Vibrational Distribution of $N_2(B^3\Pi_g)$ Produced from Dissociative Recombination of N_2O^+ in a Helium Flowing Afterglow

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$N_2(B^3\Pi_g\text{-}A^3\Sigma_u^+)$ emission resulting from a dissociative recombination (DR) process of N_2O^+ has been observed in a He afterglow reaction of N_2O. The vibrational population of $N_2(B:v'=0\text{-}10)$ exhibited a bimodal distribution with peaks at $v'=1$ and 4, probably associated with the $N_2(B) + O(^1D)$ and $N_2(B) + O(^3P)$ processes, respectively.

Electron-ion recombination is an important loss process of charged species in natural plasma including interstellar gas clouds and planetary ionospheres and in man-made plasmas such as laser plasmas and combustion flames.[1] Although a DR process of N_2O^+ is important for understanding loss processes of N_2O^+ in natural and man-made plasmas, there has been only one preliminary spectroscopic study by Taieb and Broida.[2] They observed $N_2(B^3\Pi_g\text{-}A^3\Sigma_u^+)$ neutral emission from the $v'=2\text{-}5$ levels in a He afterglow reaction of N_2O. The quenching effects of SF_6 and of microwave heating which increases the electron temperature and reduces the electron-ion recombination rate led them to the conclusion that $N_2(B)$ is produced by electron-ion recombination. Although $N_2(B)$ can be formed by electron recombination with N_2O^+ and N_2^+, the ratio of the intensity of the $N_2(B\text{-}A)$ emission was much greater than that of the $N_2^+(B\text{-}X)$ one. Therefore, they predicted that the e^-/N_2O^+ DR is a major source of $N_2(B\text{-}A)$ emission. However, the contribution from the e^-/N_2^+ recombination cannot be excluded from possible formation mechanisms of $N_2(B)$, because the precursor $N_2^+(X)$ ions are produced through not only $N_2^+(B\text{-}X)$ radiative cascade but also through a direct mechanism.

In the present study, DR of N_2O^+ is studied in a He flowing afterglow by observing $N_2(B\text{-}A)$ emission in a wider spectral range than that in the previous study of Taieb and Broida.[2] The contribution of the e^-/N_2^+ recombination is examined by using N_2 gas. The vibrational distribution of $N_2(B:v'=0\text{-}10)$ is determined.

The flowing-afterglow apparatus used in this study was the same as that used for the study of DR of CO_2^+.[3] In brief, the positive N_2O^+ ions were produced by the $He(2^3S)/N_2O$ Penning ionization, and He^+/N_2O and He_2^+/N_2O charge-transfer reactions by the addition of N_2O into the He afterglow 10 cm downstream from a center of the microwave discharge. On the other hand, electrons were formed via a direct microwave discharge of He and Penning ionization of N_2O. They were completely thermalized by collisions with buffer He gas before arriving at the reaction zone. The partial pressure in the reaction zone was 1.0 Torr (=133.3 Pa) for He and 5-50 mTorr for N_2O. Under these operating conditions, the electron density was measured to be $\sim 10^{10}/cm^3$ by using a single Langmuir probe. The emission spectra were dispersed in the 400-1100 nm region with a Spex 1250 M monochromator. A Hamamatsu Photonics (HP) R376 photolumiplier was used in the measurement of 400-800 nm region, while a red sensitive HP R316-02 one was employed in the measurement of 800-1100 nm region. Emission spectrum presented here was corrected for the wavelength response of the detection system.

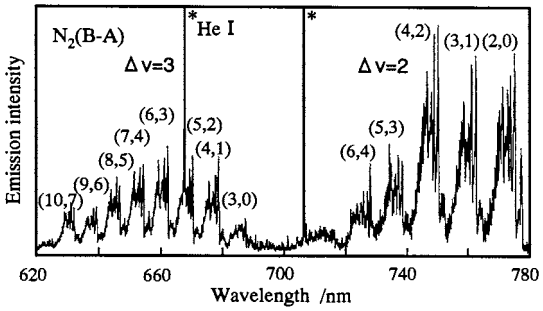

Figure 1. $N_2(B^3\Pi_g\text{-}A^3\Sigma_u^+)$ emission obtained from the He afterglow reaction of N_2O at a total pressure of 1 Torr.

