

Relative Formation Rate Constants and Electronic-State Distributions of Ne* Produced from the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ Ion-Ion Neutralization Reactions in the He Flowing Afterglow

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Relative formation rate constants, $k_0(u)$, and electronic-state distributions, $N(u)$, of Ne* for upper u states in the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ ion-ion neutralization (I-IN) reactions were determined by observing Ne* atomic emissions in the 200–990 nm region. Ne* emissions from forty-two $ns(n=4$ and $5)$, $ns'(n=4$ and $5)$, $np(n=3$ and $4)$, $np'(n=3$ and $4)$, and $4d$ states in the 18.38–20.71 eV region were identified in the Ne⁺/SF₆⁻ reaction, whereas those from forty-five $ns(n=4$ and $5)$, $ns'(n=4$ and $5)$, $np(n=3$ and $4)$, $np'(n=3$ and $4)$, $nd(n=3–5)$, and $nd'(n=3$ and $4)$ states in the 18.38–21.02 eV region were observed in the Ne⁺/C₆F₆⁻ reaction. Major product Ne* states were $4s'$, $3d$, and $3d'$ states in the Ne⁺/SF₆⁻ reaction, whereas they were $3p$, $4s'$, $3d$, $3d'$, and $5d$ states in the Ne⁺/C₆F₆⁻ reaction. The electronic-state distributions of Ne* in the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ reactions suggested that Ne* atoms are not formed through long-lived Ne⁺-SF₆⁻ and Ne⁺-C₆F₆⁻ complexes, where excess energies are distributed to products statistically. It was concluded that electronic-state distributions of Ne* are governed by the transition probability from the attractive Ne⁺-SF₆⁻ and Ne⁺-C₆F₆⁻ entrance potentials to flat Ne⁺-SF₆⁻ and Ne⁺-C₆F₆⁻ exit potentials at crossing points.

Key words: Neon ion, SF₆⁻, C₆F₆⁻, Ion-ion neutralization reaction, Flowing afterglow, Ne* atomic emission, Radiative cascade, Relative formation rate constant, Electronic-state distribution, Curve crossing

1. Introduction

Due to a strong mutual Coulombic attractive force, reaction rate constants of recombination reactions between positive and negative ions are extremely large ($\alpha \approx 2 \times 10^{-7} \times (300/T)^{1/2} \text{ cm}^3 \text{ s}^{-1}$)^{1,2)} in comparison with those of ion-molecule reactions ($k \approx 10^{-11}–10^{-9} \text{ cm}^3 \text{ s}^{-1}$). Therefore, ion-ion reactions play a significant role as a loss process of ions in natural plasmas including interstellar gas clouds and in man-made plasmas such as static and flowing

afterglows and laser plasmas. Until now reaction rate constants or cross sections of ion-ion reactions have been measured for various reaction systems, and several theoretical models have been proposed to explain the experimental data.^{1–5)} However, only very few optical spectroscopic studies have been carried out on the product-state distributions in ion-ion recombination reactions.^{6,7)}

Two-body ion-ion reactions between an atomic ion A and molecules BC leading to excited neutral species are classified into the following two cases:

Excimer formation via dissociative recombination reaction



Mutual neutralization reaction



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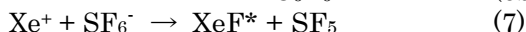
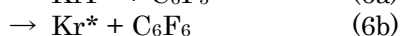
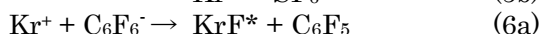
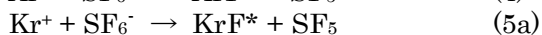
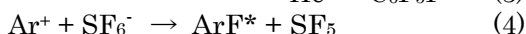
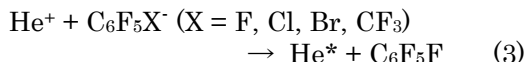
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In process (1), a new A–B bond is created, while such a rearrangement does not occur, and only mutual neutralization takes place by an electron transfer from a negative ion to a positive ion in process (2).

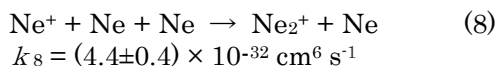
We have previously studied the following two-body ion–ion recombination and neutralization reactions by using a flowing-afterglow method.^{6–13)}



In this study, the formation of Ne* in the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ I-IN reactions are investigated by observing Ne* emissions in the He flowing afterglow. The relative formation rate constants and electronic-state distributions are determined. The observed electronic-state distributions are compared with our previous results for the He⁺/C₆F₅X⁻ (X = F, Cl, Br, CF₃) I-IN reactions (3) leading to excited He* atoms.¹³⁾ Based on the observed electronic-state distributions, reaction dynamics is discussed.

2. Experimental

The flowing-afterglow apparatus used in this study was essentially identical with that reported previously.^{13,14)} We have previously studied Ne afterglow reactions of simple molecules.^{15–18)} Then, we found that metastable Ne(³P_{0,2}) atoms are major active species at low Ne buffer gas pressure below about 0.2 Torr (1 Torr = 133.3 Pa), whereas not only Ne(³P_{0,2}) atoms but also Ne⁺ and Ne₂⁺ ions exist as active species at Ne gas pressures above that. The [Ne₂⁺]/[Ne⁺] ratio increased with increasing the Ne gas pressure, because Ne₂⁺ molecular ions are formed by the Ne⁺/2Ne three-body reaction.²⁰⁾



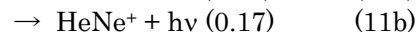
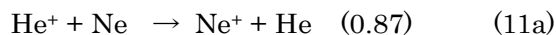
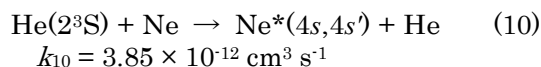
Both Ne⁺ and Ne₂⁺ can participate in the reaction as positive ion in the Ne afterglow at Ne gas pressures above 0.2 Torr. To exclude the contribution of Ne₂⁺, we used here He afterglow reaction of Ne. We initially generated such He

active species as He(2³S), He⁺, and He₂⁺ and electrons by a microwave discharge of high purity He gas (>99.9999%) in a He flowing afterglow at a microwave power of 100 W.^{14,18)} The contribution of such charged species as He⁺, He₂⁺, and electrons to the observed emissions was examined by using a charged-particle collector grid placed between the discharge section and the reaction zone. A small amount of Ne gas (26 mTorr) was added from the first gas inlet placed 10 cm downstream from the center of microwave discharge. We used a low Ne partial pressure to suppress the formation of Ne₂⁺ by the three-body reaction (9).

