The Influence of Vibrational Excitation of $NO^+(X^1\Sigma^+:v'')$ on the Formation of $NO(A^2\Sigma^+)$ by the NO^+ + SF_6^- Neutralization Reaction at Thermal Energy

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The $NO(A^2\Sigma^+\text{-}X^2\Pi_r)$ emission resulting from the mutual ion-ion neutralization reaction between $NO^+(X^1\Sigma^+)$ and SF_6^- has been measured at various source gas pressures of NO^+ in a flowing afterglow in order to examine the influence of vibrational excitation in $NO^+(X:v'')$. 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.

Although mutual neutralization reactions between positive and negative ions are a significant loss process of ions in natural and manmade plasmas, little information has been obtained on the internal state distribution of neutral products.[1,2] In order to obtain information on the internal state distribution of electronically excited products in ion-ion neutralization reactions, we have recently made an optical spectroscopic study on the formation of $NO(A^2\Sigma^+)$ by the $NO^+(X^1\Sigma^+)/SF_6^-$ neutralization reaction using a flowing-afterglow method:[3]

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

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

$$He(2^3S) + NO \rightarrow NO^+ + He + e^-, \quad (2)$$

$$He(2^3S) + N_2O \rightarrow NO^+ + N + He + e^-, \quad (3)$$

$$e^- + SF_6 \rightarrow SF_6^-, \ (k_4 = 2.2 \times 10^{-7}\ cm^3s^{-1}\ [\text{Ref. } 4]). \quad (4)$$

In our measurement, 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 with a low effective Boltzmann rotational temperature of 600±50 K. The low vibrational and rotational excitation in NO(A) led us to conclude that most of the excess energy is released as the relative translational energy of the neutral products. In the present communication, the effects of vibrational excitation in $NO^+(X:v'')$ were investigated for process (1) by reducing the source gas pressure of NO^+. This is the first optical spectroscopic study on the influence of the vibrational excitation of the positive ion in the ion-ion recombination reaction.

The flowing-afterglow apparatus used in this study was the same as that reported previously.[2,3] Although NO^+ can be formed by the $He(2^3S)/NO$ Penning ionization by using NO as a source gas of NO^+, it was not used in the present study because of a significant increase in the background NO(A-X) emission due to the $He(2^3S)/NO$ reaction with decreasing the NO pressure and a large vibrational quenching rate constant of $NO^+(X:v''>0)$ for NO ($5 \times 10^{-10}\ cm^3s^{-1}$).[5] The partial pressures in the reaction zone were 1.0 Torr for He, 0.2-39 mTorr for N_2O, and 6.5 mTorr for SF_6.

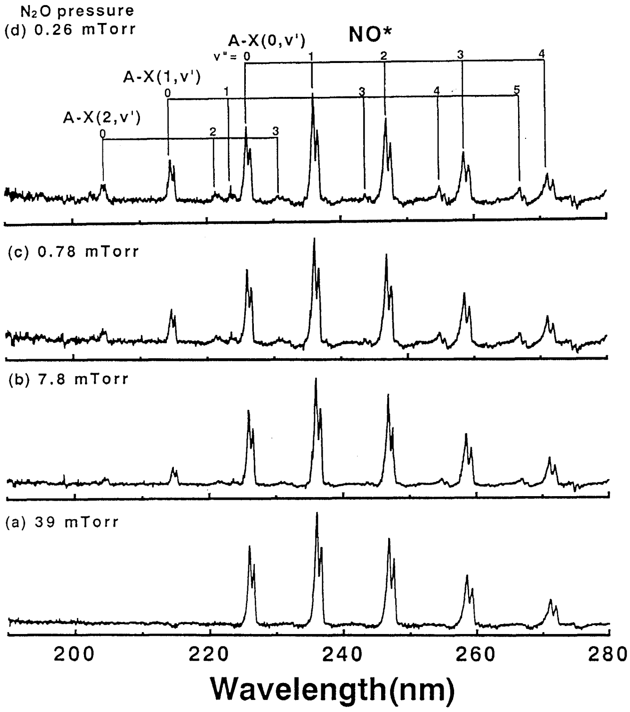

Figure 1. Emission spectra of NO(A-X) resulting from the $NO^+(X^1\Sigma^+)/SF_6^-$ reaction at different N_2O pressures.

