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Spin-orbit State Selectivity in the Formation of RgCl(B,C,D) Excimers from Ion-Ion Recombination Reactions of Rg⁺ with C₆F₅Cl⁻ in the Flowing Afterglow

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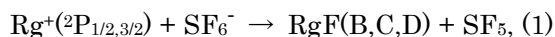
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RgCl(B,C,D) excimers were produced for Rg = Ar, Kr, and Xe by the positive ion-negative ion recombination reactions of Rg⁺(²P_{1/2,3/2}) with C₆F₅Cl⁻ in the flowing afterglow. Spin-orbit state selectivity of RgCl(B,C,D) excimers by the Rg⁺(²P_{1/2}) and Rg⁺(²P_{3/2}) components was examined by using appropriate filter gases of one spin-orbit component. The RgCl(B,D) ratio was determined to be 0.35:0.65, 0.05:0.95, and 0.24:0.76 in the Ag⁺(²P_{1/2}), Kr⁺(²P_{1/2}), and Xe⁺(²P_{1/2}) reactions, whereas the RgCl(B,C) ratio was estimated to be 0.74:0.26, 0.71:0.29, and 0.70:0.30 in the Ag⁺(²P_{3/2}), Kr⁺(²P_{3/2}), and Xe⁺(²P_{3/2}) reactions, respectively. The Rg⁺(²P_{1/2}) reactions had a high propensity to give RgCl(D) plus a lesser amount of RgCl(B), whereas the Rg⁺(²P_{3/2}) reactions gave only RgCl(B,C). These results show that Rg⁺(²P_{1/2}) + Cl⁻ and Rg⁺(²P_{3/2}) + Cl⁻ characters are conserved well for the formation of RgCl* in the ion-ion recombination reactions between Rg⁺(²P_{1/2,3/2}) and C₆F₅Cl⁻. Higher conservation of Rg⁺(²P_{1/2}) character in the Rg⁺(²P_{1/2})/C₆F₅Cl⁻ reactions than that in the Rg(³P_{0,2})/halides reactions is discussed by using correlation diagram between entrance and exit product channels.

Key words: Positive ion-negative ion reaction, Recombination reaction, RgCl* excimer, Ar⁺, Kr⁺, Xe⁺, C₆F₅Cl⁻, Flowing afterglow, Emission spectroscopy, Spin-orbit state selectivity, Correlation diagram

1. Introduction

We have successfully applied the flowing afterglow apparatus to the study on two-body dissociative ionic-recombination reactions¹⁻⁴⁾



where Rg represents Ar, Kr, or Xe atom. Positive Rg⁺(²P_{1/2,3/2}) ions were formed by He(2³S)/Rg Penning ionization and negative SF₆⁻ ions were produced by attachment of Penning electrons to SF₆. The spin-orbit state selectivity in the KrF* and XeF* formation was examined by selecting one of the spin-orbit components of Kr⁺ and Xe⁺, ²P_{1/2} or ²P_{3/2}. It was found that Kr⁺ and Xe⁺ ions in the ²P_{1/2} level

preferentially give the D state, while those in the ²P_{3/2} level give only the B and C states. The high spin-orbit state selectivity was explained by the conservation of Rg⁺(²P_{1/2}) + F⁻ and Rg⁺(²P_{3/2}) + F⁻ characters.

In this study, ion-ion recombination reactions of Ar⁺(²P_{1/2,3/2}), Kr⁺(²P_{1/2,3/2}), and Xe⁺(²P_{1/2,3/2}) with C₆F₅Cl⁻ are studied by observing RgCl* excimer emissions in the flowing afterglow. By using various filter gases of one spin-orbit component, effects of spin-orbit state are examined. Results obtained are compared with previous data for the formation of RgX* (X = halogen) excimers from the ion-ion recombination reactions of Rg⁺(²P_{1/2,3/2})/SF₆⁻ (Rg = Kr, Xe)²⁾ and from energy-transfer reactions of Ar(³P_{0,2}) with simple halides.⁵⁻⁷⁾

2. Experimental

2.1 Chemicals

Rare gases, filter gases used for spin-orbit state selection, and an electron scavenger C₆F₅Cl used in this study were obtained from

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Japanese chemical companies: He (purity >99.9999%, Taiyo Sanso), Ar (99.999%, Nippon Sanso), Kr (99.995%, Nippon Sanso), Xe (99.99%, Nippon Sanso), N₂ (99.9999%, Taiyo Sanso), O₂ (99.9%, Nippon Sanso), C₂H₂ (99%, Eto Sanso), CH₄ (99.9%, Nippon Sanso), and C₆F₅Cl (Kishida Kagaku, 95%). These reagents were used without further purification.

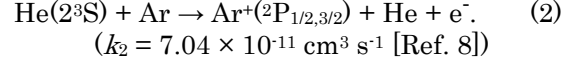
2.2 Flowing-afterglow apparatus and experimental procedure

Two-types of flowing-afterglow experiments were carried out for the Ar⁺(²P_{1/2,3/2}) reactions. One is an Ar afterglow experiment shown in Fig. 1(a), whereas the other is a He afterglow experiment shown in Fig. 1(b).

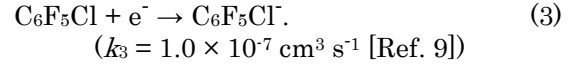
In the Ar afterglow experiment, such Ar active species as metastable Ar(³P_{0,2}) atoms and Ar⁺ ions were generated by a microwave discharge of Ar gas at the output power of 80 W, and the C₆F₅Cl gas was introduced from the second gas inlet placed 20 cm downstream from the center of microwave discharge. Effects of charged particles were examined by using a pair of charged-particle collector grids placed between the discharge section and the reaction zone. The partial pressures in the reaction zone were 0.18–1.0 Torr (1 Torr = 133.33 Pa) for Ar and 3–5 mTorr for C₆F₅Cl.

In the He afterglow experiment such He active species as He(2³S), He⁺, and He₂⁺ were generated by a microwave discharge of high purity He gas at the output power of 70 W. He⁺ and He₂⁺ ions in the discharge flow were

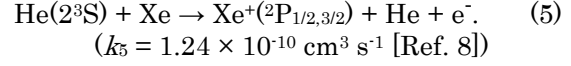
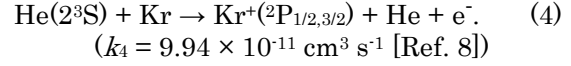
trapped by using charged-particle collector grids. Therefore, only neutral He(2³S) atoms can arrive at the reaction zone as He active species. A small amount of Ar gas was added to the He flow 10 cm downstream from the center of microwave discharge. The positive Ar⁺(²P_{1/2,3/2}) ion was produced by the He(2³S)/Ar, Penning ionization.



An electron attachment gas, C₆F₅Cl, was added from the second gas inlet, where C₆F₅Cl⁻ ion was formed by a fast non-dissociative electron attachment.



Kr⁺(²P_{1/2,3/2}) and Xe⁺(²P_{1/2,3/2}) reactions were carried out using similar He afterglow apparatus. In these cases, Kr⁺(²P_{1/2,3/2}) and Xe⁺(²P_{1/2,3/2}) ions were formed by He(2³S)/Kr and He(2³S)/Xe Penning ionization, respectively.



The partial pressures in the reaction zone were 1.0 Torr (1 Torr = 133.33 Pa) for He, 5–40 mTorr for Rg (Rg = Ar, Kr, and Xe), and 3–5 mTorr for C₆F₅Cl. The greatest advantage of the He afterglow experiment is that we can save expensive rare gases, Kr and Xe for the Kr⁺(²P_{1/2,3/2}) and Xe⁺(²P_{1/2,3/2}) reactions.

When the effects of incident spin-orbit states in Ar⁺(²P_{1/2,3/2}), Kr⁺(²P_{1/2,3/2}), and Xe⁺(²P_{1/2,3/2}) were examined, one of the spin-orbit states was isolated before reaching the second gas inlet. For the isolation of Ar⁺(²P_{3/2}), Kr⁺(²P_{1/2}), Xe⁺(²P_{1/2}), and Xe⁺(²P_{3/2}), N₂, O₂, C₂H₂, and CH₄ were used as filter gases, respectively, because the quenching rate constants of the ²P_{1/2} and ²P_{3/2} states are different at least one order of magnitude.

