Jet Collisional Excitation of Nitrogen Molecules in a Corona Excited Supersonic Expansion

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Transient molecules such as molecular ion and radical etc. are believed to play important roles in the reaction dynamics as intermediates.[1] Thus, many experimental techniques have been employed to produce the short lived species. One of the most convenient methods is to transfer the stable precursor into the highly excited energy states from which the transient molecules are formed.[2]

For the generation of transient molecules, a technique of collisional excitation has been developed using metastable inert gases as an energy transferring agent. Cossart and Cossart-Magos have observed the emission spectra of highly excited CO^+ from the jet collision between the metastable Ne atom and CO molecule generated from Geissler-type electric discharge.[3] The same technique has been applied to the generation of CS^+ from the collision of metastable He atom with long-lived CS radical.[4] Recently, Tokeshi *et al*. employed the ion-molecule collisions to observe the emission spectra ($A^2\Delta$-$X^2\Pi$) of CH radical produced in collision of Ar^+ with aliphatic compounds.[5] Very recently, we have reported the generation of nitrogen molecular ions using two different types of nozzles in a corona excited supersonic expansion.[6~8]

In this work, we have further developed the technique of jet collisional excitation in a corona excited supersonic expansion in which the effectiveness of collisional energy transfer has been substantially improved.

Experimental Section

Figure 1 illustrates the schematic diagram of the experimental setup employed in this work which is similar to those described elsewhere.[6,7] Briefly it consists of two different size of Engelking type nozzles,[9,10] a high vacuum expansion chamber and pumping system, and a spectrometer for observing the vibronic emission spectra of the transient molecules at the excited electronic states.

The nozzles were made of thick walled quartz tube of 12 mm outer diameter, narrowed one end by flame heating to a capillary of the desirable pinhole size. Two nozzles perpendicular to each other were placed inside the chamber to produce the target and colliding jets. A pinhole type of nozzles of 0.2 mm and 0.3 mm opening have been employed for the generation of metastable helium atomic and the excited nitrogen molecular jets, respectively. The sharpened stainless steel rod was inserted into the center of the each nozzle tube through the teflon holders and connected to the high voltage electric dc power supply (Bertan model 210-05R).

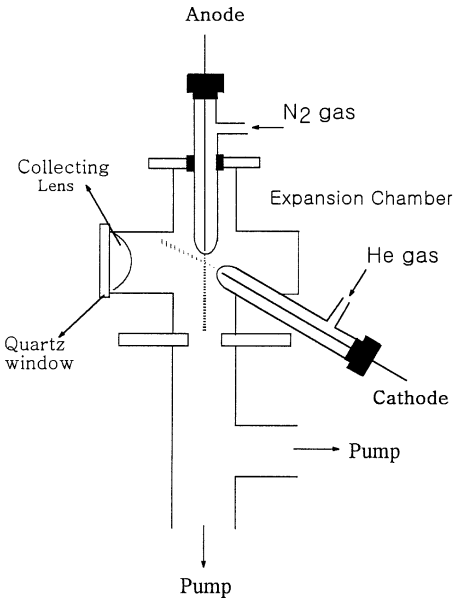

Figure 1. The schematic diagram of the jet collision in a corona excited supersonic expansion.

The rods inside the nozzles for the nitrogen and helium gases were used as an anode and a cathode, respectively. The distance between both nozzles was adjusted for the maximum excitation of the nitrogen molecules by the metastable helium atomic jet. The quartz lens of 38 mm diameter and 50 mm focal length was placed at the another arm of the chamber perpendicular to both nozzles. Both the metastable helium atomic and the excited nitrogen molecular jets were generated in a corona excited supersonic expansion.

The chamber was evacuated by two mechanical vacuum pumps (WS Automa model W2V80) of the capacity of 800 L/min, resulting in the pressure of 0.5 Torr during the expansion. The backing pressure of the nitrogen gas was kept at 2.0 atm while the helium pressure was varied from 1.0 to 10 Torr. for the maximum emission intensity of the nitrogen molecular ion.

The bright jet was obtained by an electric dc discharge at 600 V and 10 mA with 150 kΩ ballast resister. The emanating light from the downstream nitrogen jet was collimated by a quartz lens placed inside the expansion chamber and focussed onto the slit of the monochromator (Jobin Yvon U-1000) employing two 1800 lines/mm gratings, and detected with a photomultiplier tube (Hamamatsu R212UH) and a photon counting system. During the scans, the slits were set to 200 μm, providing effective resolution of 2.0 cm^{-1} at the