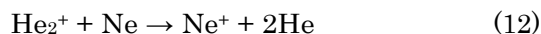


The booster pump used in the present apparatus was equipped with a continuously variable gate valve. The flow tube pressure was varied from 0.9 Torr to 7.3 Torr by opening or closing the gate valve.

By the reactions of He(2³S), He⁺, and He₂⁺ with Ne, the following energy-transfer and charge-transfer reactions take place near the Ne gas inlet.^{15,19,20)}



$$k_{11\text{a}} = (1.20 \times 10^{-15}) \pm 30\% \text{ cm}^3 \text{ s}^{-1}$$



$$k_{12} = (6.00 \times 10^{-10}) \pm 30\% \text{ cm}^3 \text{ s}^{-1}$$

Since the rate constant of reaction (12) is larger than that of (11) by five orders of magnitude, Ne⁺ atomic ions are preferentially formed by reaction (12) in our He flowing-afterglow reaction of Ne.

We added an electron scavenger SF₆ or C₆F₆ from the second gas inlet placed further 10 cm downstream from the first gas inlet. The partial pressure of SF₆ or C₆F₆ was 3–5 mTorr. Around the second gas inlet, SF₆⁻ or C₆F₆⁻ anions were formed by a fast electron attachment to SF₆ or C₆F₆,

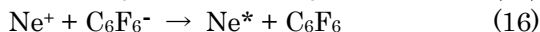
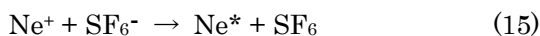


$$k_{13} = 2.2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \quad (\text{Ref. 21})$$



$$k_{14} = 2.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \quad (\text{Ref. 22})$$

Then, excited Ne^* atoms can be formed through the following I-IN reactions around the second gas inlet:



Under our experimental conditions, excited Ne^* states can be formed by energy-transfer reaction (10) and I-IN reaction (15) or (16). Without applying an electrostatic potential to the charged-particle collector grids, Ne^* emissions resulting from both reactions (10) and (15) or (16) are observed, whereas those resulting only from reaction (10) are obtained by applying an electrostatic static potential to grids. Thus, the Ne^* emissions resulting only from I-IN reaction (15) or (16) are obtained by subtracting the contribution of energy-transfer reaction (10). There are two spin-orbit components in the ground state of Ne^+ , $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$, with recombination energies of 21.56 and 21.66 eV, respectively. Their relative concentration was not estimated in this study.

A reaction flame around the second gas inlet was dispersed in the 200–990 nm region with a Spex 1250M monochromator equipped with cooled photomultipliers (Hamamatsu Photonics R376 and R316-02). The monochromator and the optical detection system were corrected by using standard D_2 and halogen lamps. All spectra presented here were corrected for the wavelength response of the detection system.

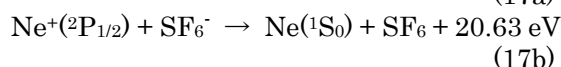
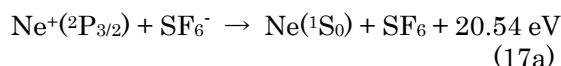
3. Results and Discussion

3.1 Emission spectra of Ne^* resulting from the $\text{Ne}^+/\text{SF}_6^-$ and $\text{Ne}^+/\text{C}_6\text{F}_6^-$ I-IN reactions

Figure 1(a) shows a typical emission spectrum resulting from the $\text{He}(2^3\text{S})/\text{Ne} + \text{Ne}^+/\text{SF}_6^-$ reactions in the 500–700 nm region at a He gas pressure of 7.3 Torr, where Ne^* lines from the $3p$, $3p'$, $4d$, and $5s'$ states and a He line are identified. Most of the observed Ne^* lines become weak, when charged species were removed from the He afterglow on applying an electrostatic potential to the grid, as shown in Fig. 1(b). Emission spectrum resulting from the $\text{Ne}^+/\text{SF}_6^-$ I-IN reaction is shown in Fig. 1(c), which is obtained by subtracting spectrum (b) from spectrum (a).

The upper electronic states of the observed Ne^* lines in the 500–970 nm region and their excitation energies are listed in Table 1. The spectral assignment was made by referring to

reported atomic spectral tables,^{23,24} and the excitation energies of Ne^* were obtained from reported tables.^{24,25} In the present study, we identified forty-two ns ($n=4$ and 5), ns' ($n=4$ and 5), np ($n=3$ and 4), np' ($n=3$ and 4), and $4d$ levels of Ne^* in the 18.38–20.71 eV region. The recombination energies of $\text{Ne}^+(^2\text{P}_{3/2})$ and $\text{Ne}^+(^2\text{P}_{1/2})$ are 21.56 and 21.66 eV, respectively, and the electron affinity of SF_6 is 1.03 eV.²⁶ Therefore, the total available energies in the $\text{Ne}^+(^2\text{P}_{3/2})/\text{SF}_6^-$ and $\text{Ne}^+(^2\text{P}_{1/2})/\text{SF}_6^-$ I-IN reactions, $\Delta H_0^\circ + 3RT$, are 20.62 eV and 20.71 eV, respectively.



