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The Influence of Vibrational Excitation of $NO^+(X^1\Sigma^+ : v'')$ on the Formation of NO^* by the $NO^+ + C_6F_6^-$ Neutralization Reaction at Thermal Energy

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The $NO(A^2\Sigma^+\text{-}X^2\Pi_r, C^2\Pi_r\text{-}X^2\Pi_r, D^2\Sigma^+\text{-}X^2\Pi_r)$ emissions resulting from the mutual ion–ion neutralization reaction between $NO^+(X^1\Sigma^+)$ and $C_6F_6^-$ have been measured at various source gas pressures of NO^+ in a flowing afterglow in order to examine the influence of vibrational excitation in $NO^+(X : v'')$. N_2O was used as a source gas of $NO^+(X)$. The NO(A-X, C-X, D-X) emissions from only the $v' = 0$ level were observed at high N_2O pressures above ca. 60 mTorr (1 Torr = 133.322 Pa), where only $NO^+(X : v'' = 0)$ was present. On the other hand, the NO(A-X) emission from $v' = 1$, 2 and the NO(D-X) emission from $v' = 1$ appeared at low N_2O pressures below ca. 60 mTorr, where $NO^+(X : v'' > 0)$ was present. It was found that vibrational excitation in $NO^+(X : v'')$ results in vibrational excitation of the product $NO(A, D : v' = v'')$ molecule because of favorable Franck–Condon factors for the $NO^+(X : v'') \rightarrow NO(A, D : v' = v'')$ neutralization. The fact that the vibrational excitation of NO(D) is slightly higher than that of NO(A) indicated that the relative coupling strength between $NO^+(X : v'' > 0) + C_6F_6^-$ and $NO(D : v' = v'') + C_6F_6$ to that between $NO^+(X : v'' = 0) + C_6F_6^-$ and $NO(D : v' = 0) + C_6F_6$ is larger than that in the corresponding processes leading to $NO(A : v' = v'')$. The lack of vibrational excitation of NO(C) was explained by the predissociation of $NO(C : v' > 0)$.

Mutual neutralization reactions between positive and negative ions contribute significantly to the loss of charged particles from natural and manmade plasmas because of their large reaction rate coefficients due to a long-range Coulombic attractive force. Many neutral reactions having large reaction rate coefficients proceed through harpoon-type mechanism (1) via an ion-pair intermediate $[A^+{\cdot}BC^-]$:[1)]

$$A + BC \rightarrow [A^+{\cdot}BC^-] \rightarrow AB + C. \tag{1}$$

Since the nature of the $[A^+{\cdot}BC^-]$ ion-pair is believed to govern the reaction dynamics, the studies of neutralization reactions between positive and negative ions are of great significance in understanding of chemical reaction dynamics between neutral species. Although reaction rate coefficients of ion–ion neutralization reactions have been measured for various reaction systems, little information has been obtained on the internal state distribution of neutral products.[2—4)] We have recently studied the formation processes of NO^* by the $NO^+(X^1\Sigma^+)/SF_6^-$ and $NO^+(X^1\Sigma^+)/C_6F_6^-$ neutralization reactions by observing NO^* emissions in a helium flowing afterglow:[5,6)]

$$NO^+(X^1\Sigma^+ : v'' = 0) + SF_6^- \rightarrow NO^* + SF_6, \tag{2}$$

$$NO^+(X^1\Sigma^+ : v'' = 0) + C_6F_6^- \rightarrow NO^* + C_6F_6. \tag{3}$$

The positive NO^+ ion was generated by $He(2^3S)$ Penning ionization of NO or N_2O, while the negative SF_6^- or $C_6F_6^-$ ion was formed by a fast nondissociative electron attachment to SF_6 or C_6F_6 10 cm downstream from the NO or N_2O gas inlet:

$$He(2^3S) + NO \rightarrow NO^+ + He + e^-, \tag{4}$$

$$He(2^3S) + N_2O \rightarrow NO^+ + N + He + e^-, \tag{5}$$

$$e^- + SF_6 \rightarrow SF_6^-, \quad (k_6 = 3.1 \times 10^{-7}\ \mathrm{cm^3\,s^{-1}}\ [\text{Ref. 7}]), \tag{6}$$

$$e^- + C_6F_6 \rightarrow C_6F_6^-, \quad (k_7 = 2.1 \times 10^{-7}\ \mathrm{cm^3\,s^{-1}}\ [\text{Ref. 8}]). \tag{7}$$

In our measurements, a sufficient amount of NO or N_2O was injected into the flow tube in order to collisionally relax the $NO^+(X^1\Sigma^+ : v'' > 0)$ states to the ground vibrational state. Only the $NO(A^2\Sigma^+\text{-}X^2\Pi_r)$ emission from the $v' = 0$ level was excited in the $NO^+(X^1\Sigma^+)/SF_6^-$ reaction (2) with a low effective Boltzmann rotational temperature of 600±50 K. On the other hand, the $NO(A^2\Sigma^+\text{-}X^2\Pi_r, C^2\Pi_r\text{-}X^2\Pi_r, D^2\Sigma^+\text{-}X^2\Pi_r)$ emissions from the $v' = 0$ level were excited in the $NO^+(X^1\Sigma^+)/C_6F_6^-$ reaction (3) with low effective Boltzmann rotational temperatures of 400±150 K. The low vibrational and rotational excitation in NO(A, C, D) led us to conclude that most of the excess energy is released as the relative translational energy of the neutral products.

