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Development of Corona Excited Supersonic Jet System for the Vibronic Emission Spectra of Transient Molecules

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One of the most interesting subjects in modern molecular spectroscopy is to observe the spectrum of transient molecules in the gas phase.¹ For this purpose, numerous experimental techniques have been developed so far. Among the techniques developed, the supersonic free jet expansion has been proven to be a powerful spectroscopic tool for obtaining the spectrum of gas phase molecular species since early work² on the NO₂, allowing the study of rotationally resolved spectra of large molecules at low temperature. The spectral simplification and stabilization associated with the rare gas expansion usually cannot be obtained in any other way. The majority of these supersonic expansion applications have been carried out in the ultraviolet and visible frequency regions because of the sensitivity of fluorescence-based detection schemes.

Transient molecules are characterized as existing in low concentrations and in abnormal conditions, and thus their

observation requires that available instrumentation be pushed to its limit.¹ The supersonic expansion method has been applied to the fluorescence spectra of radicals,³ ions,^{4,5} and clusters⁶ in free jets. In these cases, excitation occurs either before or after expansion. For example, in the Engelking-type corona discharge,⁷ pyrolysis jet,⁸ Hg-photosensitized reactions inside the throat of a Campargue-type free jet,⁹ and laser metal vaporization cluster sources,¹⁰ the gases are excited before expansion, whereas in cw^{4,5} and pulsed electron beams,¹¹ as well as VUV and multiphoton ionization devices,¹² excitation occurs outside the expansion region. Very recently, Cossart and Cossart-Magos¹³ have developed a new emission source which is effective for the molecular ions using Penning-type electric discharge in a supersonic free jet. Of the emission sources, the only one giving enough continuous photon intensity for high resolution studies of weak transitions in a jet was the Engelking-type corona discharge which has been widely used for the observation of the vibronic emission spectrum of transient molecules.¹⁴ However, this device has suffered from destabilizing the discharge of messy precursor over a long period.

Recently, we have chosen¹⁵ to develop in our laboratory an emission source for the vibronic spectra of transient molecules using a corona discharge in a jet and a long path length of monochromator. It would be useful for obtaining the vibronic emission spectra of transient molecules as well as stable molecules. This communication details the design of the instrumentation developed.

Figure 1 shows the schematic diagram of the corona excited supersonic jet system which is mainly divided into three parts; electric discharge, supersonic expansion and spectrometer. For the generation of transient molecules in a jet from the precursor molecules, we have employed a conventional corona discharge system which is similar to that developed by Engelking.⁷ A conventional corona discharge¹⁶ coupled with a supersonic expansion is consisted of a thin metal rod, terminated with a sharp point, mounted inside an insulating and inert tube. A small pinhole or slit is cut into the end of the tube, forming a supersonic nozzle. The metal tip is placed very close to the exit hole and a high positive voltage is applied to the rod. Thus, the nozzle body, in this work, was formed from a thick-walled quartz tube of 12 mm outer diameter, 2 mm thickness, and 250 mm length, narrowed by flame heating at one end to a capillary of the desired pinhole size. The nozzle was connected to threaded adaptor (Ace glass model 5027-05). A long and sharpened anode, made of a 1.6 mm diameter stainless steel rod was inserted through a rubber o-ring into the quartz nozzle for the generation and excitation of transient molecules. The o-ring was tightened by a teflon bushing with a hole in center through which the anode was connected to the high voltage electric dc power supply (Bertan model 210-05R).

The position of the metal tip used for the anode has been proven to be critical for the stability of the discharge over a long period. For example, in Engelking type corona discharge the metal tip is located inside the nozzle and the molecules are excited before expansion, which substantially reduces the stability of the discharge when organic compounds are used as precursors. The messy fragments generated by an electric discharge of the organic precursor easily block the narrow hole of the nozzle. Thus, in this design we put