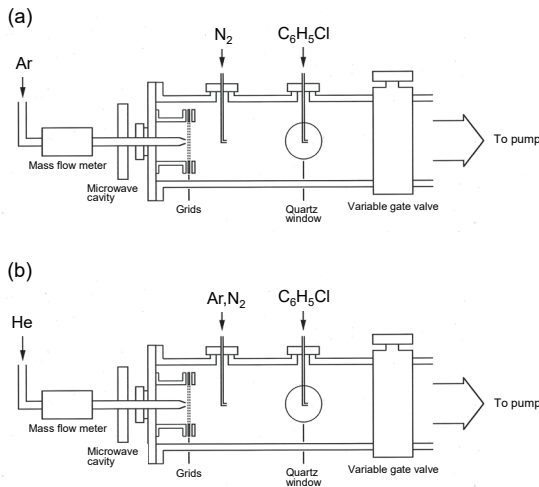
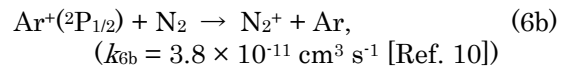
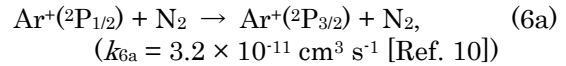
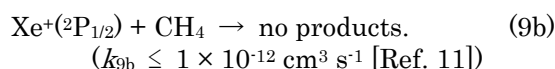
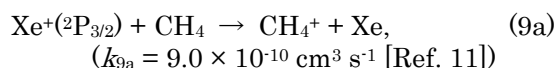
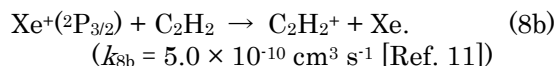
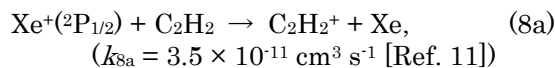
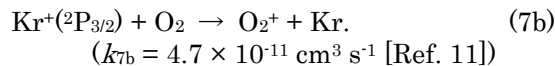
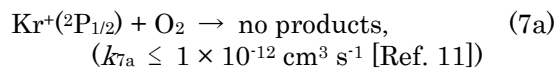
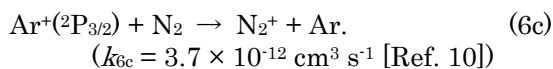


Fig. 1. (a) Ar and (b) He flowing-afterglow apparatuses for the study on the Ar⁺(²P_{1/2,3/2})/C₆F₅Cl⁻ ion-ion recombination reaction. N₂ was added as a filter gas of the Ar⁺(²P_{1/2}) component.



These filter gases were injected from the first gas inlet, as shown in Figs (1a) and (1b) for the case of N_2 in the $\text{Ar}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction. The partial pressures of the filter gases were 10–200 mTorr.

The emission spectra, observed around the $\text{C}_6\text{F}_5\text{Cl}$ gas inlet, were dispersed in the 120–840 nm region with McPherson 218 and Spex 1250M monochromators. Photon signals from a cooled photomultiplier were analyzed with a microcomputer.

We used ionization potentials of Ar, Kr, Xe, and $\text{C}_6\text{F}_5\text{Cl}$, electron affinity of $\text{C}_6\text{F}_5\text{Cl}$, dissociation energy of $\text{D}(\text{C}_6\text{F}_5-\text{Cl})$, excitation energies of RgCl^* reported in Refs. 12–18 for the calculations of energetics in each reaction.

3. Results and Discussion

3.1 Formation of ArCl^* excimer from the $\text{Ar}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction in the Ar and He afterglow

Figures 2(a)–2(d) show emission spectra of $\text{C}_6\text{F}_5\text{Cl}$ in an Ar flowing afterglow at various Ar gas pressures. At the lowest Ar pressure of 0.18 Torr, very weak unidentified atomic lines are observed. At higher Ar gas pressures of 0.42–1.0 Torr, three transitions of ArCl^* excimer and Cl^* lines are identified in the 130–210 nm region. The intensities of ArCl^* and Cl^* increase with increasing the Ar pressure from 0.42 Torr to 0.68 Torr, and then decrease with further increasing Ar pressure from 0.68 Torr to 1.0 Torr. ArCl^* excimer bands, on which present work focuses, consists of the strong $\text{B}(1/2)-\text{X}(1/2)$ transition in the 160–180 nm region, the weak $\text{D}(1/2)-\text{X}(1/2)$ transition in the

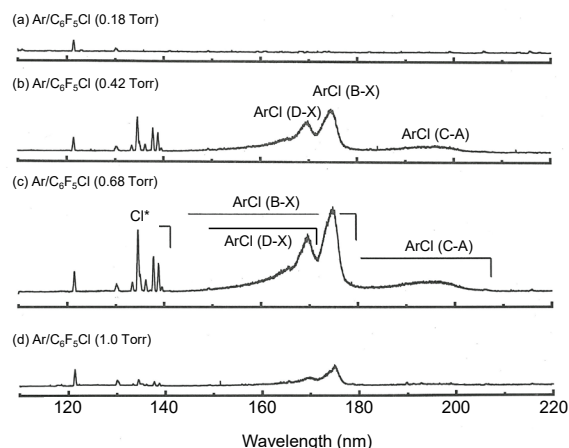
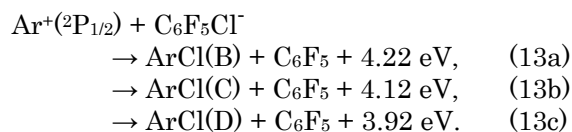
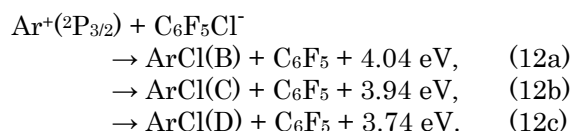
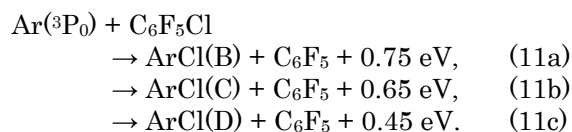
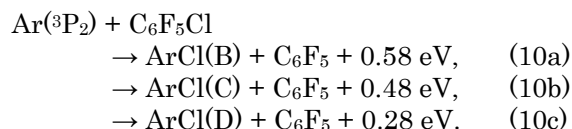


Fig. 2. Emission spectra resulting from the $\text{Ar}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction in the 110–220 nm region at various Ar gas pressures.

140–173 nm region, and the weak broad $\text{C}(3/2)-\text{A}(3/2)$ transition in the 180–207 nm region. Since the B, C, and D states of RgX^* are strongly bound, whereas the X and A states of RgX^* are repulsive,^{16–18} continuous bands without vibrational structures are observed for the $\text{ArCl}(\text{B-X}, \text{D-X}, \text{C-A})$ bound-free transitions.

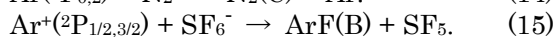
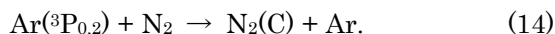
Possible excitation sources of ArCl^* emissions are metastable $\text{Ar}(^3\text{P}_2)$ and $\text{Ar}(^3\text{P}_0)$ atoms and $\text{Ar}^+(^2\text{P}_{3/2})$ and $\text{Ar}^+(^2\text{P}_{1/2})$ ions. The energetics for the formation of $\text{ArCl}(\text{B,C,D})$ from the $\text{Ar}(^3\text{P}_{0,2})/\text{C}_6\text{F}_5\text{Cl}^-$ and $\text{Ar}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction is as follows:



Based on energetics, both metastable $\text{Ar}(^3\text{P}_{0,2})$ atoms and $\text{Ar}^+(^2\text{P}_{3/2,1/2})$ ions can be excitation

sources of ArCl^* . Figures 3(a) and 3(b) show emission spectra at an Ar pressure of 0.68 Torr without and after ion trapping using ion collector grids, respectively. ArCl^* and Cl^* emissions disappear almost completely in Fig. 3(b), indicating that only charged $\text{Ar}^+(^2\text{P}_{3/2,1/2})$ ions take part in the formation of ArCl^* and Cl^* at 0.68 Torr.

