Formation of the He(3s,3p,3d) States by Ion-Ion Neutralization Reaction of He^+ with $C_6F_6^-$ in the Helium Flowing Afterglow

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(Received November 18, 1996)

The ion-ion neutralization reaction of He^+ with $C_6F_6^-$ has been spectroscopically studied in a He flowing afterglow. Six He(3s, 3p, 3d) states in the energy range of 22.72-23.09 eV were produced. The electronic state population decreased rapidly with increasing the excitation energy of the product He^* atoms. The total triplet/singlet ratio of He^* was 1.7.

We have recently studied ion-ion recombination and neutralization reactions by observing emission spectra of excited products in a flowing afterglow.[1,2] We found that recombination and mutual neutralization processes compete with each other in the $Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ reaction:[3]

$$Kr^+(^2P_{1/2,3/2}) + C_6F_6^- \rightarrow KrF(B,D) + C_6F_5, \quad \text{(Recombination)} \quad (1a)$$
$$\rightarrow Kr(5p[3/2,5/2]) + C_6F_6. \quad \text{(Neutralization)} \quad (1b)$$

The branching ratios of (1a):(1b) were 0.001:0.999, respectively. The small branching ratio of process (1a) was explained as due to a high $C_6F_6^- \rightarrow C_6F_5 + F^-$ dissociation energy (2.40 eV).

In the present study, the ion-ion neutralization reaction of He^+ with $C_6F_6^-$ has been spectroscopically studied in a He flowing afterglow. Since no HeF^* excimer is formed, only mutual neutralization channels are open for the $He^+/C_6F_6^-$ reaction. This is the first spectroscopic study on the ion-ion neutralization reaction of He^+ with a negative ion leading to excited He^* states.

The flowing-afterglow apparatus used in this study was the same as that reported previously.[1-3] In brief, the positive He^+ ions and electrons were produced by a microwave discharge of high purity He gas, while the negative $C_6F_6^-$ ions were formed by a fast nondissociative electron attachment to C_6F_6 20 cm downstream from the center of the discharge:

$$e^- + C_6F_6 \xrightarrow{k_2} C_6F_6^- \quad (2) \quad (k_2 = 2.1 \times 10^{-7}\ cm^3s^{-1}\ \text{[Ref. 4]}).$$

The partial pressure in the reaction zone was 1.0 Torr(=133.3 Pa) for He and 3-10 mTorr for C_6F_6. Under the operating conditions, the electron density in the reaction zone was evaluated to be $\sim 10^{10}/cm^3$ by using a single Langmuir probe. Since thermal electrons were completely scavenged through process (2), the density of $C_6F_6^-$ was expected to be nearly the same as that of the electron density. The emission spectrum near the C_6F_6 gas inlet was dispersed in the 200-840 nm region with a Spex 1250 M monochromator. The relative sensitivity of the monochromator and the photomultiplier was calibrated by using a standard halogen lamp.

When emission spectrum in a He afterglow was observed without the addition of C_6F_6, the following six series of He^* lines with excitation energies of 22.72-24.53 eV were observed in the UV and visible regions: $ns^1S \rightarrow 2p^1P(n=3\text{-}6)$, $ns^3S \rightarrow 2p^3P(n=3\text{-}10)$, $np^1P \rightarrow 2s^1S(n=3\text{-}9)$, $np^3P \rightarrow 2s^3S(n=3\text{-}13)$, $nd^1D \rightarrow 2p^1P(n=3\text{-}13)$, and $nd^3D \rightarrow 2p^3P(n=3\text{-}16)$. The dependence of emission intensities on the electron density indicated that these emissions arose from the $He^+/2e^-$ collisional-radiative recombination process, as reported for the $nd^3D \rightarrow 2p^3P$ and $np^3P \rightarrow 2s^3S$ series in the He afterglow.[5,6] In the collisional-radiative recombination process, an electron acts as a third body. By the addition of C_6F_6 into the He afterglow, He^* lines with high excitation energies of 23.59-24.53 eV disappeared, and only six lines with low excitation energies of 22.72-23.09 eV are observed, as shown in Figure 1. This indicates that electrons are completely scavenged by C_6F_6, so that the contribution of the $He^+/2e^-$ recombination reaction is negligible in Figure 1. Possible precursors of He^* are $He(2^3S)$, He^+, and He_2^+. When He^+ and He_2^+ were removed from the He discharge flow using ion collector grids placed between the discharge and the reaction zone, these He^* lines disappeared. On the basis of this finding, possible formation processes of He^* are the following $He^+/C_6F_6^-$ and/or $He_2^+/C_6F_6^-$ ion-ion neutralization reactions:

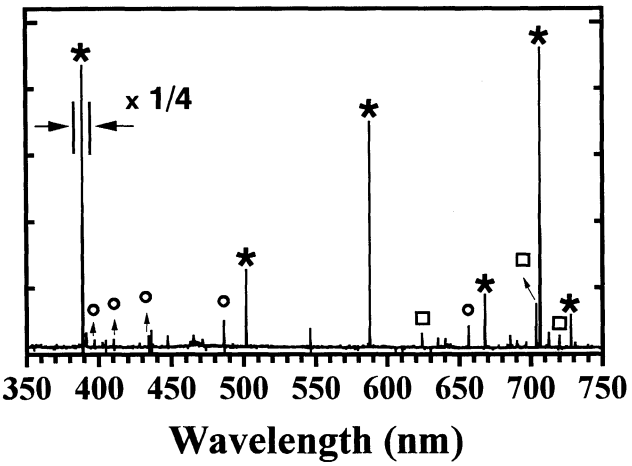

Figure 1. Emission spectrum resulting from the ion-ion neutralization reaction of He^+ with $C_6F_6^-$ in the He afterglow. Lines marked with *, O, and □ are He*, H*(impurity), and F* lines, respectively. Spectra were uncorrected for the relative sensitivity.

