Formation of the He_2(c,d,e,f,C,D,E,F) States by Ion-Ion Neutralization Reaction of He_2^+ with $C_6F_6^-$ in the Helium Flowing Afterglow

Masaharu Tsuji,* Erika Oda, 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

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The ion-ion neutralization reaction of He_2^+ with $C_6F_6^-$ has been spectroscopically studied in a He flowing afterglow. The He_2(C,D,E,F,c,d,e,f) states in the energy range of 19.22-20.62 eV were produced. There was a great similarity in the product electronic state distribution between the $He_2^+/C_6F_6^-$ and $He^+/C_6F_6^-$ reactions leading to He_2* and He*, respectively.

We have recently studied ion-ion recombination and neutralization reactions by observing emission spectra from excited products in a flowing afterglow.[1,2] It was found that the He(3s,3p,3d) states are produced from the ion-ion neutralization reaction of atomic $He^+(^2S_{1/2})$ ions with $C_6F_6^-$:[3]

$$He^+ + C_6F_6^- \rightarrow He(3s,3p,3d) + C_6F_6. \quad (1)$$

The total triplet/singlet ratio was about 1.7. In the present study, the ion-ion neutralization reaction of He_2^+ with $C_6F_6^-$ has been spectroscopically studied in a He flowing afterglow. The results obtained are compared with those of the $He^+/C_6F_6^-$ reaction.[3] This is the first spectroscopic study on the ion-ion neutralization reaction of the molecular He_2^+ ion with a negative ion leading to excited He_2* molecule.

The flowing-afterglow apparatus used in this study was the same as that reported previously.[1,2] In brief, He(2^3S), He^+, and electrons were generated by a microwave discharge of He. The positive He_2^+ ions were formed by the three-body reaction of He^+ with 2He in a flow tube:

$$He^+ + 2He \xrightarrow{k_2} He_2^+ + He, \quad (2)$$
($k_2 = 8.3 \times 10^{-32}$ cm^{6}molecule^{-2}s^{-1} [Ref. 4]).

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:

$$e^- + C_6F_6 \xrightarrow{k_3} C_6F_6^-, \quad (3)$$
($k_3 = 2.1 \times 10^{-7}$ cm^{3}molecule^{-1}s^{-1} [Ref. 5]).

The partial pressure in the reaction zone was 2~3 Torr (1 Torr=133.3 Pa) for He and 2~5 mTorr for C_6F_6. Since thermal electrons were completely scavenged through process (3), the density of $C_6F_6^-$ was expected to be nearly the same as that of the electron density (~10^{10} cm^{-3}), measured by using a single Langmuir probe. Emission spectra near the C_6F_6 gas inlet were dispersed in the 200-1100 nm region with a Spex 1250 M monochromator.

When emission spectra in a He flowing afterglow were observed at high He pressures of 2~3 Torr without the addition of C_6F_6, several He_2* systems with excitation energies of 19.52-21.84 eV have been observed in the 320-950 nm region. Most of these He_2* systems has been found by Collins and Robertson in the high-pressure He flowing afterglow.[6] The dependence of emission intensities on the electron density indicated that these emissions arose from the $He_2^+/2e^-$ collisional radiative association:

