Formation of High Rydberg He(np ^{3}P:n=5-12) Atoms by the Three-Body Collisional-Radiative Recombination of He^+ in the Helium Flowing Afterglow

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The He(np ^{3}P→2s ^{3}S) emission lines from n=5-12 have been observed in a He flowing afterglow. A comparison of the He-pressure dependence of the emission intensity with those predicted from the two-body [He^+][e^-] and three-body [He^+][e^-][He] and [He^+][e^-][e^-] recombination processes indicated that the high Rydberg He(np ^{3}P:n=5-12) states are produced from the last three-body collisional-radiative (CR) recombination reaction.

There has been a continuing interest in electron-ion recombination processes of He^+ because they are an important loss process of charged species from natural plasmas in space and man-made plasmas such as discharges containing He atoms.[1-5] The main purpose of these previous studies has been placed upon the determination of recombination coefficients at various He pressures and temperatures. Therefore, there are only a few experimental studies that have been determined the final electronic states of the neutral He^* atoms.[6,7] A flowing-afterglow method fitted with an optical detection system is an ideal technique to study the final electronic states in electron-ion recombination reactions. Collins and Robertson[6] have observed the He(nd ^{3}D →2p ^{3}P) emission lines from n=3-14 in the He flowing afterglow in the spectral range of 349-588 nm. They predicted that these emission lines arise from the three-body CR reaction. However, no definite experimental evidence of this prediction has been obtained because they did not directly measure the electron density. To the best of our knowledge, no optical spectroscopic study on the electron-ion recombination processes in the He afterglow has been carried out in the UV region below 300 nm.

In the present study, electron-ion recombination processes in the He flowing afterglow have been studied by observing He^* emission below 300 nm. A Rydberg series of He^* lines, which have not been observed previously, appears in the 265-296 nm region. The responsible recombination process is determined by measuring the changes in [He^+] and [e^-] at various He pressures.

The flowing-afterglow apparatus used in the present study was identical with that reported previously,[8,9] except for an addition of a Langmuir probe in order to directly measure the electron density in the reaction zone. A pair of grids were placed between the discharge section and the reaction zone in order to examine the effects of charged species on the observed emissions. The emission spectra at 20 cm downstream from the center of the discharge were dispersed in the spectral range of 120-300 nm with a McPherson 218 monochromator. The He pressure in the reaction zone was measured using a Pirani gauge calibrated against a capacitance manometer.

Figure 1 shows a typical emission spectrum observed in the UV region at a He gas pressure of 1.3 Torr. The spectrum consists of intense He* atomic lines due to the He(np ^{3}P→2s ^{3}S:n=5-12) transitions in the 265-296 nm region and the (1,0) band of the OH(A-X) transition in the 280-290 nm region. The latter emission results from the electron-H_2O^+ dissociative recombination process, where H_2O^+ is produced by the reactions of He(2^3S), He^+, and He_2^+ with H_2O (impurity). These He(np ^{3}P→2s ^{3}S) lines disappeared, when positive ions in the He afterglow were trapped by applying a positive electrostatic potential to the grid. A similar disappearance occurred, when thermal electrons in the He afterglow were removed by the application of a negative potential to the grid or by the addition of a small amount of a thermal-electron scavenger (SF_6) to the reaction zone. These results imply that the He(np ^{3}P:n=5-12) states are produced by some electron-ion recombination processes.

