Collisional Excitation of Benzyl Radical in a Corona Excited Supersonic Expansion

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Many techniques have been developed to produce transient molecules[1] since they are believed to play important roles as reaction intermediates in chemical reaction. The method frequently employed is to decompose stable precursor molecules using methods such as microwave discharge, electric discharge, photolysis, and chemical reaction, etc.

As an emission source, Engelking and coworkers[2,3] have developed a very simple supersonic nozzle system coupled with high voltage electric discharge for the excitation of molecules in a jet, which is called a corona excited supersonic expansion (CESE). This has been frequently used for the observation of vibronic emission spectra of transient molecules[4~9] because it gives strong photon intensity for the high resolution studies of weak transitions. Nevertheless, this method is only suitable for the transition of large Franck-Condon factor as well as of small excitation energy. Besides these limitations, excitation into vibrationally excited electronic state is not always possible for large molecules due to the efficient collisional relaxation process at the nozzle throat during expansion.[8,9] Thus, the vibronic emission spectra obtained with Engelking type nozzle in a corona excited supersonic expansion are similar to the laser dispersed fluorescence spectra while pumping the origin band of the electronic transition.[10]

Recently, a technique using jet collision in a supersonic expansion chamber has been developed for the excitation method. Molecular collision between target molecules and metastable rare gas produces vibronically excited target molecules which subsequently fluoresce. Cossart and Cossart-Magos[11] have observed the emission spectra of highly excited CO^+ in the gas phase from the jet collision between metastable Ne atom and CO. The same technique has been also applied for the generation[12] of CS^+ from long-lived CS radical in collision with the metastable He atomic jet. Recently, Li and coworkers[13,14] have detected the dissociative excitation of small molecules, in the jet collisional process, of the energy transfer between rare gas atom and small precursor molecules. Tokeshi *et al.*[15] have obtained the emission spectra in the visible region of CH produced in collision of aliphatic compounds with Ar^*. Very recently, we have reported the development of the jet collision experiment to obtain the nitrogen molecular ions from the electronically excited nitrogen molecules using a metastable He jet generated in the Engelking type nozzle[16] and graphite tube nozzle.[17] Up to the present, however, most of the collisional excitation experiments have been confined to the small molecules.

The benzyl radical is a prototypical aromatic radical having seven delocalized π electrons and has been subjected to many spectroscopic studies.[18~20] However, most of studies on the benzyl radical have been focussed on the first excited electronic state (1^2A_2). Miller group[21] analyzed the vibronic coupling between the second excited state (2^2B_2) and the vibrationally excited states of the first excited electronic state from their high resolution spectra. Carrick and Selco[22] have recently applied the CESE technique to obtain the rotationally cooled vibronic emission spectra of the benzyl radical. Owing to the efficient cooling effect, however, it was extremely difficult to observe the hot vibronic bands originating from the vibronically excited state by which the molecular structures at the excited states can be obtained.

Thus, in this study, we have tried to obtain the vibronic emission spectra of the benzyl radical in which the intensity of the hot vibronic bands have been significantly increased by the jet collision with the metastable He atomic jet.

The experimental apparatus employed in this work is similar to those described previously.[23] Briefly, it consisted of a collision chamber, two Engelking type nozzles, and a spectrometer. The collision chamber is the six-way cross type made of thick Pyrex glass tubes of 50 mm inner diameter. The chamber was evacuated by two mechanical vacuum pumps (WS Automa W2V80) of the capacity of 800 L/min each, resulting in the pressure of 1.5 Torr during the expansion with 2.0 atm of He backing pressure. The Engelking type nozzles were made of thick quartz tube of 12.7 mm outer diameter according to the methods described previously.[23] Both nozzles perpendicular to each other were placed inside the chamber to produce the benzyl radical and the metastable He jets, respectively. The distance between the head of the both nozzles was adjusted for the maximum excitation of the benzyl radical. For the maximum collection of the fluorescence, a collecting quartz lens of 38 mm diameter and 50 mm focal length was placed at the another arm of the chamber which is also perpendicular to the both nozzles.

