayed on a chart recorder. By sampling the ion signals at different times in the afterglow the time history of the ions was obtained.

The gas-handling system was analogous to that developed by Alpert.[13] A 2-in. oil diffusion pump with Sorbent-A oil trap was connected to the quadrupole mass spectrometer by means of 2-in.-diam stainless-steel tubing. The effective pumping speed at the mass spectrometer was estimated to

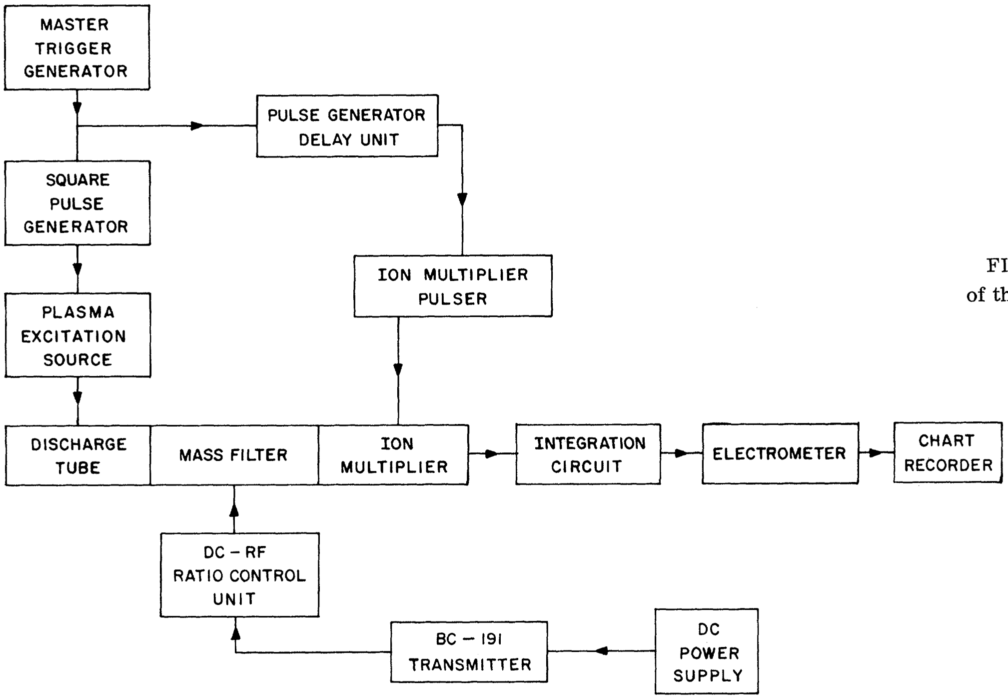

FIG. 1. Block diagram of the measuring system.

be about 10 liters/sec. A variable leak valve in conjunction with an automatic pressure controller was employed to maintain a constant pressure in the discharge region. A capacitance manometer was used to measure the gas pressure. The vacuum system together with the mass spectrometer was baked out at 300 °C for several days. The ultimate pressure obtained was 4×10^{-9} Torr, and the rate of rise of contamination pressure was less than 5×10^{-10} Torr per hour. The high-purity gas supplied in a 2-liter glass flask by General Electric contained the following major impurities: $\leq 0.01\%$ of Xe, $\leq 0.01\%$ of Ar, and $\leq 0.002\%$ of N_2 according to the manufacturer's specifications. All other impurities were less than 0.0005%.

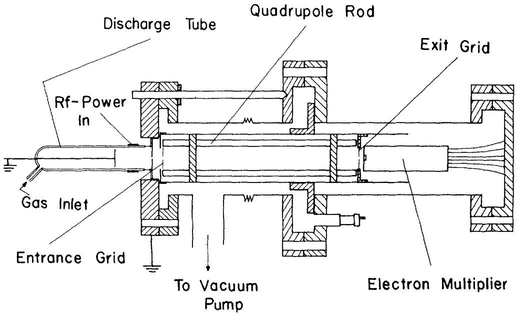

FIG. 2. Schematic of the discharge tube and the mass spectrometer.

