# Emission Spectrum of $NeAr_2^+$ Cluster Ion Produced in the Flowing Afterglow

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$NeAr^+$ emission systems resulting from the three-body $Ne^+/2Ar$ and $Ne^+/Ar/He$ reactions were observed in the He flowing afterglow. At high Ar stagnation pressures above ~1 atm, a new broad band appeared in the 210-275 nm region. It was ascribed to the bound-free $C_2$-X, B-X, $C_1$-$A_1$, $C_2$-$A_2$, and B-$A_2$ transitions of the $NeAr_2^+$ cluster ion.

The emissions of rare-gas heterocluster-ions have received considerable attention due to the importance of their intense radiation for laser applications. We have recently studied clustering reactions of $He^+$ with Ar atoms by observing VUV emission in the He afterglow.[1] At high Ar pressures, besides the $HeAr^+$(B-X,B-$A_2$) bands due to the three-body $He^+/2Ar$ reaction, new broad bands were found in the longer wavelength region of the $HeAr^+$(B-X,B-$A_2$) bands. They were attributed to the B-X and B-$A_2$ transitions of the $HeAr_n^+$(n=2,3) cluster ion. It is interesting whether similar emissions are produced from the $NeAr_n^+$ system because these emissions are possible candidates of new gas lasers in the UV region.

The emission spectrum of the $NeAr^+$ cluster ion has been first observed by Tanaka *et al.* in an electric discharge of Ne/Ar mixtures.[2] Five bands, observed in the 210-225 nm region, were ascribed to transitions between three loosely bound states derived from the $Ne^+(^2P_{1/2})$ + $Ar(^1S_0)$ and $Ne^+(^2P_{3/2})$ + $Ar(^1S_0)$ dissociation limits and three loosely bound states correlating with the $Ne(^1S_0)$ + $Ar^+(^2P_{1/2})$ and $Ne(^1S_0)$ + $Ar^+(^2P_{3/2})$ dissociation limits. In the present study, clustering reactions of $Ne^+$ with Ar atoms have been studied in the He afterglow. We reported here the first observation of the emission from the $NeAr_2^+$ cluster ion.

The flowing-afterglow apparatus used in this study was similar to that reported previously.[1] Active species of helium [$He(2^3S)$, $He^+$, and $He_2^+$] were generated by a microwave discharge of high purity helium gas in a discharge flow operated at 1.4-1.7 Torr (1 Torr=133.3 Pa). The contribution of ionic active species to the observed emissions was examined by using an ion-collector grid placed between the discharge section and the reaction zone. A small amount of Ne was introduced from the first gas inlet placed 10 cm downstream from the center of the microwave discharge. Although $He(2^3S)$ and $He_2^+$ are efficiently deactivated by excitation-transfer and charge-transfer reactions, (1) and (2), respectively, $He^+$ is not removed due to a small rate coefficient of charge-transfer reaction (3):

$$He(2^3S) + Ne \rightarrow Ne^* + He, \quad (1)$$
$$k_1 = 5.1 \times 10^{-12}\ cm^3 \cdot s^{-1} \text{ (Ref. 3)},$$
$$He_2^+ + Ne \longrightarrow Ne^+ + 2He, \quad (2)$$
$$k_2 = (1.4\text{~}6.0) \times 10^{-10}\ cm^3 \cdot s^{-1} \text{ (Ref. 4)},$$
$$He^+ + Ne \longrightarrow Ne^+ + He, \quad (3)$$
$$k_3 \leq 1 \times 10^{-13}\ cm^3 \cdot s^{-1} \text{ (Ref. 4)}.$$

Since near-resonant $Ne^*$ atoms formed in reaction (1) decay radiatively before arriving at the second gas inlet, the remaining $He^+$ ions and the $Ne^+(^2P_{1/2,3/2})$ ions flowed downstream. A high purity Ar gas (purity 99.9999%) was admixed from the second gas inlet placed 10 cm downstream from the first gas inlet. The partial pressures of Ne, and Ar were measured to be 0.05 and 0.2-0.7 Torr, respectively, by using a capacitance manometer located 25 cm downstream from the second gas inlet. The actual Ar pressure just at an exit opening of a stainless steel nozzle with 0.60 mm in diameter was expected to be much higher than that measured 25 cm downstream and it was probably close to stagnation pressures of 0.7-3.8 atm. The emission spectrum observed around the Ar gas inlet was dispersed in the 115-400 nm region with either a McPherson 218 or Spex 1250M monochromator. The relative sensitivity was calibrated by using known band intensities of the $NO^+(A^1\Pi\text{-}X^1\Sigma^+)$ system and a standard $D_2$ lamp.