In order to further confirm the excitation source of ArCl^* emission in the Ar flowing afterglow, the Ar pressure dependence of ArCl(B-X) emission was compared with those of $\text{N}_2(\text{C-B})$ emission due to the $\text{Ar}(^3\text{P}_{0,2})/\text{N}_2$ reaction^{19,20} and ArF(B-X) emission due to the $\text{Ar}^+(^2\text{P}_{1/2,3/2})/\text{SF}_6^-$ reaction (Fig. 4).^{1,2}



The ArCl(B-X) and ArF(B-X) bands by the $\text{Ar}^+(^2\text{P}_{1/2,3/2})$ reaction appeared at an Ar pressure of ~ 0.2 Torr with a single intensity peak at ~ 0.65 Torr, while the $\text{N}_2(\text{C-B})$ band by the $\text{Ar}(^3\text{P}_{0,2})/\text{N}_2$ reaction appeared at a lower Ar pressure of ~ 0.05 Torr with two intensity peaks at 0.15 and 0.7 Torr. A similar Ar pressure dependence between ArCl(B-X) and ArF(B-X) emissions suggests that ArCl(B) excimer is

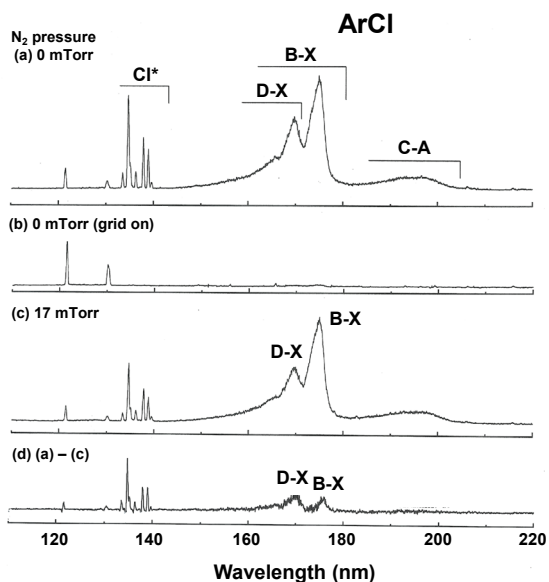


Fig. 3. Emission spectra resulting from the (a) $\text{Ar}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction in the Ar afterglow, (b) ion-collection in spectrum (a), (c) by the addition of 17 mTorr of N_2 , and (d) $\text{Ar}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction. Spectrum (d) was obtained by subtracting spectrum (c) from spectrum (a).

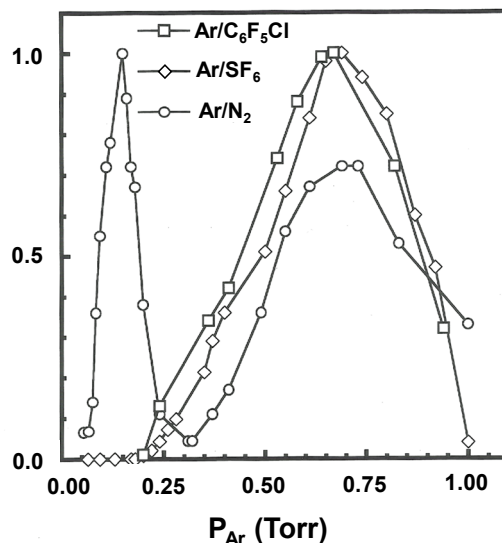


Fig. 4. Dependence of emission intensities of ArCl(B-X) band from the $\text{Ar}^+/\text{C}_6\text{F}_5\text{Cl}^-$ reaction, ArF(B-X) band from the $\text{Ar}^+/\text{SF}_6^-$ reaction, and $\text{N}_2(\text{C-B})$ band from the $\text{Ar}(^3\text{P}_{0,2})/\text{N}_2$ reaction in the Ar flowing afterglow.

formed by the $\text{Ar}^+(^2\text{P}_{1/2,3/2})$ reaction. An important finding in this work is that product channels leading to ArCl(B,C,D) excimers, processes (10) and (11), are closed in the $\text{Ar}(^3\text{P}_{0,2})/\text{C}_6\text{F}_5\text{Cl}$ reaction, even though they are energetically allowed.

Figure A1 in Appendix shows effects of N_2 addition on the emission spectra of ArCl^* resulting from the $\text{Ar}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction. With increasing the N_2 pressure, the $[\text{Ar}^+(^2\text{P}_{3/2})]/[\text{Ar}^+(^2\text{P}_{1/2})]$ ratio is expected to be enhanced. Without addition of N_2 (Fig. A1(a)), the weak ArCl(D-X) band appears as a shoulder band of the main ArCl(B-X) band, and the weak broad ArCl(C-A) band is observed in the longer wavelength region of the ArCl(B-X) band. With increasing the partial pressure of N_2 from 21 mTorr to 93 mTorr (Fig. A1(b)–1(e)), the intensity of ArCl(D-X) band decreases more rapidly than those of ArCl(B-X) and ArCl(C-A) bands, and the ArCl(D-X) band almost disappears at the highest N_2 pressure of 140 mTorr (Fig. A1(f)). This shows that the ArCl(D-X) band is produced from the $\text{Ar}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction, whereas ArCl(B-X) and ArCl(C-A) bands arise from the $\text{Ar}^+(^2\text{P}_{3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction.

A similar disappearance of the ArCl(D-X) band by the N_2 addition is found in the $\text{Ar}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction in the He

afterglow (Fig. A2(a)–2(d) in Appendix). With increasing the N₂ pressure, ArCl(D–X) band decreases more rapidly than those of ArCl(B–X, C–A) bands, and it nearly disappears at N₂ pressure of 19 mTorr. From the intensity ratio between the ArCl(B–X) and ArCl(C–A) bands in the Ar and He afterglow, the branching ratio of ArCl(B) and ArCl(C) in processes (12a) and (12b) was estimated to be 0.74:0.26, respectively.

Figure 3(c) shows emission spectrum of C₆F₅Cl in the Ar flowing afterglow after addition of 17 mTorr of N₂. ArCl(B–X, C–A, D–X) emissions reduced their intensities in comparison with those in Fig. 3(a) obtained without N₂ addition. Decay rate of Ar^{+(2P_{1/2})} is about 20 times faster than that of Ar^{+(2P_{3/2})} by the N₂ addition. Thus, we examined the contribution of the Ar^{+(2P_{1/2})} reaction by assuming that ArCl* emission resulting only from the Ar^{+(2P_{1/2})}/C₆F₅Cl[−] reaction is attenuated by the addition of a small amount of N₂ (17 mTorr). Figure 3(d) shows emission spectrum of the Ar^{+(2P_{1/2})}/C₆F₅Cl[−] reaction obtained by subtracting spectrum (c) from spectrum (a). In Fig. 3(d), weak ArCl(B–X) and ArCl(D–X) bands are observed, and the intensity of the ArCl(D–X) band is stronger than that of the ArCl(B–X) one. From the intensity ratio of the two band systems, the branching ratio of ArCl(B) and ArCl(D) in processes (13a) and (13c) was estimated to be 0.35:0.65, respectively.

3.2 Formation of KrCl* excimer from the Kr^{+(2P_{1/2,3/2})}/C₆F₅Cl[−] reaction in the He afterglow

Figure 5(a) shows emission spectrum resulting from the Kr^{+(2P_{1/2,3/2})}/C₆F₅Cl[−] reaction in the He afterglow. The strong KrCl(B–X) band, the very weak KrCl(D–X) band, and the weak broad KrCl(C–A) band are identified in the 160–225, 160–200, and 225–275 nm region, respectively. Figures 5(b) and 5(c), respectively, show emission spectra obtained by addition of O₂ at partial pressures of 50 and 100 mTorr to enhance the [Kr^{+(2P_{1/2})}]/[Kr^{+(2P_{3/2})}] ratio. With increasing the partial pressure of O₂, KrCl(D–X)/KrCl(B–X) intensity ratio increases. By the addition of a sufficient amount of O₂ (~200 mTorr), the KrCl(D–X)/KrCl(B–X) intensity ratio further increases and becomes constant, as shown in Fig. 5(d). Based on these experiments, the branching ratio of KrCl(B) and KrCl(C) in processes (16a) and (16b), and that of KrCl(B) and KrCl(D) in processes (17a)

and (17c) were evaluated to be 0.71:0.29 and 0.05:0.95, respectively.