More recently, we have investigated the effects of vibrational excitation in $NO^+(X: v'')$ for the NO^+/SF_6^- reaction by reducing the source gas pressure of NO^+.[9] It was found that vibrational excitation in $NO^+(X: v'')$ results in vibrational excitation of the product $NO(A: v' = v'')$ molecule with a low rotational excitation:

$$NO^+(X^1\Sigma^+: v'' = 0\text{—}2) + SF_6^- \rightarrow NO(A^2\Sigma^+: v' = v'') + SF_6. \quad (8)$$

In the present study, the effects of vibrational excitation in $NO^+(X: v'')$ was studied for the $NO^+/C_6F_6^-$ reaction by reducing the source gas pressure of NO^+:

$$NO^+(X^1\Sigma^+: v'' > 0) + C_6F_6^- \rightarrow NO(A^2\Sigma^+,\ C^2\Pi_r,\ D^2\Sigma^+: v') + C_6F_6. \quad (9)$$

The results obtained are compared with those for the NO^+/SF_6^- reaction.

Experimental

The flowing-afterglow apparatus used in this study was the same as that reported previously.[5,6,10,11] The $NO^+(X)$ cation can be formed by both the $He(2^3S)/NO$ and $He(2^3S)/N_2O$ Penning ionization (4) and (5) using NO and N_2O as source gases of NO^+. However, when NO was used, a strong background NO(A-X) emission due to the $He(2^3S)/NO$ reaction was observed at low NO pressures.[5,6] On the other hand, when N_2O was used, much weaker background NO(A-X,B-X) emissions due to some secondary reactions such as the $N(^4S)/O(^3P)/He$ reaction appeared at all N_2O pressures.[5,6] Therefore, N_2O was more suitable as a source gas of NO^+. Since the vibrational quenching rate coefficient of $NO^+(X: v'' > 0)$ for N_2O (ca. 2×10^{-10} $cm^3\,s^{-1}$) is smaller than that for NO (5×10^{-10} $cm^3\,s^{-1}$),[12] N_2O was more useful for the study of reactions with $NO^+(X: v'' > 0)$. On the basis of the above two facts, only N_2O was used as a source gas of $NO^+(X: v'' > 0)$ in the present study. The partial pressures in the reaction zone were 1.0 Torr for He, 2—150 mTorr for N_2O, and 1—10 mTorr for C_6F_6. When C_6F_6 was not added into the He afterglow, an electron density, $[e^-]$, was measured to be about 10^{10} cm^{-3} using a single Langmuir probe.[13,14] Since thermal electrons were completely scavenged through process (7), the density of $C_6F_6^-$ was expected to be almost the same as that of the electron density.

The emission spectra, observed around the C_6F_6 gas inlet, were dispersed in the 180—700 nm region with a Spex 1.25 m monochromator. Digital photon signals from a cooled photomultiplier were stored and analyzed with a microcomputer. Emissions due to the ion–ion recombination reaction were exclusively obtained by subtracting weak underlying background NO(A-X, B-X) emissions, as reported previously.[5,6]

Results and Discussion

Emission spectra of NO^* resulting from the $NO^+(X^1\Sigma^+)/C_6F_6^-$ neutralization reaction were measured over the N_2O pressure range of 2—150 mTorr. For example, Fig. 1(a)—(c) show emission spectra of NO^* obtained at N_2O pressures of 8, 27, and 63 mTorr, respectively. At high N_2O pressures above ca. 60 mTorr, a strong $NO(A^2\Sigma^+\text{-}X^2\Pi_r)$ emission and weak $NO(C^2\Pi_r\text{-}X^2\Pi_r,\ D^2\Sigma^+\text{-}X^2\Pi_r)$ emissions are found from only the ground $v' = 0$ levels, which is consistent with our previous work.[6] The NO(A-X) emission from the $v' = 1$ and 2 levels and the NO(D-X) emission from the $v' = 1$ level appear at lower N_2O pressures, where $NO^+(X: v'' > 0)$ was present. Although the NO(A-X) emission is observed up to $v' = 2$, the NO(D-X) emission from $v' = 2$ cannot be found. Since the NO(D-X) emission is much weaker than the NO(A-X) emission, its emission intensity is probably too weak to be detected in this study. No NO(C-X) emission from $v' > 0$ is observed even at the lowest N_2O pressure of 2 mTorr. It is known that the NO(C-X) emissions from $v' > 0$ are extremely weak due to predissociation.[15,16] Thus, the lack of NO(C-X) emission from $v' > 0$ was attributed to the predissociation of vibrationally excited levels.

