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Collisional Excitation using Metastable Helium Jet Produced in a Graphite Tube Nozzle

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The graphite tube nozzle has been developed for the generation of metastable He jet by which the nitrogen molecules initially excited in a jet with Engelking type nozzle have been further excited in a corona excited supersonic expansion. The excitation process of nitrogen molecules in the jet collision has been discussed in detail by observing the emission intensity from the vibronic emission spectra of nitrogen molecules and nitrogen molecular ions upon helium jet collision.

Introduction

The transient molecules are of considerable interest in chemistry because they are believed to play important roles in chemical reaction as reaction intermediates.[1] So far, many experimental techniques have been developed to produce these short lived molecules because they only exist under abnormal conditions. One of the most popular methods obtaining these molecules is to decompose the stable precursor by providing the molecules with the external energy using the methods such as microwave discharge, electric discharge, chemical reaction, photolysis, etc.[2]

As one of the most convenient devices, Engelking has recently developed the supersonic nozzle system using an electric discharge, which is called a corana excited supersonic expansion.[3,4] This has been widely used for the observation of the vibronic emission spectra of rotationally cooled transient molecules in the gas phase because it gives enough continuous photon intensity for the high resolution studies of weak transitions in a jet.[5-8] Nevertheless, this method is only suitable for the transitions of large Franck-Condon factor as well as of small excitation energy. In addition to these limitation in this scheme, the excitation is only possible to the energy states with long lifetime because of the rapid collisional relaxation process occurring at the high pressure region after excitation by electron impact.[7]

A technique using a jet collision in an expansion chamber has been devised as another method for the effective energy transfer. Cossart and Cossart-Magos[9] have succeeded the observation of the emission spectra of highly excited CO^+ in the gas phase employing jet collision between metastable Ne atom and CO molecule generated from Geissler type electric discharge. The same technique has been applied for the generation of CS^+ by collison of the metastable He atom with long-lived CS radical.[10] Li and coworkers have applied the jet collision process to the energy transfer reaction between rare gas atom and small precursor molecules for observation of the dissociative excitation of small molecules.[11-13] This method was also used for the collision between small molecules under molecular beam conditions.[14] Recently, Tokeshi *et al.* employed the ion-molecule collisions to generate the unstable molecular ion for observing the emission spectra of CH produced in collisions of Ar^+ with aliphatic compounds.[15]

Very recently, we have reported the development of excitation technique using jet collision in a corona excited supersonic expansion.[16] In this scheme, two identical Engelking type nozzles were employed for the excitation of both target and colliding jets. The nitrogen molecules initially excited by the electron impact were further excited by the collision of metastable He atomic jet, leading to produce the nitrogen molecular ions at the excited state. Although this method has been turned out to be very effective for highly excitation process, there exists a technical difficulty in maintaining the electrical discharge at both nozzles.

In this work we have modified the excitation scheme using the graphite tube nozzle instead of Engelking type nozzle for the colliding atomic jet. The target nitrogen molecules initially excited using Engelking type nozzle in a corona excited supersonic expansion are further excited to nitrogen molecular ions *via* jet collision with metastable He atoms.

