Emission Spectra of $HeAr_n^+$ (n=1-3) Cluster Ions Produced from the Helium Afterglow Reactions of Ar

Masaharu Tsuji,* Makoto Tanaka, Masafumi Nakamura, and Yukio Nishimura
Institute of Advanced Material Study and Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816

(Received June 16, 1995)

The $HeAr^+(B^2\Sigma^+\text{-}X^2\Sigma^+, B^2\Sigma^+\text{-}A_2{}^2\Pi_{1/2})$ emissions resulting from the two-body He^+/Ar and three-body $He^+/Ar/He$ reactions were observed in the He afterglow reaction of Ar at low Ar pressures below ~0.14 Torr. At high Ar pressures, new broad bands appeared in the 143-168 nm region. They were ascribed to the B-X and $B\text{-}A_2$ transitions of the $HeAr_n^+$ (n=2,3) cluster ions.

Recently, there have been continuing interests in structures and reactivities of small cluster ions. The emission spectrum of the $HeAr^+$ cluster ion has been first observed by Tanaka *et al.* in an electric discharge of He/Ar mixtures.[1] A detailed rotational analysis was subsequently made by Dabrowski *et al.*[2] Two bands, observed in the 140-143 and 144-146 nm region, were ascribed to transitions between a loosely bound state derived from the $He^+(^2S_{1/2})$ + $Ar(^1S_0)$ dissociation limit and two loosely bound states correlating with the $He(^1S_0)$ + $Ar^+(^2P_{1/2})$ and $He(^1S_0)$ + $Ar^+(^2P_{3/2})$ dissociation limits. Although He^+, He_2^+, and $He(2^3S)$ could participate in the formation of $HeAr^+(B)$, no definite conclusion on the excitation mechanism could be obtained because of simultaneous occurrence of complicated excitation and quenching processes in discharge plasma.

In the present study, the formation of electronically excited $HeAr_n^+$(n=1-3) ions has been studied by observing VUV emission in the He afterglow. At low Ar pressures, only the $HeAr^+(B\text{-}X,B\text{-}A_2)$ transitions are observed. The responsible active species and the excitation processes are determined. At high Ar pressures, new broad bands are found in the longer wavelength region of the $HeAr^+(B\text{-}X,B\text{-}A_2)$ bands. They are attributed to the B-X and $B\text{-}A_2$ transitions of $HeAr_n^+$(n=2,3). This is the first observation of electronic emissions from polyatomic rare-gas heterocluster-ions.

The flowing-afterglow apparatus used in this study was similar to that reported previously.[3] 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 0.3-1.2 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. The sample Ar gas was admixed with the discharge flow about 20 cm downstream from the center of the discharge. The partial pressure of Ar was varied in the range of 0.03-0.33 Torr. The emission spectra at a few mm downstream from the Ar gas inlet were dispersed in the 110-200 nm region with a McPherson 218 monochromator.

Figure 1(a) shows a typical emission spectrum obtained from the He afterglow reaction of Ar at a low Ar pressure of 0.11 Torr. The spectrum consists of two broad bands in the 140-143 and 144-146 nm region. Since the observed wavelengths agree with those reported by Tanaka *et al.*,[1] the bands in the 140-143 and 144-146 nm region were ascribed to the $B^2\Sigma^+\text{-}X^2\Sigma^+$ and $B^2\Sigma^+\text{-}A_2{}^2\Pi_{1/2}$ transitions of $HeAr^+$, respectively. The $HeAr^+(B\text{-}X,B\text{-}A_2)$ bands disappeared when ionic active species were removed from the discharge flow. This implies that He^+ and/or He_2^+ are responsible for the excitation of $HeAr^+(B)$. Although He^+ has a sufficient recombination energy of 24.59 eV to produce $HeAr^+(B{:}v'=0)$ with a ΔH° value of 24.43 eV from the $He(^1S_0)$ + $Ar(^1S_0)$ dissociation limit, the recombination energy of He_2^+(18.3-20.3 eV)[3] is insufficient to excite $HeAr^+(B)$. On the basis of the above facts, only the He^+ ion is responsible for the formation of $HeAr^+(B)$. Possible excitation processes of $HeAr^+(B)$ are the following two-body radiative association and three-body clustering processes:

