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6. For PTPase assay, *p*-nitrophenyl phosphate (pNPP) was used as a substrate. The enzyme was added to the reaction mixture containing pNPP in reaction buffer (10 mM pNPP, 100 mM HEPES, 10 mM DTT, 5 mM EDTA, pH 7.0). The reaction was quenched by addition of 1.0 mL of 0.5 N NaOH solution and the absorbance was measured at 405 nm. *p*-Nitrophenol released was quantitated using a standard curve determined for *p*-nitrophenol.

## New Excitation Technique using Jet Collision in a Supersonic Expansion

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The spectroscopic studies of highly excited transient molecules are of considerable interest in both theoretical and experimental chemists because they are believed to play very important roles in explaining the reaction mechanism.<sup>1</sup> One of the most powerful methods for observing these molecules is to use the technique of emission spectroscopy which has greatly contributed to the understanding of molecular structure.<sup>2</sup> In emission spectroscopy, the molecules are excited to high energy states by taking energy from the external sources such as microwave discharge, electric discharge, chemical reaction, photolysis, etc.<sup>3</sup> Of these, the method of electric discharge has been long employed for the generation and excitation of transient molecules.

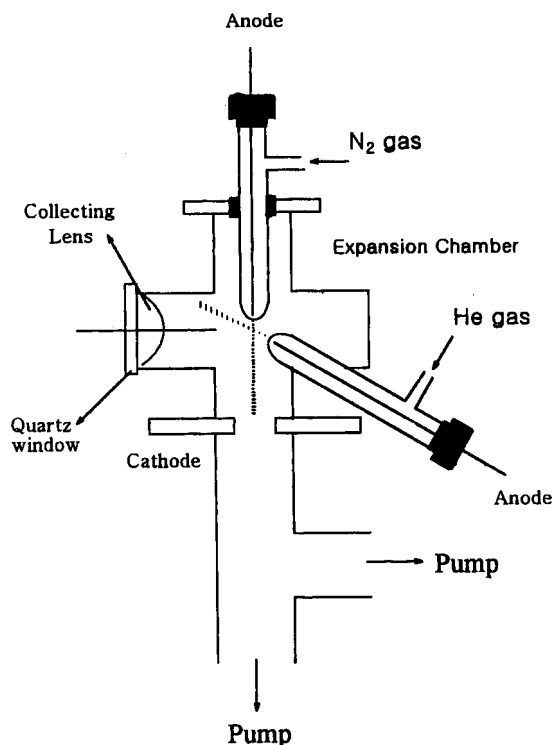
The supersonic free jet expansion has been proven to be a powerful spectroscopic tool for obtaining the spectrum of molecular species in the gas phase since the early work on NO<sub>2</sub> by Smalley *et al.*<sup>3</sup> The spectral simplification and stabilization associated with the inert gas expansion usually cannot be obtained in any other ways. The combination of supersonic expansion technique with the emission method has had an enormous impact on the repertoire of spectroscopic molecular studies that can be carried out. Of the emission sources developed so far for these purposes, the only one giving enough continuous photon intensity for high resolution studies of weak transitions in a jet is the Engelking-type corona discharge which has been widely used for the observation of the vibronic emission spectrum of transient molecules.<sup>4,5</sup> This has been applied for the observation of vibronic emission spectra of rotationally cooled transient molecules in the gas phase.<sup>6,7,8</sup> Nevertheless, this method is only suitable for the transitions of large Franck-Condon factor as well as of small excitation energy.

A technique using a jet collision in an expansion chamber has been devised as a method of more effective energy transfer. Recently, Cossart and Cossart-Magos<sup>9</sup> have succeeded the observation of the emission spectra of highly excited CO<sup>+</sup> employing jet collision of metastable Ne atom

and CO molecule generated from Geissler-type electric discharge. The same technique has been applied for the generation of CS<sup>+</sup> from the collision of metastable He atom with long-lived CS radical.<sup>10</sup> Similar methods have been used for the study of the energy transfer reaction between N<sub>2</sub> and CO under molecular beam conditions.<sup>11</sup> Very recently, Tokeshi *et al.* employed the ion-molecule collisions to generate the unstable molecular ion for observing the emission spectra of CH (A<sup>2</sup>Δ-X<sup>2</sup>Π) produced in collisions of Ar<sup>+</sup> with aliphatic compounds.<sup>12</sup>

Recently, we have determined to develop in our laboratory new excitation technique which is useful for the vibronic emission spectra of highly excited transient molecules using jet collision in a corona excited supersonic expansion.

Figure 1 shows the schematic diagram of the jet collision in a corona excited supersonic expansion. The experimental apparatus used in this experiment are similar to those reported previously.<sup>13</sup> The collision chamber was made of six-way cross Pyrex tube of 50 mm inner diameter. The nozzle was made of thick walled quartz tube of 12 mm outer diameter and 2 mm thickness, narrowed one end by flame heating to a capillary of the desired pinhole size, and connected with threaded adaptor (Ace glass model 5027-05). The anode located in the center of the nozzle tube with teflon holder was connected to the high voltage electric dc power supply (Bertan model 210-05R). The cathode made of a copper rod of 1.5 mm diameter and 100 mm length was placed to the parallel with target molecular jet through the Pyrex glass joint tube. Two nozzles perpendicular to each other were placed inside the chamber to produce the target and colliding jets. In this experiment, pinhole nozzles of 0.3 mm and 0.5 mm opening have been employed for the generation of metastable helium atomic and excited nitrogen molecular jets, respectively. The distance between the head of both nozzles was adjusted for the maximum excitation of the nitrogen molecules by the metastable He