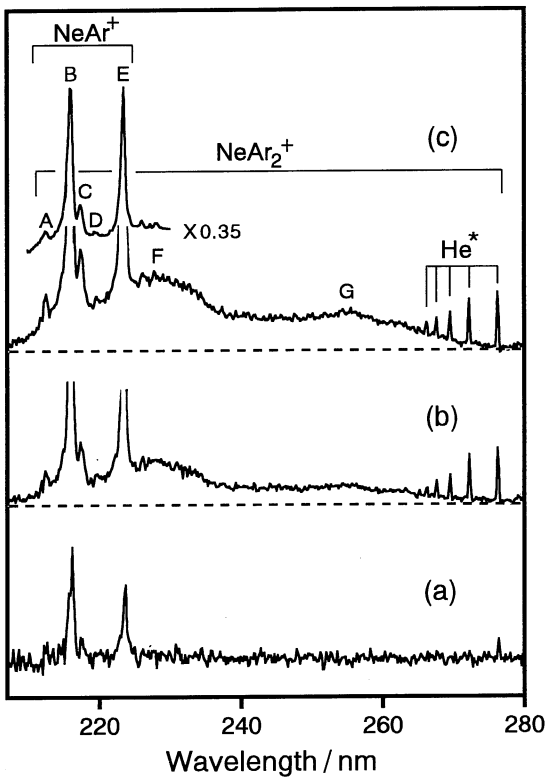


**Figure 1.** Emission spectra of $NeAr^+$ and $NeAr_2^+$ observed in the He afterglow at a He pressure of 1.4 Torr, a Ne pressure of 0.05 Torr, and Ar stagnation pressures of (a) 1.8 atm, (b) 3.0 atm, and (c) 3.8 atm.

Figures 1(a), 1(b), and 1(c) show emission spectra obtained at Ar stagnation pressures of 1.8, 3.0, and 3.8 atm, respectively. In the all spectra, strong bands with five peaks (A-E) are observed in the 210-225 nm region, as shown in Figure 1(c). Since the observed wavelengths agree with those reported by Tanaka *et al.*,[2] they were ascribed to the $C_2(1/2)$-X(1/2), B(1/2)-X(1/2), $C_1(3/2)$-$A_1(3/2)$, $C_2(1/2)$-$A_2(1/2)$, and B(1/2)-$A_2(1/2)$

transitions of $NeAr^+$, which were ascribed to the A, B, C, D, and E bands, respectively.[2,5] Here, the $NeAr^+(X\ 1/2,A_1\ 3/2)$, $NeAr^+(A_2\ 1/2)$, $NeAr^+(B\ 1/2,C_1\ 3/2)$, and $NeAr^+(C_2\ 1/2)$ states are correlated with the $Ne(^1S_0) + Ar^+(^2P_{3/2})$, $Ne(^1S_0) + Ar^+(^2P_{1/2})$, $Ne^+(^2P_{3/2}) + Ar(^1S_0)$, and $Ne^+(^2P_{1/2}) + Ar(^1S_0)$ dissociation limits, respectively. All of the $NeAr^+$ bands disappeared when ionic active species were removed from the discharge flow. This implies that $Ne^+$ is responsible for the excitation of $NeAr^+$. The most probable excitation processes of $NeAr^+$ are the following three-body clustering processes under the present experimental conditions:

$$Ne^+(^2P_{1/2}) + Ar + He \rightarrow NeAr^+(C_2) + He, \quad (4a)$$
$$Ne^+(^2P_{3/2}) + Ar + He \rightarrow NeAr^+(B,C_1) + He, \quad (4b)$$
$$Ne^+(^2P_{1/2}) + 2Ar \rightarrow NeAr^+(C_2) + Ar, \quad (5a)$$
$$Ne^+(^2P_{3/2}) + 2Ar \rightarrow NeAr^+(B,C_1) + Ar. \quad (5b)$$

The relative intensities of the B, C, and E bands to those of the A and D bands are much stronger than those observed in the discharge experiment of Tanaka *et al.*[2] This suggests that the $[Ne^+(^2P_{1/2})]/[Ne^+(^2P_{3/2})]$ ratio in the present experiment is much lower than that in their discharge experiment. The $HeAr^{+*}$ emission systems resulting from the two-body $He^+$/Ar radiative association were found at low He and Ar pressures in the previous study.[1] However, such a low pressure experiment was not possible because a high He pressure was required to generate a sufficient amount of molecular $Ne^+$ ion by charge-transfer reaction (2).

