



Formation of NO(A 2 Σ +,C 2 Π r ,D 2 Σ +) by the ion–ion neutralization reactions of NO+ with C6F5CI–, C6F5Br–, and C6F– 5 at thermal energy

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Citation: The Journal of Chemical Physics **105**, 2701 (1996); doi: 10.1063/1.472133 View online: http://dx.doi.org/10.1063/1.472133 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/105/7?ver=pdfcov Published by the AIP Publishing

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Formation of NO($A^{2}\Sigma^{+}$, $C^{2}\Pi_{r}$, $D^{2}\Sigma^{+}$) by the ion–ion neutralization reactions of NO⁺ with C₆F₅Cl⁻, C₆F₅Br⁻, and C₆F₅⁻ at thermal energy

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(Received 18 December 1995; accepted 6 May 1996)

The ion-ion neutralization reactions of NO⁺($X^{1}\Sigma^{+}:v''=0$) with C₆F₅Cl⁻, C₆F₅Br⁻, and C₆F₅ have been spectroscopically studied in the flowing helium afterglow. The NO($A^{2}\Sigma^{+} - X^{2}\Pi_{r}, C^{2}\Pi_{r} - X^{2}\Pi_{r}, D^{2}\Sigma^{+} - X^{2}\Pi_{r}$) emission systems are observed in the NO⁺/C₆F₅Cl⁻ reaction with the branching ratios of 0.96, 0.017, and 0.028, respectively, while only the NO(A - X) emission system is found in the NO⁺/C₆F₅Br⁻ and NO⁺/C₆F₅⁻ reactions. The vibrational and rotational distributions of NO(A, C, D) indicate that only 1%–11% of the excess energy is deposited into vibration and rotation of NO(A, C, D) for all the reactions. In the NO⁺/C₆F₅X⁻ (X=Cl,Br) reactions, a major part of the excess energy is expected to be partitioned into the relative translational energy of the neutral products and the vibrational energy of C₆F₅X. A comparison of the observed vibrational and rotational distributions with the statistical prior ones indicates that the reaction dynamics is not governed by a simple statistical theory because of the large impact parameter. The excitation mechanism of NO(A, C, D) in the ion–ion neutralization reactions of NO⁺ with C₆F₅X⁻ (X=F,Cl,Br,CF₃) and C₆F₅⁻ is discussed. © *1996 American Institute of Physics*. [S0021-9606(96)01331-1]

I. INTRODUCTION

Mutual neutralization reactions between positive and negative ions are important because they remove efficiently charges from cold plasmas. Since the first study in 1896 by Thomson and Rutherford,¹ ion–ion neutralization reactions have been investigated by using flowing-afterglow and merged-beam methods.^{2–9} The major purpose of these studies was the determination of reaction rate constants. There are only a few optical spectroscopic studies that have determined the final states of the reaction products.^{10–12} Smith *et al.*¹³ have spectroscopically studied ion–ion neutralization process (1) by using a flowing-afterglow method

$$NO^{+}(X^{1}\Sigma^{+}) + NO_{2}^{-} \rightarrow NO(A^{2}\Sigma^{+}: v'=0) + NO_{2}. \quad (1)$$

Only the NO($A^{2}\Sigma^{+}-X^{2}\Pi_{r}$) emission from v'=0 was observed. We have recently investigated the excitation processes of NO by ion–ion neutralization reactions of NO⁺ with such negative ions as SF₆⁻, C₆F₆⁻, and C₆F₅CF₃⁻ by using the flowing-afterglow method^{14–17}

NO⁺(X¹Σ⁺)+C₆F₅CF₃⁻ →NO(A²Σ⁺,C²Π_r,D²Σ⁺:v'=0)+C₆F₅CF₃. (4) Only the NO($A^{2}\Sigma^{+}-X^{2}\Pi_{r}$) emission system from v'=0 was observed for the reaction with SF₆⁻, while the NO($A^{2}\Sigma^{+}-X^{2}\Pi_{r}, C^{2}\Pi_{r}-X^{2}\Pi_{r}, D^{2}\Sigma^{+}-X^{2}\Pi_{r}$) emission systems from v'=0 were found for the reactions with C₆F₆⁻ and C₆F₅CF₃⁻. This shows that the product electronic state distribution in the ion–ion neutralization reactions depends strongly on the negative ion.

In order to obtain further information about the electronic state selectivity of NO^{*} in the ion–ion neutralization processes, the formation of NO^{*} by the reactions of NO⁺ with $C_6F_5Cl^-$, $C_6F_5Br^-$, and $C_6F_5^-$ have been studied here. The electronic state distributions and the rovibrational distributions in each reaction are determined. The observed vibrational and rotational distributions are compared with statistical prior ones in order to obtain dynamical features of the ion–ion neutralization reactions. The results obtained are compared with our previous data for reactions (3) and (4).

II. EXPERIMENT

The flowing-afterglow apparatus used in this study is identical with that used for the ion–ion neutralizations of NO⁺ with SF₆⁻ and C₆F₆⁻.^{14,15} In brief, the metastable He(2³S) atoms and He⁺ and He₂⁺ ions were generated by a microwave discharge of the high purity He gas in a discharge flow operated at 0.5–1.5 Torr (1 Torr=133.3 Pa). All experiments were carried out by removing the He⁺ and He₂⁺ ions by using a pair of ion-collector grids placed between the discharge section and the reaction zone.

 N_2O or NO was admixed with the discharge flow about 10 cm downstream from the center of the discharge, whereas

J. Chem. Phys. 105 (7), 15 August 1996

0021-9606/96/105(7)/2701/9/\$10.00

 C_6F_5X (X=Cl,Br,I) were introduced 10 cm further downstream from an inlet of N₂O or NO. The partial pressure of N₂O or NO in the reaction zone was 15–50 mTorr, while those of C_6F_5X (X=Cl,Br,I) were 1–5 mTorr, as measured by a capacitance manometer. Typical operating pressures were 1.0 Torr for He, 50 mTorr for N₂O, 17 mTorr for NO, and 3 mTorr for C_6F_5X (X=Cl,Br,I).