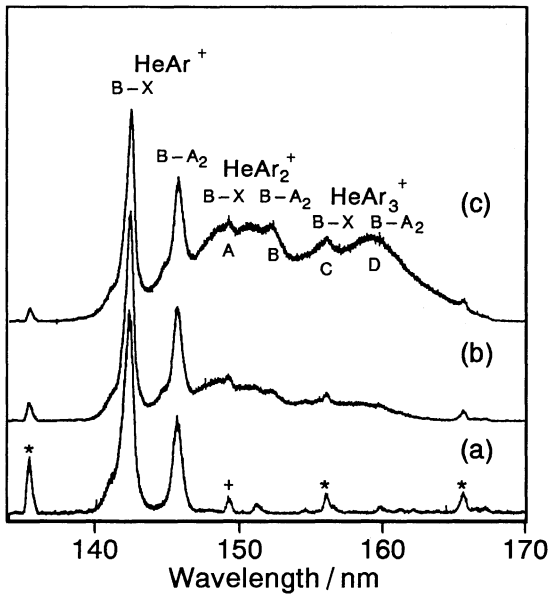

Figure 1. Emission spectra observed from the He afterglow reactions of Ar at a He pressure of 0.55 Torr and Ar pressures of (a) 0.11 Torr, (b) 0.20 Torr, and (c) 0.29 Torr. Lines marked with * and + are CI and NI atomic lines (impurity lines). Uncorrected for the relative sensitivity.

$$He^+ + Ar \rightarrow HeAr^+(B) + h\nu, \quad (1)$$

$$He^+ + Ar + He \rightarrow HeAr^+(B) + He. \quad (2)$$

In order to examine the relative contribution of the above two processes, the dependence of the emission intensity of $HeAr^+(B\text{-}X)$ on the He pressure was compared with that of $N_2^+(C^2\Sigma_u^+\text{-}X^2\Sigma_g^+)$ resulting from the two-body He^+/N_2 charge-transfer reaction.[4] The He-pressure dependence of the emission intensity of $HeAr^+(B\text{-}X)$ was similar to that of $N_2^+(C\text{-}X)$ at low He pressure below ~0.7 Torr, while the former emission increased more rapidly than the latter one above that. It was therefore concluded that two-body process (1) was dominant below ~0.7 Torr, while three-body process (2) became significant above that.

The $HeAr^+(B\text{-}X,B\text{-}A_2)$ emissions, measured at higher Ar

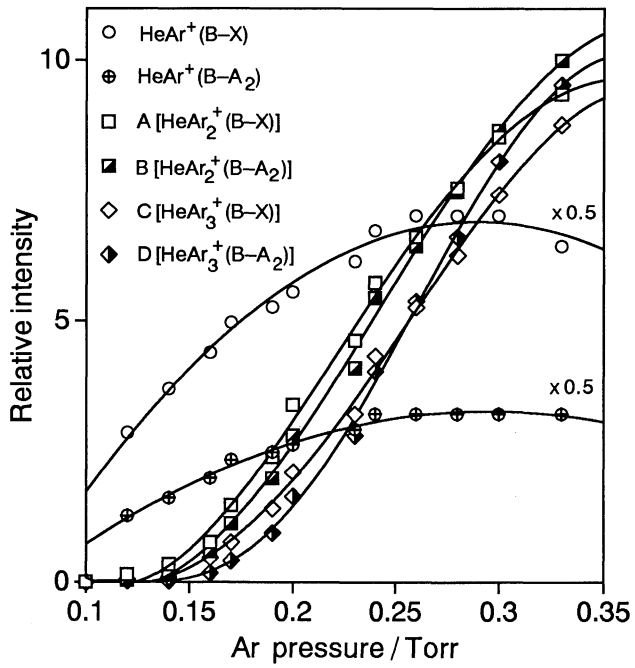

Figure 2. The dependence of the emission intensities of $HeAr^+(B\text{-}X,B\text{-}A_2)$ and peaks A-D in Figure 1 on the Ar pressure at a He buffer gas pressure of 0.55 Torr.

pressures of 0.20 and 0.29 Torr, are shown in Figures 1(b) and 1(c), respectively. It should be noted that a new broad band appears in the 143-168 nm region partially overlapping with the $HeAr^+(B\text{-}X,B\text{-}A_2)$ emissions. The band consists of two components in the 143-153 and 153-168 nm region. With increasing the Ar pressure, the intensity of longer wavelength side becomes strong for both components and two sets of peaks, A,B and C,D in Figure 1(c), become prominent. Figure 2 shows the dependence of emission intensities of $HeAr^+(B\text{-}X,B\text{-}A_2)$ and peaks A, B, C, and D on the Ar gas pressure. Peaks A and B appear at an Ar pressure of ~0.12 Torr and their intensities increase more rapidly than those of $HeAr^+(B\text{-}X,B\text{-}A_2)$ with increasing the Ar pressure. Peaks C and D start from a higher pressure of ~0.14 Torr and they depend more strongly on the Ar gas pressure than peaks A and B. The new bands 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 bands are associated with $HeAr_2^+$ and $HeAr_3^+$ cluster ions resulting from the sequential collisions of $HeAr^+(B)$ and $HeAr_2^+(B)$ with 2Ar:

$$He^+ + 2Ar \rightarrow HeAr^+(B) + Ar, \quad (3)$$

$$HeAr^+(B) + 2Ar \rightarrow HeAr_2^+(B) + Ar, \quad (4)$$

$$HeAr_2^+(B) + 2Ar \rightarrow HeAr_3^+(B) + Ar. \quad (5)$$

Here, the $HeAr_2^+(B)$ and $HeAr_3^+(B)$ states are correlated with the $HeAr^+(B)$ + $Ar(^1S_0)$ and $HeAr_2^+(B)$ + $Ar(^1S_0)$ dissociation limits, respectively. The relative intensities of the $HeAr_n^+(n=2,3)$ bands to that of $HeAr^{+*}$ reduced greatly with increasing the He pressure. Thus, the lack of the $HeAr_n^+(n=2,3)$ bands in the measurements of Tanaka *et al.*[1] is probably due to high He/Ar ratios (8~10:1) and high total pressures of 9-11 Torr.

Although no emission from triatomic rare gas ions has been observed, extensive experimental and theoretical studies have been carried out on the emission spectra of isovalent triatomic Rg_2X^* excimers (Rg=rare gas, X=halogen).[5-8] In most cases, triatomic excimers appeared at high rare-gas pressures in the longer wavelength region of the main diatomic RgX^* excimers. The Rg_2X^* spectra were much broader than the RgX^* ones. These spectral characters of Rg_2X^* are the same as those of the new broad band observed in the 143-153 nm region. This strongly supports our prediction that the responsible emitting species of the new band with peaks A and B is $HeAr_2^{+*}$.

The $HeAr_n^+(n=2,3)$ spectra are very broad with red side tail-bands. These spectral features probably reflect a bound-free character of the transition, which has already been known for the Rg_2X^* excimers.[5-8] The broad $HeAr_n^+(n=2,3)$ bands consist of two components A,B and C,D with energy separations of ~1020 and ~1245 cm^{-1}, respectively. These values are smaller than the energy separation between $HeAr^+(X)$ and $HeAr^+(A_2)$, ~1495 cm^{-1}.[2] If the $HeAr_n^+(B)$ states are vibrationally excited up to near the dissociation limits of $HeAr_{n-1}^+(B)$ + $Ar(^1S_0)$, the short wavelength onsets of the $HeAr_n^+(B\text{-}X)$ transitions will be close to those of the $HeAr_{n-1}^+(B\text{-}X)$ transitions. Actually, the short wavelength onsets of the $HeAr_2^{+*}$ and $HeAr_3^{+*}$ bands are close to the B-X transitions of $HeAr^+$ and $HeAr_2^+$, respectively, as shown in Figure 1(c). It is therefore reasonable to assume that peaks A and C are transitions from the weakly bound $HeAr_2^+(B)$ and $HeAr_3^+(B)$ states to the ground $HeAr_2^+(X)$ and $HeAr_3^+(X)$ states. Peaks B and D are probably associated with the corresponding transitions to the $HeAr_2^+(A_2)$ and $HeAr_3^+(A_2)$ states, which are correlated with the $HeAr^+(A_2)$ + $Ar(^1S_0)$ and $HeAr_2^+(A_2)$ + $Ar(^1S_0)$ dissociation limits. The peak shifts of A and C from the $HeAr^+(B\text{-}X)$ band are ~3050 and 6100 cm^{-1}, indicating that the addition of the first and the second Ar atom to $HeAr^+(B)$ gives a similar perturbation for the $HeAr^+(B,X)$ potentials. It is clear from Figure 2 that the intensities of B and D are enhanced compared with those of A and C with increasing the Ar pressure. This is probably due to the fact that the vibrational relaxation of $HeAr_2^+(B)$ and $HeAr_3^+(B)$ by collisions with the Ar gas enhances the intensities of the $B\text{-}A_2$ transitions.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture (No. 06453026) and the Iwatani Naoji Foundation.

References and Notes

1 Y. Tanaka, K. Yoshino, and D. E. Freeman, *J. Chem. Phys.*, **62**, 4484 (1975).
2 I. Dabrowski, G. Herzberg, and K. Yoshino, *J. Mol. Spectrosc.*, **89**, 491 (1981).
3 M. Tsuji, in "Techniques of Chemistry," ed by J. M. Farrar and W. H. Saunders, Jr., Wiley, New York (1988), Vol. 20, Chap. 9, 489.
4 H. Sekiya, M. Tsuji, and Y. Nishimura, *J. Chem. Phys.*, **87**, 325 (1987).
5 J. A. Margano, J. H. Jacob, M. Rokin, and A. Hawryluk, *Appl. Phys. Lett.*, **31**, 26 (1977).
6 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, **68**, 3850 (1978).
7 D. C. Lorents, D. L. Huestis, M. V. McCusker, H. H. Nakano, and R. W. Hill, *J. Chem. Phys.*, **68**, 4657 (1978).
8 D. L. Huestis and N. E. Schotter, *J. Chem. Phys.*, **69**, 3100 (1978).