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He_3^+ and He_4^+ in 300°K Helium Plasmas: Their Effect on Recombination Loss of Electrons*

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The work reported here establishes the existence of He_3^+ and He_4^+ at room temperature (300°K) in a helium afterglow. The data presented in this paper indicate that the often-measured electron-ion recombination coefficient in 300°K helium afterglows is mainly attributable to electron recombination with He_3^+ rather than, as is usually assumed, with the dominant ion He_2^+.

The electron-ion recombination coefficient in 300°K helium plasmas has been widely studied for the past 20 years by several different groups.[1-6] The measured recombination rate has usually been assigned to He_2^+ if the gas pressure is greater than a few Torr. Results are presented in this paper which indicate that at room temperature and pressures greater than a few Torr, the measured recombination rate can be attributed to electron recombination with He_3^+ even though it is a minority ion.

In 1968, Patterson[7] reported measurements of an ion observed in helium at gas temperatures below 200°K. He concluded that this ion was the triatomic helium ion He_3^+. A mass-12 ion, assumed to be He_3^+, was seen in a flowing afterglow.[8] Isotope measurements have confirmed that He_3^+ and He_4^+ exist in a helium afterglow at a temperature of about 80°K.[9] There have been several other mass-spectrometric observations of mass 12 in helium plasmas[10,11] where the authors have postulated that the observed ion was He_3^+. Unfortunately, in those experiments the presence of other impurities as well as the relative abundance of the mass-12 ion makes it more likely that the observations pertained to C^+.

The work reported here establishes the existence of He_3^+ and He_4^+ at room temperature (300°K) in a helium afterglow. The equilibrium concentration ratios of these ions have also been determined.

He_3^+ and He_4^+ have atomic mass units of 12 and 16, respectively. As is well known, C^+ and O^+ have the same respective masses. Consequently, in order to avoid misinterpretation of the data the isotope of helium ^3He was used in this study. Figure 1(a) shows a time-integrated mass spectrum taken at 15 Torr. Mass 7 ($^{4,3}He_2^+$) is due to a trace of ^4He. The ions observed are He_2^+ and two ions at masses 9 and 12. In order to establish the identity of the latter masses, ^4He was added. The resulting expanded mass scan is shown in Fig. 1(b). Masses 9, 10, 11, and part of 12 are He_3^+ while the remainder of mass 12, and masses 13 and 14 are He_4^+. The superscripts on the chemical terms in Fig. 1(b) indicate the mass structure of the molecular ion. The absence of O^+ (mass 16) indicates that the mass-12 peak is not due to C^+. A quadrupole mass filter which employed a Bendix Channeltron as an ion detector was used to obtain these mass

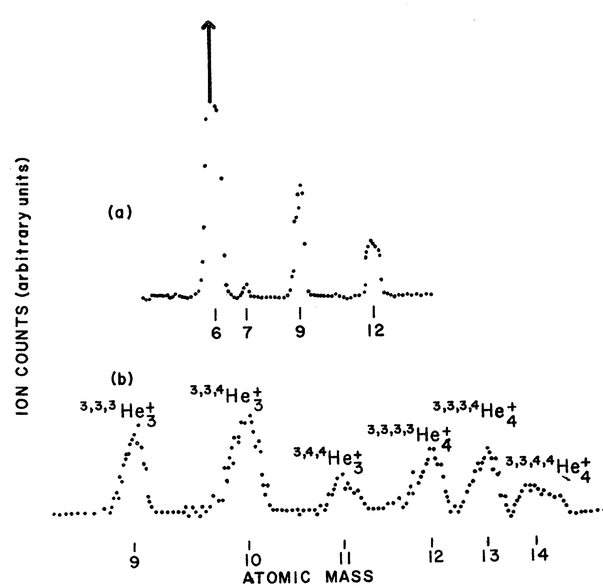

FIG. 1. (a) Time-integrated mass spectra of ^3He afterglow. (b) Time-integrated mass spectra of ^3He and ^4He afterglow. (b) was taken at a different scan speed than (a).

spectra and the ion density ratios. A complete description of the experimental techniques and equipment will be contained in a future publication.[12] It was typically possible to measure the decay of He_2^+ in the afterglow over eight decades of ion current.

The equation describing electron loss by recombination when He_2^+ and He_3^+ are the only ions present is

$$dn_e/dt = -\alpha_2 n_e[He_2^+] - \alpha_3 n_e[He_3^+], \qquad (1)$$

where the electron density is n_e, the brackets indicate densities, and α_2, α_3 are the respective electron-ion recombination coefficients. If $n_e \sim [He_2^+] \gg [He_3^+]$, then Eq. (1) becomes

$$dn_e/dt = -\alpha_{eff} n_e^2, \qquad (2)$$

where $\alpha_{eff} = \alpha_2 + \alpha_3[He_3^+]/[He_2^+]$. Using the recombination coefficient for He_3^+, including its temperature dependence,[13] one finds $\alpha_3 \sim 10^{-7}$ cm^3/sec. The $[He_3^+]/[He_2^+]$ ratio as observed in this work is $\sim 10^{-3}$; hence, α_{eff} is at least $\sim 10^{-10}$ cm^3/sec, which is within the rather wide range of measured values.[1-6] We propose that the term $\alpha_3[He_3^+]/[He_2^+]$ in α_{eff} represents the pressure-dependent recombination mechanism reported by Berlande et al.,[14] instead of the three-body electron-ion recombination with He_2^+ (the third body being a neutral helium atom) as they proposed. Recently, Dolgov-Savel'ev et al.[15] have reported an experiment with the rare gases in which they have determined the net electronic recombination coefficient. All the rare gases except helium gave results consistent with previously published work. Helium alone showed an anomalous pressure dependence that is consistent with the results presented in this paper.