At low N₂O and NO gas pressures, the vibrationally excited NO⁺($X^{1}\Sigma^{+}$) states arrived at the reaction zone,¹⁷ because the vibrational relaxation rate of NO⁺($X:v' \ge 1$) is slow for the buffer He gas, while it is fast for NO and N₂O

NO⁺(X¹Σ⁺:v"≥1)+He→NO⁺(X¹Σ⁺:v"=0)+He,

$$k_5 < 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$$
 (Ref. 18), (5)

$$NO^{+}(X^{1}\Sigma^{+}:v'' \ge 1) + NO \rightarrow NO^{+}(X^{1}\Sigma^{+}:v'' = 0) + NO,$$
(6)

$$k_6 = 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
 (Ref. 18),

NO⁺ $(X \ ^{1}\Sigma^{+}: v'' \ge 1) + N_2O \rightarrow \text{products},$

$$k_7 \approx 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$
 (Ref. 18). (7)

The spectral features of NO(A-X) were independent of the NO or N₂O gas pressure above 10 mTorr indicating that all of the reactant NO⁺ ions were relaxed completely to the NO⁺($X^{1}\Sigma^{+}:v''=0$) level. Thus all experiments were carried out at NO and N₂O pressures above 10 mTorr, where the contribution of NO⁺($X^{1}\Sigma^{+}:v'' \ge 1$) was negligible.

In our flowing-afterglow experiment, electron/positive ion plasma was created between the two gas inlets of N_2O or NO and C_6F_5X (X=Cl,Br,I) due to the following Penning ionization:

$$\text{He}(2^{3}S) + \text{N}_{2}O \rightarrow \text{N}_{2}O^{+} + \text{He} + e^{-}, \quad (47\%)$$
 (8a)

$$\rightarrow \mathrm{NO}^{+} + \mathrm{N} + \mathrm{He} + e^{-}, \quad (51\%) \qquad (8b)$$

$$\text{He}(2^{3}S) + \text{NO} \rightarrow \text{NO}^{+} + \text{He} + e^{-}.$$
 (100%) (9)

The branching ratios of Eqs. (8a), (8b), and (9) are obtained from mass spectroscopic data of West *et al.*¹⁹ The electron/ positive ion plasma was converted completely to positive ion/negative ion one by the addition of C_6F_5X (Cl,Br,I) with large thermal electron attachment coefficients. The following nondissociative electron attachment leading to parent anions occurs for C_6F_5Cl and C_6F_5Br , while dissociative electron attachment leading to $C_6F_5^-$ preferentially takes place for $C_6F_5I^8$

$$e^{-} + C_6 F_5 Cl \rightarrow C_6 F_5 Cl^{-} (100\%)$$

 $k_{10} = 8.4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1},$ (10)

$$e^{-} + C_6 F_5 Br \rightarrow C_6 F_5 Br^{-}, \quad (\geq 97\%)$$
 (11a)

$$k_{11b} \rightarrow Br^{-} + C_6 F_5, \quad (\leq 3\%)$$

 $k_{11a} + k_{11b} = 8.3 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1},$



FIG. 1. Emission spectra of NO^{*} resulting from the He afterglow reaction (a) with C_6F_5Cl addition and (b) without C_6F_5Cl addition. Spectrum (c) is the difference spectrum between (a) and (b) [(a)–(b)]. The optical resolution is 0.19 nm (FWHM).

$$e^{-} + C_{6}F_{5}I \rightarrow C_{6}F_{5}^{-} + I, \quad (\geq 95\%)$$
(12a)
$$\stackrel{k_{12b}}{\rightarrow} C_{6}F_{5}I^{-}, \quad (\leq 5\%)$$

$$k_{12a} + k_{12b} = 3.1 \times 10^{-8} \text{ cm}^{3} \text{ s}^{-1}.$$
(12b)

The emission spectra resulting from ion–ion neutralization reactions around the C_6F_5X gas inlet, were dispersed in the 190–700 nm region with a Spex 1250M monochromator. All emission spectra presented here are corrected for the relative sensitivity of the optical detection system.

III. RESULTS AND DISCUSSION

A. Excitation processes of NO in the He afterglow

Figures 1(a) and 1(b) show typical emission spectra in the 190-280 nm region obtained by the addition of N₂O into the He afterglow from the first gas inlet with and without addition of C₆F₅Cl from the second gas inlet, respectively, where only $He(2^{3}S)$ was involved as an initial active species. The very weak NO($A^{2}\Sigma^{+} - X^{2}\Pi_{r}$) γ system from v'=0 and the NO($B^{2}\Pi_{r}-X^{2}\Pi_{r}$) β system from v'=0,1are identified in Fig. 1(b) with reference to reported spectral data.^{20–22} Most of these NO(A-X) and NO(B-X) emissions probably result from the three-body $N(^4S)/O(^3P)/M$ (M =He, N_2O) reactions.^{23,24} By the addition of a small amount of C₆F₅Cl into the reaction zone, the NO(A ${}^{2}\Sigma^{+}-X {}^{2}\Pi_{r})$ system is enhanced strongly, as shown in Fig. 1(a). In order to subtract the contribution from the weak underlying NO(A-X,B-X) emissions, Fig. 1(b) is subtracted from Fig. 1(a). The resulting spectrum is shown in Fig. 1(c). It is clear from Fig. 1(c) that the NO(A-X) emission from v'=0 and 1 appears by the C_6F_5Cl addition. All emission spectra presented below were obtained by using the same subtraction method.