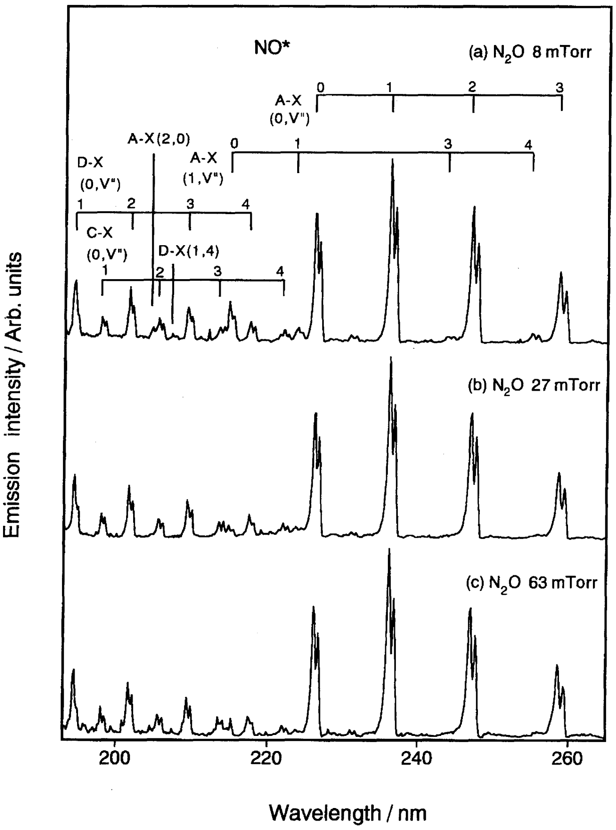

Fig. 1. NO(A-X, C-X, D-X) emissions resulting from the $NO^+(X^1\Sigma^+: v'' = 0\text{—}2)/C_6F_6^-$ reaction at various N_2O pressures.

A weak NO(A-X) emission from the $v' = 0$ and 1 levels was observed from the He afterglow reaction of N_2O without the addition of C_6F_6, as reported previously.[5,6] Its intensity distribution was independent of the N_2O pressure in the 2—150 mTorr and the He pressure in the 0.5—2.0 Torr, indicating that the vibrational relaxation of $NO(A: v' = 1)$ by collisions with N_2O and He was insignificant during its radiative lifetime of 187 ns.[16] The radiative lifetimes of $NO(A: v' = 2, 3)$ and $NO(D: v' = 0\text{—}3)$ are 165—177 and 10.1—16.1 ns, respectively.[16] Since these values are shorter than that of $NO(A: v' = 1)$, the vibrational relaxation of $NO(A: v' = 2, 3)$ and $NO(D: v' = 0\text{—}3)$ by collisions with N_2O and He are expected to be insignificant under the present experimental conditions.

The band intensity (photons s^{-1}) of a transition from a (v', J') level to a (v'', J'') level is given by[17]

$$I_{v'J'v''J''} \propto N_{v'J'} R_e^2(\bar{r}_{v'v''}) q_{v'v''} \nu^3_{v'J'v''J''} S_{J'J''}/(2J'+1). \tag{10}$$

Here, $N_{v'J'}$ is a rotational distribution of a given vibrational level v', $R_e(\bar{r}_{v'v''})$ is the electronic transition moment, $q_{v'v''}$ is the Franck–Condon (FC) factor, $\nu_{v'J'v''J''}$ is the transition frequency, and $S_{J'J''}$ is the rotational line strength. The $S_{J'J''}$ values were deduced from the formula given by Kovács.[18] For the low resolution spectra obtained here, the integrated intensities of vibrational bands were treated according to

$$I_{v'v''} \propto N_{v'} R_e^2(\bar{r}_{v'v''}) q_{v'v''} \nu^3_{v'v''} \propto N_{v'} A_{v'v''}, \tag{11}$$

where $A_{v'v''}$ is the Einstein coefficients of a transition. The relative vibrational populations of NO(A : v' = 0—2) were estimated from known Einstein coefficients of the NO(A-X) transition.[19] On the other hand, those of NO(D : v' = 0, 1) were evaluated using known FC factors of the NO(D-X) transition[20] and assuming the $R_e(\bar{r}_{v'v''})$ values to be constant. Figures 2 and 3 show the dependence of $N_{v'}$ of NO-(A : v' = 0—2) and NO(D : v' = 0, 1) on the N_2O pressure below 63 mTorr. The vibrational excitation of NO(A, D) increases with decreasing the N_2O pressure. The $N_{v'}$ values of NO(A, D) obtained by extrapolating N_2O pressure to zero are given in Table 1. For comparison, corresponding data for NO(A) from the $NO^+(X^1\Sigma^+)/SF_6^-$ reaction are also given in Table 1. The N_1 value of NO(D) is larger than that of NO(A). The N_1 and N_2 values of NO(A) in the $NO^+(X^1\Sigma^+)/C_6F_6^-$ reaction are smaller than those in the $NO^+(X^1\Sigma^+)/SF_6^-$ reaction, indicating that the relative reaction rate coefficients of NO^+(X : $v'' > 0$) in the former reaction are smaller than those in the latter reaction.