The emission spectra, observed around the SF_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 due to the N/O/He reaction.[3]

Figure 1 shows emission spectra of NO(A-X) resulting from the $NO^+(X^1\Sigma^+)/SF_6^-$ neutralization reaction at four different N_2O pressures. At a high N_2O pressure of 39 mTorr, only the NO(A-X) emission from v'=0 is found, which is consistent with our previous work.[3] It should be noted that the NO(A-X) emission from the v'=1 and 2 levels appear at low N_2O pressures and their intensities increase with decreasing the N_2O pressure. Figure 2 shows the relative vibrational populations of NO(A:v'=0-2) at four N_2O pressures estimated from known Einstein coefficients of the NO(A-X) transition.[6] The vibrational excitation of NO(A) increases with decreasing the N_2O pressure.

$NO^+(X^1\Sigma^+:v''>0)$ must be involved due to the incomplete vibrational relaxation because the collisional quenching rate constant of $NO^+(X:v''>0)$ is unmeasurably small for the buffer He gas ($1 \times <10^{-13}\ cm^3s^{-1}$).[5] With increasing the N_2O pressure, $NO^+(X:v''>0)$ is expected to relax to the $NO^+(X:v''=0)$ level by

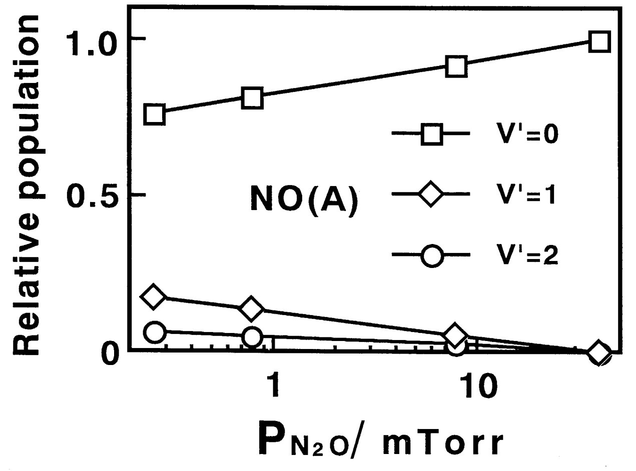

Figure 2. The dependence of relative vibrational populations of NO(A:v'=0-2) produced from the $NO^+(X^1\Sigma^+)/SF_6^-$ reaction on the N_2O pressure. The relative vibrational populations are normalized to unity.

collisions with the N_2O gas:

$$NO^+(X:v''>0) + N_2O(X:0,0,0) \rightarrow NO^+(X:v''=0) + N_2O(X:v_i''>0), \quad (5)$$
$$k_5 = \sim 2 \times 10^{-10}\ cm^3s^{-1}\ \text{(Ref. 5).}$$

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

$$NO^+(X^1\Sigma^+:v''>0) + SF_6^- \rightarrow NO(A^2\Sigma^+:v'=1,2) + SF_6. \quad (6)$$

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). The ΔH^0 values of reactions (1) and (6) leading to NO(A:v'=0-2) are 2.15-2.73, 2.44-3.02, and 2.73-3.31 eV for the reactions with $NO^+(X:v''=0$, 1, and 2), respectively. Although these energies are sufficient to produce NO(A) up to highly vibrationally excited levels, no significant vibrational excitation in NO(A) was found. This implies that vibrational excitation in $NO^+(X:v'')$ gives a small vibrational excitation in NO(A). We have previously reported that the lack of the vibrational excitation of NO(A) in the $NO^+(X:v''=0)/SF_6^-$ reaction is due to a nearly complete energy release to the relative translational energy because of a strong mutual Coulombic attractive force.[3] Combining this fact with a similar low vibrational excitation of NO(A) observed here, it is reasonable to assume that the vibrational energy of $NO^+(X:v''\geq 0)$ ion is conserved well in the same vibrational states of NO(A:v') after an electron transfer from SF_6^- to NO^+ because of a small energy difference in the vibrational frequency between $NO^+(X:\omega_e=2376.42\ cm^{-1})$ and $NO(A:\omega_e=2374.31\ cm^{-1})$:[7]

$$NO^+(X^1\Sigma^+:v''=0\text{-}2) + SF_6^- \rightarrow NO(A^2\Sigma^+:v'=v'') + SF_6. \quad (7)$$