On the basis of the reaction scheme given in Sec. II and the energetics, the NO(A, C, D) states can be formed by dis-

(11b)



FIG. 2. Emission spectra of NO* resulting from the NO⁺/ $C_6F_5X^-(X=F,Cl,Br,CF_3)$ and NO⁺/ $C_6F_5^-$ reactions. The optical resolution is 0.19 nm (FWHM).

sociative ion–ion neutralization reactions (13a)-(13c) and/or nondissociative ion–ion neutralization reactions (14a)-(14c)

$$N_2O^+ + C_6F_5Cl^- \rightarrow NO(A) + N + C_6F_5Cl + 2.00 \text{ eV},$$
(13a)

$$\rightarrow \text{NO}(C) + \text{N} + \text{C}_6\text{F}_5\text{Cl} + 0.99 \text{ eV},$$
(13b)

$$\rightarrow \text{NO}(D) + \text{N} + \text{C}_6\text{F}_5\text{Cl} + 0.87 \text{ eV},$$
(13c)

$$NO^{+}+C_{6}F_{5}Cl^{-} \rightarrow NO(A)+C_{6}F_{5}Cl+3.30 \text{ eV},$$
 (14a)

 $\rightarrow \text{NO}(C) + \text{C}_6\text{F}_5\text{Cl} + 2.29 \text{ eV}, \qquad (14b)$

$$\rightarrow$$
 NO(D) + C₆F₅Cl+2.17 eV. (14c)

Since the dissociation energy of $D(C_6F_5-Cl)$ is 3.99 eV,²⁵ dissociative neutralization reactions leading to C_6F_5+Cl are closed in the above processes. In order to examine the contribution from NO⁺/C₆F₅Cl⁻ reactions (14a)–(14c), the source gas of positive ions was changed from N₂O to NO. Since only the NO⁺ ion is formed in the He(2³S)/NO Penning ionization,¹⁹ the contribution from reactions (13a)–(13c) can be removed completely. The emission spectrum of NO^{*} obtained by using NO was the same as that found by using N₂O. This implies reactions (14a)–(14c) dominate the formation of NO^{*}. In order to examine the contribution from N₂O⁺/C₆F₅Cl⁻ reactions (13a)–(13c), NO^{*} emission was

measured in the Ar afterglow, where only the N_2O^+ ion was generated by the Ar^+/N_2O charge-transfer reaction²⁶ and thermal electrons were produced by a microwave discharge of Ar. No evidence of the NO* formation due to the $N_2O^+/C_6F_5Cl^-$ reaction was found. It was therefore concluded that only ion-ion neutralization reactions (14a)-(14c) participate in the excitation of NO(A, C, D). Although the same emission spectra of NO(A, C, D) were obtained by using NO and N₂O as source gases of NO⁺, the signal to noise ratio of the observed spectra was much better by using N2O because background NO* emissions were much weaker. When $C_6F_5Br^-$ and $C_6F_5^-$ were used as negative ions, the same emission spectra of NO* were obtained by using N2O and NO. No evidence of the NO* formation by the $N_2O^+/C_6F_5Br^-$ and $N_2O^+/C_6F_5^-$ reactions was found when N_2O^+ was selectively formed from the Ar^+/N_2O reaction. These findings led us to conclude that NO* was excited by the NO⁺/C₆F₅Br⁻ and NO⁺/C₆F₅⁻ reactions.

Figure 2 shows emission spectra resulting from the ion– ion neutralization reactions of NO⁺ with C₆F₅Cl⁻, C₆F₅Br⁻, and C₆F₅⁻. For comparison, our previous data for C₆F₆⁻ and C₆F₅CF₃⁻ are also given. The v' = 0 v'' progression of the NO(*A*-*X*) emission system is observed strongly in all spectra. Although the NO($C {}^{2}\Pi_{r} - X {}^{2}\Pi_{r}, D {}^{2}\Sigma^{+} - X {}^{2}\Pi_{r})$ systems can be clearly identified in the NO⁺/C₆F₆⁻ and NO⁺/C₆F₅CF₃⁻ reactions, these systems and the NO(*A*-*X*) system from v' > 0 are either weak or absent for the other



FIG. 3. Expanded spectra of NO^{*} in the 190–230 nm region resulting from the NO⁺/C₆F₅X⁻(X=F,Cl,Br,CF₃) and NO⁺/C₆F₅⁻ reactions. The optical resolution is 0.36 nm (FWHM).



FIG. 4. Potential energy diagram of NO and NO $^+$. Adopted from Refs. 22 and 27.

three reactions. In order to examine whether the NO(C-X,D-X) systems and the NO(A-X) system from v' > 0 are present or absent, higher-sensitivity measurements of the spectra in the 190–230 nm region were carried out. The spectra obtained are shown in Fig. 3 along with our previous data for C₆F₆⁻ and C₆F₅CF₃⁻, where the NO(C-X,D-X) systems appear strongly. Although weak NO(C-X,D-X) emissions from v'=0 and NO(A-X) emission from v'=1 are identified for C₆F₅Cl⁻, only very weak NO(A-X) emission from v'=1 is observed for C₆F₅Br⁻. Summarizing the above facts, neutralization processes (15a) and (16) are found in the NO⁺/C₆F₅Br⁻ and NO⁺/C₆F₅⁻ reactions, though processes (15b) and (15c) cannot be observed

$$NO^+ + C_6F_5Br^- \rightarrow NO(A) + C_6F_5Br + 3.31 \text{ eV},$$
 (15a)

$$\rightarrow$$
NO(C)+C₆F₅Br+2.30 eV, (15b)

$$\rightarrow$$
NO(D)+C₆F₅Br+2.18 eV, (15c)

$$NO^+ + C_6F_5^- \rightarrow NO(A) + C_6F_5 + 0.38 \text{ eV},$$
 (16)

Since $D(C_6F_5-Br)$ is 3.5 eV,²⁵ dissociative neutralization reactions leading to C_6F_5+Br are excluded from the possible processes.

