Electron-Ion Recombination of Xe^+ and XeH^+ Ions*

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The properties of Xe^+ and XeH^+ ions were studied in xenon and helium-hydrogen-xenon mixtures, respectively, by means of the stationary-afterglow method. The time dependence of the number density of these ions was measured by mass-spectrometric techniques. The temporal behavior of the intensity of the 4671-Å spectral line of xenon was determined by light-spectrometric techniques. The studies established for the first time the occurrence of the collisional recombination process $Xe^+ + 2e \rightarrow Xe^* + e \rightarrow Xe + e + h\nu$ and that of the dissociative recombination process $XeH^+ + e \rightarrow Xe^* + H \rightarrow Xe + H + h\nu$.

I. INTRODUCTION

The recombination of positive ions with electrons has been studied by many investigators for many years. In 1949 Biondi and Brown[1] were the first to use microwave techniques for the study of electron-ion recombination processes. They measured the time dependence of the electron density in decaying plasmas. These studies led to the discovery of the dissociative recombination process[1,2]

$$X_2^+ + e \rightarrow X^* + X \rightarrow 2X + h\nu, \qquad (1)$$

where the superscripts + and * refer to ionized and excited states of the atom, respectively.

Subsequent studies have shown that the collisional recombination process

$$X^+ + 2e \rightarrow X^* + e \rightarrow X + e + h\nu \qquad (2)$$

and the radiative recombination process

$$X^+ + e \rightarrow X^* + h\nu_1 \rightarrow X + h\nu_1 + h\nu_2 \qquad (3)$$

are two other recombination processes which may be important when discussing volume losses of charged particles.[2] It has been shown that He^+, Ne^+, and Ar^+ are lost as a consequence of process (2), while Ne_2^+ and Ar_2^+ ions recombine with electrons through process (1).[2-6] It can, therefore, be expected that the processes (2) and/or (3) are the recombination processes of all atomic rare gas ions and that the volume loss of molecular rare-gas ions is due to process (1). The recombination processes involving He_2^+ ions have not been definitely established as yet.[2,7,8] The present paper gives the results of studies concerning the recombination mechanism of the rare gas-hydride ion XeH^+. To the best of our knowledge no studies concerning the recombination of this type of ion with electrons have been published. The method used is simultaneous measurement of the time dependence of the number density of the XeH^+ ions and that of the intensity of spectral lines emitted during the decay period of a plasma produced in helium-hydrogen-xenon mixtures. The production mechanism of XeH^+ has been studied by several authors.[9,10] Moran and Friedman[11] calculated that the dissociation energy of XeH^+ is 2.66 eV, which means that this ion is a very stable ion at room temperature decaying plasmas.

Veatch and Oskam[12] observed that H_3^+ was the dominant ion during the decay period of plasmas produced in helium-hydrogen mixtures at pressures of a few Torr for hydrogen concentrations larger than about 0.1%. This is due to the fact that H_2^+ ions are rapidly converted into H_3^+ ions via the process[9]

$$H_2^+ + H_2 \rightarrow H_3^+ + H. \qquad (4)$$

When a small percentage of xenon atoms is added to the helium-hydrogen mixture, the H_3^+ ions are converted into XeH^+ ions through the process[9,10]

$$H_3^+ + Xe \rightarrow XeH^+ + H_2. \qquad (5)$$

The XeH^+ ion is a stable ion having the smallest energy in this triple gas mixture. It should, therefore, be possible to obtain experimental conditions such that the rare-gas-hydride ion XeH^+ is the dominant ion during the plasma decay period. This makes it possible to establish the recombination process of this ion.

II. EXPERIMENTAL METHOD

The experimental tube used to study the time dependence of the ions during the afterglow period consists of a differentially pumped mass spectrometer that samples ions diffusing to the walls of a discharge tube. The mass spectrometer used is of the electric-quadrupole type.

The discharge region is the glass cylinder with metal endplates. One endplate is a molybdenum electrode, while the other is made of kovar metal and contains a small hole (60-μ diameter and 40-μ length) through which the ions effuse into the mass-spectrometer region.

The gas-handling system is analogous to that developed by Alpert.[13] The ultimate pressure was about 10^{-9} Torr following a system bakeout at 325 °C for a period of 24 h. Research-grade hydrogen, helium, and xenon were used (purchased from Air Reduction Co.). The final cleaning of the discharge region was achieved by covering the discharge tube wall with a molybdenum layer obtained from sputtering the discharge electrode. This cleaning process was continued until the impurity-ion signal was less than 0.5% of that of the dominant ion throughout the afterglow. This condition was necessary to achieve reproducibility of the data. The gas pressure was measured by a capacitance manometer that controlled a servo-operated valve to maintain a constant preset pressure in the discharge tube.