A typical emission spectrum observed 10 cm downstream from an inlet of N_2O is shown in Figure 1, where the $\Delta v=2$ and 3 sequences of the $N_2(B^3\Pi_g\text{-}A^3\Sigma_u^+)$ transition from $v'=2\text{-}10$ is identified. Although Taieb and Broida[2] observed $N_2(B\text{-}A)$ emission from the $v'=2\text{-}5$ levels, the $v'=0\text{-}10$ levels are identified in the 570-1080 nm region in this study. When a small amount of an electron scavenger, SF_6, was added into the observation region, the $N_2(B\text{-}A)$ emission reduced its intensity by factors of 5-8. This implies that almost all $N_2(B)$ is formed though some electron-ion recombination processes. In addition to DR of N_2O^+ (1), the following radiative recombination (2a), collisional radiative recombination (2b), and three-body recombination (2c) of N_2^+ are possible as the formation processes of $N_2(B:v'=0\text{-}10)$:

$$e^- + N_2O^+ \rightarrow N_2(B:v'=0\text{-}10) + O, \quad (1)$$
$$e^- + N_2^+ \rightarrow N_2(B:v'=0\text{-}10) + h\nu, \quad (2a)$$
$$e^- + N_2^+ + e^- \rightarrow N_2(B:v'=0\text{-}10) + e^-, \quad (2b)$$
$$e^- + N_2^+ + M \rightarrow N_2(B:v'=0\text{-}10) + M \ (M=He \text{ or } N_2O). \quad (2c)$$

Taieb and Broida[2] concluded that processes (2a)-(2c) were unimportant because the ratio of the intensity of the $N_2(B\text{-}A)$ emission was much greater than that of the $N_2^+(B\text{-}X)$ one. In order to examine the contribution of processes (2a)-(2c), sample N_2O gas was replaced by N_2 gas. No evidence of processes (2a)-(2c) was found at low N_2 flow rates, where the $e^-/N_2^+\cdot N_2$ DR process leading to $N_2(B)$[4] was insignificant. It was therefore concluded that the responsible recombination process for the formation of $N_2(B:v'=0\text{-}10)$ is DR of N_2O^+ (1).

In order to examine the vibrational distribution of the precursor $N_2O^+(X^2\Pi_g:v_1",v_2",v_3")$ ion, laser induced fluorescence (LIF) of $N_2O^+(A^2\Sigma^+\text{-}X^2\Pi_i)$ was observed in a He afterglow using a similar LIF apparatus reported previously.[5] Only the LIF bands from the ground $N_2O^+(X^2\Pi_g:0,0,0)$ level were observed. This finding led us to conclude that $N_2O^+(X^2\Pi_g:v_1",v_2",v_3")$ ions were completely relaxed to the ground vibrational level by collisions with He and N_2O before arriving at the recombination reaction zone.

The energetics for the formation of $N_2(B^3\Pi_g)$ via DR of $N_2O^+(X^2\Pi_g:0,0,0)$ is as follows:

$$e^- + N_2O^+(X^2\Pi_g:0,0,0)$$
$$\rightarrow N_2(B:v'=0\text{-}10) + O(^3P), \quad \Delta H^o = -3.80 \sim -1.85 \text{ eV}, \quad (3a)$$
$$\rightarrow N_2(B:v'=0\text{-}10) + O(^1D), \quad \Delta H^o = -1.84 \sim 0.11 \text{ eV}. \quad (3b)$$

The total available energies for processes (3a) and (3b) were estimated to be 1.92~3.87 eV and -0.05~1.91 eV, respectively, by taking account of the relative kinetic energy and the rotational energy of $N_2O^+(X)$ at 300 K (5/2RT).