Figure 4 shows a potential-energy diagram of NO and NO⁺, and the energies of NO⁺+C₆F₅X⁻ (X=F,Cl,Br,CF₃) and NO⁺+C₆F₅⁻ ion pairs at infinite intermolecular distances. Among a number of emitting excited states in NO,^{22,27} the $A^{2}\Sigma^{+}$, $B^{2}\Pi_{r}$, $C^{2}\Pi_{r}$, $D^{2}\Sigma^{+}$, and $E^{2}\Sigma^{+}$ states can be detected by observing the $A \rightarrow X$, $B \rightarrow X$, $C \rightarrow X$, $D \rightarrow X$, and $E \rightarrow A$ emission systems in the ultraviolet and visible region. Although the NO(A - X) transition was observed in all reactions, no reactions exhibited the

TABLE I. Relative formation rates of NO^{*} in the ion–ion neutralization reactions of NO⁺ with $C_6F_5X^-(X=F_5Cl,Br,CF_3)$ and $C_6F_5^-$.

		Relative formation rate			
Anion		NO($A^{2}\Sigma^{+}$)	NO($C^2 \Pi_r$)	NO($D^{2}\Sigma^{+}$)	
$C_6F_6^-$	Ref. 15	1.00	0.13 ± 0.04	0.24 ± 0.04	
$C_6F_5Cl^-$	This work	1.00	0.018 ± 0.002	0.029 ± 0.003	
$C_6F_5Br^-$	This work	1.00	0.00	0.00	
$C_6F_5^-$	This work	1.00			
$\mathrm{C_6F_5CF_3^-}$	Ref. 16	1.00	0.041 ± 0.03	0.060 ± 0.010	

NO(B-X, E-A) transitions. The NO(C-X, D-X) transitions were detected in the NO⁺/C₆F₅X⁻ (X=F,Cl,CF₃) reactions.

B. Internal state distributions of NO*

The relative formation rates of NO(A, C, D) in each reaction were determined by comparing the total emission intensities of the NO(A-X, C-X, D-X) systems. The results obtained are given in Table I along with our previous results for $C_6F_6^-$ and $C_6F_5CF_3^-$. These values were obtained assuming that the $C \rightarrow A$ and $D \rightarrow A$ radiative-cascade processes are negligible for the formation of NO(A).^{14,15} The relative formation rates of NO(A, C, D) were unchanged in the He pressure range 0.5–1.5 Torr, leading us to conclude that the electronic quenching of NO(A, C, D) by collisions with the buffer He gas is insignificant during short radiative lifetimes of $\tau = (192 - 202) \pm 14$ ns for NO(A ${}^{2}\Sigma^{+}: v' = 0, 1), {}^{20} \leq 2.7$ ± 1.5 ns for NO($C^2 \Pi_r : v' = 0$),²⁸ and 16.1 ± 0.7 ns for NO($D^{2}\Sigma^{+}:v'=0$).²⁸ The relative formation rates of NO(C,D) decrease with increasing mass of halogen atom substituted to the C₆F₅ group and they become zero for the case of the heaviest $C_6F_5Br^-$ ion. The relative formation rates of NO(C,D) increase again by the substitution of a heavy CF₃ molecule.

Although only the v'=0 level is found for NO(*C*,*D*) in the NO⁺/C₆F₅Cl⁻ reaction, both the v'=0 and v'=1 levels are observed for NO(*A*) in the NO⁺/C₆F₅Cl⁻ and NO⁺/C₆F₅Br⁻ reactions. The relative vibrational populations of NO(*A*:v'=0,1) were determined from the intensity ratio



FIG. 5. The observed and calculated spectra of the (0,1) band of NO($A^{2}\Sigma^{+}-X^{2}\Pi_{r}$) obtained from the NO⁺/C₆F₅Cl⁻ reaction at thermal energy. The optical resolution is 0.085 nm (FWHM).

TABLE II. Observed and calculated prior vibrational populations of NO(A, C, D) produced from the ion–ion neutralization reactions of NO⁺ with C₆F₅X⁻(X=F,Cl,Br,CF₃) and C₆F₅⁻.^a

			NO(A)		NO(C)		NO(D)	
Anion			v'=0	v'=1	v'=0	v'=1	v'=0	v'=1
$C_6F_6^-$	Ref. 15	Obs. Calc.	1.00 1.00	0.00 $2.6(-2)^{b}$	1.00 1.00	0.00 2.6(-3)	1.00 1.00	0.00 2.0(-3)
C ₆ F ₅ Cl ⁻	This work	Obs. Calc.	1.00 1.00	2.1(-3) 4.1(-2)	1.00 1.00	0.00 7.8(-3)	1.00 1.00	0.00 7.1(-3)
$C_6F_5Br^-$	This work	Obs. Calc.	1.00 1.00	1.1(-2) 4.2(-2)	0.00 1.00	0.00 8.1(-3)	0.00 1.00	0.00 7.3(-3)
$C_6F_5^-$	This work	Obs. Calc.	1.00 1.00	0.00 1.2(-21)				
$C_6F_5CF_3^-$	Ref. 16	Obs. Calc.	1.00 1.00	0.00 8.3(-3)	1.00 1.00	0.00 3.8(-4)	1.00 1.00	0.00 2.4(-4)

^aValues in parentheses are power of 10 multiplying the entry.

^bThis value was erroneously reported as 0.26 in Ref. 15.

between the (0,0) and (1,0) bands of NO(A-X) and their known Einstein coefficients.²⁰ The N_1/N_0 ratios are very small, as shown in Table II, for both reactions. The rotational distributions of NO(A, C, D) resulting from the reactions with $C_6F_5Cl^-$, $C_6F_5Br^-$, and $C_6F_5^-$ were determined by a computer simulation of the NO(A-X, C-X, D-X) emissions. The simulation method was the same as that reported previously.^{14,15} As a representative result, the observed NO(A-X) spectrum in the NO⁺/C₆F₅Cl⁻ reaction is compared with the best fit one (Fig. 5). The observed NO(A -X, C-X, D-X) spectra can be reproduced by single Boltzmann rotational temperatures given in Table III. For comparison, the rotational temperatures of NO* formed in the reactions with $C_6F_6^-$ and $C_6F_5CF_3^-$ are given in Table III. It should be noted that the rotational temperatures are relatively low for all the reactions. The T_r values of NO(A), NO(C), and NO(D) in the v'=0 levels are independent of the negative ion.