Low-energy Ne^* states in the 18.38–20.57 eV region can be produced through both the $\text{Ne}^+(^2\text{P}_{3/2})/\text{SF}_6^-$ and $\text{Ne}^+(^2\text{P}_{1/2})/\text{SF}_6^-$ reactions. On the other hand, high energy Ne^* states in the 20.66–20.71 eV region can only be formed through the $\text{Ne}^+(^2\text{P}_{1/2})/\text{SF}_6^-$ reaction. These results show that the upper $\text{Ne}^+(^2\text{P}_{1/2})$ spin-orbit component participates in the formation of Ne^* in our experimental condition. In Table 1, both nL and nL' states of Ne^* with $2p^5(^2\text{P}_{3/2})nL$

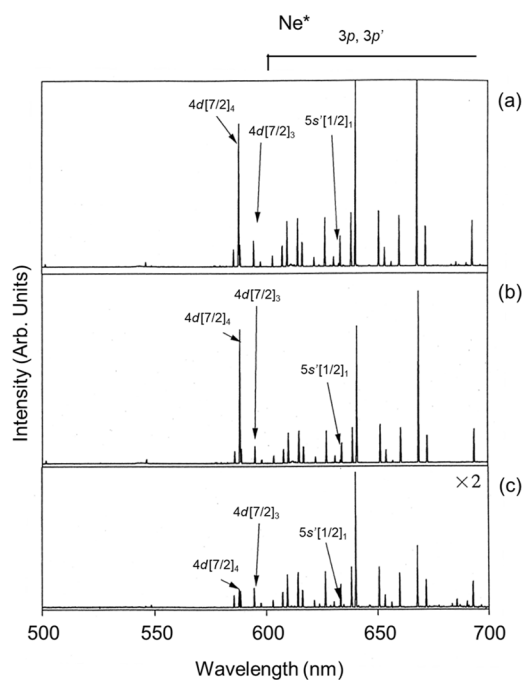


Fig. 1. Emission spectra resulting from (a) $\text{He}(2^3\text{S})/\text{Ne} + \text{Ne}^+/\text{SF}_6^-$, (b) $\text{He}(2^3\text{S})/\text{Ne}$, and (c) $\text{Ne}^+/\text{SF}_6^-$ reactions in the 500–700 nm region.

Table 1. Relative formation rate constants and electronic-state distribution of Ne* in the Ne⁺/SF₆⁻ I-IN reaction in the He flowing afterglow.

Energy / eV	State	<i>J</i>	<i>k</i> (<i>u</i>)	<i>k</i> (<i>u</i> : cascade)	<i>k</i> ₀ (<i>u</i>)	<i>N</i> (<i>u</i>)	ln(<i>N</i> (<i>u</i>)/ <i>g</i> _{<i>u</i>})	∑ _{<i>l</i>} <i>A</i> _{<i>ul</i>} (s ⁻¹) ^a
18.38	3 <i>p</i> [1/2]	1	1.11E-01	8.87E-02	2.26E-02	3.94E-02	-4.33	3.93E+07
18.56	3 <i>p</i> [5/2]	3	1.00E-01	1.00E-01	0.00E+00			5.15E+07
18.58	3 <i>p</i> [5/2]	2	7.15E-02	7.15E-02	0.00E+00			4.90E+07
18.61	3 <i>p</i> [3/2]	1	2.34E-01	2.34E-01	0.00E+00			5.12E+07
18.64	3 <i>p</i> [3/2]	2	8.79E-02	8.79E-02	0.00E+00			4.98E+07
18.69	3 <i>p</i> '[3/2]	1	5.13E-01	5.13E-01	0.00E+00			5.08E+07
18.70	3 <i>p</i> '[3/2]	2	2.06E-01	2.06E-01	0.00E+00			5.27E+07
18.71	3 <i>p</i> [1/2]	0	1.32E-02	1.32E-02	0.00E+00			6.06E+07
18.73	3 <i>p</i> '[1/2]	1	2.46E-01	2.46E-01	0.00E+00			5.49E+07
18.97	3 <i>p</i> '[1/2]	0	1.86E-02	1.86E-02	0.00E+00			6.24E+07
19.66	4 <i>s</i> [3/2] ^o	2	1.04E-01	3.73E-02	6.66E-02	1.81E-01	-3.32	2.52E+07
19.76	4 <i>s</i> '[1/2] ^o	0	2.93E-02		2.93E-02	7.98E-02	-2.53	2.52E+07
19.78	4 <i>s</i> '[1/2] ^o	1	1.00E+00		1.00E+00	5.77E-01	-1.65	1.19E+08
20.03	3 <i>d</i> [1/2] ^o	1	2.45E-02		2.45E-02	2.18E-02	-4.93	7.71E+07
20.03	3 <i>d</i> [7/2] ^o	4	3.95E-02		3.95E-02	5.43E-02	-5.11	4.99E+07
20.03	3 <i>d</i> [7/2] ^o	3	2.45E-02		2.45E-02	3.46E-02	-5.31	4.85E+07
20.04	3 <i>d</i> [3/2] ^o	2	1.06E-02		1.06E-02	1.44E-02	-5.85	5.05E+07
20.04	3 <i>d</i> [3/2] ^o	1	9.80E-02		9.80E-02	5.53E-02	-3.99	1.22E+08
20.05	3 <i>d</i> [5/2] ^o	2	6.78E-02		6.78E-02	9.98E-02	-3.91	4.66E+07
20.05	3 <i>d</i> [5/2] ^o	3	1.95E-02		1.95E-02	2.87E-02	-5.50	4.66E+07
20.14	3 <i>d</i> '[5/2] ^o	2	7.09E-01		7.09E-01	1.00E+00	-1.61	4.86E+07
20.14	3 <i>d</i> '[5/2] ^o	3	1.00E-02		1.00E-02	1.43E-02	-6.19	4.79E+07
20.14	3 <i>d</i> '[3/2] ^o	2	2.89E-01		2.89E-01	4.08E-01	-2.51	4.85E+07
20.15	4 <i>p</i> [1/2]	1	1.05E-03	1.05E-03	0.00E+00			4.84E+06
20.19	4 <i>p</i> [5/2]	3	1.07E-03	1.07E-03	0.00E+00			7.35E+06
20.20	4 <i>p</i> [5/2]	2	3.94E-03	3.94E-03	0.00E+00			7.01E+06
20.21	4 <i>p</i> [3/2]	1	2.40E-03	2.40E-03	0.00E+00			7.77E+06
20.21	4 <i>p</i> [3/2]	2	1.99E-03	1.99E-03	0.00E+00			8.81E+06
20.26	4 <i>p</i> [1/2]	0	7.31E-04	7.31E-04	0.00E+00			1.14E+07
20.29	4 <i>p</i> '[3/2]	1	1.41E-03	1.41E-03	0.00E+00			7.67E+06
20.30	4 <i>p</i> '[1/2]	1	9.19E-04	9.19E-04	0.00E+00			8.40E+06
20.30	4 <i>p</i> '[3/2]	2	2.46E-03	2.46E-03	0.00E+00			7.55E+06
20.37	4 <i>p</i> '[1/2]	0	3.09E-04	3.09E-04	0.00E+00			1.58E+07
20.56	5 <i>s</i> [3/2] ^o	2	1.54E-03		1.54E-03	8.01E-03	-6.44	1.32E+07
20.57	5 <i>s</i> [3/2] ^o	1	8.09E-02		8.09E-02	1.07E-01	-3.34	5.20E+07
20.66	5 <i>s</i> '[1/2] ^o	1	3.45E-02		3.45E-02	5.77E-02	-3.95	4.10E+07
20.70	4 <i>d</i> [1/2] ^o	1	1.72E-03		1.72E-03	1.78E-03	-7.43	6.60E+07
20.71	4 <i>d</i> [7/2] ^o	4	1.67E-03		1.67E-03	6.35E-03	-7.26	1.81E+07
20.71	4 <i>d</i> [7/2] ^o	3	1.47E-03		1.47E-03	5.84E-03	-7.09	1.73E+07
20.71	4 <i>d</i> [3/2] ^o	2	1.40E-03		1.40E-03	5.29E-03	-6.85	1.82E+07
20.71	4 <i>d</i> [5/2] ^o	2	4.73E-04		4.73E-04	1.91E-03	-7.87	1.69E+07
20.71	4 <i>d</i> [5/2] ^o	3	7.38E-04		7.38E-04	2.98E-03	-7.76	1.70E+07