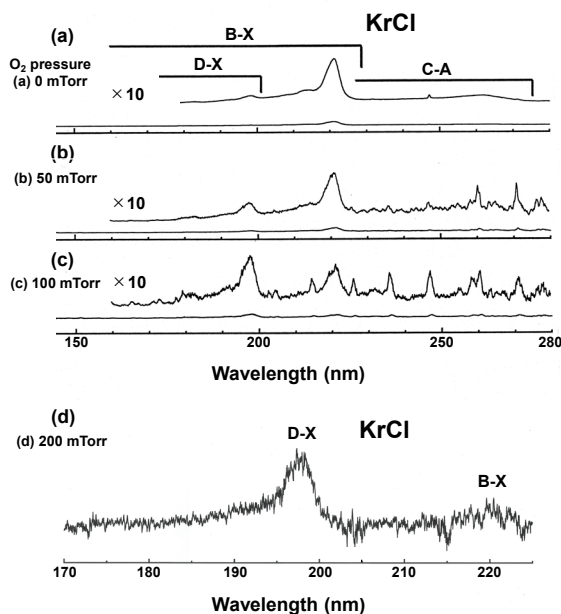
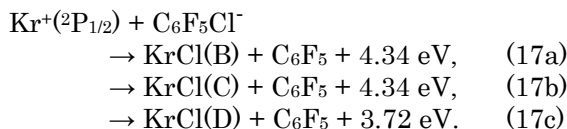
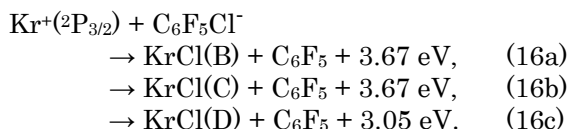


Fig. 5. Emission spectra resulting from the Kr⁺/C₆F₅Cl[−] reaction in the 150–280 nm or 170–230 nm region. (a) without O₂ addition, (b) 50 mTorr O₂ addition, (c) 100 mTorr O₂ addition, (d) 200 mTorr O₂ addition.

3.3 Formation of XeCl* excimer from the Xe^{+(2P_{1/2,3/2})}/C₆F₅Cl[−] reaction in the He afterglow

Figure 6(a) shows emission spectrum resulting from the Xe^{+(2P_{1/2,3/2})}/C₆F₅Cl[−] reaction in the He afterglow. XeCl* excimer bands consist of the strong XeCl(B–X) band in the 250–320 nm region, the very weak XeCl(D–X) band in the 200–240 nm region, and the weak broad XeCl(C–A) band in the 320–450 nm region. Figures 6(b) and 6(c) show emission spectra obtained by selecting one-spin-orbit component using C₂H₂ or CH₄ filter gases, respectively. In the Xe^{+(2P_{1/2})}/C₆F₅Cl[−] reaction shown in Fig. 6(b), the XeCl(B–X) band greatly reduces its intensity by removal of the Xe^{+(2P_{3/2})}

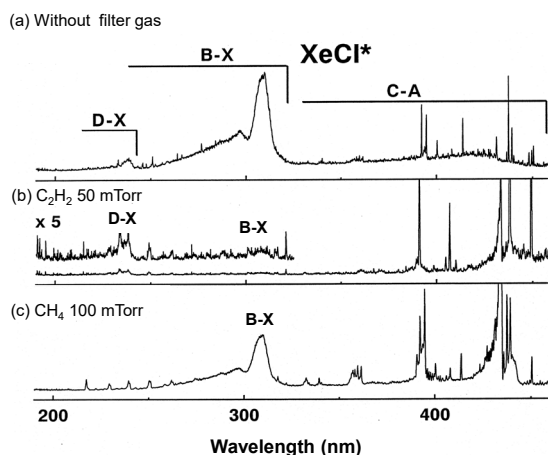
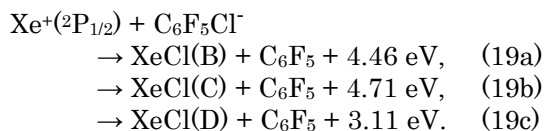
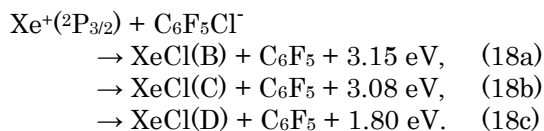


Fig. 6. Emission spectra resulting from the Xe⁺/C₆F₅Cl[−] reaction in the 200–450 nm region. (a) Xe⁺(²P_{1/2,3/2)/C₆F₅Cl[−] reaction without addition of filter gas, (b) Xe⁺(²P_{1/2)/C₆F₅Cl[−] reaction by addition of 50 mTorr C₂H₂, (c) Xe⁺(²P_{3/2)/C₆F₅Cl[−] reaction by addition of 100 mTorr CH₄.}}}

component, whereas the XeCl(D–X) band remains its intensity. On the other hand, in the Xe⁺(²P_{3/2)/C₆F₅Cl[−] reaction shown in Fig. 6(c), XeCl(B–X) and XeCl(C–A) bands remain their intensities, whereas the XeCl(D–X) band disappears. The branching ratio of XeCl(B) and XeCl(C) in processes (18a) and (18b) and that of XeCl(B) and XeCl(D) in processes (19a) and (19c) were evaluated to be 0.70:0.30 and 0.24:0.76, respectively.}



3.4 Branching ratios of RgX(B,C,D) excimers in the ion-ion recombination reactions and chemiluminescent reactions

In Table 1 are summarized the branching ratios of RgX(B,C,D) excimers in the Rg⁺(²P_{1/2})/C₆F₅Cl[−] and Rg⁺(²P_{3/2})/C₆F₅Cl[−] reactions. For comparison, corresponding data for the Rg⁺/SF₆[−] reactions and chemiluminescent reactions of metastable Rg(³P_{0,2}) atoms with diatomic and polyatomic halides RX are also given.

The initial formation ratio of two spin-orbit components of Kr⁺ and Xe⁺, [²P_{1/2}]/[²P_{3/2}], in the Penning ionization (4) and (5) was estimated to be 0.56 for Kr⁺ and 0.49 for Xe⁺ from the analysis of Penning ionization electron spectra.²¹⁾ We found previously that RgF(B–X) emissions are formed highly selectively by the Rg⁺(²P_{3/2})/SF₆[−] reactions, whereas RgF(D–X) emissions preferentially results from the Rg⁺(²P_{1/2})/SF₆[−] reactions for Rg = Kr and Xe.²⁾ Therefore, the [Rg⁺(²P_{1/2})]/[Rg⁺(²P_{3/2})] ratios can be estimated by using intensity ratios of RgF(D–X)/RgF(B–X) excimers resulting from spin-orbit state selective Rg⁺(²P_{1/2,3/2})/SF₆[−] reactions, assuming that no significant difference exists between the rate constant for the formation of RgF(D) from the Rg⁺(²P_{1/2})/SF₆[−] reaction and that of RgF(B) from the Rg⁺(²P_{3/2})/SF₆[−] reaction. We found that the RgF(B–X) emission is much stronger than that of RgF(D–X) emissions, as reported previously.²⁾ It was therefore concluded that the lower Rg⁺(²P_{3/2}) state is major component in the present experiments, although a small amount of upper Rg⁺(²P_{1/2}) state is involved in all cases.

It is clear that the B and D states are formed by the Rg⁺(²P_{1/2})/C₆F₅Cl[−] reactions with the D state being strongly favored, whereas the B and C state are produced by the Rg⁺(²P_{3/2})/C₆F₅Cl[−] reactions with the branching ratio of about 7:3, respectively in all cases. The Γ(D) values for the Ar⁺(²P_{1/2})/C₆F₅Cl[−] and Xe⁺(²P_{1/2})/C₆F₅Cl[−] reactions, 0.65 and 0.76, respectively, are smaller than that for the Kr⁺(²P_{1/2})/C₆F₅Cl[−] reaction, 0.95. The Γ(D) value for the Kr⁺(²P_{1/2})/C₆F₅Cl[−] reaction, 0.95, is the same as that for the Kr⁺(²P_{1/2})/SF₆[−] reaction, whereas the Γ(D) value for the Xe⁺(²P_{1/2})/C₆F₅Cl[−] reaction, 0.76, is smaller than that for the Xe⁺(²P_{1/2})/SF₆[−] reaction, 0.94.