It should be noted that a new weak broad band appears in the 210-275 nm region at high Ar stagnation pressures partially overlapping with the $NeAr^+$ bands. The broad band consists of two components in the 210-240 and 240-275 nm region, which are denoted by F and G, respectively, in Figure 1(c). The dependencies of emission intensities of the $NeAr^+$(B-X) bands and peaks F and G on the Ar stagnation pressure were measured at a constant Ne pressure. Peaks F and G appeared at an Ar stagnation pressure of ~1 atm and their intensities increased more rapidly than that of the $NeAr^+$(B-X) band with increasing the Ar stagnation pressure. These contrasting pressure dependencies confirm the suggestion that further collisions with Ar atoms are necessary for the formation of the broad band. The broad band also disappeared by removing ionic active species in the discharge flow. On the basis of the above findings, it is highly likely that the new broad band in the 210-275 nm region is associated with the $C_2$-X, B-X, $C_1$-$A_1$, $C_2$-$A_2$, and B-$A_2$ transitions of $NeAr_2^+$ cluster ion resulting from the three-body reaction of $NeAr^+(B\ 1/2, C_1\ 3/2, C_2\ 1/2)$ with 2Ar:

$$NeAr^+(B,C_1,C_2) + 2Ar \xrightarrow{k_6} NeAr_2^+(B,C_1,C_2) + Ar. \quad (6)$$

Here, the $NeAr_2^+(X,A_1,A_2,B,C_1,C_2)$ states are correlated with the $NeAr^+(X\ 1/2,A_1\ 3/2,A_2\ 1/2,B\ 1/2,C_1\ 3/2,C_2\ 1/2) + Ar(^1S_0)$ dissociation limits, respectively. Since the $NeAr^+$(B-X,B-$A_2$) transitions are much stronger than the $NeAr^+$($C_2$-X,$C_1$-$A_1$,$C_2$-$A_2$) transitions, the $NeAr_2^+$(B-X,B-$A_2$) transitions will be much stronger than the $NeAr_2^+$($C_2$-X,$C_1$-$A_1$,$C_2$-$A_2$) transitions. It is therefore reasonable to assume that the B-X and B-$A_2$ transitions of $NeAr_2^+$ dominantly contribute to the formation of the broad band.

Since $He^+$ is not quenched by Ne, the $HeAr^+$(B-X,B-$A_2$) bands due to the following three-body reaction were observed in the 143-153 nm region:

$$HeAr^+(B) + 2Ar \xrightarrow{k_7} HeAr_2^+(B) + Ar. \quad (7)$$

Assuming that the collisional quenching of $HeAr_2^+(B)$ was insignificant, the $k_6/k_7$ ratio was estimated to be 0.056 by comparing the intensity ratio of $NeAr_2^+$($C_2$-X,B-X,$C_1$-$A_1$,$C_2$-$A_2$,B-$A_2$)/$NeAr^+$($C_2$-X,B-X,$C_1$-$A_1$,$C_2$-$A_2$,B-$A_2$) with that of $HeAr_2^+$(B-X,B-$A_2$)/$HeAr^+$(B-X,B-$A_2$). This implies that clustering reaction (6) is much more inefficient than reaction (7).

The $NeAr_2^+$ spectra are very broad with red side tail-bands. These spectral features probably reflect a bound-free character of the transitions, which has already been known for the isoelectronic $Ar_2F^*$ excimer.[6-8] If the $NeAr_2^+(B,C_2)$ states are vibrationally excited up to near the dissociation limits of $NeAr^+(B,C_2) + Ar(^1S_0)$, the short wavelength onsets of the $NeAr_2^+$($C_2$-X,B-X) transitions will be close to those of the $NeAr^+$($C_2$-X,B-X) transitions. Actually, the short wavelength onset of broad band F is close to the $C_2$-X and B-X transitions of $NeAr^+$, as shown in Figures 1(b) and 1(c). It is therefore reasonable to assume that broad band F arises from transitions between the weakly bound $NeAr_2^+(B,C_2)$ states and the repulsive $NeAr_2^+(X)$ state. Peak G increased more rapidly than peak F with increasing the Ar stagnation pressure, as shown in Figure 1. A similar increase in peak G was found when Ne was mixed with Ar in order to examine the effects of the collisional relaxation of $NeAr_2^+(B,C_1,C_2)$. This led us to conclude that the vibrational relaxation by collisions with Ar or Ne takes part in the formation of peak G at high Ar and Ne stagnation pressures.

In conclusion, the clustering reaction leading to $NeAr_2^+(B,C_1,C_2)$ was investigated in the He afterglow. At high Ar stagnation pressures, a new broad band, which was ascribed to the $C_2$-X, B-X, $C_1$-$A_1$, $C_2$-$A_2$, and B-$A_2$ transitions of $NeAr_2^+$, was found in the 210-275 nm region. We are planning to make theoretical calculations in order to confirm this assignment and to obtain information about the equilibrium geometry of $NeAr_2^+$.

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## References and Notes

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