a) Ref. 24. ∑_{*l*} *A*_{*ul*} is the Einstein coefficient for spontaneous emission.

Table 2. Relative formation rate constants and electronic-state distribution of Ne* in the Ne⁺/C₆F₆⁻ I-IN reaction in the He flowing afterglow.

Energy / eV	State	J	$k(u)$	$k(u: \text{cascade})$	$k_0(u)$	$N(u)$	$\ln(N(u)/g_u)$	ΣA_i (s ⁻¹) ^{a)}
18.38	3p[1/2]	1	1.82E-01	7.58E-02	1.06E-01	3.22E-01	-2.23	3.93E+07
18.56	3p[5/2]	3	1.63E-01	1.12E-01	5.14E-02	1.19E-01	-4.08	5.15E+07
18.58	3p[5/2]	2	1.14E-01	7.13E-02	4.26E-02	1.03E-01	-3.88	4.90E+07
18.61	3p[3/2]	1	1.11E-01	1.11E-01	0.00E+00			5.12E+07
18.64	3p[3/2]	2	8.62E-02	8.35E-02	2.76E-03	6.59E-03	-6.63	4.98E+07
18.69	3p'[3/2]	1	1.87E-01	1.87E-01	0.00E+00			5.08E+07
18.70	3p'[3/2]	2	1.43E-01	1.43E-01	0.00E+00			5.27E+07
18.71	3p[1/2]	0	2.18E-02	2.18E-02	0.00E+00			6.06E+07
18.73	3p'[1/2]	1	1.48E-01	1.48E-01	0.00E+00			5.49E+07
18.97	3p'[1/2]	0	2.49E-02	2.49E-02	0.00E+00			6.24E+07
19.66	4s[3/2] ^o	2	1.31E-01	5.00E-02	8.07E-02	3.81E-01	-2.58	2.52E+07
19.69	4s[3/2] ^o	1	5.54E-02	2.28E-04	5.52E-02	6.78E-02	-3.79	9.68E+07
19.76	4s'[1/2] ^o	0	7.18E-02	2.88E-04	7.15E-02	3.38E-01	-1.09	2.52E+07
19.78	4s'[1/2] ^o	1	1.00E+00	8.53E-04	9.99E-01	1.00E+00	-1.10	1.19E+08
20.03	3d[1/2] ^o	1	2.83E-02	3.91E-06	2.83E-02	4.36E-02	-4.23	7.71E+07
20.03	3d[7/2] ^o	4	3.38E-02		3.38E-02	8.06E-02	-4.72	4.99E+07
20.03	3d[7/2] ^o	3	2.07E-02	4.65E-07	2.07E-02	5.07E-02	-4.93	4.85E+07
20.04	3d[3/2] ^o	2	1.17E-02	7.54E-07	1.17E-02	2.75E-02	-5.20	5.05E+07
20.04	3d[3/2] ^o	1	1.49E-01		1.49E-01	1.45E-01	-3.03	1.22E+08
20.05	3d[5/2] ^o	2	1.30E-02		1.30E-02	3.31E-02	-5.02	4.66E+07
20.05	3d[5/2] ^o	3	2.33E-02		2.33E-02	5.94E-02	-4.77	4.66E+07
20.14	3d'[5/2] ^o	2	1.64E-01		1.64E-01	4.01E-01	-2.52	4.86E+07
20.14	3d'[3/2] ^o	2	1.14E-01		1.14E-01	2.80E-01	-2.88	4.85E+07
20.14	3d'[3/2] ^o	1	2.34E-02		2.34E-02	3.29E-02	-4.51	8.47E+07
20.15	4p[1/2]	1	1.88E-03	1.88E-03	0.00E+00			4.84E+06
20.19	4p[5/2]	3	4.21E-03	4.21E-03	0.00E+00			7.35E+06
20.20	4p[5/2]	2	1.33E-02	1.33E-02	0.00E+00			7.01E+06
20.21	4p[3/2]	1	1.76E-02	1.76E-02	0.00E+00			7.77E+06
20.21	4p[3/2]	2	2.13E-03	2.13E-03	0.00E+00			8.81E+06
20.26	4p[1/2]	0	7.06E-04	7.06E-04	0.00E+00			1.14E+07
20.29	4p'[3/2]	1	5.51E-03	5.51E-03	0.00E+00			7.67E+06
20.30	4p'[1/2]	1	4.69E-03	4.69E-03	0.00E+00			8.40E+06
20.30	4p'[3/2]	2	1.25E-02	1.25E-02	0.00E+00			7.55E+06
20.37	4p'[1/2]	0	1.67E-03	1.67E-03	0.00E+00			1.58E+07
20.56	5s[3/2] ^o	2	6.83E-03		6.83E-03	6.16E-02	-4.40	1.32E+07
20.57	5s[3/2] ^o	1	1.97E-02		1.97E-02	4.51E-02	-4.20	5.20E+07
20.66	5s'[1/2] ^o	1	1.74E-01		1.74E-01	5.05E-01	-1.78	4.10E+07
20.70	4d[1/2] ^o	1	5.30E-03		5.30E-03	9.55E-03	-5.75	6.60E+07
20.71	4d[7/2] ^o	4	5.45E-03		5.45E-03	3.58E-02	-5.53	1.81E+07
20.71	4d[7/2] ^o	3	4.21E-03		4.21E-03	2.90E-02	-5.49	1.73E+07
20.71	4d[3/2] ^o	2	3.21E-03		3.21E-03	2.10E-02	-5.47	1.82E+07
20.71	4d[5/2] ^o	2	3.89E-02		3.89E-02	2.73E-01	-2.91	1.69E+07
20.81	4d'[3/2] ^o	1	2.12E-03		2.12E-03	5.79E-03	-6.25	4.35E+07
21.02	5d[7/2] ^o	3	3.54E-03		3.54E-03	6.49E-02	-4.68	6.48E+06
21.02	5d[5/2] ^o	2	3.39E-02		3.39E-02	6.34E-01	-2.07	6.36E+06