In the chemiluminescent reactions of metastable Ar(³P_{0,2}) and Kr(³P_{0,2}) atoms with halides RX, spin-orbit selectivity is also found. In these cases, Ar(³P₂) and Kr(³P₂) reactions give only B and C states, whereas mixtures of B and D states are formed in the Ar(³P₀) and Kr(³P₀) reactions. The Γ(D) values in the Ar(³P₀) and Kr(³P₀) reactions range from 0.23 to 0.73, which are about the same or smaller than those obtained in the Rg⁺(²P_{1/2})/C₆F₅Cl[−] reactions (0.65–0.95). It should be noted that a significant difference is observed in the spin-orbit selectivity between the Xe(³P₀)/RX and the Xe⁺(²P_{1/2})/C₆F₅Cl[−] reactions. In strong contrast to the Ar(³P₀) and Kr(³P₀) reactions,

Table 1. Branching ratios of RgX(B,C,D) excimers in ion-ion recombination reactions and chemiluminescent (CL) reactions.

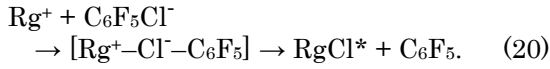
Ion-ion reactions		$\Gamma(B)$	$\Gamma(C)$	$\Gamma(D)$	CL Reaction		$\Gamma(B)$	$\Gamma(C)$	$\Gamma(D)$
$\text{Ar}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$	This work	0.35		0.65	$\text{Ar}(^3\text{P}_0)/\text{Cl}_2$	Ref. 5	0.52	0.13	0.35
$\text{Ar}^+(^2\text{P}_{3/2})/\text{C}_6\text{F}_5\text{Cl}^-$	This work	0.74	0.26		$\text{Ar}(^3\text{P}_2)/\text{Cl}_2$	Ref. 5	0.70	0.30	
$\text{Kr}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$	This work	0.05		0.95	$\text{Ar}(^3\text{P}_0)/\text{SOCl}_2$	Ref. 5	0.40	0.09	0.51
$\text{Kr}^+(^2\text{P}_{3/2})/\text{C}_6\text{F}_5\text{Cl}^-$	This work	0.71	0.29		$\text{Ar}(^3\text{P}_2)/\text{SOCl}_2$	Ref. 5	0.69	0.31	
$\text{Xe}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$	This work	0.24		0.76	$\text{Ar}(^3\text{P}_0)/\text{PCl}_3$	Ref. 5	0.23	0.04	0.73
$\text{Xe}^+(^2\text{P}_{3/2})/\text{C}_6\text{F}_5\text{Cl}^-$	This work	0.70	0.30		$\text{Ar}(^3\text{P}_2)/\text{PCl}_3$	Ref. 5	0.27	0.73	
$\text{Kr}^+(^2\text{P}_{1/2})/\text{SF}_6^-$	Ref. 2	0.05		0.95	$\text{Ar}(^3\text{P}_0)/\text{CCl}_4$	Ref. 5	0.26	0.08	0.66
$\text{Kr}^+(^2\text{P}_{3/2})/\text{SF}_6^-$	Ref. 2	0.62	0.38		$\text{Ar}(^3\text{P}_2)/\text{CCl}_4$	Ref. 5	0.33	0.67	
$\text{Xe}^+(^2\text{P}_{1/2})/\text{SF}_6^-$	Ref. 2	0.06		0.94	$\text{Ar}(^3\text{P}_0)/\text{F}_2$	Ref. 5	0.49	0.28	0.23
$\text{Xe}^+(^2\text{P}_{3/2})/\text{SF}_6^-$	Ref. 2	0.68	0.32		$\text{Ar}(^3\text{P}_2)/\text{F}_2$	Ref. 5	0.50	0.50	
					$\text{Kr}(^3\text{P}_0)/\text{Cl}_2$	Ref. 6	0.42		0.58
					$\text{Kr}(^3\text{P}_2)/\text{Cl}_2$	Ref. 6	0.52	0.48	
					$\text{Kr}(^3\text{P}_0)/\text{SOCl}_2$	Ref. 6	0.46		0.54
					$\text{Kr}(^3\text{P}_2)/\text{SOCl}_2$	Ref. 6	0.60	0.40	
					$\text{Kr}(^3\text{P}_0)/\text{PCl}_3$	Ref. 8	1.00		
					$\text{Kr}(^3\text{P}_2)/\text{PCl}_3$	Ref. 6	0.33	0.67	
					$\text{Kr}(^3\text{P}_0)/\text{CCl}_4$	Ref. 6	0.50		0.50
					$\text{Kr}(^3\text{P}_2)/\text{CCl}_4$	Ref. 8	0.40	0.60	
					$\text{Xe}(^3\text{P}_0)/\text{F}_2$	Ref. 7	≥ 0.90		≤ 0.10
					$\text{Xe}(^3\text{P}_2)/\text{F}_2$	Ref. 7	1.00 (B + C)		
					$\text{Xe}(^3\text{P}_0)/\text{Br}_2^{\text{a)}$	Ref. 7	≥ 0.75		≤ 0.25
					$\text{Xe}(^3\text{P}_2)/\text{Br}_2$	Ref. 7	1.00 (B + C)		
					$\text{Xe}(^3\text{P}_0)/\text{Cl}_2$	Ref. 7	1.00 (B + C)		
					$\text{Xe}(^3\text{P}_2)/\text{Cl}_2$	Ref. 7	1.00 (B + C)		
					$\text{Xe}(^3\text{P}_0)/\text{HCl}$	Ref. 7	1.00 (B + C)		
					$\text{Xe}(^3\text{P}_2)/\text{HCl}$	Ref. 7	1.00 (B + C)		
					$\text{Xe}(^3\text{P}_0)/\text{PCl}_3$	Ref. 7	1.00 (B + C)		
					$\text{Xe}(^3\text{P}_2)/\text{PCl}_3$	Ref. 7	1.00 (B + C)		
					$\text{Xe}(^3\text{P}_0)/\text{CF}_3\text{Cl}$	Ref. 7	1.00 (B + C)		
					$\text{Xe}(^3\text{P}_2)/\text{CF}_3\text{Cl}$	Ref. 7	1.00 (B + C)		

^{a)} From peak intensity.

the $\Gamma(\text{D})$ values in the $\text{Xe}(^3\text{P}_0)/\text{RX}$ reactions are zero except for F_2 (≤ 0.10) and Br_2 (≤ 0.25). The $\Gamma(\text{B}) + \Gamma(\text{C})$ values in the $\text{Xe}(^3\text{P}_2)/\text{RX}$ reactions are 1.00 for all reagents, as in the cases of the $\text{Ar}(^3\text{P}_2)$ and $\text{Kr}(^3\text{P}_2)$ reactions and the $\text{Xe}^+(^2\text{P}_{3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction.

3.3 Reaction dynamics for the formation of RgCl(B,C,D) excimers in the reactions of $\text{Rg}^+(^2\text{P}_{1/2,3/2})$ with $\text{C}_6\text{F}_5\text{Cl}^-$

The formation of RgCl^* excimers from the $\text{Rg}^+/\text{C}_6\text{F}_5\text{Cl}^-$ reactions must proceed through the $[\text{Rg}^+-\text{Cl}^--\text{C}_6\text{F}_5]$ intermediates.