Experimental Details

Figure 1 illustrates the schematic diagram of the jet col-

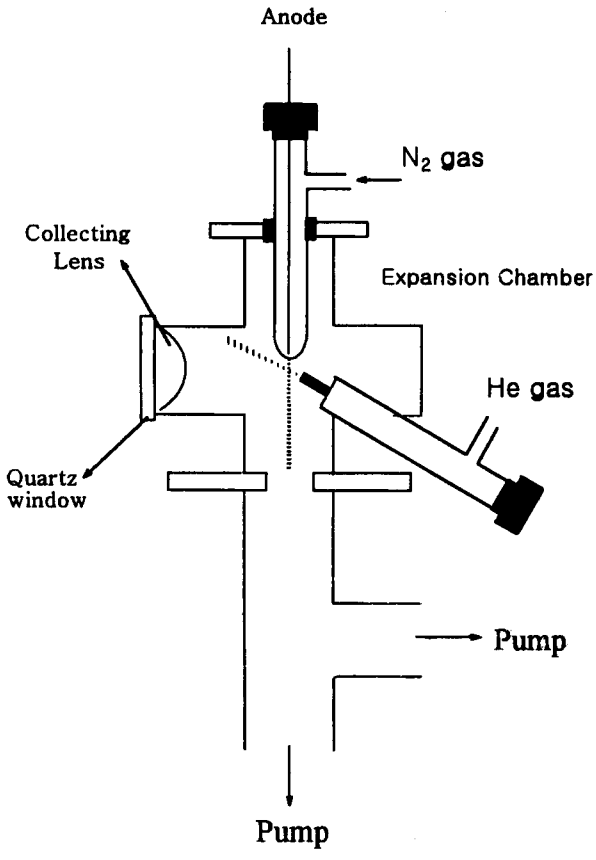

Figure 1. The schematic diagram of the jet collision using Engelking type nozzle for the target jet and graphite tube nozzle for the colliding jet in a corona excited supersonic expansion.

lision between nitrogen molecules and He gas in a corona excited supersonic expansion. The experimental apparatus used in this work are similar to those reported previously.[16] It consisted of an Engelking type nozzle for the excitation of target nitrogen molecules, graphite tube nozzle for the colliding He atomic jet, a high vacuum collision chamber, and a spectrometer for the vibronic emission spectra of the target molecules in a jet. The Engelking type nozzle was made according to the method previously published.[16] The graphite tube nozzle was made of a 25.4 mm long and 6.4 mm outer diameter graphite of spectroscopic grade. The tube has 0.7 mm inner diameter hole in the center for the He atomic jet. The graphite tube was epoxy glued to the Pyrex glass tube of 12.7 mm outer diameter for the coupling with the collision chamber. The graphite tube was acting as a cathode by externally wiring to the ground of the high voltage power supply. The direction of the Engelking type nozzle was perpendicular to that of the graphite tube nozzle. Also, the nitrogen molecular jet was parallel with the pumping direction for the maximum pumping efficiency. In this experiment, pinhole opening size of 0.3 mm has been employed for the nitrogen molecular jet. The collision effect appeared to increase by shortening the distance between the head of graphite tube nozzle and the nitrogen jet. However, the electrical current of the discharge increases substantially at the very short disctance, which degrades significantly the quality of the spectrum observed. The distance between the head of both nozzles was adjusted for the maximum signal to noise ratio of the spectrum, and fixed at 1.0 cm during the experiment. Both the metastable He atomic and the excited nitrogen molecular jets were generated using the Engelking type and the graphite tube nozzles, respectively, 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 each, 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 observation of emission intensity of the nitrogen molecular ion. The helium pressure was ranged from 1.0 Torr to 0.1 atm. The bright jet was obtained by an electric dc discharge at 1000 V and 2-3 mA with 200 kΩ ballast resister. The collecting quartz lens of 38 mm diameter and 50 mm focal length was placed inside the another arm of the collision chamber which is perpendicular to both direction of the jets. The eminating light from the nitrogen jet after the collision was focused onto the slit of the spectrometer using a combination of two mirrors and a lens. The optics were aligned to obtain the maximum total fluorescence from the jet. The vibronic emission spectra from the jet have been recorded with the double type monochromator (Jobin Yvon U-1000) using a head-on photomultiplier tube (Hamamatsu R649) in a cooled housing. The visible vibronic emission spectra were obtained by scanning 22,000 to 26,000 cm^{-1} at the step of 2.0 cm^{-1} and 100 μm of slit width over 10 min.