^{a)} Ref. 24. $\Sigma_l A_{ul}$ is the Einstein coefficient for spontaneous emission.

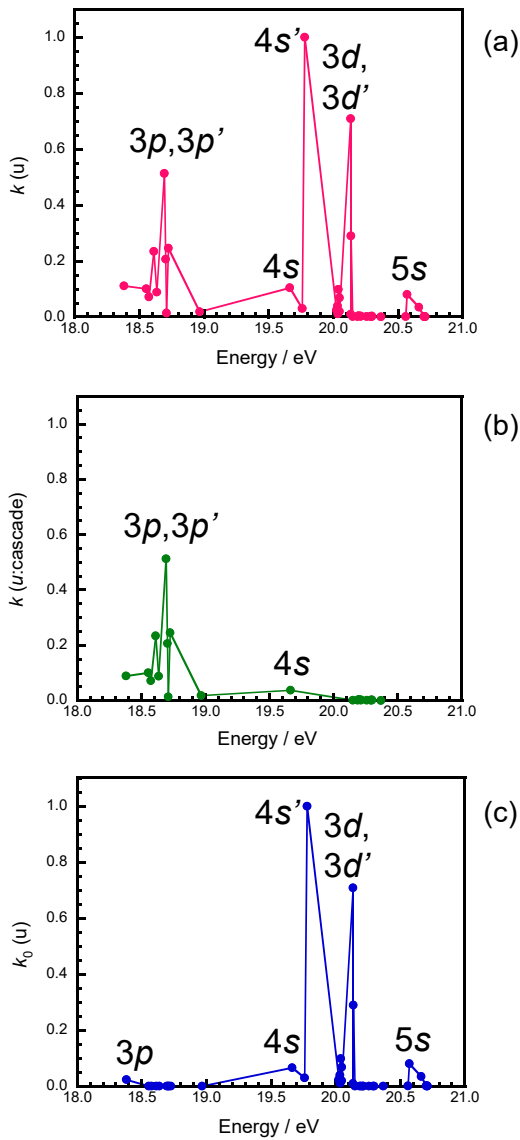


Fig. 3. Dependence of relative formation rate constants on the excitation energy of Ne* in the Ne⁺/SF₆⁻ reaction: (a) including radiative cascade, (b) radiative cascade, and (c) excluding radiative cascade.

$k(u:cascade)$, and $k_0(u)$ values on the excitation energy of Ne* in the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ reactions, respectively. A comparison between $k(u)$ and $k_0(u)$ values in Tables 1 and 2, and Figs. 3 and 4 suggests that some 3p and all 3p', 4p, and 4p' levels are formed only through radiative cascade from upper levels in the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ reactions. The cascade-free $k_0(u)$ values indicate that favorable states in the Ne⁺/SF₆⁻ reaction are 4s', 3d, and 3d' states, whereas those in the Ne⁺/C₆F₆⁻ reaction are 3p, 4s, 4s', 3d, 3d', and 5s' states. Among them, the 4s' state at 19.78 eV is

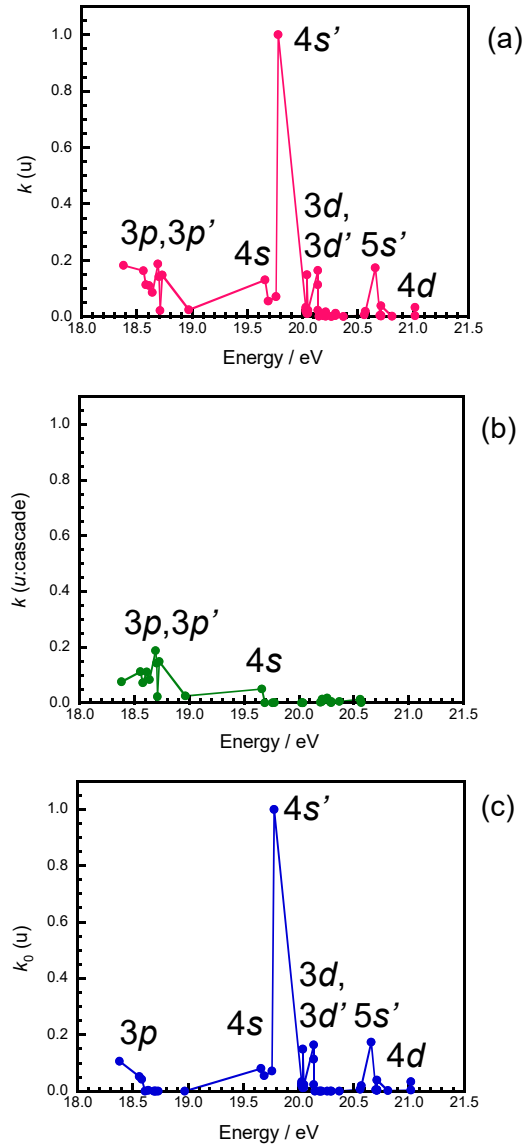


Fig. 4. Dependence of relative formation rate constants on the excitation energy of Ne* in the Ne⁺/C₆F₆⁻ reaction: (a) including radiative cascade, (b) radiative cascade, and (c) excluding radiative cascade.

the most favorable in both reactions.