The vibrational and rotational distributions of NO(A-X, C-X, D-X) were independent of the He buffer gas pressure over the range of 0.5–1.5 Torr. In order to further examine the effects of the collisional relaxation, the vibrational and rotational distributions of NO(A) produced from the He(2 ³S)/NO reaction in the He flowing afterglow at 0.5–1.5 Torr were compared with those measured using a beam apparatus²⁹ at 3 mTorr. The vibrational and rotational

distributions of NO(*A*) were identical between the two experiments. On the basis of these findings, the vibrational and rotational relaxation of NO(*A*,*C*,*D*) by collisions with He atoms is insignificant during short radiative lifetimes of 2.7–202 ns^{20,28} under the operating conditions.

By using established rovibrational distributions of NO(A, C, D), we determined the average vibrational and rotational energies of NO(A, C, D) and their average fractions of the total excess energy, which are denoted by $\langle E_v \rangle$, $\langle f_v \rangle$, $\langle E_r \rangle$, and $\langle f_r \rangle$, respectively. The same relations as those reported previously^{14–16} were used for the evaluation of these values. The $\langle E_n \rangle$, $\langle f_n \rangle$, $\langle E_r \rangle$, and $\langle f_r \rangle$ values obtained are given in Table IV together with our previous data for $C_6F_6^$ and $C_6F_5CF_3^-$. Either no or very small amount of the excess energy is deposited into the vibrational mode of NO(A), while no energy is partitioned into the vibration of NO(C,D)because of the lack of emission from $v' \ge 1$. Since the $\langle f_v \rangle$ and $\langle f_r \rangle$ values are very small for all cases, the $\langle f_v \rangle + \langle f_r \rangle$ values are small ($\leq 11\%$). On the basis of these facts, most of the excess energy must be released as the internal energy of C_6F_5X (X=F,Cl,Br,CF₃) and C_6F_5 and/or the relative translational energy of the products.

Since the formation of NO(A, C, D) takes place via strongly attractive ion-pair potentials, long lived (NO⁺-C₆F₅X⁻) and (NO⁺-C₆F₅⁻) complexes can be postulated. According to a simple statistical theory,^{30–32} the rota-

TABLE III. Rotational temperatures of NO^{*} produced from the ion-ion neutralization reactions of NO⁺ with $C_6F_5X^-(X=F,Cl,Br,CF_3)$ and $C_6F_5^-$.

		T_r (K)			
Anion		NO(A:v'=0)	NO(A:v'=1)	NO(C:v'=0)	NO(D:v'=0)
$C_6F_6^-$	Ref. 15	500±50		300±50	400±50
$C_6F_5Cl^-$	This work	500 ± 50	500 ± 50	300 ± 50	400 ± 50
$C_6F_5Br^-$	This work	500 ± 50	400 ± 50		
$C_6F_5^-$	This work	500 ± 50			
$C_6F_5CF_3^-$	Ref. 16	500±50		300±50	400±50

TABLE IV. Average vibrational and rotational energies deposited into NO(*A*,*C*,*D*) and their fractions of the total available energies in the ion–ion neutralization reactions of NO⁺ with $C_6F_5X^-(X=F,Cl,Br,CF_3)$ and $C_6F_5^-$.

Anion		NO*	$E_v \; ({\rm meV})$	$E_r \; (\mathrm{meV})$	$\langle f_v \rangle$	$\langle f_r \rangle$
$C_6F_6^-$	Ref. 15	NO(A)	0	43±4	0	0.015
		NO(C)	0	26±4	0	0.014
		NO(D)	0	34 ± 4	0	0.019
$C_6F_5Cl^-$	This work	NO(A)	0.6	43±4	0.0002	0.013
		NO(C)	0	26±4	0	0.011
		NO(D)	0	34 ± 4	0	0.016
$C_6F_5Br^-$	This work	NO(A)	3.2	43±4	0.001	0.013
$C_6F_5^-$	This work	NO(A)	0	43 ± 4	0	0.11
$C_6F_5CF_3^-$	Ref. 16	NO(A)	0	43±4	0	0.015
		NO(C)	0	26±4	0	0.014
		NO(D)	0	34±4	0	0.019

tional and vibrational populations of a given (v', J') level are given by the relations

$$P_{v'}^{0} \propto [E_{\text{tot}} - E(A, C, D; v')]^{s+3},$$
(17a)

$$P_{J'}^{0} \propto (2J'+1) [E_{\text{tot}} - E(A, C, D; v', J')]^{s+2}.$$
(17b)

Here, E_{tot} is the total excess energy released in each process, E(A, C, D: v', J') is a rovibrational energy of the (v', J')level, and *s* is the number of normal modes (3n-6 for an n)atom nonlinear molecule:s = 30 for C_6F_5X and s = 27 for C_6F_5). By using Eq. (17a), the prior vibrational distributions for the lowest v' = 0 and 1 levels are estimated for each exothermic process, as shown in Table II. The statistical theory predicts very low vibrational excitation of NO(A, C, D), being consistent with the experimental observation. However, it was found that NO(A) from the $NO^+/C_6F_5Br^-$ reaction is more vibrationally excited than that from the $NO^+/C_6F_6^-$ and $NO^+/C_6F_5Cl^-$ reactions, even though similar vibrational excitation is expected among the three reactions based upon the statistical theory.

