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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 He₂⁺ ions are involved as active ionic species in a helium afterglow. Although it was difficult to separate the He⁺ reaction from the He₂⁺ one, a new convenient method to isolate the He⁺ reaction is presented here. In our method, Ar, whose rate coefficient for He₂⁺ is much larger than that for He⁺, was premixed with the He flow to remove He₂⁺ ions efficiently. This method was successfully applied to the formation of N₂⁺(B²Σ⁺) by the He⁺ + N₂ 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(2³S) atoms and the He⁺ and He₂⁺ 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(2³S), He⁺, and He₂⁺ 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(2³S) atoms and charge-transfer reactions by He⁺ and He₂⁺ ions.^{2,3)} Although the reactions between neutral He(2³S) atoms and charged He⁺ and He₂⁺ 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 He₂⁺ 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 demonstrated by a selective observation of the N₂⁺(B²Σ⁺-X²Σ⁺) emission resulting from the He⁺/N₂ 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 N₂ 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(2³S), He⁺, and He₂⁺. By the addition of Ar, active species of He in region B become only He⁺. The partial pressures of He, Ar, and N₂ 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

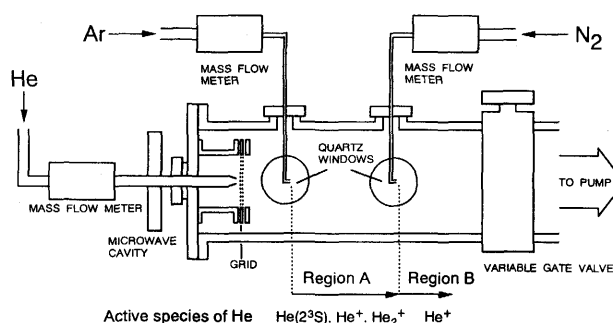


Fig. 1. Flowing afterglow apparatus for studying the He⁺ reactions.

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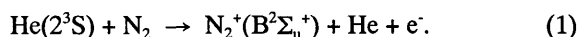
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Hamamatsu Photonics R376 photomultiplier. Photon signals from the photomultiplier were amplified and converted to digital signals using an AD converter. They are stored and analyzed using a microcomputer. The relative sensitivity of the monochromator and the optical detection system was corrected by using standard D₂ and halogen lamps.

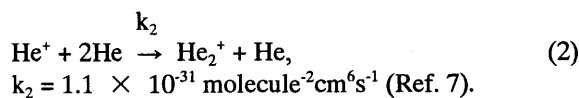
Results and Discussion

When N₂ was added into a He flowing afterglow 20 cm downstream from the center of the discharge without premixing Ar gas, a strong N₂⁺(B²Σ_u⁺-X²Σ_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 Δν = -2 sequence of N₂⁺(B-X) from ν′=0-6 is identified. These findings are consistent with previous studies on the helium-afterglow reaction of N₂.⁴⁻⁶⁾ Active species in Fig. 2(a) are He(2³S), He⁺, and He₂⁺. When the He⁺ and He₂⁺ ions are trapped using the ion-collector grids, the N₂⁺(B-X) emission from ν′=0,1 reduces its intensity by about 45-65% and that from ν′=2-6 disappeared, as shown in Fig. 2(b). The N₂⁺(B-X) emission from ν′=0,1 observed in Fig. 2(b) entirely arises from the He(2³S)/N₂ Penning ionization (1):

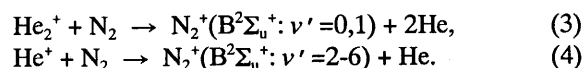


These findings indicate that about 45-65% of N₂⁺(B-X) from ν′=0,1 and all of the N₂⁺(B-X) emission from ν′=2-6 result from charge-transfer reactions of He⁺ and/or He₂⁺ with N₂.

Since He₂⁺ ions are formed via the following secondary three-body reaction, the N₂⁺(B-X) emission resulting from the He₂⁺/N₂ reaction is expected to be strongly enhanced at high He pressures:



Piper et al.⁴⁾ and Endoh et al.⁶⁾ measured the dependence of the intensity distribution of N₂⁺(B²Σ_u⁺; ν′) on the He buffer gas pressure. Both groups found that the populations of the low N₂⁺(B²Σ_u⁺; ν′=0,1) levels are significantly enhanced with increasing the He pressure relative to those of the high N₂⁺(B²Σ_u⁺; ν′≥2) levels. It was therefore concluded that the N₂⁺(B²Σ_u⁺; ν′=0,1) levels are dominantly formed by the He₂⁺/N₂ reaction (3), while the N₂⁺(B²Σ_u⁺; ν′=2-6) levels are produced by the He⁺/N₂ reaction (4):



However, there is a large possibility that the N₂⁺(B; ν′=0,1) levels are also excited by the He⁺/N₂ reaction (5):