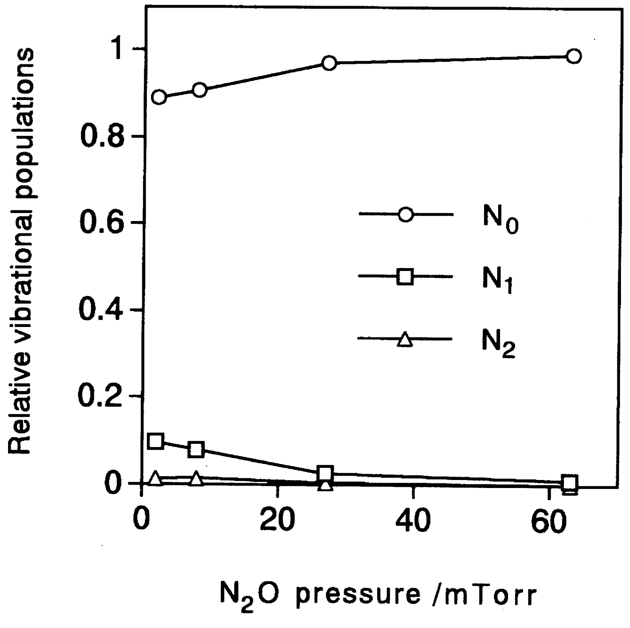

Fig. 2. The dependence of relative vibrational populations of NO(A : v' = 0—2) on the N_2O pressure in the $NO^+(X^1\Sigma^+$: v'' = 0—2)/$C_6F_6^-$ reaction.

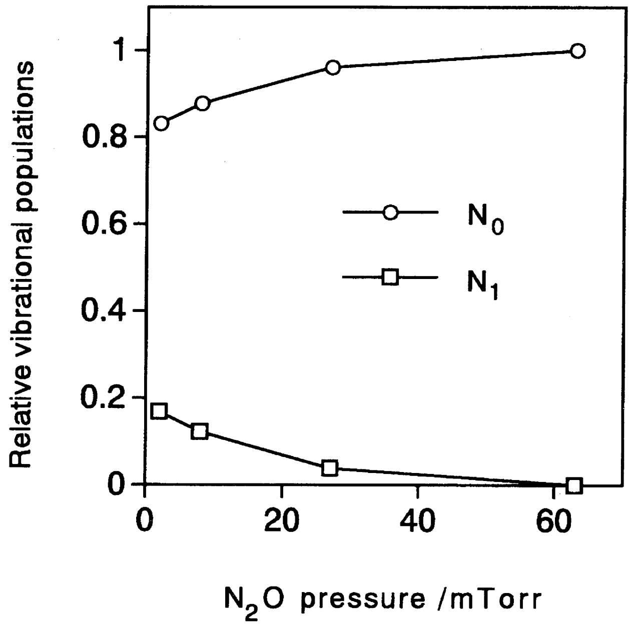

Fig. 3. The dependence of relative vibrational populations of NO(D : v' = 0, 1) on the N_2O pressure in the $NO^+(X^1\Sigma^+$: v'' = 0, 1)/$C_6F_6^-$ reaction.

Table 1. Vibrational Distributions of NO(A, D) in the $NO^+(X^1\Sigma^+$: v'')/$C_6F_6^-$ and $NO^+(X^1\Sigma^+$: v'')/SF_6^- Reactions Obtained by Extrapolating the $N_{v'}$ Data to Zero N_2O Pressure

		NO($A^2\Sigma^+$)			NO($D^2\Sigma^+$)	
$N_{v'}$		N_0	N_1	N_2	N_0	N_1
$NO^+/C_6F_6^-$	This work	0.88	0.11	0.01	0.82	0.18
NO^+/SF_6^-	Ref. 9	0.71	0.20	0.09		

It is known that $NO^+(X^1\Sigma^+$: $v'' > 0$) survives in a He flowing afterglow because the collisional quenching rate constant of NO^+(X : $v'' > 0$) is unmeasurably small for the buffer He gas ($< 1\times10^{-13}$ $cm^3\,s^{-1}$).[12,21] Thus, $NO^+(X^1\Sigma^+$: $v'' > 0$) must be involved at low N_2O pressures due to the incomplete vibrational relaxation. With increasing N_2O pressure, NO^+(X : $v''>0$) is expected to be relaxed to the NO^+(X : v'' = 0) level by collisions with the N_2O gas:

$$NO^+(X:v''>0)+N_2O(X:0,0,0) \rightarrow NO^+(X:v''=0)+N_2O(X:v_i''>0), \tag{12}$$