The use of the mass spectrometer for the study of ionic processes in plasmas was based on the assumption that the measured ion current was determined by the microscopic properties of the plasma. The ion current measured by the mass spectrometer was obtained by sampling the ions through an orifice in the flange at one end of the discharge tube. In the measurements reported here this flange, which was grounded, was externally connected to the other internal electrode (Fig. 2). Therefore, no external electric field is applied to the plasma during the decay period. The ion current effusing through the orifice was determined by the undisturbed ambipolar flow of the ions to the wall. For the fundamental diffusion mode, assuming 100% ion transmission efficiency for the mass spectrometer, this ion current $i(t)$ is given by the relation

$$i(t) = (\pi e A/H) D_a n(0, 0, t) \quad , \tag{2}$$

where $n(0, 0, t)$ is the instantaneous ion density at the center of the discharge tube, A is the area of the ion sampling orifice, D_a is the ambipolar diffusion constant, and H is the length of the plasma container. The above relation (2) is valid only when the spatial distribution of the ion number density is independent of time.

The rate of change of atomic and molecular ion densities is given by

$$\frac{\partial}{\partial t} n_1(\vec{r}, t) = -\alpha_1 n_1(\vec{r}, t) n_e(\vec{r}, t)$$

$$-KN^2 n_1(\vec{r}, t) + D_{a1}\nabla^2 n_1(\vec{r}, t) \ , \qquad (3)$$

$$\frac{\partial}{\partial t} n_2(\vec{r}, t) = KN^2 n_1(\vec{r}, t) - \alpha_2 n_2(\vec{r}, t) n_e(\vec{r}, t)$$

$$+ D_{a2}\nabla^2 n_2(\vec{r}, t) \ , \qquad (4)$$

where n_1, n_2, n_e, and N are the number densities of Kr^+, Kr_2^+, electrons, and neutral atoms, respectively. D_a is the ambipolar diffusion coefficient,[14–16] K is the rate constant for the conversion of Kr^+ into Kr_2^+ by process (1), and α is the electron-ion recombination coefficient. It is assumed that the production of Kr^+ during the decay period by mutual collision between metastable krypton atoms can be neglected.

During the late afterglow period, the loss of Kr^+ by recombination with electrons can be neglected. The time dependence of the fundamental mode solution of (3) is given by

$$n_1 = n_{10} e^{(-t/\tau)} \ , \qquad (5)$$

where n_{10} is the initial Kr^+-ion density. The time constant τ for the decay of Kr^+-ion number density is given by the relation

$$P_0/\tau = 1.25 \times 10^{33} K P_0^3 + D_{a1} P_0/\Lambda^2 \ . \qquad (6)$$

Here, Λ is the characteristic diffusion length of the plasma container and P_0 is the krypton pressure (in Torr) reduced to 273 °K. For the discharge tube used in the present studies $\Lambda^2 = 0.174$ cm^2.

If the conversion of Kr^+ into Kr_2^+ occurs by a three-body collision, a plot of P_0/τ versus P_0^3 should be a straight line. The slope of this line gives the conversion-rate constant K, while the intercept at $P_0 = 0$ yields $D_{a1}P_0/\Lambda^2$. The mobility value of Kr^+ in krypton is obtained from the relation

$$\mu_0 = 7.63 (D_{a1} P_0 / T_g) \ cm^2 V^{-1} sec^{-1} \ , \qquad (7)$$

where T_g is the Maxwellian temperature of the ions, which is assumed to be equal to the gas temperature.

