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A New Technique for a Selective Observation of Charge-Transfer Reactions by He^+ in a Helium Afterglow

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The He^+ and He_2^+ ions are involved as active ionic species in a helium afterglow. Although it was difficult to separate the He^+ reaction from the He_2^+ one, a new convenient method to isolate the He^+ reaction is presented here. In our method, Ar, whose rate coefficient for He_2^+ is much larger than that for He^+, was premixed with the He flow to remove He_2^+ ions efficiently. This method was successfully applied to the formation of $N_2^+(B^2\Sigma^+)$ by the $He^+ + N_2$ reaction at thermal energy.

Introduction

Studies on gas-phase elementary reactions induced by active species of rare gases are significant for understanding chemical reactions in discharge plasmas, combustion flame, and interstellar space in a microscopic level. Active species generated in discharge plasma of He are the metastable $He(2^3S)$ atoms and the He^+ and He_2^+ ions. A flowing afterglow method, which was developed by Ferguson et al.[1] in NOAA for studying reactions by rare gas metastable atoms and ions in an upper atmosphere, is a useful technique for studying reactions of $He(2^3S)$, He^+, and He_2^+ at thermal energy.

Optical spectroscopic studies in a helium afterglow have extensively been carried out in order to clarify excitation transfer reactions and Penning ionization by the metastable $He(2^3S)$ atoms and charge-transfer reactions by He^+ and He_2^+ ions.[2,3] Although the reactions between neutral $He(2^3S)$ atoms and charged He^+ and He_2^+ ions can be distinguished by using ion collector grids placed between the discharge section and the reaction zone, it was difficult to completely separate the ionic reactions between He^+ and He_2^+ ions.[2-6] We communicate here a new convenient method to isolate the He^+ reaction in a helium afterglow. The usefulness of this technique is demonstrating by a selective observation of the $N_2^+(B^2\Sigma^+-X^2\Sigma^+)$ emission resulting from the He^+/N_2 charge-transfer reaction.

Experimental

The flowing afterglow apparatus used in this study is shown in Fig. 1. It consists of a main stainless steel flow tube [internal diameter (i.d.) 60 mm] and a quartz discharge tube (i.d. 11 mm), which are continuously evacuated using a 10,000 l min^{-1} mechanical booster pump. Helium active species were generated by a microwave discharge in the quartz tube. Ar and N_2 gases were added to the flow tube 10 and 20 cm downstream from the center of the discharge, respectively. Active species of He in region A are $He(2^3S)$, He^+, and He_2^+. By the addition of Ar, active species of He in region B become only He^+. The partial pressures of He, Ar, and N_2 in the reaction zone were measured to be 0.96, 0.080, and 0.003 Torr, respectively. A pair of ion-collector grids were installed between the discharge section and the reaction zone. The contribution of the ionic active species was examined by applying an electrostatic potential to an ion-collector grid.

Emission spectra just around the gas inlet were measured in the UV and visible region using a Spex 1.25 m scanning monochromator equipped with a 1200 line/mm grating blazed at 500 nm and a cooled

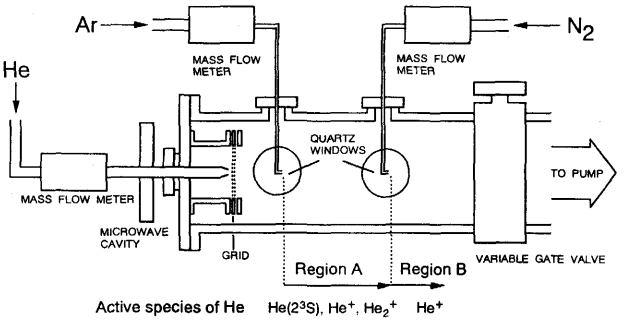

Fig. 1. Flowing afterglow apparatus for studying the He^+ reactions.

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Hamamatsu Photonics R376 photomultiplier. Photon signals from the photomultiplier were amplified and converted to digital signals using an AD converter. They are stored and analyzed using a microcomputer. The relative sensitivity of the monochromator and the optical detection system was corrected by using standard D_2 and halogen lamps.

Results and Discussion

When N_2 was added into a He flowing afterglow 20 cm downstream from the center of the discharge without premixing Ar gas, a strong $N_2^+(B^2\Sigma_u^+\text{-}X^2\Sigma_g^+)$ emission system was observed in the 330-600 nm region. Figure 2(a) shows a typical emission spectrum in the 440-475 nm region obtained at a total pressure of 1 Torr, where the Δv = -2 sequence of N_2^+(B-X) from v'=0-6 is identified. These findings are consistent with previous studies on the helium-afterglow reaction of N_2.[4-6] Active species in Fig. 2(a) are $He(2^3S)$, He^+, and He_2^+. When the He^+ and He_2^+ ions are trapped using the ion-collector grids, the N_2^+(B-X) emission from v'=0,1 reduces its intensity by about 45-65% and that from v'=2-6 disappeared, as shown in Fig. 2(b). The N_2^+(B-X) emission from v'=0,1 observed in Fig. 2(b) entirely arises from the $He(2^3S)/N_2$ Penning ionization (1):

$$He(2^3S) + N_2 \rightarrow N_2^+(B^2\Sigma_u^+) + He + e^-. \quad (1)$$

These findings indicate that about 45-65% of N_2^+(B-X) from v'=0,1 and all of the N_2^+(B-X) emission from v'=2-6 result from charge-transfer reactions of He^+ and/or He_2^+ with N_2.