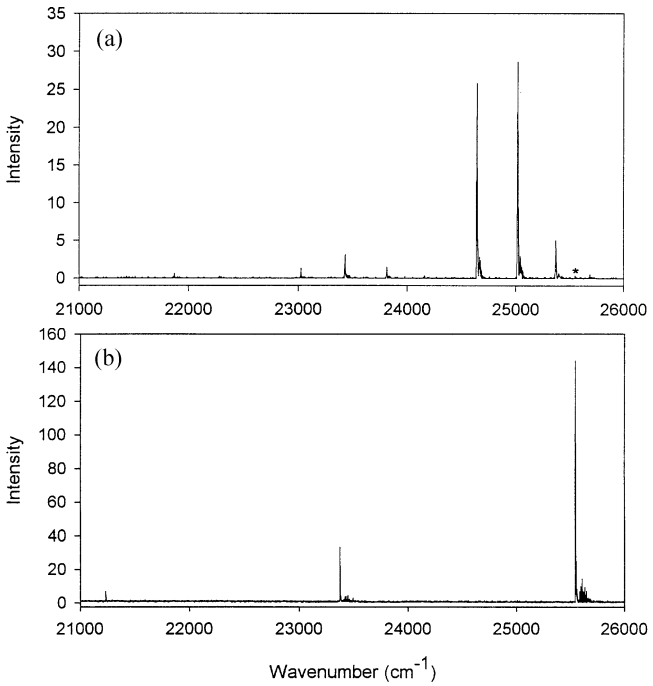

Figure 2. A portion of the vibronic emission spectra (a) obtained from the pure nitrogen jet without collisional excitation in a corona excited supersonic expansion, (b) obtained from the nitrogen jet while a metastable helium atomic jet collides with the excited nitrogen molecular jet at the right angle. The weak band belonging to the nitrogen molecular ions is represented by an asterisk in (a).

visible region. The spectral region from 18000 to 26000 cm^{-1} was scanned in about one hour in 2.0 cm^{-1} steps to obtain the final spectra shown in Figure 2.

Results and Discussion

We have focused our attention on the emission intensity of the bands from the vibronic emission spectra taken from the nitrogen jet upon collisional energy transfer by metastable helium jet. The spectrum(a) in Figure 2 was obtained from the pure nitrogen jet in a corona excited supersonic expansion without collisional excitation by metastable helium. This exhibits the vibronic bands belonging to the nitrogen molecules as well as the nitrogen molecular ions.[11] Most of the strong bands belong to the nitrogen molecules in the transition of $C^3\Pi_u \rightarrow B^3\Pi_g$ (second positive system).[11] The very weak band indicated by an asterisk is from the nitrogen molecular ions in the transition of $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ (first negative system).[11]

The C and B states of nitrogen molecule are 11.05 eV and 7.39 eV high from the ground state, respectively. For the nitrogen molecular ion, the B state is 3.16 eV high from the ground state. Since the ionization energy of the nitrogen molecule is 27.10 eV, a total of 19.21 eV and 22.87 eV are required to generate the nitrogen molecular ions at the B state from the C and B states of the nitrogen molecules, respectively.[12]

The excitation of nitrogen molecules and helium atoms in a corona discharge is possibly proceeded according to the following processes.

$$N_2 \text{ (X state)} + e^- \rightarrow N_2^* \text{ (C state)}$$
$$He + e^- \rightarrow He^* \text{ (2s}^3\text{S, 19.82 eV)}$$

The production of a metastable He at the 2s^{3}S state from the ground state by an electric discharge is well-known process.[13] On the other hand, the nitrogen molecular ions is possibly generated either from the nitrogen molecules at the excited state

$$N_2^* \text{ (C state)} + e^- \rightarrow N_2^+ \text{ (B state)}$$

or from the nitrogen molecules at the ground state.

$$N_2 \text{ (X state)} + e^- \rightarrow N_2^+ \text{ (B state)}$$

Also, it may be possible to generate the ions from the nitrogen molecules at the B state. But the most feasible way is from the ground state because of much larger number of population at the ground state in the jet. It should be understood that in a corona discharge using Engelking type nozzle with anode inside the nozzle throat, the number of molecules being excited by electron impact in a jet is proportional to the difference between production and destruction during the expansion. Thus, the total emission intensity reflects the population of molecules at the given states.

In order to observe the collisional excitation effect on the nitrogen molecular jet, we have taken the vibronic emission spectrum from the target jet in collision with the colliding jet. The spectrum in Figure 2(b) was obtained from the target jet while the helium atomic jet collides with the nitrogen molecular jet at the right angle. For this purpose, the length of helium atomic jet from the head of nozzle to the collision point was varied by moving the nozzle horizontally while fixing the focusing point to the spectrometer. At the short length, we have observed very strong emission intensity of molecular ions while the emission from nitrogen molecules completely disappeared as shown in Figure 2(b). The molecular ion exhibits a different bandshape from the molecule. The strong emission intensity of nitrogen molecular ions results from the energy transfer by the metastable helium atoms to the nitrogen molecules at the C state since the He energy (19.82 eV) is enough to produce the nitrogen molecular ions at the excited electronic state.[13] The excitation process by collisional energy transfer of metastable helium is represented as follows.

$$N_2^* \text{ (C state)} + He^* \text{ (2s}^3\text{S)} \rightarrow N_2^+ \text{ (B state)} + He$$

The effectiveness of energy transfer from the metastable helium to the nitrogen molecule was significantly reduced with increasing jet length due to the dispersion of the jet flow.[14] Also, the increasing backing pressure of helium deflects the supersonic jet flow after the collision, which deteriorates the optical alignment of the emission to the spectrometer.

In summary, we have excited the nitrogen molecule to molecular ion by using collisional excitation with metastable He jet which was generated in a corona excited supersonic expansion. From the observation, it has been found that the

collisional energy transfer is very effective with employing the corona discharge between two Engelking type nozzles, which may be useful for the generation of transient molecules at the excited electronic states.[8]

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