During the decay period of the afterglow plasma, molecular ions are continuously produced by conversion of Kr^+ into Kr_2^+, and are lost by recombination with electrons within the volume of the plasma and by ambipolar diffusion to the walls of the discharge tube. Because of the large value for the electron-molecular ion recombination coefficient α_2 coupled with the small value of the ambipolar diffusion constant,[17] the decay of the Kr_2^+ number density with time $n_2(t)$ will not be exponential, except at low-charged-particle density, i.e., at very late times in the afterglow period.

RESULTS AND DISCUSSION

The ionic mass analysis of plasmas produced in commercially available krypton showed the presence of Kr^+, Kr_2^+, Xe^+, Xe_2^+, and $(XeKr)^+$ ions as the major constituents. The presence of a small amount of xenon is manifested by a rapid exponential decay of Kr_2^+ ions, since it was found that the cross section for the reaction $Kr_2^+ + Xe \rightarrow Xe^+ + 2Kr$ is large ($2.5 \times 10^{-10} cm^3 sec^{-1}$). It was found that the xenon impurities could be removed by the cataphoretic segregation process.[18] Therefore, the gas admitted to the discharge tube was purified by using a cataphoresis discharge at a pressure of 20–40 Torr in a 1-m-long, 1.0-cm-i.d. Pyrex discharge tube (discharge current = 60 mA). The mass analysis of such cataphoretically cleaned krypton discharges showed only the presence of Kr^+ and Kr_2^+ ions. The density of impurity ions was at least two orders of magnitude smaller. Figure 3 shows the time dependence of the number density of atomic krypton ions at different gas pressures. The time dependence of the ion density is exponential over two orders of magnitude. The decay time constants τ were measured over a pressure range of 1–4 Torr. The measured values of P_0/τ against P_0^3 are plotted in Fig. 4. The data show that the conversion of Kr^+ into Kr_2^+ proceeds according to the three-body reaction

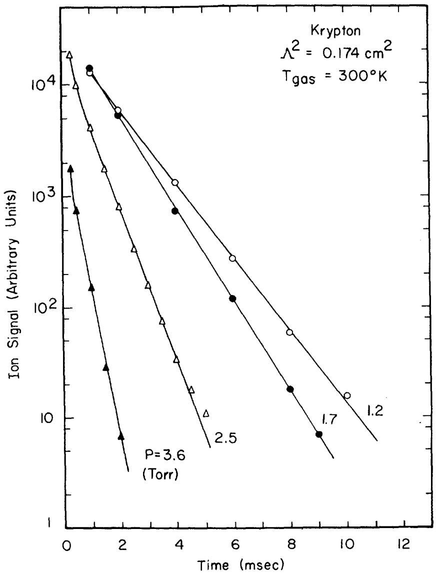

FIG. 3. Time dependence of atomic krypton ion signals in the afterglows of pulsed discharges in krypton.

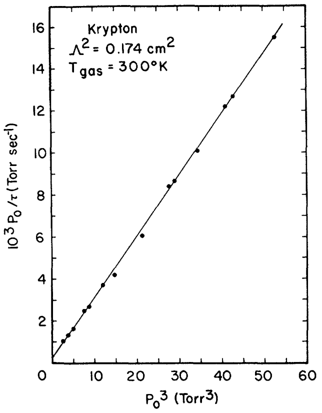

FIG. 4. A plot of P_0/τ as a function of P_0^3.

$$Kr^+ + 2KR \rightarrow Kr_2^+ + Kr. \quad . \tag{8}$$

For this reaction, the slope of the line yields for the rate constant the value $K = 2.3 \times 10^{-31}$ cm^6 sec^{-1}. The intercept at $P_0 = 0$ corresponds to a value of $D_{a1}P_0 = (41 \pm 4)$ cm^2 Torr sec^{-1} at a gas temperature of 300 °K. From (6), this value of the ambipolar diffusion coefficient yields for the mobility value of atomic krypton ions in krypton $\mu_0(Kr^+) = 1.0 \pm 0.1$ cm^{2}V^{-1}sec^{-1}. This value of the mobility is in agreement with values reported by other authors.[6–9]

The accuracy of the determination of $D_a P_0$ is not very good in the present measurements because of the small value of $D_a P_0/\Lambda^2$ compared to the large rate constant for conversion of atomic into molecular ions. However, the accuracy for the determination of the rate of conversion is good.