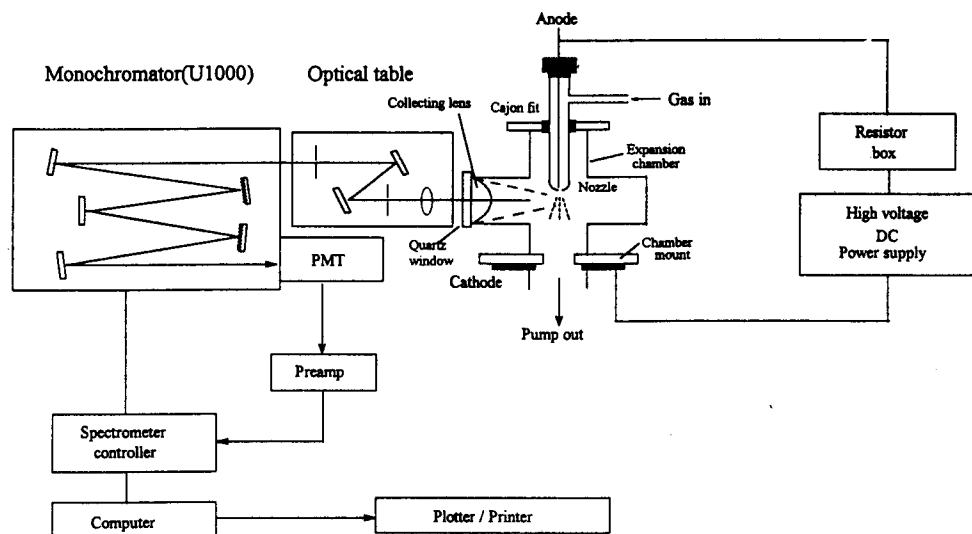


Figure 1. The schematic diagram of the corona excited supersonic jet system.

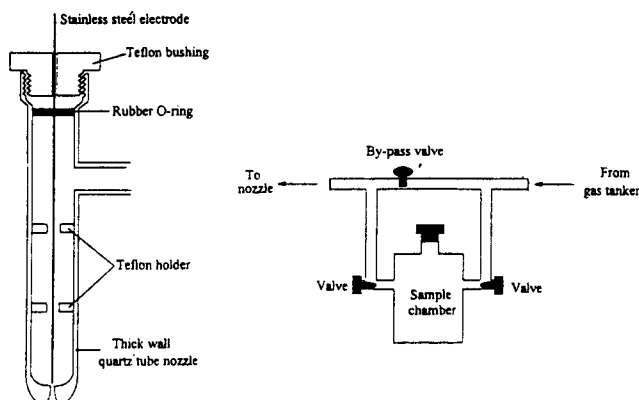


Figure 2. The details of the nozzle structure.

the metal tip outside the nozzle. Even though the length of the metal tip exposed outside the nozzle is less than 0.5 mm, it changes the mechanism, leading to excitation after expansion. However, it is very important to let the metal tip be centered at the hole for the straightly downstream beam. The anode was firmly fixed into the center of nozzle by using teflon holders inside the nozzle. The teflon holder made of 3 mm thickness of teflon disk of whose diameter is exactly same as the inner diameter of the nozzle has a center hole for the anode and several small holes for the gas flow. The nozzle was positioned into the expansion chamber via a Cajon fit attached to the stainless steel flange. The cathode was located at under the chamber supporter made by an acrylic plate to avoid seeing the arching by the spectrometer during the discharge. The arching was more severe when the surface of the cathode was contaminated by foreign compounds.

When a dilute mixture of a precursor molecule in a rare gas was expanded through the orifice, an electrical discharge produced not only molecular fragments but also vibrationally excited molecules. The details of the nozzle system is shown in Figure 2. The anode was connected via a 200 k Ω ballast resistor to the high voltage electric dc power supply which

has a maximum 5 kV and 40 mA capacity. The expansion gas is supplied from 3 atm rare gas reservoir seeded with a small quantity of stable precursor molecules vaporized inside the vaporizing vessel. The concentration of the precursor in a carrier gas can be controlled by immersing the sample in a temperature-controllable water bath or adjusting the opening of the bypass valve. Since the discharge occurs in the high pressure region of the nozzle, molecules undergo collisional relaxation into the vibrational ground level of the electronic excited state before they emit. Thus, it has an advantage of observing the transitions from a single vibronic state.

For the rotational cooling, the supersonic expansion chamber was made of six-way cross pyrex tube of 50 mm inner diameter. The chamber was evacuated by a 800 L/min mechanical vacuum pump (WS Automa model W2V80), resulting in the pressure range of 1.5-1.8 Torr during the operation with 2.0 atm of backing pressure. The emitting light from the downstream jet was collected through a collecting quartz lens of 38 mm diameter and 50 mm focal length placed at focal length from the tip of the nozzle, and focused onto the slit of the double-type monochromator using a combination of two mirrors and a lens.