A block diagram of the measuring system is shown in Fig. 1. The time sequence of events begins with the master pulser and ends at the multichannel scaler. The discharge was produced by a high-voltage dc pulse applied between the discharge-tube electrodes. The ions passing through the quadrupole mass spectrometer are detected by a Bendix magnetic electron-multiplier model No. M310B. The resulting anode pulses, each due to a single ion, are amplified by a wide-band amplifier and those above a minimum pulse height are selected by a discriminator in order to reduce the background count rate. The pulses from the discriminator are then fed into a multichannel scaler. The afterglow is divided into 100, 200, or 400 time intervals which have a minimum duration of 25 μsec. As the multichannel scaler advances from channel to channel, the number of pulses in the corresponding time intervals in the afterglow are recorded in the memory section. By accumulating the afterglow counts for a sufficient number of afterglow repetitions, a statistically significant number of counts can be recorded in each channel of the memory.

The time dependence of the intensity of the spectral lines studied was obtained using a half-meter Ebert light spectrometer. The photomultiplier has a S-20 photocathode and is thermoelectrically cooled to reduce the dark count rate. The signal pulses resulting from single photons are detected and counted using the same technique as used for ions.

III. RESULTS AND DISCUSSION

The ionic composition during the decay period of plasmas produced in xenon and in helium-hydrogen as well as in helium-hydrogen-xenon mixtures for various pressures and mixtures was first determined. For pressures smaller than about 1 Torr, the Xe^+ ion was the dominant ion in pure xenon. For helium pressures larger than about 4 Torr and hydrogen concentration larger than about 0.1%, the H_3^+ ion was the major ion in helium-hydrogen mixtures. For the triple mixture consisting of helium containing 10% hydrogen and 1% xenon the XeH^+ ion was the only ion detected during the decay period provided the total pressure was larger than about 3 Torr.

The two spectral lines in the visible spectrum from 3000 to 7000 Å during the decay period of plasmas produced in pure xenon and in the triple mixture had a wavelength of 4671 Å ($7p_{23}\rightarrow 6s_{12}$) and 4624 Å ($7p_{12}\rightarrow 6s_{12}$). The intensity of the 4671-Å line was in general twice that of the 4624-Å line, while the time dependence of their intensities was identical during the plasma decay period. Figures 2 and 3 show the relation between the intensity of the 4671-Å line and the number density of Xe^+ and XeH^+, respectively. The log-log plot is obtained by measuring the time dependencies of the spectral line intensity and that of the $Xe^+(XeH^+)$ number density under identical experimental conditions. Each measuring point in Figs. 2 and 3 gives the line intensity and the $Xe^+(XeH^+)$ density at the same time in the plasma decay period.

The intensity of spectral lines emitted as a consequence of a specific electron-ion recombination process will be proportional to the number of ions recombining with electrons per second by this

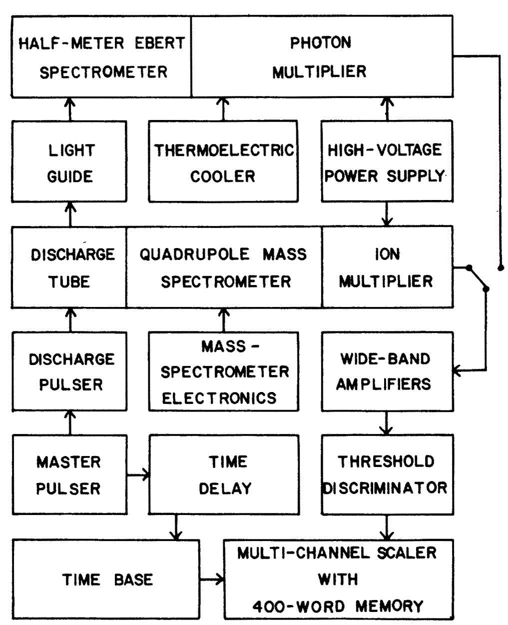

FIG. 1. Block diagram of the experimental system.

process. This means that the time-dependent part of the light intensity $I_a(t)$ will be proportional to the product of the recombination coefficient α, and ion density $n_i(t)$, and the electron density, i.e.,

$$I_a(t) \propto \alpha n_i(t) n_e(t). \quad (6)$$

The radiative recombination process (3) will result in a spectral-line emission intensity proportional to the product of the electron density and that of the ion involved. The same dependence will be found for spectral emission owing to the dissociative recombination process (1). The collisional recombination process (2), however, will result in a different relation between the intensity of the produced spectral lines and the densities of the charged particles participating in the recombination process, since the recombination coefficient α for this process is a function of electron density. Previously, it was established that the recombination of He^+, Ne^+, and Ar^+ with electrons occurred via the collisional recombination process with a recombination coefficient proportional to the electron density.[4-6]