As a representative result, the prior rotational distribution of NO(A:v'=0) in the NO⁺/C₆F₅Cl⁻ reaction is compared with the observed one in Fig. 6(a). The calculated prior distribution is more excited than the observed one. Similar results have also been obtained for NO(A:v'=1), NO(C:v'=0), and NO(D:v'=0) in the NO⁺/C₆F₅Cl⁻ reaction and NO(A:v'=0,1) in the NO⁺/C₆F₅Br⁻ reaction. On the other hand, the prior distribution of NO(A) from the NO⁺/C₆F₅⁻ reaction is less excited than the observed one. The deviation from the prior distribution can often be represented in the form of linear surprisal,^{30–32}

$$I(g_{J'}) = -\ln[(P(J')/P^0(J')] = \lambda^0 + \theta_{v'}g_{J'}, \qquad (18)$$

where $g_{J'} = E_{J'}/(E_{tot} - E_{v'})$. As an example, the surprisal plot for NO(A:v'=0) in the NO⁺/C₆F₅Cl⁻ reaction is shown in Fig. 6(b). A satisfactory linear relationship is found. Similar linear relationships were found for the other cases. From the slopes of the surprisal plots, the linear rotational surprisal parameters $\theta_{v'}$ are obtained for each neutralization process (Table V). As described above, there are significant discrepancies between the observed vibrational and rotational distributions and the statistical ones. It was there-



FIG. 6. (a) Observed and calculated prior rotational distributions and (b) surprisal plot for NO(A:v'=0) produced from the NO⁺/C₆F₅Cl⁻ reaction.

fore concluded that the formation of NO^{*} by the ion–ion neutralization reactions of NO⁺ with $C_6F_5Cl^-$, $C_6F_5Br^-$, and $C_6F_5^-$ does not proceed through long-lived ion-pair complexes, where the excess energy is randomized statistically to neutral products. The ion–ion neutralization reactions have an enormous cross section, due to the strong coulombic attraction between the ion pair. Because of the large impact parameter, the conservation of angular momentum inhibits close contact, i.e., a strong collision. Therefore the excess energy will not be randomized statistically in the reaction products.

C. Reaction mechanism

The ion-ion neutralization reactions studied here proceed through $V(NO^+, C_6F_5X^-)$ and $V(NO^+, C_6F_5^-)$ ion-pair

TABLE V. Rotational surprisal parameters for NO(A, C, D) produced from the ion–ion neutralization reactions of NO⁺ with C₆F₅Cl⁻, C₆F₅Br⁻, and C₆F₅⁻.

	$\theta_{v'}$				
Anion	NO(A:v'=0)	NO(A:v'=1)	NO(C:v'=0)	NO(D:v'=0)	
$C_6F_5Cl^-$	44.0	37.1	55.5	29.9	
$C_6F_5Br^-$	44.2	55.1			
$C_6F_5^-$	-31.1				

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FIG. 7. The entrance $NO^++C_6F_5X^-(X=F,Cl,Br,CF_3)$ and $NO^++C_6F_5^-$ ionpair potentials and the exit $NO^*+C_6F_5X(X=F,Cl,Br,CF_3)$ and $NO^*+C_6F_5$ potentials.

potentials, as shown in Fig. 7. NO* arises from diversion of trajectories from the entrance $V(NO^+, C_6F_5X^-)$ or $V(NO^+, C_6F_5^-)$ potential to the exit $V(NO^*, C_6F_5X)$ or $V(NO^*, C_6F_5)$ potentials due to a strong coupling between the two potentials. Thus the electronic state distribution of NO* reflects the different crossing point of the strongly attractive ion-pair entrance potentials and rather flat covalent exit potentials at the crossing points and the coupling between each pair of states. The NO⁺-C_6F_5X⁻ (X=Cl,Br) and NO⁺-C_6F_5⁻ separations at crossing points R_c are calculated using the same relation as that reported previously.^{14,15} In the calculations, the following electron affinities were used: $C_6F_5Cl (0.48 \text{ eV})$,³³ $C_6F_5Br (0.47 \text{ eV})$,³³ and $C_6F_5 (3.4 \text{ eV})$.³⁴

The ion-ion neutralization reactions proceed through an approach of the NO⁺($X^{1}\Sigma^{+}$) and C₆F₅X⁻ or C₆F₅⁻ ion pair under their mutual Coulombic field followed by an electron transfer from C₆F₅X⁻ or C₆F₅⁻ to NO⁺. Since the Born-Oppenheimer approximation holds during a fast electron transfer, the relative motion of an ion pair is unchanged after the neutralization. Therefore, a large kinetic energy resulting from the strong mutual Coulombic force is conserved at the instant of electron transfer. The electron transfer occurs at relatively large intermolecular separations of 4.3–38 Å,

TABLE VI. Crossing points in the ion–ion neutralization reactions of NO⁺ with $C_6F_5Cl^-$, $C_6F_5Br^-$, and $C_6F_5^-$.

	R_c (Å)				
NO*	$NO^+/C_6F_5Cl^-$	$\mathrm{NO}^+/\mathrm{C}_6\mathrm{F}_5\mathrm{Br}^-$	$NO^{+}/C_{6}F_{5}^{-}$		
NO(A)	4.35	4.34	37.8		
NO(B)	$(4.57)^{a}$	(4.56)	(65.2)		
NO(C)	6.27	(6.24)			
NO(D)	6.61	(6.65)			
NO(E)	(11.7)	(11.6)			

 ${}^{a}R_{c}$ values for unobserved NO* states are given in parentheses.

where interactions between neutral NO^{*} and C_6F_5X or C_6F_5 molecules are small. Thus, a large amount of the kinetic energy will remain in the neutral products.

Under the Born-Oppenheimer approximation, the internuclear separations of NO⁺(X), C₆F₅X⁻, and C₆F₅⁻ are also unchanged just after the neutralization, since the equilibrium nuclear separation of NO⁺(X ¹ Σ ⁺:1.063 22 Å) is close to those of NO(A ${}^{2}\Sigma^{+}$:1.0634 Å), NO(C ${}^{2}\Pi_{r}$:1.062 Å), and NO($D^{2}\Sigma^{+}$:1.0618 Å),²² the formation of NO(A, C, D) with the largest Franck–Condon factors for the $NO^+(X^{1}\Sigma^+) \rightarrow NO(A, C, D)$ neutralization will be most favorable. This prediction is consistent with the preferential formation of NO(A, C, D) in the v' = 0 levels. Although no vibrational excitation of NO(A) was found in the $NO^+/C_6F_6^-$, $NO^+/C_6F_5^-$, and $NO^+/C_6F_5CF_3^-$ reactions, the very low vibrational excitation of NO(A) was observed in the NO⁺/C₆F₅Cl⁻ and NO⁺/C₆F₅Br⁻ reactions. For the latter reactions, the NO(A) formation occurs via curve crossings at shorter range than that for the former reactions, so that the $NO^+(X)$ potential is slightly perturbed by an access of the negative ion.