Patterson[7] has shown that He_3^+ and He_2^+ are in equilibrium over a temperature range of 125 to 200°K. Equation (3) shows that under conditions of equilibrium the ratio of He_3^+ to He_2^+ increases linearly with pressure:

$$He_2^+ + 2\,He \rightarrow He_3^+ + He. \qquad (3)$$

Figure 2 shows the ratio of mass-resolved ion currents $j[He_3^+]/j[He_2^+]$ for a plasma of ^3He. It is seen that within the scatter of the data, $j[He_3^+]/j[He_2^+]$ does increase linearly with pressure. Since there are no other known mechanisms of He_3^+ formation, this indicates that the ions He_3^+ and He_2^+ were in a relative equilibrium during the afterglow. The relative concentrations of He_2^+, He_3^+, and He_4^+ were nearly identical during the afterglow.

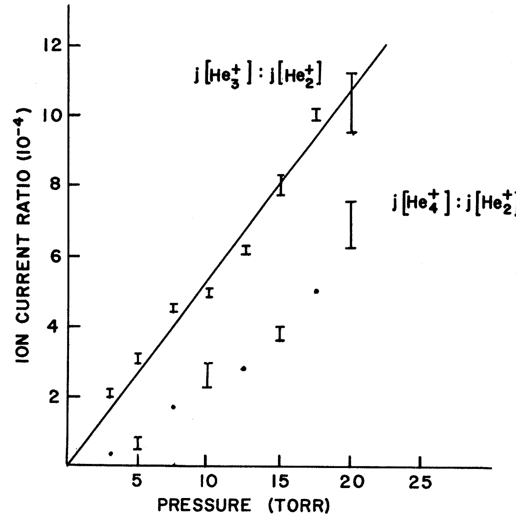

FIG. 2. Ion current ratios $j[He_3^+]/j[He_2^+]$ and $j[He_4^+]/j[He_2^+]$ as a function of helium pressure for a 300°K afterglow. The error bars represent experimental reproducibility.

The relation between the equilibrium constant and the appropriate equilibrium densities is defined by

$$K(T) = [He_2^+]^*[He]^*/[He_3^+]^*. \qquad (4)$$

The asterisks indicate equilibrium conditions.

The equilibrium constant obtained from Fig. 2 is $K = 0.6\times10^{21}$ cm^{-3} $\pm13.2\%$. The $\pm13.2\%$ is the standard deviation obtained in fitting a straight line to $j[He_3^+]/j[He_2^+]$ versus pressure in Fig. 2. This value of K was obtained by assuming a fundamental diffusion mode for all charged species and equal diffusion coefficients for He_2^+ and He_3^+. It is probable that the diffusion coefficient of He_3^+ is greater than that of He_2^+.[7] However, it is estimated that this will introduce an error no greater than 50% in the determination of K. An additional source of error in the evaluated K is due to possible differences in ion detection efficiency of the Channeltron for different ions. In light of these uncertainties the value of K at 300°K is

$$0.5\times10^{21} < K(300°K) < 1.0\times10^{21}\ cm^{-3}. \qquad (5)$$

Equation (8) of Ref. 7 predicts an equilibrium constant at 300°K of $0.67\times10^{21} < K < 6.7\times10^{21}$ cm^{-3}, where the bracketing of K results from the stated uncertainty in the dissociation energy of He_3^+ as given in that work. Equation (8) of Ref. 7 requires information about He_3^+ which can be obtained from Poshusta, Haugen, and Zetik.[16]

The recombination coefficient, α_3, as taken from Ref. 13 is

$$\alpha_3 = (3.37 \pm 1.50)\times 10^{-6}(T_e/80)^{-\chi}\ \mathrm{cm^3/sec},\quad 0.98 < \chi < 1.60, \tag{6}$$

where T_e is the electron temperature in degrees Kelvin. This value of α_3 was measured at a gas temperature near 80°K. It is possible that α_3 will also have a gas-temperature dependence due to excitation of vibrational and rotational modes of He_3^+.

Using Eqs. (4), (5), and (6), one finds

$$1.2\times 10^{-11}p \leq \alpha_3[He_3^+]/[He_2^+] \leq 7.1\times 10^{-11}p\ \mathrm{cm^3/sec}. \tag{7}$$

where the pressure p is in Torr. The inequalities of Eq. (7) result from the uncertainties of α_3 as indicated in Eq. (6). Error incurred in determining the ratio $[He_3^+]/[He_2^+]$ has not been included. Equation (7) is to be compared with the pressure-dependent recombination term of Ref 14,

$$k_{He}n_{He} = (6.4 \pm 1.6)\times 10^{-11}p\ \mathrm{cm^3/sec}. \tag{8}$$

The overlap of this value with the inequality given by Eq. (7) indicates that He_3^+ may indeed control the recombination loss of electrons in room-temperature helium plasmas. Even though there is agreement between Eqs. (7) and (8), it must be noted that neither the gas-temperature dependence of α_3 nor the recombination of He_4^+ was included in Eq. (7).

Figure 2 also shows the ratio $j[He_4^+]/j[He_2^+]$. At this time it is not possible to make a definite statement concerning the mechanism for formation of He_4^+ at 300°K. Data concerning the behavior of He_4^+ at 77°K will be published.[12]

It is the hypothesis of this paper that in 300°K helium afterglows with pressures greater than 1 Torr, He_3^+ is the ion primarily responsible for electron recombination. Recombination of electrons with He_4^+ will serve to increase the net recombination loss, and the effective recombination coefficient will still increase monotonically with pressure (although not necessarily linearly).

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