The formation dynamics of RgX^* excimers from the $\text{Rg}(^3\text{P}_{0,2})/\text{X}_2$ reaction using a correlation diagram is shown in Fig. A3 (Appendix), where RgX^* excimers are formed through $\text{Rg}^+(^2\text{P}_{1/2,3/2}) + \text{X}_2^-$ ion-pairs intermediates. It is known that changing the designation of the states to C_s geometry for RX^- molecules with A' or A'' symmetry does not alter the broad interpretation for X_2^- with higher symmetry.⁵⁻⁷ Figure 7 shows the schematic potential diagram of the $\text{Rg}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ recombination process, where the Ω designation given in Fig. A3 remains for the

$\text{Rg}(^3\text{P}_{0,2}) + \text{C}_6\text{F}_5\text{Cl}$, $\text{Rg}^+(^2\text{P}_{1/2,3/2}) + \text{C}_6\text{F}_5\text{Cl}^-$, and $\text{RgCl}(\text{B,C,D}) + \text{C}_6\text{F}_5$ systems. The $\text{RgCl}(\text{D})$ state correlates to the $\text{Rg}^+(^2\text{P}_{1/2}) + \text{Cl}^-$ ion pair, while the $\text{RgCl}(\text{B,C})$ states correlate to the $\text{Rg}^+(^2\text{P}_{3/2}) + \text{Cl}^-$ ion pair based upon ab initio calculations.¹⁶⁻¹⁸⁾

There are quasi continuous $\text{Rg} + \text{C}_6\text{F}_5\text{Cl}^*$ (excited states) product channels below the $V[\text{Rg}^+, \text{C}_6\text{F}_5\text{Cl}^-]$ ion-pair potentials for a relatively large molecule such as $\text{C}_6\text{F}_5\text{Cl}$. Here, excited states of $\text{C}_6\text{F}_5\text{Cl}$ involve superexcited states above the first ionization potential of 9.72 eV. In addition to the $\text{Rg} + \text{C}_6\text{F}_5\text{Cl}^*$ product channels, a number of $\text{Rg}^{**}(\text{Rydberg states}) + \text{C}_6\text{F}_5\text{Cl}$ potentials are present above the $\text{Rg}(^3\text{P}_{0,2}) + \text{C}_6\text{F}_5\text{Cl}$ potentials as product channels, because the potential energies of $\text{Rg}^+(^2\text{P}_{3/2}) + \text{C}_6\text{F}_5\text{Cl}^-$ are higher than those of $\text{Rg}(^3\text{P}_0) + \text{C}_6\text{F}_5\text{Cl}$ by 1.9–3.3 eV. They are also shown by hatched lines in Fig. 7. In the $\text{Ar}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$, $\text{Kr}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$, and $\text{Xe}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions, the following states exist as candidates for Rg^{**} and some of them can interact with the entrance $V[\text{Rg}^+(^2\text{P}_{1/2,3/2}), \text{C}_6\text{F}_5\text{Cl}^-]$ ion-pair potentials: total 59 4s, 4p, 3d, 5s, 5p, 4d, 6s, and 4f states for Ar^{**} , 51 5s, 5p, 4d, 6s, 6p, 5d, 7s, and 4f states for Kr^{**} , and 48 6s, 6p, 5d, 7s, 7p, 6d, 8s, and 4f states for Xe^{**} . As shown in Table 1, most of $\text{Rg}(^3\text{P}_{0,2})/\text{RX}$ reactions give RgX^* excimers via

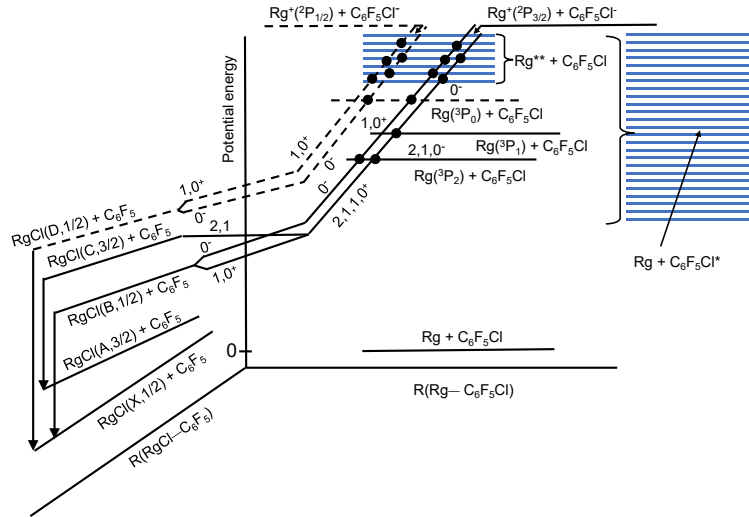
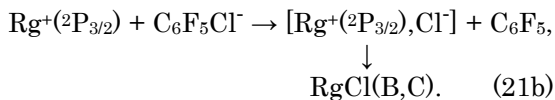
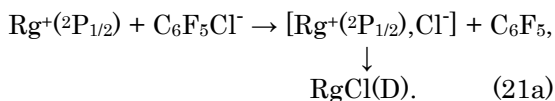


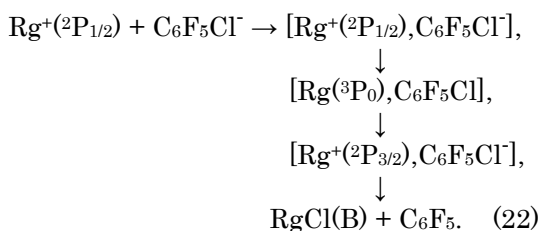
Fig. 7. Correlation diagram of the diabatic potentials for the $\text{Rg}(^3\text{P}_{0,2})/\text{C}_6\text{F}_5\text{Cl}$ and $\text{Rg}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions. The states with $\text{Rg}^+(^2\text{P}_{1/2})$ ion-core configuration are shown by dashed lines. The dark circles show positions of strong interactions of the diabatic potentials. Ω values shown in Fig. A3 for the $\text{Rg}(^3\text{P}_{0,2})/\text{X}_2$ and $\text{Rg}^+(^2\text{P}_{1/2,3/2})/\text{X}_2^-$ reactions in collinear geometry are used.

$[\text{Rg}^+(^2\text{P}_{1/2,3/2}), \text{RX}]$ ion-pair intermediates. In the $\text{Xe}^{**}(6p, 6p', 7p)/\text{RX}$ reactions,^{22,23)} XeX^* excimer formation via $V[\text{Xe}^+(^2\text{P}_{1/2,3/2}), \text{RX}]$ ion-pair potentials has also been observed, indicating that higher energy entrance $V[\text{Xe}^{**}(6p, 6p', 7p), \text{RX}]$ potentials really couple with the $V[\text{Xe}^+(^2\text{P}_{1/2,3/2}), \text{RX}]$ ion-pair potentials. If the attractive ion-pair potentials strongly couple with some of these $V[\text{Rg}, \text{C}_6\text{F}_5\text{Cl}^*]$ or $V[\text{Rg}^{**}, \text{C}_6\text{F}_5\text{Cl}]$ potentials, this coupling diverts trajectories from the ion-pair potential to the $V[\text{Rg}, \text{C}_6\text{F}_5\text{Cl}^*]$ or $V[\text{Rg}^{**}, \text{C}_6\text{F}_5\text{Cl}]$ potentials. The preferential formation of $\text{RgCl}(\text{D})$ from the $\text{Rg}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions and the selective formation of $\text{RgF}(\text{B}, \text{C})$ from the $\text{Rg}^+(^2\text{P}_{3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions imply that trajectory loss by interactions with $V[\text{Rg}, \text{C}_6\text{F}_5\text{Cl}^*]$ or $V[\text{Rg}^{**}, \text{C}_6\text{F}_5\text{Cl}]$ potentials is small, so that the RgCl^* excimers could be formed through diabatic pathways predicted from the potential diagram.



On the basis of this finding, the electronic configuration of rare gas ion is conserved well during the $\text{Rg}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions.

The formation of a small amount of $\text{RgCl}(\text{B})$ from the $\text{Rg}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction suggests that the conservation of ion configuration is partially broken. One possible route for the formation of $\text{RgCl}(\text{B})$ from the $\text{Rg}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction shown in Fig. 7 is the first curve crossing between the $\Omega = 0^-$ entrance $V[\text{Rg}^+(^2\text{P}_{1/2}), \text{C}_6\text{F}_5\text{Cl}^-]$ potential and the $\Omega = 0^-$ potential arising from $\text{Rg}(^3\text{P}_0) + \text{C}_6\text{F}_5\text{Cl}$ followed by the second curve crossing between the $\Omega = 0^-$ potential from $\text{Rg}(^3\text{P}_0) + \text{C}_6\text{F}_5\text{Cl}$ and the $\Omega = 0^-$ potential arising from $\text{Rg}^+(^2\text{P}_{3/2}) + \text{C}_6\text{F}_5\text{Cl}^-$.