NO(A:v'=0-2) is formed via curve crossings between strongly attractive entrance potentials and flat exit ones. Since the vibrational frequencies of $NO^+(X)$ and NO(A) are nearly the same, the entrance $NO^+(X:v'=0) + SF_6^-$, $NO^+(X:v'=1) + SF_6^-$, and $NO^+(X:v'=2) + SF_6^-$ potentials cross the exit $NO(A^2\Sigma^+:v'=0) + SF_6$, $NO(A^2\Sigma^+:v'=1) + SF_6$, and $NO(A^2\Sigma^+:v'=2) + SF_6$ ones at the same intermolecular distances of 5.26 Å using an electron affinity of SF_6(1.05 eV).[8] On the basis of the present findings, NO(A:v'=0-2) is dominantly formed via curve crossings at the same intermolecular distances.

The rotational distributions of NO(A:v'=0-2) were determined by a computer simulation of the observed spectra. The simulation method used in the present study was identical to that reported previously.[3] The rotational distributions of NO(A:v'=0, 1, and 2) can be reproduced by effective rotational temperatures (T_r) of 600±100, 500±100, and 600±100 K, respectively. The rotational temperatures were independent of the He and N_2O pressures, indicating that rotational relaxation by collisions with He and N_2O is insignificant within short radiative lifetimes of =177-202 ns for NO(A:v'=0-2)[6,9] under the operating condition. The T_r value for v'=0 was the same as that for the $NO^+(X:v''=0)/SF_6^-$ reaction,[3] which is consistent with our prediction that NO(A:v''=0) is not formed by the $NO^+(X:v''=1,2)/SF_6^-$ reaction. The relatively low rotational excitation in NO(A) suggests that the vibrational energy of $NO^+(X:v''>0)$ is not deposited into the rotational mode of NO(A) after electron transfer from SF_6^- to $NO^+(X:v''>0)$.

We are planning to measure the influence of vibrational excitation in $NO^+(X)$ for the other ion-ion recombination reactions such as $NO^+/C_6F_6^-$ and $NO^+/C_6F_6CF_3^-$ leading to the NO(A,C,D) states.[10,11]

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References and Notes

1 M. R. Flannery, in "Adv. Atom. Mol. Opt. Phys.," ed by B. Bederson and A. Dargano, Academic Press, New York, (1994), Vol. 32, p. 117.
2 M. Tsuji, in "Trends in Physical Chemistry" Vol. 5, Council of Scientific Information, Trivandrum, India, in press.
3 M. Tsuji, H. Ishimi, M. Nakamura, Y. Nishimura, and H. Obase, *J. Chem. Phys.*, **102**, 2480 (1995).
4 D. Smith, N. G. Adams, and E. Alge, *J. Phys.*, B **17**, 461 (1984).
5 W. Federer, W. Dobler, F. Howorka, W. Lindinger, M. Durup-Ferguson, and E. E. Ferguson, *J. Chem. Phys.*, **83**, 1032 (1985).
6 L. G. Piper and L. M. Cowles, *J. Chem. Phys.*, **85**, 2419 (1986).
7 K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules," Van Nostrand, New York (1979).
8 E. P. Grimsrud, S. Chowdhury, and P. Kebarle, *J. Chem. Phys.*, **83**, 1059 (1985).
9 A. J. Smith and F. H. Read, *J. Phys.*, B **11**, 3263 (1978).
10 M. Tsuji, H. Ishimi, Y. Nishimura, and H. Obase, *J. Chem. Phys.*, **102**, 6013 (1995).
11 M. Tsuji, H. Ishimi, Y. Nishimura, and H. Obase, *Int. J. Mass Spectrom. Ion Process.*, in press.