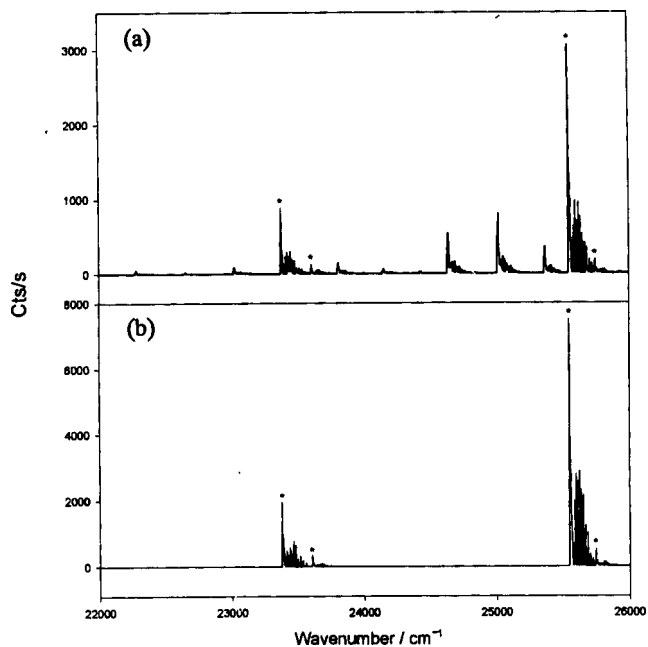


**Figure 1.** The schematic diagram of the jet collision in a corona excited supersonic expansion.

atomic jet. The collecting 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 He 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 1.5 Torr during the operation. The backing pressure of the nitrogen was kept at 2.0 atm while the helium pressure was varied for the maximum emission intensity of the nitrogen molecular ion. The helium pressure was ranged from 1.0 Torr to 1.0 atm. The bright jet was obtained by an electric dc discharge at 1050 V and 10 mA with 200 k $\Omega$  ballast resistor. The emanating light from the nitrogen jet was focused on to the slit of the spectrometer using a combination of two mirrors and a lens. The vibronic emission spectrum of nitrogen molecules were recorded with the double type monochromator (Jobin Yvon U-1000) using a head-on photomultiplier tube (Hamamatsu R649) in a cooled housing. The visible emission spectra shown in Figure 2 were obtained by scanning 22,000 to 26,000  $\text{cm}^{-1}$  at the step of 2.0  $\text{cm}^{-1}$  and 100  $\mu\text{m}$  of slit width over 10 min.

We have focused our attention on measuring the intensity change of the bands from the vibronic emission spectrum taken from the nitrogen jet upon collisional energy transfer by a metastable helium. The spectra observed in this experiment<sup>14</sup> exhibit the vibronic bands belonging to not only the nitrogen molecules in the transitions of  $C^3\Pi_u \rightarrow B^3\Pi_g$  (second positive system) but also the nitrogen molecular ions in the transition of  $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$  (first negative system), cited  $\text{CO}^+$  employing jet collision of metastable Ne atom



**Figure 2.** The vibronic emission spectra (a) obtained from the pure nitrogen 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 bands belonging to the molecular ions are represented by an asterisk.

1) statistics of the homonuclear diatomic molecules as well as a bandhead in the P-branch. The spectrum in Figure 2(a) was obtained from the corona excited supersonic expansion of the pure nitrogen molecules without collision of helium atomic jet. This is a typical spectrum observed from the nitrogen molecules in a corona discharge. The nitrogen molecules at the ground state are excited by electron impact to higher electronic states (C state), from which the molecules undergo a radiative relaxation to the B state. The C and B states are 11.05 eV and 7.39 eV higher from the ground electronic state ( $X^1\Sigma_g^+$ ), respectively.<sup>15</sup> The same explanation is applied to the generation of nitrogen molecular ions at the excited electronic states.

The spectrum in Figure 2(b) was observed from the target jet while the helium atomic jet collides with the target jet at the right angle. In this process, the metastable helium atomic jet transfers its energy to the nitrogen molecules at the C state. It is well-known that the helium atoms excited to the several highly excited states initially by electron impact collisionally relax to the metastable state ( $2s^3S$ ) which is 19.82 eV high from the ground state and has a relatively long lifetime.<sup>16</sup> This energy is high enough to produce the nitrogen molecular ions at the excited state (B state) from the nitrogen molecules at the C state through single collision. The ionization energy of the nitrogen molecule is 27.10 eV. Thus, a total of 19.21 eV and 30.26 eV are required to produce the nitrogen molecular ion at the B state from the nitrogen molecule at the C and ground states, respectively, since the B state of the nitrogen molecular ion is 3.16 eV high from the ground state. The disappearance of the vibronic bands of the nitrogen molecules as shown in citation of the nitrogen molecules by the metastable He

the nitrogen molecular ions from the nitrogen molecules after the collisional energy transfer by helium. Also, we have observed the substantial increase in the rotational temperature of the bands upon collisional excitation by a metastable helium as expected. The details of energy transfer process will be published elsewhere.

In summary, we have tried to develop the excitation technique useful for highly excited transient molecules using the collision with a metastable helium atomic jet in a corona excited supersonic expansion. The nitrogen molecules were excited and ionized by collision with metastable helium atomic jet. From the comparison of the spectra observed, it has been concluded that the energy transfer from helium atom to nitrogen molecule is quite effective in this experimental scheme.

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