$$k_{12} \approx 2\times10^{-10}\ cm^3\,s^{-1}\ \text{(Ref. 12)}.$$

Thus, NO^+(X : $v'' > 0$) must be responsible for the excitation of NO(A : v' = 1, 2) and NO(D : v' = 1):

$$NO^+(X^1\Sigma^+:v''>0)+C_6F_6^- \rightarrow NO(A:v'=1,2)+C_6F_6, \tag{13a}$$

$$\rightarrow NO(D:v'=1)+C_6F_6. \tag{13b}$$

The vibrational distributions of the reactant NO^+(X : v'') ion at low N_2O pressures could not be determined in the present study. However, it is reasonable to assume that the NO^+(X) ion is dominantly populated in the low lying v'' = 0—2 levels because of a smooth increase in the relative populations of

$NO(A:v'=1,\ 2)$ and $NO(D:v'=1)$ with decreasing N_2O pressure. The ΔH° values of reaction processes leading to the observed $NO(A:v'=0\text{—}2)$, $NO(C:v'=0)$, and $NO(D:v'=0,\ 1)$ levels were estimated using an electron affinity of C_6F_6(0.52 eV)[22] and known spectroscopic constants of $NO(A^2\Sigma^+$, $C^2\Pi_r$, $D^2\Sigma^+)$ and $NO^+(X^1\Sigma^+)$:[23]

$$NO^+(X:v''=0)+C_6F_6^- \rightarrow NO(A:v'=0\text{—}2)+C_6F_6+(2.68\text{—}3.26)\ \text{eV}, \quad (14a)$$

$$NO^+(X:v''=1)+C_6F_6^- \rightarrow NO(A:v'=0\text{—}2)+C_6F_6+(2.97\text{—}3.55)\ \text{eV}, \quad (14b)$$

$$NO^+(X:v''=2)+C_6F_6^- \rightarrow NO(A:v'=0\text{—}2)+C_6F_6+(3.26\text{—}3.84)\ \text{eV}, \quad (14c)$$

$$NO^+(X:v''=0)+C_6F_6^- \rightarrow NO(C:v'=0)+C_6F_6+2.25\ \text{eV}, \quad (15a)$$

$$NO^+(X:v''=1)+C_6F_6^- \rightarrow NO(C:v'=0)+C_6F_6+2.54\ \text{eV}, \quad (15b)$$

$$NO^+(X:v''=2)+C_6F_6^- \rightarrow NO(C:v'=0)+C_6F_6+2.82\ \text{eV}, \quad (15c)$$

$$NO^+(X:v''=0)+C_6F_6^- \rightarrow NO(D:v'=0,\ 1)+C_6F_6+(1.85\text{—}2.13)\ \text{eV}, \quad (16a)$$

$$NO^+(X:v''=1)+C_6F_6^- \rightarrow NO(D:v'=0,\ 1)+C_6F_6+(2.14\text{—}2.42)\ \text{eV}, \quad (16b)$$

$$NO^+(X:v''=2)+C_6F_6^- \rightarrow NO(D:v'=0,\ 1)+C_6F_6+(2.43\text{—}2.71)\ \text{eV}. \quad (16c)$$

On the basis of the calculated ΔH° values, high excess energies are released in the above neutralization processes.

$NO(A:v'=0\text{—}2)$ and $NO(D:v'=0,\ 1)$ are formed via curve crossings between strongly attractive Coulombic entrance potentials and flat exit ones, as shown in Fig. 4. The crossing points R_c were calculated from the relation

$$R_c = e^2/(IP-EA), \quad (17)$$

where IP is the ionization potential of NO^* and EA is the electron affinity of C_6F_6. By using an EA value of C_6F_6 (0.52 eV),[22] the R_c values for the formation of each NO^* state were calculated. Since the vibrational frequencies of $NO^+(X)$ and $NO(A,\ D)$ are nearly the same, the entrance $NO^+(X:v''=0\text{—}2)+C_6F_6^-$ potentials cross the exit $NO(A:v'=v'')+C_6F_6$ and $NO(D:v'=v'')+C_6F_6$ ones at almost the same intermolecular distances of 4.4 and 6.7 Å, respectively.