Figure 5 is a typical plot of the time dependence of Kr^+ and Kr_2^+ ions in the afterglow. As a consequence of the large value for the electron-ion recombination coefficient of Kr_2^+ coupled with its small value of the ambipolar diffusion constant, the time dependence of the Kr_2^+ ions is not exponential over the density range covered in these measurements. Consequently, it was not possible to determine the mobility value of Kr_2^+ ions in krypton.

It is of interest to compare the measured conversion rate with the theoretical calculations of Niles and Robertson,[3] Mahan,[4] and Smirnov.[5] Although the theoretical value obtained by Niles and Robertson for the conversion rate in helium is in agreement with experiment,[3] their predictionof $K = 0.443 \times 10^{-31}$ cm^{6}sec^{-1} for the conversion rate in krypton is much too small when compared with the experimental value of 2.3×10^{-31} cm^{6}sec^{-1} obtained above. The same comment holds for the conversion rates obtained for neon and argon.[19] This may be due to lack of knowledge of the accurate values for a number of parameters involved in their calculation.

The substitution of the value for the polarizability[20] and the mass of krypton-gas atom into the theoretical expression for the conversion coefficient proposed by Smirnov,[5] yields a value of 6.3×10^{-31} cm^{6}sec^{-1} for K. This is appreciably higher than the present experimental value. Mahan's[4] formulation for the rate of formation of diatomic molecule incorporates the polarizability of the gas atoms and the resonant charge-transfer rate. The charge-transfer-rate constant was obtained by multiplying the cross section tabulated by Dalgarno[20] by the average relative velocity of the colliding particles. Using this computed charge-transfer-rate constant and the polarizability taken from Pitzer[21] we obtain from Mahan's formula a value of 2.57×10^{-31} cm^{6}sec^{-1} for the rate of formation of Kr_2^+. This is in very good agreement with the experimental value of 2.3×10^{-31} cm^{6}sec^{-1}.

CONCLUSION

Mass spectrometric studies of decaying krypton plasma show that the conversion of atomic krypton ions into molecular krypton ions proceeds through the three-body reaction $Kr^+ + 2Kr \rightarrow Kr_2^+ + Kr$. The experimentally determined value for the rate of conversion is 2.3×10^{-31} cm^{6}sec^{-1} and is in very good agreement with the theoretical value obtained from Mahan[4] formula. The mobility of atomic krypton ions in krypton was found to be $\mu_0(Kr^+)$

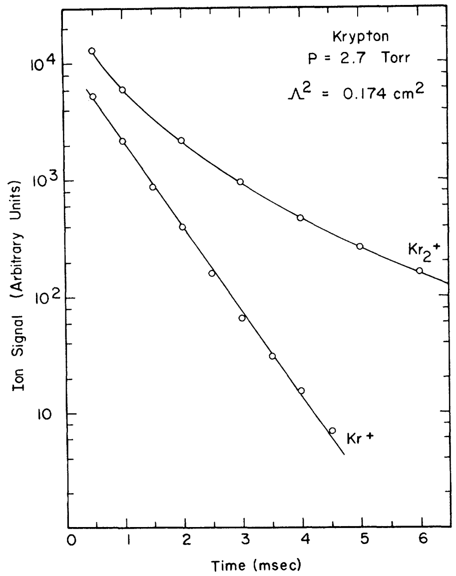

FIG. 5. Time dependence of krypton-ion signals in the afterglow.

$= 1 \pm 0.1\ \mathrm{cm^2\,V^{-1}\,sec^{-1}}$, which is in agreement with the values reported previously.

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