The benzyl radical was generated from the gas mixture of toluene and inert gas He by corona discharge. The toluene (Aldrich, reagent grade) was vaporized at room temperature inside the sample vessel under 2.0 atm of He gas. The concentration of the toluene in the gas mixture was adjusted for the maximum intensity of emission monitored from the $6b_1^0$ band which is the strongest band in the spectra of the benzyl radical in the transition of $1^2A_2 \rightarrow 1^2B_2$. The sharpened long stainless steel anode placed inside the nozzle was connected with the 3.0 kV dc power supply *via* 150 kΩ current limiting ballast resister. The cathode was located inside the other Engelking type nozzle which has been used for the generation of metastable He ($2s^3S$, 19.82 eV) in a jet. In this work, pinhole nozzles of 0.5 mm and 0.3 mm opening have been used for the generation of benzyl radical and metastable He atomic jet, respectively. The typical discharge condition was 5 mA at 2.0 kV dc potential.

In order to observe the collision efficiency, the gas pressure of the metastable He jet was varied over a wide range. As expected, the collisional excitation effect was increased with the He pressure. However, the direction of the benzyl radical jet was getting deflected with increasing He pressure, causing poor optical alignment with the spectrometer. Thus, we have fixed the He pressure at 10 Torr during the jet collision. Also, the He jet was focused onto the jet of benzyl radical within 2-3 mm from the emission point to the spectrometer.

The vibronic emission spectrum of the benzyl radical was obtained with a long path monochromator (Jobin Yvon U 1000) equipped with a cooled PMT (Hamamatsu R649). The light emanating from the downstream area of the jet ~7 mm below the nozzle head was collimated and focused onto the slit of the spectrometer. The spectrometer was scanned from 18000 to 24000 cm^{-1} at the step of 0.5 cm^{-1} with 100 μm of slit width over 30 min. The frequency of spectrometer was calibrated with the He atomic lines[24] recorded at the same time with the benzyl radical in a jet and believed to be accurate within ±0.5 cm^{-1}.

Figure 1 shows the benzyl radical spectrum obtained without jet collision. This is a typical vibronic emission spectrum in the transition of $1^2A_2 \rightarrow 1^2B_2$ taken with the Engelking type nozzle in a corona excited supersonic expansion. It consists of an origin band at 22000 cm^{-1} as well as many strong vibronic bands including $6a_1^0$ and $6b_1^0$ which exhibit the strongest intensity. It is well known that the origin band shows weaker intensity compared to the $6a_1^0$ and $6b_1^0$ bands in the vibronic emission spectra of the benzyl radical.[25] Any vibronic bands with observable intensity cannot be found to the blue of the origin, confirming the efficient vibrational relaxation at the nozzle throat. The band positions measured in this study are accurate within ±1.0 cm^{-1} from those reported previously.[25] Also from the comparison of bandshapes, we can easily identify that the origin band has similar bandshape to the $6a_1^0$, but different from the $6b_1^0$, which suggests that the origin and $6a_1^0$ bands belong to the same symmetry.[26,27]

The spectrum in Figure 2 was obtained from the benzyl radical jet while the metastable He jet was colliding with the benzyl radical jet. The experimental conditions were exactly the same for the both cases except for the jet collision.

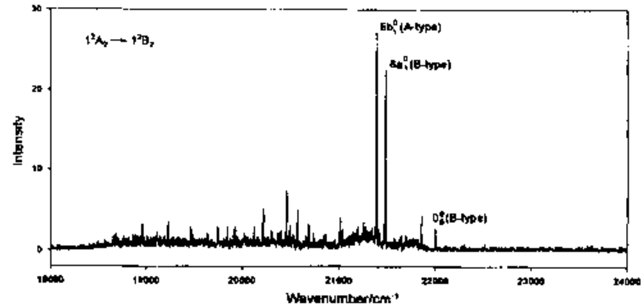

Figure 1. The vibronic emission spectrum of the benzyl radical in the transition of $1^2A_2 \rightarrow 1^2B_2$ obtained from the benzyl radical jet without He jet collision in a corona excited supersonic expansion.