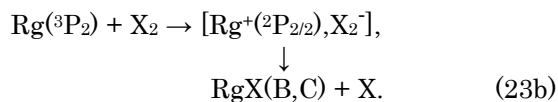
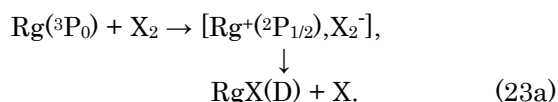


Other possibilities are similar interactions

between the entrance $V[\text{Rg}^+(^2\text{P}_{1/2}), \text{RX}]$ potential and some $V[\text{Rg}^{**}, \text{RX}]$ potential followed by interaction between $V[\text{Rg}^{**}, \text{RX}]$ and $V[\text{Rg}^+(^2\text{P}_{3/2}), \text{RX}]$ potentials.

The smaller $\Gamma(\text{D})$ values in the $\text{Ar}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ and $\text{Xe}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions than that in the $\text{Kr}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction suggest that conversion of ion-core configuration via curve crossings occurs with higher probability in the former reactions.

The spin-orbit state selectivity for the excimer formation in the reactions of metastable $\text{Rg}(^3\text{P}_{0,2})$ atoms with RX has been studied by Setser and his co-workers.⁵⁻⁷⁾ They discussed the electronic state selectivity of RgX^* excimer in the $\text{Rg}(^3\text{P}_{0,2})$ reactions by both the J state and the ion core. As an example, Figure A3 in Appendix shows a schematic diagram of the RgX^* formation from the $\text{Rg}(^3\text{P}_{0,2})/\text{X}_2$ reactions obtained by assuming a collinear approach. A similar potential diagram will be applicable to the formation of RgX^* from the other $\text{Rg}(^3\text{P}_{0,2})/\text{RX}$ reactions with a lower molecular symmetry. The formation of RgX^* by the $\text{Rg}(^3\text{P}_{0,2})/\text{X}_2$ reactions proceeds through harpoon-type reactions via $[\text{Rg}^+, \text{X}_2^-]$ ion-pair intermediates. The metastable $\text{Rg}(^3\text{P}_0)$ and $\text{Rg}(^3\text{P}_2)$ atoms have $\text{Rg}^+(^2\text{P}_{1/2})$ and $\text{Rg}^+(^2\text{P}_{3/2})$ ion cores, respectively. If the ion-core configurations of $\text{Rg}(^3\text{P}_0)$ and $\text{Rg}(^3\text{P}_2)$ are conserved, the $\text{Rg}(^3\text{P}_0)$ atoms should yield the $\text{RgX}(\text{D})$ state through an $[\text{Rg}^+(^2\text{P}_{1/2}), \text{X}_2^-]$ intermediate, whereas the $\text{RgX}(\text{B}, \text{C})$ states would be formed through an $[\text{Rg}^+(^2\text{P}_{3/2}), \text{X}_2^-]$ intermediate.



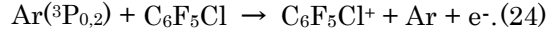
Thus, the formation of D state from the $\text{Rg}(^3\text{P}_0)/\text{X}_2$ reactions and the B and C states from the $\text{Rg}(^3\text{P}_2)/\text{X}_2$ reactions has been explained by the conservation of ion-core configurations. The formation of B from the $\text{Rg}(^3\text{P}_0)$ reactions, which does not conserve the ion-core configuration, was attributed to a crossing between the $\Omega = 0^-$ entrance $V[\text{Rg}(^3\text{P}_0), \text{X}_2]$ potential and the $\Omega = 0^-$ $V[\text{Rg}^+(^2\text{P}_{3/2}), \text{X}_2^-]$ potential. In the $\text{Rg}(^3\text{P}_0)/\text{X}_2$ reactions, the crossing between the entrance $\Omega = 0^-$ potential and the outer $\Omega = 0^-$

$V[\text{Rg}^+(^2\text{P}_{3/2}), \text{X}_2^-]$ potential occurs before the formation of the $[\text{Rg}^+(^2\text{P}_{1/2}), \text{X}_2^-]$ intermediate. Therefore, for the formation of RgX(D) state, trajectories via $V[\text{Rg}(^3\text{P}_0), \text{X}_2]$ potential must pass through the outer crossing with the $V[\text{Rg}^+(^2\text{P}_{3/2}), \text{X}_2^-]$ potential and continue to the inner $V[\text{Rg}^+(^2\text{P}_{1/2}), \text{X}_2^-]$ potential.

In general, this diagram can also be applied to RX reagents as shown in Fig 7 for C₆F₅Cl. It should be noted that such an outer crossing is unnecessary for the formation of $[\text{Rg}^+(^2\text{P}_{1/2}), \text{RX}]$ intermediate in the $\text{Rg}^+(^2\text{P}_{1/2})/\text{RX}^-$ ionic-recombination reactions. Therefore, loss of initial trajectories by outer crossing is absent, so that a high propensity for the formation of RgCl(D) can be achieved in the $\text{Rg}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions in comparison with that in the $\text{Rg}(^3\text{P}_0)/\text{RX}$ reaction. Higher propensity of RgX*(D) is especially found in the $\text{Xe}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction in comparison with that in the $\text{Xe}(^3\text{P}_0)/\text{RX}$ reactions (Table 1). Zong et al.⁷⁾ attributed the low propensity of RgX*(D) in the $\text{Xe}(^3\text{P}_0)/\text{RX}$ reactions to a coupling between the $V[\text{Xe}(6s' ^3\text{P}_0), \text{RX}]$ and $V[\text{Xe}(6p), \text{RX}]$ potentials in the entrance channel, because the emission spectra and the product branching ratios for XeX(B) formation from the reactions of $\text{Xe}(^3\text{P}_0)$ with RX molecules are similar to those from reactions of $\text{Xe}(6p)$ atoms. The covalent $V[\text{Xe}(6s' ^3\text{P}_0), \text{RX}]$ and $V[\text{Xe}(6p), \text{RX}]$ potentials are rather flat before crossing with strongly attractive ion-pair $V[\text{Xe}^+(^2\text{P}_{1/2}), \text{RX}^-]$ potential as reported by Nelson et al.²²⁾ The $V[\text{Xe}(6p), \text{RX}]$ potentials are located at least 0.13 eV above the $V[\text{Xe}(6s' ^3\text{P}_0), \text{RX}]$ potential. It is therefore expected that coupling between the $V[\text{Xe}(6s' ^3\text{P}_0), \text{RX}]$ and $V[\text{Xe}(6p), \text{RX}]$ potentials in the entrance channel is weak at thermal energy. On the basis of present results, ion configuration is rather well conserved in the $\text{Xe}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction, even though the entrance $V[\text{Xe}^+(^2\text{P}_{1/2}), \text{C}_6\text{F}_5\text{Cl}^-]$ potential can couple with many $V[\text{Xe}^{**}, \text{C}_6\text{F}_5\text{Cl}]$ potentials involving $V[\text{Xe}(6p), \text{C}_6\text{F}_5\text{Cl}]$ potential. It is therefore reasonable to assume that the low propensity of RgX*(D) in the $\text{Xe}(^3\text{P}_0)/\text{RX}$ reactions arises from strong coupling of the entrance $\Omega = 0^- (\text{A}'') V[\text{Xe}(^3\text{P}_0), \text{RX}]$ potential with outer $\Omega = 0^- (\text{A}'') V[\text{Xe}^+(^2\text{P}_{3/2}), \text{RX}^-]$ potential.

In the $\text{Ar}(^3\text{P}_{0,2})/\text{C}_6\text{F}_5\text{Cl}$ reactions, no ArCl(B,C,D) formation was observed, even though they are energetically allowed. One possibility is the main product channel is Penning ionization leading to $\text{C}_6\text{F}_5\text{Cl}^+$, because the ionization potential of C₆F₅Cl (9.72 eV) is lower than energies of $\text{Ar}(^3\text{P}_2)$:11.55 eV,

$^3\text{P}_0$:11.72 eV).