Unfortunately, to the best of our knowledge, detailed equilibrium geometries of $C_6F_5CF_3^-$ and $C_6F_5^-$ are unknown. On the other hand, some structural information on the geometry of $C_6F_6^-$ has been obtained from electron spin resonance (ESR) coupling constants measured in the condensed phase.^{35–37} The resulting geometry depends on the theoretical treatment. Both carbon skeleton distorted to a cyclohexane like chair³⁶ and undistorted carbon skeleton but out of plane C-F bonds³⁷ have been proposed for the equilibrium geometry of $C_6F_6^-$. These geometries are significantly different from that of the planer C_6F_6 molecule. For $C_6F_5Cl^-$ and C₆F₅Br⁻, some changes in the C–Cl and C–Br bond lengths are expected between the neutral molecules and anions on the basis of the ESR coupling constants,³⁸ because an excess electron is located on the C–Cl or C–Br σ^* orbital. Since the equilibrium geometries of $C_6F_5X^-$ (X=F,Cl,Br) are different from those of C_6F_5X , some energy will be released as the vibrational energy of C_6F_5X in the neutralization reaction. Consequently, almost all excess energy will be transformed into the relative kinetic energy of the neutral products and the vibrational energy of C_6F_5X .

For the production of NO(A, C, D), the symmetry of the reactant and product potentials must be matched. Although NO(A ${}^{2}\Sigma^{+}$) and NO(D ${}^{2}\Sigma^{+}$) are formed, NO(E) with the same ${}^{2}\Sigma^{+}$ symmetry is not produced in the NO⁺/C₆F₅X⁻ (X=F,Cl,Br,CF₃) reactions. It is therefore reasonable to assume that the symmetry of the product potential is not a significant factor for the electronic state selectivity of NO* in the NO⁺/C₆F₅X⁻ (X=F,Cl,Br,CF₃) reactions. Here, it was found that the electronic state selectivity of NO* is the same for the reactions with $C_6F_6^-$, $C_6F_5Cl^-$, and $C_6F_5CF_3^-$ with D_{6h} , D_{2h} , and C_s molecular symmetries, respectively. On the other hand, the electronic selectivity of $C_6F_5Br^-$ is different from that of $C_6F_5Cl^-$, even though the molecular symmetry is the same. These facts led us to conclude that molecular symmetry of negative ion is not a significant factor for assessing the electronic selectivity of NO*.

There exist two types for the electronic state selectivity in the ion-ion neutralization reactions of NO⁺ with negative ions. One is the formation of the $A^{2}\Sigma^{+}$, $B^{2}\Pi_{r}$, and $E^{2}\Sigma^{+}$ states, which is independent of the negative ion. The other is the formation of the $C^{2}\Pi_{r}$ and $D^{2}\Sigma^{+}$ states, which depends strongly on the negative ion. For the former type of reactions, the A state is formed in all reactions, even though there are significant differences in the crossing points (4.3–38 Å) as shown in Table VI and in the nature of the highest occupied molecular orbital (HOMO) in the negative ions. The formation of the A state from the NO⁺/C₆ F_5^- reaction occurs at an especially long intermolecular distance of 38 Å. A similar near-resonant ion-ion neutralization process via curve crossings at long intermolecular distances has recently been found in the He⁺/C₆F₆⁻ reaction³⁹

$$\text{He}^+ + \text{C}_6\text{F}_6^- \rightarrow \text{He}(4p\ ^3P, 4d\ ^3D, 4d\ ^1D) + \text{C}_6\text{F}_6.$$
 (19)

The B and E states are absent in all cases. The neutralization reactions leading to the A, C, D, and E states proceed through an electron jump from the HOMO orbital of the negative ion to the $3s\sigma$, $3p\pi$, $3p\sigma$, and $4s\sigma$ orbitals of NO^+ , respectively.²² The preferential formation of the A state and the lack of the high Rydberg E state in all cases imply that an electron jump from the HOMO orbital of the negative ion to the NO⁺(3s σ) orbital occurs efficiently, while that to the upper NO⁺(4s σ) orbital does not take place. One reason for the lack of the E state may be curve crossings at long intermolecular distances (≥ 11.6 Å), where interactions between the entrance and exit potentials are very weak. The lack of the B state is attributed to a low probability of two-electron transfer in the neutralization process and small Franck–Condon factors between the $NO^+(X)$ and NO(B) states, as discussed previously.¹⁴ In the $NO^+/C_6F_5X^-$ (X=F,Cl,Br) reactions, the branching ratios of the C and D states decrease with increasing the mass of the halogen atom in the anion and becomes zero for the heaviest $C_6F_5Br^-$ molecule. Although the R_c values for the formation of the C and D states are nearly the same between the $NO^+/C_6F_5Cl^-$ and $NO^+/C_6F_5Br^-$ reactions, there is a significant difference in the formation of the C and D states between the two reactions. This implies that the R_c value is not a critical factor in assessing the electronic state selectivity of the C and D states.