Figures 5, 6 and 7, 8 show the dependence of $N(u)$ and $\ln(N(u)/g_u)$ on the excitation energy of Ne* in the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ reactions, respectively. Favorable populations are obtained for the 4s, 4s', 3d, 3d', and 5s in the Ne⁺/SF₆⁻ reaction, whereas they are found for the 3p, 4s, 4s', 3d, 3d', 5s', and 5d states in the Ne⁺/C₆F₆⁻ reaction. It should be noted that the most populated states are different between the two reactions. They are the 3d' state at 20.14 eV in the Ne⁺/SF₆⁻ reaction and the 4s' state at 19.78 eV in the Ne⁺/C₆F₆⁻ reaction.

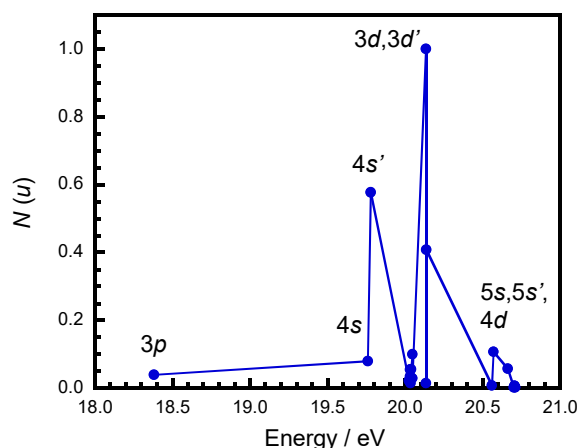


Fig. 5. Electronic-state distribution vs excitation energy of Ne* in the Ne⁺/SF₆⁻ reaction.

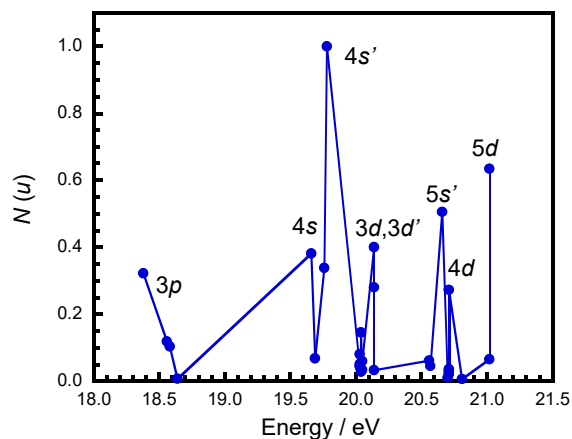


Fig. 7. Electronic-state distribution vs excitation energy of Ne* in the Ne⁺/C₆F₆⁻ reaction.

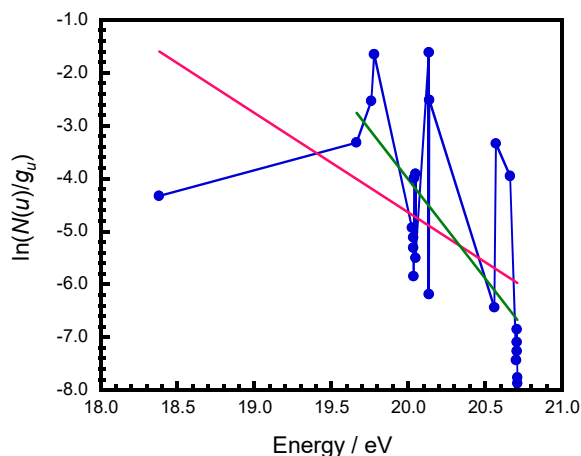


Fig. 6. $\ln(N(u)/g_u)$ vs excitation energy of Ne* in the Ne⁺/SF₆⁻ reaction.

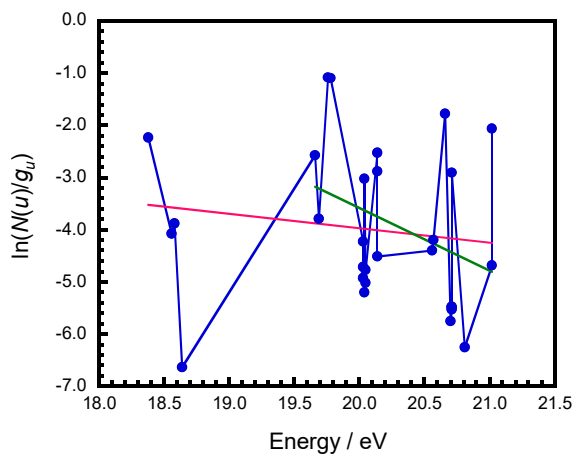


Fig. 8. $\ln(N(u)/g_u)$ vs excitation energy of Ne* in the Ne⁺/C₆F₆⁻ reaction.

In Tables 3 and 4 are summarized the total relative formation rate constants ($\sum_u k_0(u)$) and electronic-state distributions ($\sum_u N(u)$) of Ne* in the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ reactions at thermal energy. Based on the present data shown in these tables, major populated Ne* states in the Ne⁺/SF₆⁻ reaction are the 4s', 3d, and 3d' states, which occupy 40.6, 11.2, and 39.8% of $\sum_u k_0(u)$ and 23.4, 11.0, and 50.7% of $\sum_u N(u)$, respectively. On the other hand, major populated Ne* states in the Ne⁺/C₆F₆⁻ reaction are the 3p, 4s', 3d, 3d', 5s', and 5d states, which occupy 8.9, 46.8, 12.2, 13.2, 7.6, and 1.6% of $\sum_u k_0(u)$ and 10.6, 25.9, 8.5, 13.8, 9.8, and 13.5% of $\sum_u N(u)$, respectively. These results suggest that Ne* states formed in the Ne⁺/C₆F₆⁻ reaction are populated in more wider energy range than those produced in the Ne⁺/SF₆⁻ reaction. One reason for this is the larger total available energy of the Ne⁺/C₆F₆⁻ reaction than

that of the Ne⁺/SF₆⁻ reaction, so that higher energy Ne* states can be formed.