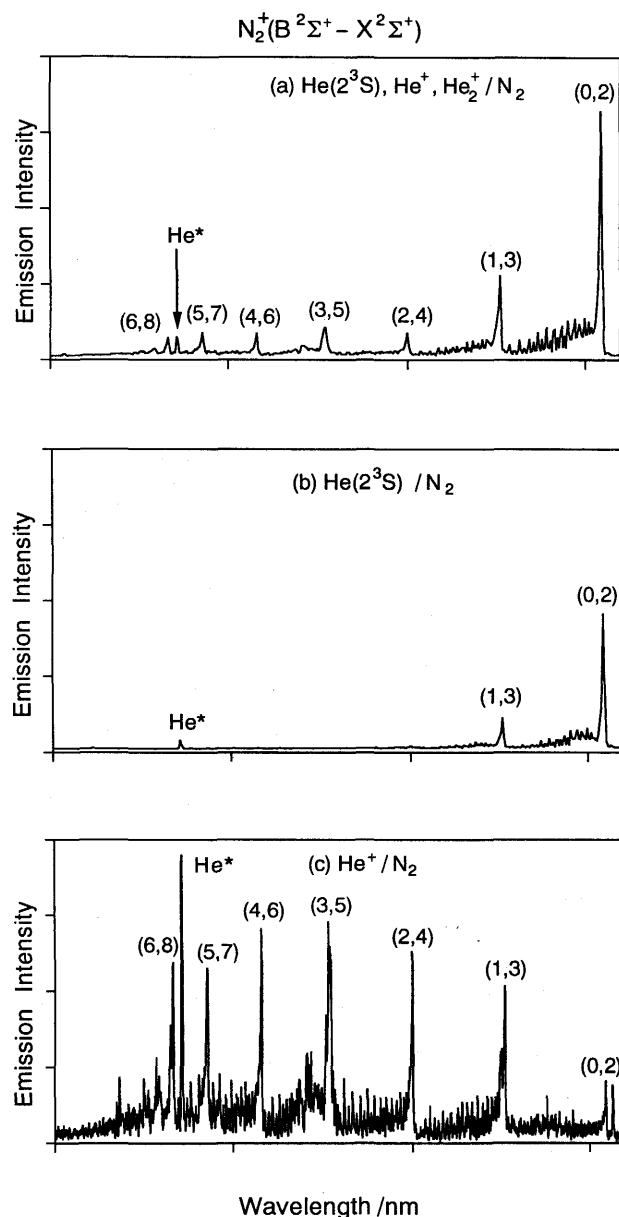
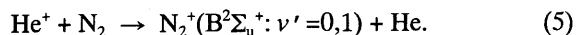


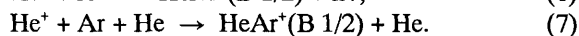
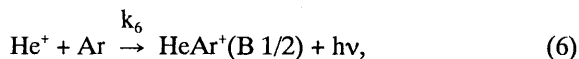
Fig. 2. Emission spectra of N₂ in a helium flowing afterglow.



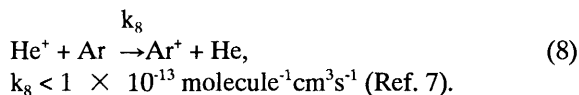
The rate constant of reaction (3) will be much larger than that of process (5). Therefore, the N₂⁺(B-X) emission from process (3) is seriously overlapped with that from process (5) even at a low He pressure, where the concentration of He₂⁺ is much lower than that of He⁺. Thus, it was difficult to isolate the N₂⁺(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

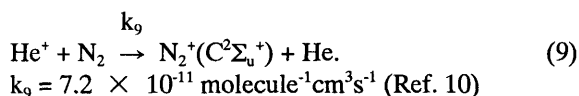
downstream from center of the discharge:



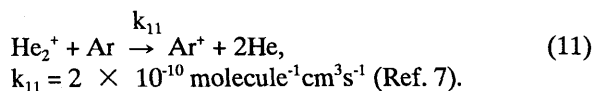
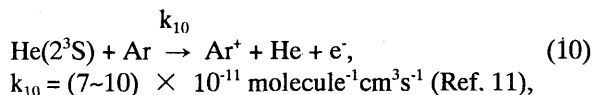
This emission was observed at 20 cm downstream from the center of the discharge, indicating that the rate constant of the He^+/Ar reaction is not sufficiently large to completely remove the He^+ ion.



Actually, we have determined the rate constant of process (6) to be $4.0 \times 10^{-13} \text{ molecule}^{-1}\text{cm}^3\text{s}^{-1}$ (Ref. 10) by comparing the total emission intensity of $\text{HeAr}^+(\text{B-X})$ with that of $\text{N}_2^+(\text{C-X})$ resulting from the following near-resonant charge-transfer reaction:



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



Thus, by the addition of Ar before the reaction zone, $\text{He}(2^3\text{S})$ 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 $\text{N}_2^+(\text{B-X})$ emission from $v'=0-6$ is identified. When ionic active species were trapped by the ion-collector grids, the $\text{N}_2^+(\text{B-X})$ emission observed in Fig. 2(c) completely disappeared, indicating that all of the $\text{N}_2^+(\text{B-X})$ emission arise from the ionic reaction. Piper et al.⁴⁾ and Endoh et al.⁶⁾ reported that the vibrational distribution of $\text{N}_2^+(\text{B-X})$ emission resulting from reaction (3) is similar to that from $\text{He}(2^3\text{S})/\text{N}_2$ Penning ionization. Since the vibrational distributions of $\text{N}_2^+(\text{B}; v'=0,1)$ in the He_2^+/N_2 reaction (3) and $\text{He}(2^3\text{S})/\text{N}_2$ Penning ionization (1) are in good agreement with that predicted from Franck-Condon factor for the $\text{N}_2(\text{X}^1\Sigma^+) \rightarrow \text{N}_2^+(\text{B}^2\Sigma_u^+)$ vertical ionization,

it was concluded that the ionization proceeds though a Franck-Condon like vertical process. Although the intensity distribution of $\text{N}_2^+(\text{B-X})$ 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 $\text{He}(2^3\text{S})$ 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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