Aquilanti et al.[24] have theoretically studied the ion–ion recombination reaction of $N_2^+(X^2\Sigma_g^+)+F^-(^1S_0)\rightarrow N_2(B^3\Pi_g:v')+F(^2P)$. Crossings between entrance and exit channels, which are responsible for the nonadiabatic transitions, were treated by Landau–Zener theory. The total cross-section for each exit channel can be calculated once the matrix element $H_{v'}$ of the nonadiabatic coupling is known at each crossing v'. The $H^2_{v'}(R)$ value can be obtained by

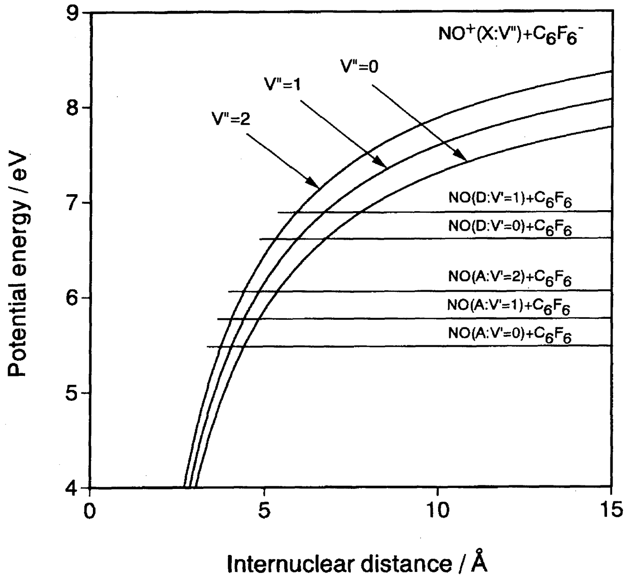

Fig. 4. The entrance $NO^+(X^1\Sigma^+:v''=0\text{—}2)+C_6F_6^-$ ion-pair potentials and the exit $NO(A^2\Sigma^+:v'=0\text{—}2)+C_6F_6$ and $NO(D^2\Sigma^+:v'=0,\ 1)+C_6F_6$ covalent potentials.

$$H^2_{v'}(R) = H^2_{el}(R)q(v'). \quad (18)$$

Here H_{el} represents the part of the nonadiabatic coupling matrix element which depends on the electronic radial wavefunctions and the term $q(v')$ is the FC factor between $N_2^+(X^2\Sigma_g^+:v''=0)$ and $N_2(B^3\Pi_g,:v')$.

The Rydberg, Klein, and Rees (RKR) FC factors for the $NO^+(X:v''=0\text{—}3)\rightarrow NO(A,\ C,\ D:v'=0\text{—}3)$ neutralization were calculated using known molecular constants of $NO^+(X)$ and $NO(A,\ C,\ D)$.[23] The results obtained are given in Table 2. It should be noted that FC factors for the $NO^+(X:v''=0)\rightarrow NO(A,\ C,\ D:v')$ neutralization are nearly unity for the transitions to $NO(A:v'=0)$, $NO(C:v'=0)$, and $NO(D:v'=0)$ because there are only small differences in the vibrational frequency between $NO^+(X:\omega_e=2376.42\ \text{cm}^{-1})$ and $NO(A:\omega_e=2374.31\ \text{cm}^{-1})$, $NO(C:\omega_e=2395\ \text{cm}^{-1})$, or $NO(D:\omega_e=2323.90\ \text{cm}^{-1})$ and the internuclear distance between $NO^+(X:r_e=1.06322\ \text{Å})$ and $NO(A:r_e=1.0634\ \text{Å},)$ $NO(C:r_e=1.062\ \text{Å})$, or $NO(D:r_e=1.0618\ \text{Å})$.[23] Therefore, the preferential formation of $NO(A,C,D:v'=0)$ is expected if $NO^+(X:v''=0)$ is not perturbed at R_c. We found that $NO(A,\ C,\ D:v'=0)$ is selectively formed by the $NO^+(X:v''=0)/C_6F_6^-$ reaction. This indicates that the $NO^+(X:v''=0)$ potential is not perturbed by an access of $C_6F_6^-$ at 4.6 Å for NO(A), 6.4 Å for NO(C), and 7.1 Å for NO(D); NO(A, C, D) in the ground vibrational states are formed via vertical FC-like neutralization processes. Since positive and negative ions are accelerated towards each other

Table 2. RKR Franck–Condon Factors for the $NO^+(X^1\Sigma^+ : v'') \rightarrow NO(A^2\Sigma^+, C^2\Pi_r, D^2\Sigma^+ : v')$ Neutralization

		$NO(A^2\Sigma^+ : v')$, $NO(C^2\Pi_r : v')$, or $NO(D^2\Sigma^+ : v')$			
		$v'=0$	$v'=1$	$v'=2$	$v'=3$
$NO^+(X^1\Sigma^+ : v'')$	$v''=0$	1.0000[a)]	0.0000	0.0000	0.0000
		0.9997[b)]	0.0002	0.0000	0.0001
		0.9996[c)]	0.0003	0.0001	0.0000
	$v''=1$	0.0000	0.9999	0.0000	0.0000
		0.0002	0.9967	0.0025	0.0002
		0.0002	0.9991	0.0001	0.0006
	$v''=2$	0.0000	0.0000	0.9999	0.0001
		0.0000	0.0027	0.9853	0.0099
		0.0002	0.0001	0.9983	0.0000
	$v''=3$	0.0000	0.0000	0.0001	0.9998
		0.0001	0.0001	0.0112	0.9590
		0.0000	0.0005	0.0000	0.9961

a) $NO^+(X^1\Sigma^+ : v'') \rightarrow NO(A^2\Sigma^+ : v')$ neutralization. b) $NO^+(X^1\Sigma^+ : v'') \rightarrow NO(C^2\Pi_r : v')$ neutralization. c) $NO^+(X^1\Sigma^+ : v'') \rightarrow NO(D^2\Sigma^+ : v')$ neutralization.

due to the Coulombic force, some amount of potential energy is converted to kinetic energy. In general, the perturbation of a target molecule is significant at low collision energies because of a long reaction time. One reason for the lack of any perturbation of the potential energy curve of $NO^+(X : v''=0)$ is the short reaction time at R_c due to the acceleration of the ion-pair.