The $\sum_u k_0(u)$ and $\sum_u N(u)$ values of the product states having the Ne⁺(²P_{3/2}) ion core and the Ne⁺(²P_{1/2}) ion core are 18:82% and 24:76%, for the Ne⁺/SF₆⁻ reaction, whereas they are 32:68% and 50:50% for the Ne⁺/C₆F₆⁻ reaction, respectively. Since both ²P_{3/2} and ²P_{1/2} spin-orbit components of Ne⁺ exist in the present experiment and their relative concentration is not determined. Therefore, it is difficult to discuss the relative contribution of the Ne⁺(²P_{3/2}) and Ne⁺(²P_{1/2}) components and conservation of ion-core configuration during the I-IN reactions. One of the spin-orbit components must be selected to discuss further the electron-transfer mechanism in these reaction systems.

Assuming a Maxwell-Boltzmann distribution, N_u is given by

Table 3. Total relative formation rate constants and electronic-state distribution of Ne^* in the $\text{Ne}^+/\text{SF}_6^-$ I-IN reaction at thermal energy.

State	Number of sublevel	$\sum_u k_0(u)$ (%)	$\sum_u N(u)$ (%)
3p	1	0.9	1.4
4s	1	2.6	6.5
4s'	2	40.6	23.4
3d	7	11.2	11.0
3d'	3	39.8	50.7
5s	2	3.3	4.1
5s'	1	1.4	2.1
4d	6	0.3	0.9

Table 4. Total relative formation rate constants and electronic-state distribution of Ne^* in the $\text{Ne}^+/\text{C}_6\text{F}_6^-$ I-IN reaction at thermal energy.

State	Number of sublevel	$\sum_u k_0(u)$ (%)	$\sum_u N(u)$ (%)
3p	4	8.9	10.6
4s	2	5.9	8.7
4s'	2	46.8	25.9
3d	7	12.2	8.5
3d'	3	13.2	13.8
5s	2	1.2	2.1
5s'	1	7.6	9.8
4d	5	2.5	7.1
4d'	1	0.1	0.1
5d	2	1.6	13.5

$$N_u = g_u \exp(-E_u/kT_e), \quad (22)$$

where E_u is the excitation energy of Ne^* . If a plot of $\ln(N_u/g_u)$ vs E_u is linear, then the distribution can be characterized by a Boltzmann electronic temperature (T_e). The dependence of $\ln(N_u/g_u)$ on E_u was fitted by straight lines as shown in Figs. 5 and 6. Although deviations from linearity are large in the present systems, Boltzmann electronic temperatures of 0.53 and 0.27 eV were obtained from slopes of the straight lines for Ne^* from the $\text{Ne}^+/\text{SF}_6^-$ reaction in the whole 18.4–20.7 eV region and high-energy 19.7–20.7 eV region, respectively. On the other hand, Boltzmann temperatures of 3.63 and 0.83 eV were obtained for Ne^* from the $\text{Ne}^+/\text{C}_6\text{F}_6^-$ reaction in the whole

18.4–21.0 eV region and high-energy 19.7–21.0 eV region, respectively. We have previously obtained Boltzmann electronic temperatures of 0.070, 0.16, 0.090, and 0.19 eV for He^* from the $\text{He}^+/\text{C}_6\text{F}_5\text{X}^-$ ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{and CF}_3$) I-IN reactions, respectively.¹³⁾ Thus, the Boltzmann electronic temperatures obtained for Ne^* from the $\text{Ne}^+/\text{SF}_6^-$ and $\text{Ne}^+/\text{C}_6\text{F}_6^-$ reactions are higher than those of the $\text{He}^+/\text{C}_6\text{F}_5\text{X}^-$ reactions.

It should be noted that many points are far from the line of best fit in Figs. 6 and 8. Thus, very small R^2 (coefficient of determination) values of 0.26 and 0.018 are obtained for the $\text{Ne}^+/\text{SF}_6^-$ reaction in the 18.4–20.7 eV region and for the $\text{Ne}^+/\text{C}_6\text{F}_6^-$ reaction 19.7–20.7 eV region, respectively. It is therefore reasonable to assume that reaction dynamics of $\text{Ne}^+/\text{SF}_6^-$ and $\text{Ne}^+/\text{C}_6\text{F}_6^-$ I-IN reactions is not governed by statistical model, where such long-lived intermediates as $\text{Ne}^+-\text{SF}_6^-$ and $\text{Ne}^+-\text{C}_6\text{F}_6^-$ are formed and excess energies are distributed to all degrees of freedom statistically. Curve crossings between strongly attractive entrance $\text{Ne}^+-\text{SF}_6^-$ and $\text{Ne}^+-\text{C}_6\text{F}_6^-$ curves and rather flat Ne^*-SF_6 and $\text{Ne}^*-\text{C}_6\text{F}_6$ exit curves and the probability of an electron transfer from an anion to a cation at crossing points would play a significant role for the electronic-state distributions of the present two I-IN reactions.

The crossing points R_c (Å) were calculated from the relation

$$R_c = e^2/(\text{IP}-\text{EA}) = 14.38/(\text{IP}-\text{EA}), \quad (23)$$

where IP is the ionization potential of Ne^* and EA is the electron affinity of X. The R_c values calculated for the formation of each Ne^* state in the $\text{Ne}^+/\text{SF}_6^-$ and $\text{Ne}^+/\text{C}_6\text{F}_6^-$ reactions are given in Tables 5 and 6. Most of the product states are produced via curve crossings at interparticle distances of 15–37 Å in the $\text{Ne}^+/\text{SF}_6^-$ reaction, whereas they are curve crossings at 5–38 Å in the $\text{Ne}^+/\text{C}_6\text{F}_6^-$ reaction. According to Landau–Zener theory, the probability of electron transfer falls off rapidly at large R_c because of the rapidly diminishing nonadiabatic coupling matrix elements, and therefore the reaction efficiencies of such high energy states as 5s, 5s', 4d, and 4d' would be small.