Since He_2^+ ions are formed via the following secondary three-body reaction, the N_2^+(B-X) emission resulting from the He_2^+/N_2 reaction is expected to be strongly enhanced at high He pressures:

$$He^+ + 2He \xrightarrow{k_2} He_2^+ + He, \quad (2)$$
$$k_2 = 1.1 \times 10^{-31} \text{ molecule}^{-2}\text{cm}^6\text{s}^{-1} \text{ (Ref. 7).}$$

Piper et al.[4] and Endoh et al.[6] measured the dependence of the intensity distribution of $N_2^+(B^2\Sigma_u^+:v')$ on the He buffer gas pressure. Both groups found that the populations of the low $N_2^+(B^2\Sigma_u^+: v'=0,1)$ levels are significantly enhanced with increasing the He pressure relative to those of the high $N_2^+(B^2\Sigma_u^+: v' \geqq 2)$ levels. It was therefore concluded that the $N_2^+(B^2\Sigma_u^+:v'=0,1)$ levels are dominantly formed by the He_2^+/N_2 reaction (3), while the $N_2^+(B^2\Sigma_u^+: v'=2\text{-}6)$ levels are produced by the He^+/N_2 reaction (4):

$$He_2^+ + N_2 \rightarrow N_2^+(B^2\Sigma_u^+: v'=0,1) + 2He, \quad (3)$$
$$He^+ + N_2 \rightarrow N_2^+(B^2\Sigma_u^+: v'=2\text{-}6) + He. \quad (4)$$

However, there is a large possibility that the $N_2^+(B:v'=0,1)$ levels are also excited by the He^+/N_2 reaction (5):

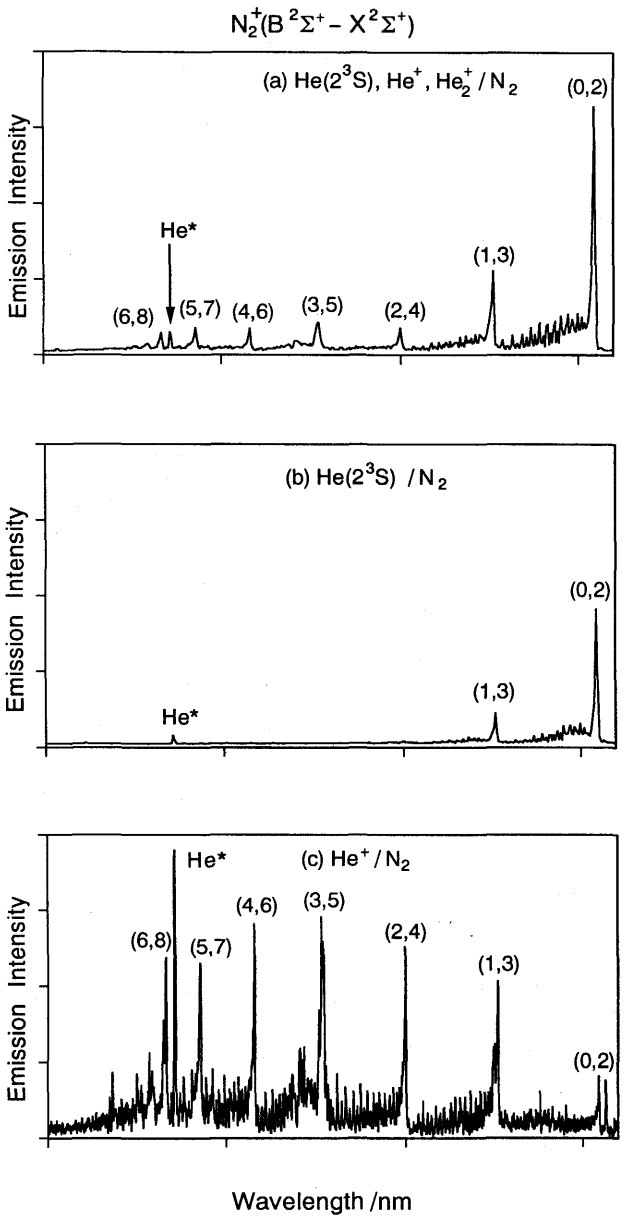

Fig. 2. Emission spectra of N_2 in a helium flowing afterglow.

$$He^+ + N_2 \rightarrow N_2^+(B^2\Sigma_u^+: v'=0,1) + He. \quad (5)$$

The rate constant of reaction (3) will be much larger than that of process (5). Therefore, the N_2^+(B-X) emission from process (3) is seriously overlapped with that from process (5) even at a low He pressure, where the concentration of He_2^+ is much lower than that of He^+. Thus, it was difficult to isolate the N_2^+(B-X) emission from process (5).