Results and Discussion

We have focused our attention on comparing the emission intensity of the vibronic bands of the spectra taken from the nirogen jet upon collisional energy transfer by a metastable helium. The spectrum in Figure 2 was obtained from the pure nitrogen molecules in a jet at a corona excited supersonic expansion without collisional energy transfer by metastable He. This spectrum exhibits the vibronic bands belonging to both the nitrogen molecules and the nitrogen molecular ions.[17] Most of the strong bands observed in the spectrum belong to the nitrogen molecules in the transition of $C^3\Pi_u \rightarrow B^3\Pi_g$ (second positive system). The bands from the nitrogen molecular ions in the transition of $B^2\Sigma_u^+ \rightarrow$

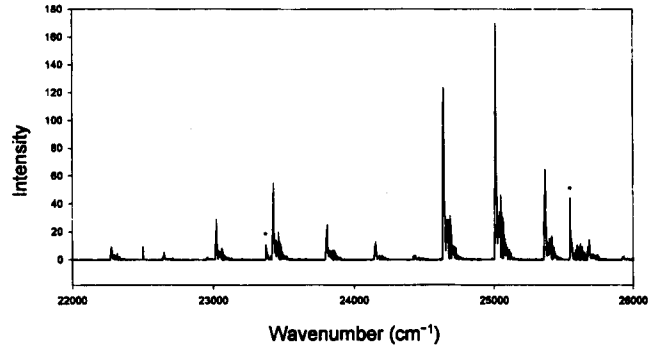

Figure 2. A portion of the vibronic emission spectra obtained from the pure nitrogen molecules using Engelking type nozzle without collisional energy transfer in a corona excited supersonic expansion. The bands from nitrogen molecular ions are indicated by asterisk.

$X^2\Sigma_g^+$ (first negative system) are indicated by asterisk. Also, the intensity alternation with rotational quantum number is clearly seen indicating that the molecule is homonuclear diatomics of $^{14}N(I=1)$.[18] The sharp bandhead in the P-branch is due to the large difference in the rotational constants between both vibronic states.[19] We can easily identify the ionic bands because the nitrogen molecular ion has slightly different bandshape from the nitrogen molecules. From the comparison with the spectrum simulated, the molecules exhibit rotational temperature of 45°K after supersonic expansion, which has a good agreement with those reported previously using the same experimental apparatus.[8] It is well known that the vibrational temperature of transient molecules is sensitive to the methods used for the decomposition of the precursor while the rotational temperature is subjected to the pressure difference of the supersonic expansion.

The C and B states of nitrogen molecule are 11.05 eV and 7.39 eV high from the ground state, respectively. In 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 needed to generate the nitrogen molecular ion at the B state from the C and B states of the nitrogen molecules, respectively.

It should be understood that in a corona discharge using Engelking type nozzle with anode inside the nozzle throat, the electrons flow in the opposite direction of the molecular jet. The number of molecules being excited by electron impact in a jet is proportional to the difference between production and destruction. The production rate increases with electric current in the discharge while the destruction rate depends on the lifetime and collision frequency. Since there is no collision process in the supersonic jet, the molecule may loose its energy by radiative process. Thus, the total emission intensity reflects the population of the molecules at the given states.

The number density of the excited molecules in a unit length of the jet increases downward and reach the maximum at the distance given by the lifetime of the molecules and the jet speed. Beyond the maximum point, the number density remains constant downward the jet with assumption that the number of molecules being decomposed is negligible. However, since the jet flow disperses downward, the density of the excited molecules in a unit area decreases, resulting in the decrease of the emission intensity at the slit of the spectrometer.

The excitation of nitrogen molecule and He atom by electron impact in a corona discharge is possibly proceeded according to the following processes.

$$N_2 \text{ (X state)} + e^- \longrightarrow N_2^* \text{ (C state)}$$

$$He + e^- \longrightarrow He^* \text{ (}2s^3S\text{, 19.82 eV)}$$

The production of a metastable He at the $2s^3S$ state from the ground state He by an electric discharge is well-known process.[20] On the other hand, the production of nitrogen molecular ions is possible from either the nitrogen molecules at the excited state

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

or the nitrogen molecules at the ground state.

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

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 large number of population at the ground state in the jet.

In order to observe the collisional effect on the nitrogen molecular jet, we have taken the vibronic emission spectra of the nitrogen molecules and ions in the jet after the collision of metastable He. For this purpose, we have varied the jet length from the head of nozzle to the collision point by moving the Engelking type nozzle vertically while fixing the focusing point of the spectrometer. At the very short length, we have observed very strong intensity of molecular bands compared to ionic bands, which is similar to that shown in Figure 2. The strong intensity of molecular bands are resulting from the energy transfer by the metastable He atoms to the ground state nitrogen molecules because the He energy (19.82 eV) is enough to produce the excited molecules. The excitation process by collisional energy transfer of metastable He is represented as follows.