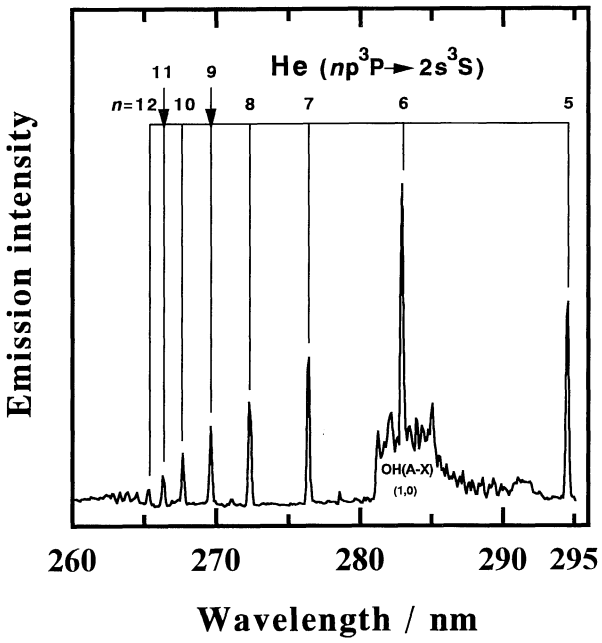

Figure 1. Emission spectrum of He^* observed in the He flowing afterglow. Uncorrected for the relative sensitivity.

Possible precursor helium ions are He^+ and He_2^+, the presence of which were confirmed by using the He^+/N_2 and He_2^+/CO_2 reference reactions.[9] The [He_2^+]/[He^+] ratio increased with increasing the He pressure because the He_2^+ ion is formed by the three-body He^+/2He reaction:

$$He^+ + He + He \rightarrow He_2^+ + He, \quad (1)$$
$$k_1 = (8.3\pm1.7) \times 10^{-32} \text{ cm}^6\text{s}^{-1} \text{ (Ref. 10).}$$

Since the excitation energies of the observed high Rydberg He(np ^{3}P:n=5-12) states from the ground He(1^1S) state are 24.03-24.49 eV, their formation from the He^+ atomic ion with a recombination energy of 24.59 eV is possible. Although the $He_2^+(X^2\Sigma_u^+:v''=0)$ dimer ion with recombination energies of 18.3-20.3 eV[9] cannot provide the He(np ^{3}P:n=5-12) states, He_2^+ in highly vibrationally excited levels can be precursor ions. The relative contribution of He^+ and $He_2^+(X^2\Sigma_u^+$:high v") was examined by the addition of a sufficient amount of Ne, Ar, or Kr at 10 cm upstream from the observation region of the He^* emission. Although He^+ is

unreactive for these rare gases, He_2^+ is removed by fast charge-transfer reactions in the He afterglow:[10]

$$He^+ + Ne, Ar, or Kr \rightarrow Products \ (k_2 < 1.0 \times 10^{-11} \ cm^3s^{-1}), \quad (2)$$

$$He_2^+ + Ne \rightarrow Ne^+ + 2He \quad (k_{3a} = 6.0 \times 10^{-10} \ cm^3s^{-1}), \quad (3a)$$

$$He_2^+ + Ar \rightarrow Ar^+ + 2He \quad (k_{3b} = 2.0 \times 10^{-10} \ cm^3s^{-1}), \quad (3b)$$

$$He_2^+ + Kr \rightarrow Kr^+ + 2He \quad (k_{3c} = 1.85 \times 10^{-11} \ cm^3s^{-1}). \quad (3c)$$

When He_2^+ was removed by the addition of Ne, Ar, or Kr, the He(np ^{3}P→2s ^{3}S:n=5-12) lines were strongly enhanced due to the generation of a significant amount of electrons by the He(2^3S)/Ne, Ar, or Kr Penning ionization. On the basis of the above results, $He_2^+(X^2\Sigma_u^+$:high v") was excluded from possible precursor ions of He(np ^{3}P:n=5-12). Thus, the remaining formation processes of He(np ^{3}P) are the following two- and three-body recombination processes:

$$He^+ + e^- \rightarrow He(np^3P) + h\nu, \quad (4)$$

$$He^+ + e^- + He \rightarrow He(np^3P) + He, \quad (5)$$

$$He^+ + e^- + e^- \rightarrow He(np^3P) + e^-. \quad (6)$$

Extensive experimental and theoretical studies[1-4] demonstrated that process (5) is important at low electron densities, while process (6) becomes significant at high electron densities. In order to determine the relative importance of the above three processes, the He-pressure dependence of the emission intensity was measured and the results obtained are compared with those of $[He^+][e^-]$, $[He^+][e^-][He]$, and $[He^+][e^-][e^-]$, as shown in Figure 2. Here, the relative value of $[He^+]$ was evaluated from the $N_2^+(C^2\Sigma_u^+$-$X^2\Sigma_g^+)$ emission resulting from the two-body He^+/N_2 charge-transfer reaction.[11] On the other hand, the electron density, $[e^-]$, was measured by using a single Langmuir probe. The absolute $[e^-]$ value was evaluated to be 3.2×10^9—2.6×10^{10} cm^{-3} at the He pressure range of 0.2-1.35 Torr by using the same procedure as that reported by Smith et al.[12,13] It

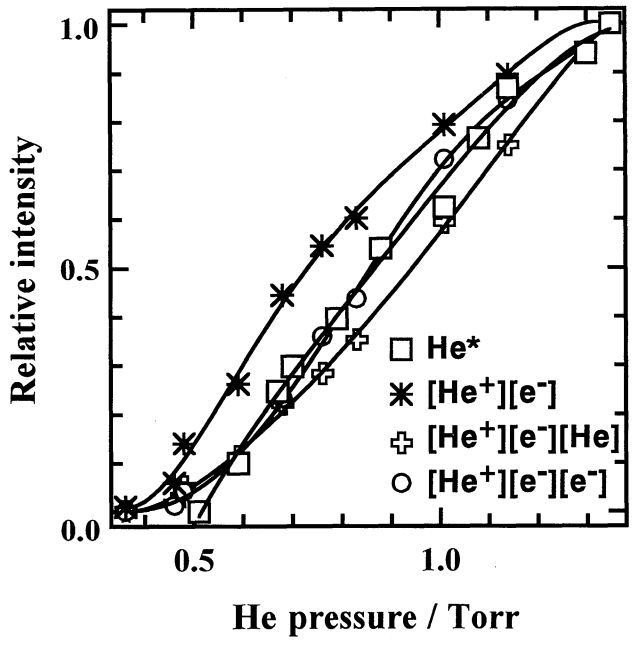

Figure 2. The dependencies of the relative emission intensity of He($7p^3P$→$2s^3S$), $[He^+][e^-]$, $[He^+][e^-][He]$, and $[He^+][e^-][e^-]$ on the He gas pressure.

should be noted that a reasonable agreement is obtained between the He-pressure dependence of the He intensity and that of $[He^+][e^-][e^-]$ at He pressures above ~0.6 Torr. It has been therefore concluded that three-body CR process (6) is most important for the excitation of He(np ^{3}P).

The present finding that He(np ^{3}P) is produced by process (6) is consistent with the previous result of Collins and Robertson[6] for the formation of the neighboring He(nd ^{3}D) states in the flowing-afterglow cell with a similar microwave-discharge source. They predicted that the He(nd ^{3}D) states are formed by three-body CR process such as (6), because the electron density in their condition (5×10^{12} cm^{-3}) is sufficiently high to give He(nd ^{3}D) via the three-body CR process. However, their evaluation of the electron density was carried out assuming a Saha equation, which holds for free electrons at high electron densities. Their value is much higher than our present data, even though there will be no significant difference in the electron density in the two similar He flowing afterglow. It is therefore highly likely that Collins and Robertson[6] overestimated the electron density in their flowing-afterglow cell. On the basis of the present data, three-body CR process (6) is a major recombination process of He^+ at low He pressure range of ~1 Torr and an electron density of ~10^{10} cm^{-3}. This finding agreed with the previous kinetic data at similar He pressures and electron densities.[5]

We have communicated here that the high Rydberg He(np ^{3}P:n=5-12) states are produced from the three-body CR process in the He flowing afterglow. We are planning to determine electronic state distributions of He^* in various Rydberg states from the spectral measurements in a wider spectral range.

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