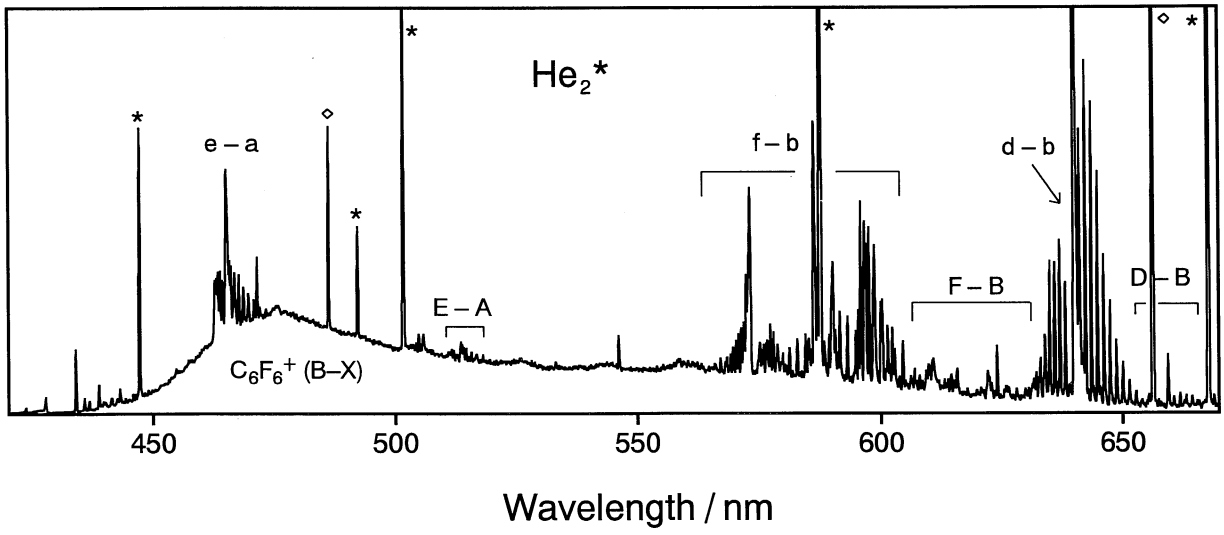

Figure 1. He_2* emissions resulting from the $He_2^+/C_6F_6^-$ neutralization reaction in a He afterglow. Lines marked with * and ◇ are He* and H*(impurity) lines, respectively. A broad $C_6F_6^+$(B-X) emission in the 430-530 nm region arises from the He(2^3S)/C_6F_6 and He_2^+/C_6F_6 reactions.

Table 1. Observed transitions and energies of the upper states of He_2^* and relative emission rate constants and crossing points in the $He_2^+/C_6F_6^-$ neutralization reaction

Transition			Energy (eV)	k_{em}	R_c (Å)
$f^3\Delta_u$	$(3d\delta) \rightarrow$	$b^3\Pi_g$	20.62	1.1	13.25
$f^3\Pi_u$	$(3d\pi) \rightarrow$	$b^3\Pi_g$	20.57	1.8	12.67
$f^3\Sigma_u^+$	$(3d\sigma) \rightarrow$	$b^3\Pi_g$	20.54	1.7	12.34
$e^3\Pi_g$	$(3p\pi) \rightarrow$	$a^3\Sigma_u^+$	20.53	1.0	12.23
$d^3\Sigma_u^+$	$(3s\sigma) \rightarrow$	$b^3\Pi_g$	20.39	5.4	10.93
$c^3\Sigma_g^+$	$(3p\sigma) \rightarrow$	$a^3\Sigma_u^+$	19.22	100	5.78
$F^1\Delta_u$	$(3d\delta) \rightarrow$	$B^1\Pi_g$	20.62	0.31	13.25
$F^1\Pi_u$	$(3d\pi) \rightarrow$	$B^1\Pi_g$	20.58	0.17	12.78
$F^1\Sigma_u^+$	$(3d\sigma) \rightarrow$	$B^1\Pi_g$	20.56	0.03	12.55
$E^1\Pi_g$	$(3p\pi) \rightarrow$	$A^1\Sigma_u^+$	20.57	0.12	12.67
$D^1\Sigma_u^+$	$(3s\sigma) \rightarrow$	$B^1\Pi_g$	20.47	0.21	11.64
$C^1\Sigma_g^+$	$(3p\sigma) \rightarrow$	$A^1\Sigma_u^+$	19.52	31	6.57