Another possibility is that interactions of the entrance $V[\text{Ar}(^3\text{P}_{0,2}), \text{C}_6\text{F}_5\text{Cl}]$ potential with many low lying $V[\text{Ar}, \text{C}_6\text{F}_5\text{Cl}^*]$ potentials occur either directly or via $V[\text{Ar}^+(^2\text{P}_{1/2,3/2}), \text{C}_6\text{F}_5\text{Cl}^-]$ ion-pair potentials with high probability, so that no trajectories leading to ArCl* remain.

The conservation of ion configuration in the $\text{Ar}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ and $\text{Xe}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions were smaller than that in the $\text{Kr}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction. This suggests that interactions of entrance $V[\text{Ar}^+(^2\text{P}_{1/2}), \text{C}_6\text{F}_5\text{Cl}^-]$ and $V[\text{Xe}^+(^2\text{P}_{1/2}), \text{C}_6\text{F}_5\text{Cl}^-]$ potentials with $V[\text{Ar}^{**}, \text{C}_6\text{F}_5\text{Cl}]$ and $V[\text{Xe}^{**}, \text{C}_6\text{F}_5\text{Cl}]$ potentials, which divert the entrance trajectories, are stronger than that in the case of $\text{Kr}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reaction.

4. Summary and Conclusion

Spin-orbit state selectivity of RgCl(B,C,D) excimers in the $\text{Rg}^+(^2\text{P}_{1/2,3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions was examined by selecting one spin-orbit component of $\text{Rg}^+(^2\text{P}_{1/2,3/2})$. The RgCl(B,D) ratio was determined to be 0.35:0.65, 0.05:0.95, and 0.24:0.76 in the $\text{Ag}^+(^2\text{P}_{1/2})$, $\text{Kr}^+(^2\text{P}_{1/2})$, and $\text{Xe}^+(^2\text{P}_{1/2})$ reactions, whereas the RgCl(B,C) ratio was estimated to be 0.74:0.26, 0.71:0.29, and 0.70:0.30 in the $\text{Ag}^+(^2\text{P}_{3/2})$, $\text{Kr}^+(^2\text{P}_{3/2})$, and $\text{Xe}^+(^2\text{P}_{3/2})$ reactions, respectively. The high propensities for the D formation from the $\text{Rg}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions and for the B and C formation from the $\text{Rg}^+(^2\text{P}_{3/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions could be explained by the conservation of the $\text{Rg}^+(^2\text{P}_{1/2}) + \text{Cl}^-$ and $\text{Rg}^+(^2\text{P}_{3/2}) + \text{Cl}^-$ characters for the formation of RgCl*. A high propensity for the formation of RgCl(D) in the $\text{Rg}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions in comparison with that in the $\text{Rg}(^3\text{P}_0)/\text{RX}$ reactions was discussed by using a correlation diagram between entrance and exit product channels. In the $\text{Rg}(^3\text{P}_0)/\text{RX}$ reactions, the crossing between the entrance $\Omega = 0^- (\text{A}'') V[\text{Rg}^+(^2\text{P}_{3/2}), \text{RX}^-]$ potential occurs before the formation of the $[\text{Rg}^+(^2\text{P}_{1/2}), \text{RX}^-]$ intermediate. Such a crossing is unnecessary for the formation of $[\text{Rg}^+(^2\text{P}_{1/2}), \text{RX}^-]$ intermediate in the ionic-recombination reactions. Therefore, a high propensity for the formation of RgCl(D) can be achieved in the $\text{Rg}^+(^2\text{P}_{1/2})/\text{C}_6\text{F}_5\text{Cl}^-$ reactions. The present results demonstrated the ionic recombination is better reaction for the selective formation of

RgX(D) excimers than the chemiluminescent reactions by the metastable Rg(3P_0) atoms.

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Appendix

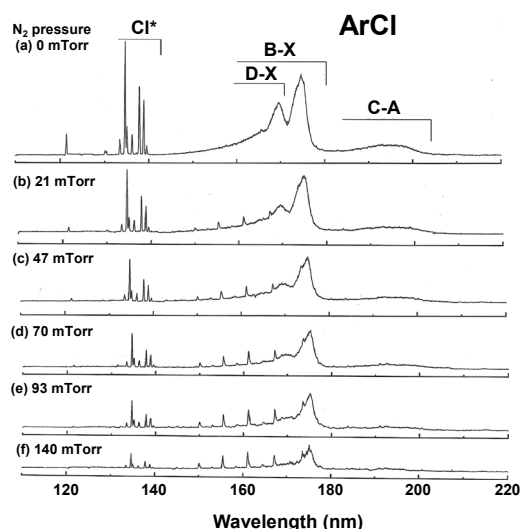


Fig. A1. Effects of N₂ addition to the emission spectra of ArCl* resulting from the Ar⁺($^2P_{1/2,3/2}$)/C₆F₅Cl⁻ reaction in the Ar afterglow.

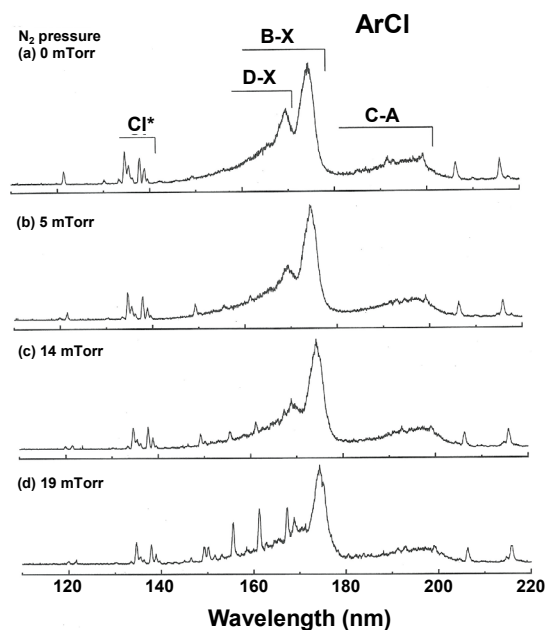


Fig. A2. Effects of N₂ addition to the emission spectra of ArCl* resulting from the Ar⁺($^2P_{1/2,3/2}$)/C₆F₅Cl⁻ reaction in the He afterglow.

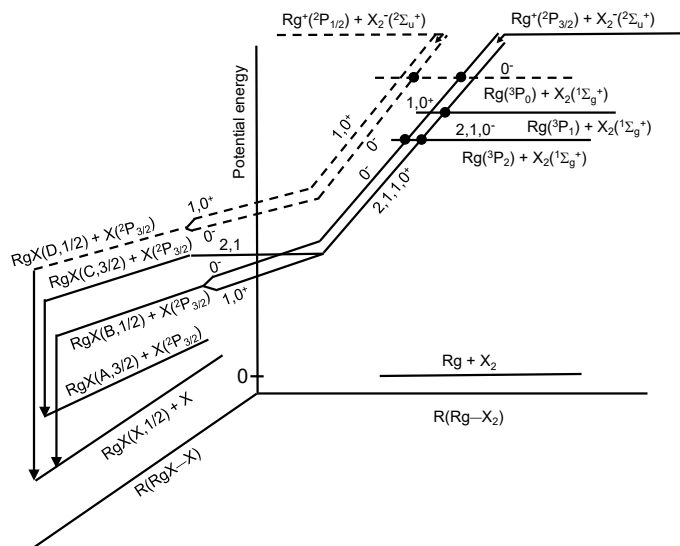


Fig. A3. Correlation diagram of the diabatic potentials for the $\text{Rg}(^3\text{P}_{0,2})/\text{X}_2$ and $\text{Rg}^+(^2\text{P}_{1/2,3/2})/\text{X}_2^-$ reactions in collinear geometry.⁵⁾ The states with $\text{Rg}^+(^2\text{P}_{1/2})$ ion-core configuration are shown by dashed lines. The dark circles show positions of expected strong interactions of the diabatic potentials. The only $\Omega = 1/2$ components correlating to $\text{X}(^2\text{P}_{3/2})$ have been included in the drawing because they are more important than $\Omega = 3/2$ components.