The functional relation between the spectral line emission intensity and the density of the charged particles responsible for the emission can easily be determined for experimental conditions such that the electron density is nearly equal to that of the recombining ion. Both the radiative recombination process and the dissociative recombination process will then produce emission having an intensity proportional to the square of the ion density. The collisional recombination process, however, will result in a different dependence of the emission intensity on the ion density. The intensity will be proportional to the ion density to the third power, provided the emission originates from electronic transitions with sufficiently small principal quantum numbers and provided the recombination coefficient is proportional to the electron density.

The data shown in Fig. 2 relate to a decaying plasma in which the Xe^+ ion density is nearly equal to the electron density. The intensity of the 4671-Å spectral line is proportional to the third power of the Xe^+ density. This functional dependence established that the recombination process involving the Xe^+ ion is, for the present experimental conditions, the collisional recombination process (2) with a recombination coefficient proportional to the electron density.

The data shown in Fig. 3 were obtained in the triple mixture for experimental conditions such that XeH^+ is equal to the electron density. The quadratic dependence of the intensity of the 4671-Å spectral line on the XeH^+ density established

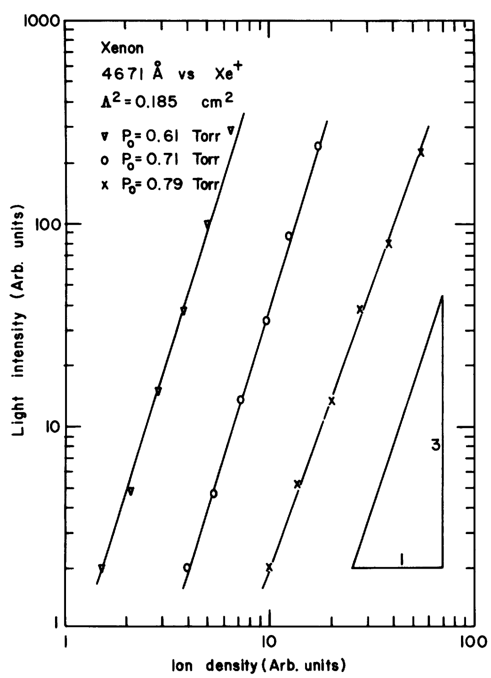

FIG. 2. Intensity of the 4671-Å line of xenon vs the Xe^+ ion density during the plasma decay period. Each data point corresponds to the values of the ion density and light intensity at a given time in the afterglow.

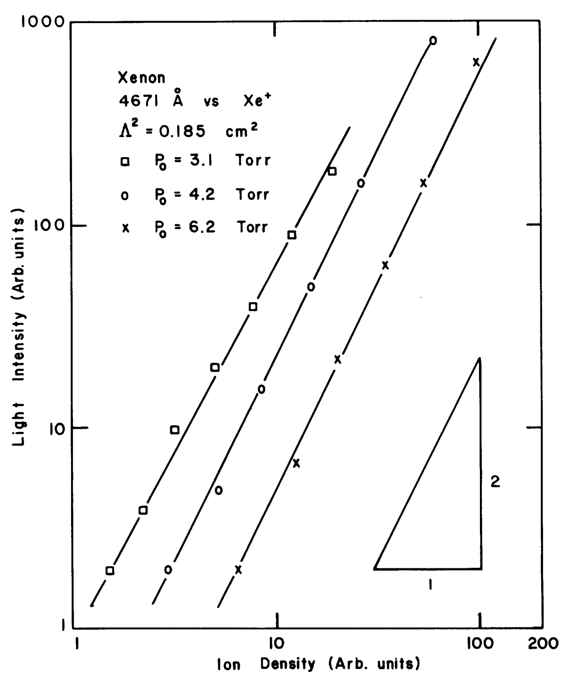

FIG. 3. Intensity of the 4671-Å line of xenon vs the XeH^+ ion density during the plasma decay period. Each data point corresponds to the values of the ion density and light intensity at a given time in the afterglow.

that the recombination process involved is the dissociative recombination process

$$XeH^+ + e \rightarrow Xe^* + H \rightarrow Xe + H + h\nu. \quad (7)$$

The energy of XeH^+ is not large enough to populate excited hydrogen states during the recombination process which would result in light emission in the wavelength region studied.

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