There is a possibility that the electronic state selectivity arises from the different electronic structure of the negative ions. Gant and Christophorou⁴⁰ have predicted the electronic configuration of the ground state of C₆F₆ is $(\pi_1)^2(\pi_2)^2(\pi_3)^2(\pi_4)$ or $(\pi_1)^2(\pi_2)^2(\pi_3)^2(\pi_5)$. According to their results, the HOMO of $C_6F_6^-$ is π_4 or π_5 . However, later ESR data in the condensed phase demonstrated that an excess electron is captured into the σ^* orbital.^{35–37} The fact that the HOMO of $C_6F_6^-$ has σ^* character has been explained by the $\sigma^* - \pi^*$ crossover. The high electronegativity of F atom leads to a lowering of the lowest unoccupied molecular orbital (LUMO) energy. However, the energy lowering occurs to a much lesser extent for π^* relative to the σ^* LUMO. Fluorine is strongly electron withdrawing by the field effect but is weakly electron pair donating (π^* donation). Therefore, significant stabilization by the field effect occurs for the σ^* orbital, while the diffuse π^* orbital is less strongly stabilized by the field effect and destabilized by the π^* donation. A similar $\sigma^* - \pi^*$ crossover also occurs for C₆F₅Cl⁻ and C₆F₅Br⁻ on the basis of the ESR data in the condensed phase.³⁸ Therefore, the excess electron is dominantly located on the C–Cl or C–Br σ^* orbital. Although the formation of C₆F₅Cl⁻, Cl⁻, C₆F₅Br⁻, and Br⁻ have been observed at low energy electron attachment, the $C_6F_5^-$ formation has not been observed due to the higher endothermicity.^{8,41} This result is consistent with the fact that the excess electron has Cl⁻ or Br⁻ σ^* character in the ground states of C₆F₅Cl⁻ and $C_6F_5Br^-$.

For an efficient electron transfer leading to NO(C,D), a favorable overlap is necessary between the σ^* orbital of $C_6F_5X^-(X)$ and the $3p\pi$ or $3p\sigma$ orbital of NO⁺ $(X^{-1}\Sigma^+)$ at the crossing points. In the case of $C_6F_6^-$, a negative charge is equally delocalized over the six C-F σ^* orbitals, while the negative charge is dominantly located on one C-Cl or C-Br σ^* orbital for the cases of C₆F₅Cl⁻ and C₆F₅Br⁻. The high branching ratios of the C and D states in the NO⁺/C₆F₆⁻ reaction in comparison with those in the NO⁺/C₆F₅Cl⁻ and $NO^+/C_6F_5Br^-$ reactions imply that a favorable overlap occurs between the delocalized σ^* orbital of $C_6F_6^-$ and the $3p\pi$ or $3p\sigma$ orbital of NO⁺, while such an overlap is inefficient for the cases of localized σ^* orbitals of C₆F₅Cl⁻ and $C_6F_5Br^-$. The lack of the C and D states in the NO⁺/C₆F₅Br⁻ reaction suggests that the $\sigma^* - 3p\pi$ and $\sigma^* - 3p\sigma$ interactions become negligibly weak by the substitution of Br with a lower electronegativity from Cl. On the basis of the above findings, different nature of the HOMO orbitals of C₆F₅X⁻ will be an important factor for assessing the electronic state selectivity in the ion-ion neutralization reactions. In order to confirm this prediction, further detailed experimental and theoretical studies will be required.

IV. SUMMARY

Ion–ion neutralization reactions of NO⁺($X^{1}\Sigma^{+}:v''=0$) with $C_6F_5X^-$ (X=Cl,Br) and $C_6F_5^-$ have been studied by using a flowing-afterglow method. The results obtained are compared with those of our previous data for the NO⁺/C₆ $F_6^$ and NO⁺/C₆F₅CF₃⁻ reactions in order to examine the dependence of the electronic state selectivity on the negative ion with a C_6F_5 group. It was demonstrated that there exist two types in the electronic state selectivity. One is the formation of the NO(A ${}^{2}\Sigma^{+}$) state, which is independent of the negative ion. The other is the formation of the NO($C^{2}\Sigma^{+}, D^{2}\Pi_{r}$) states, which depends on the negative ion. By the substitution of a heavier halogen atom to C_6F_6 , the branching ratios of the C and D states decreased: 0.27 $(C_6F_6^-)$, 0.045 $(C_6F_5Cl^-)$, and 0 $(C_6F_5Br^-)$. The significant decrease in the branching ratios of the C and D states for $C_6F_5Cl^-$ and $C_6F_5Br^-$ was explained by the weaker interactions between the localized C–Cl or C–Br σ^* orbital and the $3p\pi$ and $3p\sigma$ orbitals of NO⁺ than those between the delocalized C-F σ^* orbital and the $3p\pi$ and $3p\sigma$ orbitals of NO⁺. Only the A state was produced in the NO⁺/C₆ F_5^- reaction, because the formation of the upper C and D states is energetically closed. Only the v' = 0 level was excited in the formation of the C and D states by the $NO^+/C_6F_5Cl^-$ and $NO^+/C_6F_5Br^-$ reactions and in the formation of the A state in the NO⁺/C₆ F_5^- reaction. On the other hand, the v'=0 and 1 levels of NO(A) were produced in the NO⁺/C₆F₅Cl⁻ and $NO^+/C_6F_5Br^-$ reactions, though the relative populations of v' = 1 are small. The small vibrational excitation of NO(A) in the NO⁺/C₆F₅Cl⁻ and NO⁺/C₆F₅Br⁻ reactions can be explained as due to the perturbation of the $NO^+(X)$ potential by an access of the negative ion. The rotational temperatures of NO(A:v'=0,1), NO(C:v'=0), and NO(D:v'=0) were expressed by single Boltzmann rotational temperatures of 450 ± 100 , 300 ± 50 , and 400 ± 50 K, respectively. The vibrational and rotational distributions indicated that only 1%-11% of the total excess energy is partitioned into the rovibrational energy of NO*. It was therefore concluded that a major part of the excess energy is partitioned into the relative translational energy of the products and the vibrational energy of C₆F₅X. The observed vibrational and rotational distributions disagreed from statistical prior ones, indicating that the reaction dynamics is not governed by the simple statistical theory because of the large impact parameter.

ACKNOWLEDGMENTS

The authors are grateful to Professor Hiroshi Shimamori at Fukui Institute of Technology and Dr. Shuji Kato at Himeji Institute of Technology for their helpful discussion. This work has been supported by the Morino Foundation for molecular science (1992), the Iwatani Naoji Memorial Foundation (1993), Showa Shell Sekiyu Foundation for environmental research (1995), and a Grant-in-Aid for Scientific Research No. 06453026 from the Japanese Ministry of Education, Science, and Culture (1994–1996).

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