We found here that vibrational excitation in $NO^+(X : v'')$ gives a small vibrational excitation in NO(A, D). The $NO^+(X : v''=0)$ potential is not perturbed at crossing points of 4.6—7.1 Å in the $NO^+(X : v''=0)/C_6F_6^-$ reaction. On the basis of this finding, it is reasonable to assume that little perturbation occurs for $NO^+(X : v''>0)$ by an access of $C_6F_6^-$ to similar intermolecular distances, and that the $NO^+(X : v''>0) \rightarrow NO(A, C, D : v')$ neutralization proceeds also through vertical processes. Since the FC factors for the $NO^+(X : v''>0) \rightarrow NO(A, C, D : v')$ neutralization are nearly unity for the $v'=v''$ transitions, as shown in Table 2. It is therefore highly likely that the vibrational energy of the $NO^+(X : v'' \geq 0)$ ion is conserved well in the same vibrational states of NO(A, C, D : v') after an electron transfer from $C_6F_6^-$ to NO^+:

$$NO^+(X : v'' = 0\text{—}2) + C_6F_6^- \rightarrow NO(A : v' = v'') + C_6F_6, \quad (19a)$$

$$NO^+(X : v'' = 0) + C_6F_6^- \rightarrow NO(C : v' = v'') + C_6F_6, \quad (19b)$$

$$NO^+(X : v'' = 0, 1) + C_6F_6^- \rightarrow NO(D : v' = v'') + C_6F_6. \quad (19c)$$

Since the $NO(C : v'>0)$ states predissociate nearly completely,[15,16)] only the $NO^+(X : v''=0)/C_6F_6^-$ reaction could be observed. The N_1/N_0 ratio of NO(D) in process (19c) is larger than that of NO(A) in process (19a). This shows that the nonadiabatic coupling strength between the entrance $NO^+(X : v'')+C_6F_6^-$ potential and the exit $NO^*(v'=v'')+C_6F_6$ potential at R_c depends on the product electronic state. In the present system, the relative coupling strength between $NO^+(X : v''=1)+C_6F_6^-$ and $NO(D : v''=1)+C_6F_6$ to that between $NO^+(X : v''=0)+C_6F_6^-$ and $NO(D : v''=0)+C_6F_6$ is larger than that in the corresponding processes leading to $NO(A : v'=v'')$. In order to confirm this, detailed calculations of the nonadiabatic coupling strength will be necessary using three-dimensional potential surfaces.

The rotational distributions of NO(A : $v'=0$—2, C: $v'=0$, D : $v'=0$, 1) were determined by a computer simulation of the observed spectra using Eq. 10. Single Boltzmann rotational temperatures (T_r) were assumed for each v' level. The simulation method used in the present study was identical to that reported previously.[6)] The T_r values of NO(A : $v'=0$—2, C : $v'=0$, D : $v'=0$, 1) are given in Table 3. These values were independent of the He and N_2O pressures, indicating that rotational relaxation by collisions with He and N_2O was insignificant within short radiative lifetimes of 177—187 ns for NO(A : $v'=0$—2), ≤ 2.7 ns for NO(C : $v'=0$), and 15.0—16.1 ns for NO(D : $v'=0$, 1) under the operating conditions.[16)] If the $NO^+(X : v''>0)/C_6F_6^-$ reaction gives NO(A, C, D : $v'=0$), their T_r values may be higher than those in the $NO^+(X : v''=0)/C_6F_6^-$ reaction due to higher

Table 3. Rotational Temperatures of NO(A, C, D) in the $NO^+(X^1\Sigma^+ : v'')/C_6F_6^-$ and $NO^+(X^1\Sigma^+ : v'')/SF_6^-$ Reactions at Low N_2O Pressures

		$NO(A^2\Sigma^+)$			$NO(C^2\Pi_r)$	$NO(D^2\Sigma^+)$	
$\frac{T_r}{K}$		$v'=0$	$v'=1$	$v'=2$	$v'=0$	$v'=0$	$v'=1$
$NO^+/C_6F_6^-$	This work	500±100	500±100	500±150	300±50	600±100	500±100
NO^+/SF_6^-	Ref. 5	600±100	500±100	600±100			

excess energies. However, the T_r values for $v' = 0$ of NO(A, C, D) were the same as those for the $NO^+(X:v'' = 0)/C_6F_6^-$ reaction,[6] which is consistent with our prediction that NO(A, C, D : $v' = 0$) is not formed by the $NO^+(X:v'' > 0)/C_6F_6^-$ reaction. The relatively low rotational excitation in NO(A, C, D) suggests that the vibrational energy of $NO^+(X:v'' > 0)$ is not deposited into the rotational mode of NO(A, C, D) after electron transfer from $C_6F_6^-$ to $NO^+(X:v'' > 0)$. Since little energy is deposited into rotational energy of NO(A, C, D), most of the excess energies must be released as the relative translational energy of neutral products and internal energy of C_6F_6.