$$He_2^+ + 2e^- \rightarrow He_2^* + e^-. \quad (4)$$

A major part of the emission spectrum obtained by the addition of C_6F_6 into the He afterglow is shown in Figure 1. By the C_6F_6 addition, several He_2^* bands with high excitation energies of 21.19-21.84 eV disappeared. On the other hand, twelve He_2^* systems with low excitation energies of 19.22-20.62 eV (Table 1) were identified in the 470-980 nm region. This indicates that electrons are completely scavenged by C_6F_6, so that the contribution of reaction (4) to the observed He_2^* bands is negligible in Figure 1. 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_2^* emissions disappeared. All He_2^* bands disappeared, while He* lines due to reaction (1) remained, when Ar gas with a larger reaction rate coefficient for He_2^+(2.0×10^{-10} $cm^3molecule^{-1}s^{-1}$)[4] than that for He^+($< 1 \times 10^{-13}$ $cm^3molecule^{-1}s^{-1}$)[4] was added 10 cm upstream from the reaction zone. On the basis of above findings, it was concluded that He_2^* is produced from the following $He_2^+/C_6F_6^-$ ion-ion neutralization reactions:

$$He_2^+ + C_6F_6^- \rightarrow He_2^* + C_6F_6. \quad (5)$$

The $He_2^+/C_6F_6^-$ reaction proceeds through curve crossings between strongly attractive $He_2^+ + C_6F_6^-$ entrance ion-pair potential and flat exit Rydberg $He_2^* + C_6F_6$ potentials. The He_2^+-$C_6F_6^-$ separations at 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_2^* and EA is the electron affinity of C_6F_6. By using an EA value of C_6F_6(0.52 eV),[7] the R_c values for the formation of each He_2^* state were calculated (Table 1). It was found that an electron transfer from $C_6F_6^-$ to He_2^+ occurs at interparticle distances of 5.78-13.25 Å in the present system.

In Table 1 are given the relative emission rate constants of the observed He_2^* systems estimated from the total emission intensity of each system. The emission rate constants equal the formation ones, if there is no nonradiative decay. Dominant product channels are the formation of the lowest $c^3\Sigma_g^+$ and $C^1\Sigma_g^+$ states, which occupy 92% of the total emission rate constant. These states are formed via curve crossings at short range (6-7 Å). As minor product channels, the formation of the higher triplet and singlet states in the 20.39-20.62 eV range is found via curve crossings at long range (11-13 Å). The emission rate constants of low lying triplet states are higher than those of the related singlet states. The total triplet/singlet ratio is 3.5.

The observed He_2^* states are formed by promotion of an electron from the $2p\sigma$ orbital to the $3s\sigma$, $3p\sigma$, $3p\pi$, $3d\sigma$, $3d\pi$, or $3d\delta$ bonding orbital, as shown in Table 1. No evidence of the formation of the upper n=4 states in the 20.79-21.38 eV range[8] was found, though their formation is energetically accessible. The lack of these upper He_2^* states is probably due to the fact that the interparticle distance leading to such high energy states (15.7-44.4 Å) is too long to induce an electron jump.

No emissions from vibrational excited states of He_2^* were observed in the $He_2^+/C_6F_6^-$ reaction. The equilibrium internuclear distances of the observed He_2^* states (1.069-1.097 Å) are nearly equal to that of He_2^+ (1.081 Å).[8] Therefore, ground vibrational states of He_2^* with the largest Franck-Condon factors for the $He_2^+ \rightarrow He_2^*$ neutralization are selectively formed.

It should be noted that there is a great similarity between the $He_2^+/C_6F_6^-$ and $He^+/C_6F_6^-$ neutralization reactions leading to He_2^* and He*, respectively. In both reactions, favorable product channels are the formation of the n=3 triplet states and their relative emission rates generally decrease with increasing the excitation energy of the neutral products. The neutralization reactions of He_2^+ or He^+ with $C_6F_6^-$ proceed through an electron jump from the HOMO orbital of $C_6F_6^-$ to a vacant orbital of He_2^+ or He^+, respectively. Our results indicate that the interactions of the HOMO orbital of $C_6F_6^-$ with the $3s\sigma$, $3p\sigma$, $3p\pi$, $3d\sigma$, $3d\pi$, or $3d\delta$ molecular orbital of He_2^+ at the crossing points are as large as those with the 3s, 3p, or 3d atomic orbital of He^+.

In this letter, the relative emission rate constants of He_2^* in the $He_2^+/C_6F_6^-$ reaction were determined. No vibrational excitation of He_2^* was found. We are planning to measure the rotational distributions of each He_2^* state from a spectral simulation in order to clarify the rotational energy disposal.

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