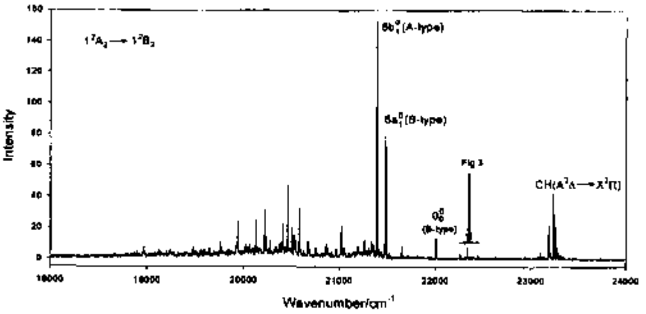

Figure 2. The vibronic emission spectrum of the benzyl radical in the transition of $1^2A_2 \rightarrow 1^2B_2$ obtained from the benzyl radical jet with collision of metastable He jet which was generated with an Engelking type nozzle in a corona excited supersonic expansion.

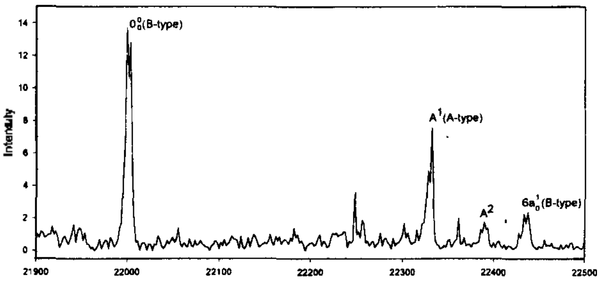

Figure 3. A portion of enlarged view of Figure 2. The bandshapes are clearly seen for the bands assigned.

From Figure 2, we can easily see that the S/N of the spectrum has been increased by a factor of 5 due to the intensive excitation process by metastable He. Besides the vibronic bands belonging to the benzyl radical as observed in Figure 1, we have found the bands belonging to the CH radical[28] in the transition of $A^2\Delta \rightarrow X^2\Pi$ which was generated from the benzyl radical during the excitation process, since the energy of He is much larger compared to the vibrational energy of the benzyl radical. In addition to CH bands, we have observed several weaker bands at ~22400 cm^{-1}. These bands are clearly shown in Figure 3 with the origin band of the benzyl radical. Since these are located at the higher wavenumber of the origin band, we can assign them as hot bands resulting from the vibrationally excited states of the lowest excited electronic state. The assignment of these bands denoted in Figure 3 has been made on the basis of the LIF works by Miller and coworkers,[21] and the high temperature emission work by Cossart-Magos and Goetz.[29]

In summary, the technique of collisional excitation developed in this laboratory has been applied to the benzyl radical using metastable He jet generated with an Engelking type nozzle in a corona excited supersonic expansion. The vibronic emission spectrum of the benzyl radical obtained with the jet collision shows the improved ratio of signal to noise of the spectra as well as the hot vibronic bands which was difficult to be observed with the CESE method. The present study also confirms that the collisional excitation is a powerful tool for the observation of the vibrationally excited electronic states of transient molecules.

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Unique Feature on the New J-Aggregate Formation of Tetrakis(2,6-difluorophenyl)porphyrin

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The aggregation of porphyrin compounds has been extensively studied because of its importance in the application to the biological and medicinal researches as well as the photoelectric applications.[1-5] Porphyrins with hydrophilic side chains are well known to form the aggregate in aqueous solution; porphyrins having anionic,[6-8] cationic,[9,10] or non-ionic[11-13] side chains form dimer or higher molecular aggregates, depending on the chemical structure of side chains upon the increase in solute concentration or the addition of acid, salt or surfactant. The aggregation is usually spectroscopically characterized by the appearance of the blue shifted (H-aggregate) or the red shifted (J-aggregate) Soret band. According to the molecular exciton theory, the frequency shift in the absorption spectrum is interpreted in terms of the angle between the aggregation axis and the transition dipole moment of each chromophore.[14] For porphyrin compounds, the H- and J-aggregates are formed when the aggregation occurs with face-to-face and edge-to-edge interactions between the neighboring units, respectively. Especially for the dicationic porphyrins with anionic side chains, the aggregation is closely related to the intermolecular ionic interaction as well as the π-π interaction, which strongly favors the J-aggregate formation.[8]

In this work, we report for the first time the aggregation

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