The vibrational distribution of $N_2(B:v'=0\text{-}10)$ in the DR process of $N_2O^+(X^2\Pi_g:0,0,0)$, $N_{v'}$, was determined from the emission intensity of a (v',v") transition of $N_2(B\text{-}A)$, $I_{v'v"}$, using the following relation:

$$I_{v'v"} = N_{v'}A_{v'}, \quad (4)$$

where $A_{v'}$ is the Einstein coefficient of the $N_2(B\text{-}A)$ transition distribution, which has been reported by Piper *et al.*[6] The emission intensity was evaluated by measuring the total area of each vibronic band. The vibrational distribution obtained is shown in Figure 2. The uncertainties of the $N_{v'}$ values were estimated

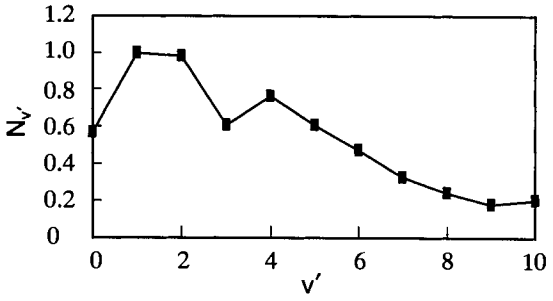

Figure 2. Vibrational distribution of $N_2(B^3\Pi_g)$ produced from DR of $N_2O^+(X^2\Pi_g:0,0,0)$ at thermal energy.

to be within ±8%. The vibrational distribution of $N_2(B)$ was independent of buffer He gas pressure in the 0.5-1.5 Torr range and N_2O pressure in the 5-50 mTorr range. It was thus concluded that the vibrational relaxation by collisions with He and N_2O was insignificant and the observed vibrational distribution reflects the nascent population. On the other hand, the rotational distribution of $N_2(B)$ was expected to be relaxed nearly completely by collisions with He and N_2O due to long radiative lifetimes of $N_2(B:\tau=4.3\text{-}12.1\ \mu s$ for $v'=0\text{-}10)$.[6] It should be noted that the observed vibrational population exhibits a bimodal distribution with peaks at v'=1 and 4. These low and high v' components are probably associated with two exit channels (3b) and (3a), respectively. The average vibrational energy deposited into $N_2(B)$ in the DR of $N_2O^+(X^2\Pi_g:0,0,0)$, $\langle E_v \rangle$, was evaluated to be 0.74 ± 0.06 eV from the observed vibrational distribution.

Two mechanisms have been proposed for DR processes of polyatomic ions.[7] One is a direct process, which proceeds through the following two-stage mechanism:

$$e^- + N_2O^+(X^2\Pi_g:0,0,0) \rightleftarrows N_2O^{**} \rightarrow N_2(B) + O, \quad (5)$$

where the free electron of energy $\varepsilon = V^{**}(N_2O^{**}) - V^+(N_2O^+)$ excites an electron of N_2O^+ and it is then resonantly captured by the ion to form a repulsive state of the doubly excited N_2O^{**} molecule, which in turn can either autoionize or predissociate into $N_2(B) + O$. The other is indirect mechanism which proceeds through the following three-stage mechanism,

$$e^- + N_2O^+(v_i^+) \rightarrow [N_2O^+(v_f)\text{-}e^-]_n$$
$$\rightarrow N_2O^{**} \rightarrow N_2(B) + O, \quad (6)$$

where the accelerating electron loses energy by vibrationally exciting ($v_i^+ \rightarrow v_f$) ion and is then captured into a Rydberg orbital of the bound N_2O^* molecule which then interacts with the doubly excited repulsive N_2O^{**} molecule via configuration mixing. According to theoretical prediction of Bate,[8] the former mechanism is significant for DR of polyatomic ions. It is therefore reasonable to assume that $N_2(B)$ is produced via a direct mechanism. The fact that favorable vibrational levels are v'=1 and 4 indicates that vibrational wavefunction of the precursor $N_2O^+(X^2\Pi_g:0,0,0)$ level is favorably overlapped with the $N_2(B:v'=1) + O(^1D)$ and $N_2(B:v'=4) + O(^3P)$ repulsive curves. Therefore, an efficient double electron capture transition into two antibonding molecular orbitals will be induced.

When C_6F_6 was added as an electron scavenger, a weak $N_2(B\text{-}A)$ emission resulting from the following $N_2O^+/C_6F_6^-$ ion-ion recombination reaction was observed:

$$N_2O^+(X^2\Pi_g:0,0,0) + C_6F_6^- \rightarrow N_2(B) + O + C_6F_6. \quad (7)$$

We are planing to compare the vibrational distributions of $N_2(B)$ between the $N_2O^+/C_6F_6^-$ reaction and the e^-/N_2O^+ one reported here in order to obtain more information on the dynamical features of the DR process of N_2O^+.

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