$$He^+ + C_6F_6^- \rightarrow He^* + C_6F_6 + (0.98\text{~}1.35)\ eV, \quad (3)$$
$$He^+ + C_6F_6^- \rightarrow He^* + C_6F_5 + F - (3.60\text{~}3.97)\ eV, \quad (4)$$
$$He_2^+ + C_6F_6^- \rightarrow He^* + He + C_6F_6 - (2.9\text{~}5.3)\ eV. \quad (5)$$

The formation of He^* through processes (4) and (5) is energetically inaccessible. It was therefore concluded that the observed He^* lines arose from process (3). We have recently found that only two Kr^* levels are selectively excited by the

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Table 1. Observed transitions, energies of the upper states, observed and calculated relative formation rate constants, and steady-state populations of He*, and crossing points in the $He^+/C_6F_6^-$ neutralization reaction[a]

Wavelength (nm)	Transition	Energy (eV)	Relative formation rate constant			Population	Crossing point (Å)
			Obs.	Model (a)	Model (b)		
501.6	$3p^1P \rightarrow 2s^1S$	23.09	4.7(-3)	8.1(-2)	1.6(-5)	7.7(-3)	14.70
667.8	$3d^1D \rightarrow 2p^1P$	23.07	4.8(-2)	4.1(-1)	1.3(-4)	9.8(-3)	14.41
587.6	$3d^3D \rightarrow 2p^3P$	23.07	4.4(-2)	1.4(-1)	4.3(-5)	2.8(-3)	14.41
388.9	$3p^3P \rightarrow 2s^3S$	23.01	1.9(-2)	2.5(-1)	7.3(-4)	1.5(-2)	13.59
728.1	$3s^1S \rightarrow 2p^1P$	22.92	9.7(-2)	2.9(-2)	1.2(-3)	3.5(-1)	12.52
706.5	$3s^3S \rightarrow 2p^3P$	22.72	7.9(-1)	9.5(-2)	1.0	6.2(-1)	10.66

[a]Values in parentheses are power of 10 multiplying the entry.

$Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ neutralization reaction.[3] Therefore, the most outstanding feature of the $He^+/C_6F_6^-$ neutralization reaction is a wider distribution in the product He* atom.

The relative formation rates of each He* levels, which are proportional to the initial relative populations, were determined from the relative intensities of He* lines. The steady-state populations of He* were evaluated by using the reported Einstein coefficients and degeneracies of the upper states.[7] The results obtained are given in Table 1. From the experimental data shown in Table 1, some general aspects are observed:

(1) Although all levels in the 22.72-23.09 eV region are formed, upper energetically accessible levels in the 23.09-24.07 eV region are not produced.

(2) The population rapidly decreases with increasing the energy of the He* level. Almost all He* atoms (97%) are populated in the low lying $3s^1S$ and $3s^3S$ states.

(3) The populations of low lying nl^3L states are higher than the nl^1L states for the 3s and 3p states. The total triplet/singlet ratio of He* is 1.7.

The $He^+/C_6F_6^-$ reaction proceeds through curve crossings between strongly attractive $He^+ + C_6F_6^-$ entrance potential and flat exit Rydberg $He^* + C_6F_6$ potentials. The crossing points R_c were calculated from the relation

$$R_c = e^2/(IP - EA), \quad (6)$$

where IP is the ionization potential of He* and EA is the electron affinity of C_6F_6. By using an EA value of C_6F_6(0.52 eV),[8] the R_c values for the formation of each He* state were calculated (Table 1). It should be noticed that an electron transfer from $C_6F_6^-$ to He^+ occurs at very long interparticle distances of 10.7-14.7 Å in the present system. The lack of the upper He*(n=4,5) states in the 23.59-24.04 eV region is probably due to the fact that the interparticle distances leading to such high energy states (30-552 Å) are too long to induce electron jump.

Since the mutual neutralization reaction proceeds through a strongly attractive potential, He* may be formed via a long-lived He^+-$C_6F_6^-$ intermediate,[9] where the excess energy is randomized statistically. Statistical prior distributions were calculated in order to examine this prediction. Two statistical models were used for the calculations of the prior distributions:

$$He^+ + C_6F_6^- \rightarrow [He^+ - C_6F_6^-] \rightarrow He^* + C_6F_6. \quad (7)$$

In model (a), the $C_6F_6^-$ anion is assumed to be an atom. On the other hand, all vibrational and rotational degrees of freedom of $C_6F_6^-$ are included in model (b) under the rigid-rotor-harmonic-oscillator approximation.[10] The final expression of the prior electronic state distribution are given by

$$P^o \propto (2J+1)(E_{excess}-E_u)^n, \quad (8)$$

where E_{excess} is a total excess energy, E_u is an energy of He*, n=1/2 for model (a), and n=69/2 for model (b). The prior distributions obtained for the above two models are given in Table 1. The observed distribution does not fit the two prior ones, indicating that the reaction dynamics is not governed by a statistical manner in the present system.

In the present communication, the electronic state distribution of He* in the $He^+/C_6F_6^-$ reaction was determined. We are planning to measure the dependence of electronic state distribution of He* on the negative $C_6F_5X^-$(X=halogen) ion.

The authors acknowledge financial support from the Mitsubishi Foundation (1996).

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