We have recently studied the He afterglow reaction of Ar.[8] We found a weak $HeAr^+$(B 1/2-X 1/2) emission resulting from the following radiative association (6) and the three-body association (7) in a vacuum ultraviolet region by the addition of Ar 10 cm

downstream from center of the discharge:

$$He^+ + Ar \xrightarrow{k_6} HeAr^+(B\ 1/2) + h\nu, \quad (6)$$
$$He^+ + Ar + He \rightarrow HeAr^+(B\ 1/2) + He. \quad (7)$$

This emission was observed at 20 cm downstream from the center of the discharge, indicating that the rate constant of the He^+/Ar reaction is not sufficiently large to completely remove the He^+ ion.

$$He^+ + Ar \xrightarrow{k_8} Ar^+ + He, \quad (8)$$
$k_8 < 1 \times 10^{-13}$ molecule^{-1}cm^{3}s^{-1} (Ref. 7).

Actually, we have determined the rate constant of process (6) to be 4.0×10^{-13} molecule^{-1}cm^{3}s^{-1} (Ref. 10) by comparing the total emission intensity of $HeAr^+$(B-X) with that of N_2^+(C-X) resulting from the following near-resonant charge-transfer reaction:

$$He^+ + N_2 \xrightarrow{k_9} N_2^+(C^2\Sigma_u^+) + He. \quad (9)$$
$k_9 = 7.2 \times 10^{-11}$ molecule^{-1}cm^{3}s^{-1} (Ref. 10)

It is known that the reaction rate constants of $He(2^3S)$/Ar and He_2^+/Ar are much larger than that of He^+/Ar:

$$He(2^3S) + Ar \xrightarrow{k_{10}} Ar^+ + He + e^-, \quad (10)$$
$k_{10} = (7\sim10) \times 10^{-11}$ molecule^{-1}cm^{3}s^{-1} (Ref. 11),

$$He_2^+ + Ar \xrightarrow{k_{11}} Ar^+ + 2He, \quad (11)$$
$k_{11} = 2 \times 10^{-10}$ molecule^{-1}cm^{3}s^{-1} (Ref. 7).

Thus, by the addition of Ar before the reaction zone, $He(2^3S)$ and He_2^+ are effectively quenched near the inlet of Ar, while most of all He^+ is expected to survive until the second N_2 gas inlet placed 10 cm further downstream from the Ar gas inlet (see Fig. 1).

Figure 2(c) shows an emission spectrum obtained by the addition of a sufficient Ar gas (1000 sccm) into the He afterglow, where the N_2^+(B-X) emission from $v'=0$-6 is identified. When ionic active species were trapped by the ion-collector grids, the N_2^+(B-X) emission observed in Fig. 2(c) completely disappeared, indicating that all of the N_2^+(B-X) emission arise from the ionic reaction. Piper et al.[4] and Endoh et al.[6] reported that the vibrational distribution of N_2^+(B-X) emission resulting from reaction (3) is similar to that from $He(2^3S)/N_2$ Penning ionization. Since the vibrational distributions of N_2^+(B: $v'=0,1$) in the He_2^+/N_2 reaction (3) and $He(2^3S)/N_2$ Penning ionization (1) are in good agreement with that predicted from Franck-Condon factor for the $N_2(X^1\Sigma^+) \rightarrow N_2^+(B^2\Sigma_u^+)$ vertical ionization, it was concluded that the ionization proceeds though a Franck-Condon like vertical process. Although the intensity distribution of N_2^+(B-X) in Fig. 2(c) is significantly different from that found in the He_2^+/N_2 reaction, it is similar to that observed from the He^+/N_2 reaction in an ion cyclotron resonance (ICR) cell.[12] This finding led us to conclude that the He^+/N_2 reaction is successfully separated from the He_2^+/N_2 reaction at thermal energy.

We found here that Ar gas can be used as an effective filter gas of $He(2^3S)$ and He_2^+ in a helium flowing afterglow. An advantage of the use of Ar gas is that no background emission, which disturbs the spectral analysis in the UV and visible region, is present. Thus, this technique will be very useful to the study of He^+ reactions in a helium flowing afterglow. Since the ionic density of He^+ in a flowing afterglow is much higher than that in the ICR cell,[12] the observed emission intensities are much stronger. This makes optical studies under much better optical resolution possible. We are planning to apply to this new technique for the other charge-transfer reactions resulting from the He^+ ion in the helium flowing afterglow.

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