For the spectrometer, we have employed the double type monochromator (Jobin Yvon model U-1000) which has effective path length of 2.0 m using 3 mirrors and 2 gratings of 1800 groves/mm. The scanning range of the spectrometer is from 11,500 cm^{-1} to 32,000 cm^{-1} , with a maximum resolving power of 0.15 cm^{-1} at 17,000 cm^{-1} which is good enough to observe the rotational contour of the vibronic band of large molecules in a jet. For the photon counting, a head-on photomultiplier tube (Hamamatsu model R649) was employed with a cooled housing. The output of the PMT was fed to the spectrometer control box via the preamplifier. The spectrometer was fully operated using a software SPECTRA-MAX¹⁷ by a personal computer.

For the test of the system, we have obtained the rotationally cooled vibronic emission spectra of N_2^+ in the gas phase which was generated in a jet from the corona discharge of

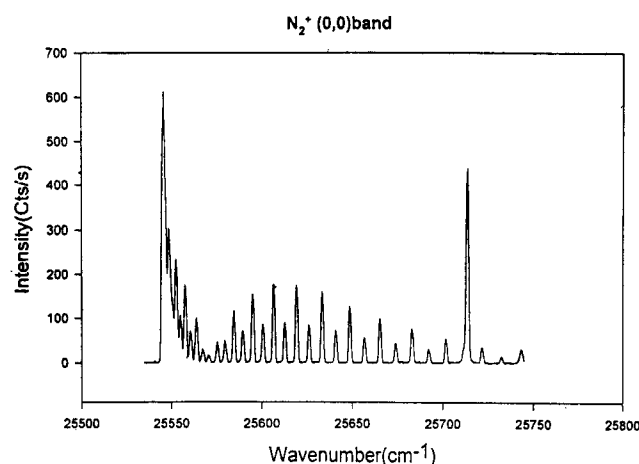


Figure 3. The vibronic emission spectra of gas phase N_2^+ generated in a jet by a corona discharge of the gas mixture of He and N_2 . The spectrum shows the origin band in the transition of $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$. The strong line at 25715 cm^{-1} is from the buffer gas He.

the the gas mixture of N_2 and the buffer gas He. The discharge conditions were adjusted for the maximum intensity of N_2^+ as well as the maximum value of N_2^+/N_2 in the spectrum observed. The maximum intensity of the N_2^+ was obtained at the 1.5 Torr of chamber pressure and 1050 V and 3 mA current. The rotational cooling was achieved employing a pinhole nozzle of 0.3 mm opening and 2.0 atm backing pressure. The supersonic beam could not be produced from the nozzle of smaller opening, since the sharpened anode partially blocks the pinhole during the operation. The visible emission spectrum shown in Figure 3 was taken by scanning $25,500$ to $25,800\text{ cm}^{-1}$ at the step of 0.05 cm^{-1} and $50\text{ }\mu\text{m}$ of slit width over 10 min. This is assigned to the origin band in the transition¹⁸ of $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ of N_2^+ showing the intensity alternation due to the nuclear spin statistics of the homonuclear diatomic molecules as well as a band-head in the P-branch which is very similar to that of the isoelectronic molecule CN.¹⁹

In summary, we have built in our laboratory the spectrometer for the vibronic emission spectra of transient molecules in the gas phase coupled with the technique of the corona discharge excited supersonic jet system. This exhibits the characteristics of simple, durable, and bright emission source for the high resolution vibronic spectra of unstable molecules.

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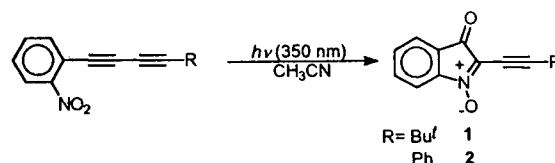
A Simple and Efficient Synthesis of Isatogens from 1-(o-Nitrophenyl)-1,3-butadiynes

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Irradiation of 1-(o-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (o-NDHD)¹⁻³ and 1-(o-nitrophenyl)-4-phenyl-1,3-butadiyne (o-NPPD)^{4,5} in CH_3CN (2 mM) for 40 min yields isatogen derivatives **1** and **2** in high yields (Scheme 1).⁶



Scheme 1.

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