The neutralization leading to NO(A, C, D) molecules takes place via an electron transfer from a singly occupied molecular orbital (SOMO) of $C_6F_6^-$ to a vacant orbital of NO^+. According to an ESR study of Symons in solid matrix at 77 K,[25] an electron is captured by C_6F_6 into a σ^*-orbital rather than a π^*-orbital. They assumed that $C_6F_6^-$ has a puckered-ring structure similar to the chair form of cyclohexane. However, a later theoretical work on $C_6F_6^-$ by Shchegoleva et al.[26] using the INDO method pointed out that a planar carbon skeleton C_6 containing out-of-plane C–F bonds fits the coupling constants in ESR better. They reported that the extra electron occupies a combination of π^* and σ^* orbitals with a prevailing π^*-component. According to recent ab initio calculations of $C_6F_6^-$ by Hiraoka et al.[27] using the UHF STO-3G method, two anions (C_{2v} and D_2 isomers) are formed by an electron attachment to C_6F_6. Energetically, the C_{2v} isomer with a planer carbon ring and out-of-plane C–F bonds is slightly more stable (0.1 kcal mol^{-1} by STO-3G and 1.6 kcal mol^{-1} by 3-21G) than the D_2 isomer. The electron in the SOMO is localized dominantly on the C_1–F_7 and C_4–F_{10} bonds. According to our calculation of $C_6F_6^-$ using the UHF-PM3 method, it has a planar structure and the excess electron was dominantly located on the P_z orbital of the C_1 and C_4 carbon in the C–F bonds.

As discussed above, the equilibrium geometry of $C_6F_6^-$ depends on the theoretical treatment. Both a carbon skeleton distorted to a cyclohexane-like chair and an undistorted carbon skeleton with out of plane C–F bonds have been proposed. Anyway, a significant change in the equilibrium structure is expected by the neutralization from $C_6F_6^-$ to C_6F_6. Chen et al.[28] estimated that the equilibrium internuclear distance of C_6F_5–F^- (ca. 1.6 Å) is larger than that of C_6F_5–F (ca. 1.4 Å) and the vertical electron affinity is longer than that of the adiabatic electron affinity by about 1 eV. Thus, the excess energies released in the neutralization processes (19a)—(19c) will be partitioned into not only the relative translational energy due to the Coulombic attractive force between the ion pair but also the vibrational energy of C_6F_6.

Conclusion

The influence of vibrational excitation in $NO^+(X:v'')$ has been studied by observing the NO($A^2\Sigma^+$-$X^2\Pi_r$, $C^2\Pi_r$-$X^2\Pi_r$, $D^2\Sigma^+$-$X^2\Pi_r$) emissions from the mutual ion–ion neutralization reaction between $NO^+(X^1\Sigma^+)$ and $C_6F_6^-$. In addition to the NO(A-X, C-X, D-X) emissions from $v' = 0$, the NO(A-X) emission from $v' = 1, 2$ and the NO(D-X) emission from $v' = 1$ appeared at low N_2O pressures, where $NO^+(X:v'' > 0)$ was present. The lack of vibrational excitation of NO(C) was explained by the predissociation of NO(C : $v' > 0$). The FC factors for the $NO^+(X:v'') \rightarrow$ NO(A, D : $v' = v''$) neutralization are nearly unity because the vibrational frequency and the internuclear distance of NO^+(X) are similar to those of NO-(A, D). Therefore, the vibrational excitation in $NO^+(X:v'')$ results in the vibrational excitation of the product NO(A, D : $v' = v''$) molecule with a low rotational excitation. It was concluded that the excess energies are partitioned into not only the relative translational energy but also the vibrational energy of C_6F_6 because of a significant different equilibrium geometry between $C_6F_6^-$ and C_6F_6. The fact that the vibrational excitation of NO(D) is higher than that of NO(A) indicated that the relative coupling strength between $NO^+(X:v'' > 0)+C_6F_6^-$ and NO(D : $v' = v''$)+C_6F_6 to that between $NO^+(X:v'' = 0)+C_6F_6^-$ and NO(D : $v' = 0$)+C_6F_6 is larger than that in the corresponding processes leading to NO(A : $v' = v''$). In order to explain this result, detailed theoretical calculations of the coupling strengths at R_c will be required.

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