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

However, the molecular ions cannot be formed from the molecules at the ground state using the energy transfer of metastable He.

With increasing jet length, the spectrum exhibits increasing intensity of ionic bands compared to those of the molecules as shown in Figure 3 because of the increasing population of excited molecules(C state) in the jet. As explained above, the metastable He has enough energy to produce the ions at the B state from the the molecules at the C state. The intensity of molecular bands was decreased because the number of excited molecules in a unit area was reduced at the dispersed jet With further increase of the length, the molecular bands disappear while the intensity of the ionic bands remains constant. This phenomena can be explained from the constant population of the excited molecules down the jet.

We have also tried to observe the intensity variation with the He pressure inside the graphite tube nozzle. The intensity of the ionic bands increases up to 2.0 mbar He pressure. In the range of 2.0-30.0 mbar pressure, the intensity of

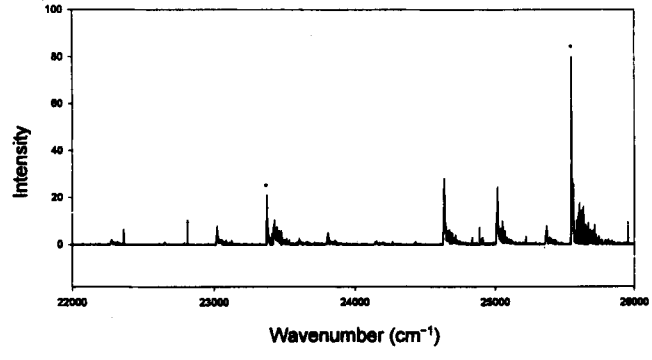

Figure 3. A portion of the vibronic emission spectra obtained from the nitrogen jet after collisional energy transfer by metastable He atomic jet. The bands from nitrogen molecular ions exhibits an increasing intensity compared to those from the molecules.

ionic bands remains constant. However, beyond 30.0 mbar pressure, the molecular jet exhibits the deflected jet flow which distort the optical alignment into the spectrometer, resulting in decrease of the reproducibility of the experiments.

In summary, we have developed a graphite tube nozzle by which a metastable He atom was generated. The nitrogen molecules initially excited in Engelking type nozzle were further excited by collisional energy transfer of a metastable He atom. The excitation of nitrogen molecules to nitrogen molecular ions were monitored by observing the emission intensity of the bands in the spectra from the nitrogen jet. From the observation, it has been found that the excitation of the nitrogen molecules at the excited state is more effective for the generation of nitrogen molecular ions, suggesting that the effective energy transfer by molecular collision may be useful for the generation of the highly excited species.

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Polymerization of Anisole Derivatives Containing Allyl or Chloromethyl Group Through Aromatic Electrophilic Substitution Reaction

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4-Allylanisole was polymerized with $AlCl_3$ as a catalyst. The polymerization was carried out in nitroethane at various temperatures with changing the ratio of the initiator to the monomer concentration. The weight average molecular weights measured by gel permeation chromatography in chloroform with polystyrene standards were between 1,500 and 4,700. ^1H NMR spectroscopy showed that the polymerization proceeded through a stepwise aromatic electrophilic substitution reaction along with a minor chain-reaction, resulting in a branched polymer. 4-Chloromethylanisole was also polymerized with $AlCl_3$ in nitroethane through an aromatic electrophilic substitution reaction to give a high molecular weight polymer (Mw=88,000).

Introduction

A few aromatic compounds having electrophiles are polymerized through aromatic electrophilic substitution reactions.[1,2] The reactions are accelerated by presence of electron donating groups on the aromatic rings. In the polymerization of a phenol-formaldehyde under basic conditions, the benzene ring of the phenol is activated by an oxide group and reacts easily with formaldehyde.[3-5] Certain aromatic compounds with alkyl halide substituents are po-