Based on the *ab initio* calculation of SF_6^- , the singly occupied molecular orbital (SOMO) of SF_6^- is totally symmetric a_{1g} with $\text{S}(3s)-\text{F}(2p\sigma^*)$ character.²⁸⁾ On the other hand, ESR data in the condensed phase demonstrated that the SOMO of C_6F_6^- has σ^* character.²⁹⁾ Since

Table 5. Curve crossing points between entrance Ne⁺(²P_{3/2,1/2})-SF₆⁻ and exit Ne*-SF₆ potentials.

Energy / eV	State	R_c (Å)	R_c (Å)
		Ne ⁺ (² P _{3/2}) /SF ₆ ⁻	Ne ⁺ (² P _{1/2}) /SF ₆ ⁻
18.38	3p[1/2]	6.69	6.40
19.66	4s[3/2] ^o	16.61	14.89
19.76	4s'[1/2] ^o	18.69	16.54
19.78	4s'[1/2] ^o	19.17	16.91
20.03	3d[1/2] ^o	28.56	23.82
20.03	3d[7/2] ^o	29.03	24.15
20.03	3d[7/2] ^o	29.04	24.16
20.04	3d[3/2] ^o	29.15	24.24
20.04	3d[3/2] ^o	29.37	24.39
20.05	3d[5/2] ^o	29.84	24.72
20.05	3d[5/2] ^o	29.86	24.72
20.14	3d'[5/2] ^o	36.50	29.11
20.14	3d'[5/2] ^o	36.52	29.12
20.14	3d'[3/2] ^o	36.63	29.20
20.56	5s[3/2] ^o		205.55
20.57	5s[3/2] ^o		241.81

I-IN reactions occur via an electron transfer from an anion to a cation, the overlapping between the SOMO orbital with S-F or C-F σ^* character and a vacant orbital to which an electron is transferred at the crossing point will be significant for the final state distribution of Ne*.

4. Summary and Conclusion

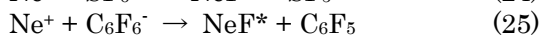
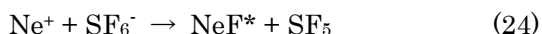
The Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ ion-ion mutual neutralization reactions were studied by observing Ne* lines in the He afterglow. Ne* emissions from forty-two ns ($n=4$ and 5), ns' ($n=4$ and 5), np ($n=3$ and 4), np' ($n=3$ and 4), and $4d$ states of Ne* in the 18.38–20.71 eV region were identified in the Ne⁺/SF₆⁻ reaction, whereas those from forty-five ns ($n=4$ and 5), ns' ($n=4$ and 5), np ($n=3$ and 4), np' ($n=3$ and 4), nd ($n=3-5$), and nd' ($n=3$ and 4) states of Ne* in the 18.38–21.02 eV region are observed in the Ne⁺/C₆F₆⁻ reaction. Major product Ne* states in the Ne⁺/SF₆⁻ reaction are $4s'$, $3d$, and $3d'$ states, whereas those in the Ne⁺/C₆F₆⁻ reaction are $3p$, $4s'$, $3d$, $3d'$, and $5d$ states. The electronic-state distributions of Ne* in the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ reactions were not expressed by a single Boltzmann distribution. Therefore, it was concluded that the reaction dynamics is mainly controlled by transition probability

Table 6. Curve crossing points between entrance Ne⁺(²P_{3/2,1/2})-C₆F₆⁻ and exit Ne*-C₆F₆ potentials.

Energy / eV	State	R_c (Å)	R_c (Å)
		Ne ⁺ (² P _{3/2}) /C ₆ F ₆ ⁻	Ne ⁺ (² P _{1/2}) /C ₆ F ₆ ⁻
18.38	3p[1/2]	5.41	5.21
18.56	3p[5/2]	5.79	5.56
18.58	3p[5/2]	5.84	5.61
18.64	3p[3/2]	5.98	5.74
19.66	4s[3/2] ^o	10.45	9.74
19.69	4s[3/2] ^o	10.64	9.90
19.76	4s'[1/2] ^o	11.24	10.42
19.78	4s'[1/2] ^o	11.41	10.57
20.03	3d[1/2] ^o	14.19	12.91
20.03	3d[7/2] ^o	14.30	13.01
20.03	3d[7/2] ^o	14.31	13.01
20.04	3d[3/2] ^o	14.33	13.03
20.04	3d[3/2] ^o	14.39	13.08
20.05	3d[5/2] ^o	14.50	13.17
20.05	3d[5/2] ^o	14.50	13.17
20.14	3d'[5/2] ^o	15.91	14.32
20.14	3d'[3/2] ^o	15.93	14.34
20.14	3d'[3/2] ^o	15.97	14.37
20.56	5s[3/2] ^o	29.96	24.79
20.57	5s[3/2] ^o	30.63	25.25
20.66	5s'[1/2] ^o	38.12	30.13
20.70	4d[1/2] ^o	42.58	32.85
20.71	4d[7/2] ^o	42.97	33.08
20.71	4d[7/2] ^o	42.99	33.09
20.71	4d[3/2] ^o	43.15	33.19
20.71	4d[5/2] ^o	43.74	33.54
20.81	4d'[3/2] ^o	61.32	42.99
21.02	5d[7/2] ^o	588.66	115.57
21.02	5d[5/2] ^o	670.25	118.40

between the strongly attractive Ne⁺-X⁻ ion-pair potentials and rather flat exit Ne*-X potentials at relatively large crossing points.

We studied here Ne* formation from the Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ I-IN reactions (15) and (16). In our previous studies on the Rg⁺/SF₆⁻ (Rg=Ar, Kr, Xe) and Rg⁺/C₆F₆⁻ (Rg=Kr) reactions (4)–(7), RgF* (Rg=Ar, Kr, Xe) excimer emissions were observed as major products in most cases.^{6-9,11} It has been known that NeF* excimer emission occurs in the vacuum ultraviolet (VUV) region (105–115 nm with a peak at 108 nm).³⁰ In the cases of Ne⁺/SF₆⁻ and Ne⁺/C₆F₆⁻ reactions, the formation of NeF* excimer with a transition energy of 11.5 eV is energetically possible.



A further optical spectroscopic study in the VUV region is necessary to clarify whether excimer formation processes (24) and (25) compete with the formation of Ne^* through I-IN processes (15) and (16) and their branching ratios. .

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