

the remained iodine was removed with NaHSO₃ solution, extracted with ether, and dried with anhydrous MgSO₄. Column chromatography (hexane) provided 0.063 g (90% yield) of **11** (isomeric ratio = 90 : 10): oil; ¹H NMR (CDCl₃) δ 7.47-7.05 (m, 10H); ¹⁹F NMR (CDCl₃, internal standard CFCl₃) δ -56.28 (s, 3F, one isomer), -60.03 (s, 3F, other isomer); MS, m/z (relative intensity) 374 (M⁺, 34), 247 (100), 227 (67), 178 (17); IR (neat) 3059, 3029, 1607, 1487, 1443, 1301, 1232, 1166, 1444, 1126, 747, 702 cm⁻¹.

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Characteristics of the Low Frequency Sequence Bands Observed in the Vibronic Emission Spectra of the Jet Cooled *p*-Fluorobenzyl Radical in the D₁→D₀ Transition

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The *p*-fluorobenzyl radical was generated from the *p*-fluorotoluene and vibronically excited in a corona excited supersonic expansion with inert buffer gases. The vibronic emission spectra of the jet cooled *p*-fluorobenzyl radical in the D₁→D₀ transition have been observed in the visible region. The spectra exhibit several low frequency sequence bands in the vicinity of the every strong vibronic band. The characteristics of the sequence bands have been examined by varying the experimental conditions such as carrier gas and nozzle size to identify the origin of the transition in the spectra.

Introduction

The identification of the transition states of the bands in the spectrum experimentally observed provides an important information on the molecular structure and motions.^{1,2} Since the properties of the potential energy surface along the rotational and vibrational potential coordinate often largely change upon electronic excitation, it is very difficult to assign the correct quantum numbers to the weak transitions of large molecule from the spectra obtained in the visible/uv region. In order to solve this difficulty, many spectroscopists have often employed supersonic cooling which has played a critical role in simplifying the otherwise congested spectra that would result from the population of low energy levels.³ For the better assignments of the transitions, on the other

hand, reliable theoretical calculations may be carried out on such molecules. These calculations provides valuable information about potential energy surfaces in both ground and electronically excited states.⁴

Bindley *et al.*⁵ obtained for the first time the vibronic emission spectra of *p*-fluorobenzyl radicals generated from the electric discharge of *p*-fluorotoluene and identified the origin band in the visible region. Also, Cossart-Magos and Cossart have made the provisional assignments on the low frequency sequence bands observed with the origin band in the gas phase discharge emission spectra of *p*-fluorobenzyl.⁶ The first low resolution excitation spectrum of *p*-fluorobenzyl radical in the visible region was reported by Charlton and Thrush.⁷ Although Fukushima and Obi⁸ have recently observed many bands from the excitation spectra of *p*-fluorobenzyl radical at very low temperature, they could assign only strong vibronic bands, leaving many bands

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unassigned.

Engelking and coworkers^{9,10} have developed a simple nozzle system which is useful for the generation and excitation of transient molecules in a corona excited supersonic expansion. This has been applied for the observation of the vibronic emission spectra of many benzyl-type transient molecules.¹¹⁻¹⁶ As a representative case, Selco and Carrick have reported the vibrational frequencies and the symmetry of the benzyl and xylyl radicals in a corona excited supersonic expansion.^{17,18} Recently, Lee and coworkers have further developed the nozzle system to obtain the vibronic emission spectra of substituted benzyl radicals with the improved ratio of signal to noise.¹⁹

In this work, we report the characteristics of the low frequency sequence bands observed in the vicinity of the every strong vibronic band of the *p*-fluorobenzyl radical in the visible region by varying the experimental conditions such as inert carrier gas and nozzle size to identify the origin of the transition in the spectra.

Experimental

The experimental setup which is similar to that used in the previous work²⁰ has been used in this work. Briefly, it consists of a pinhole type quartz nozzle coupled with high voltage dc electric discharge, a high vacuum expansion chamber, and a spectrometer for the vibronic emission spectra.

The *p*-fluorobenzyl radical was generated from the *p*-fluorotoluene and vibronically excited in the jet with an inert buffer gas in a corona excited supersonic expansion. The precursor *p*-fluorotoluene (Aldrich, reagent grade) was vaporized inside the vaporizing vessel made of thick Pyrex glass at the room temperature under 2.0 atm of inert carrier gas. The concentration of the parent compound in the carrier gas was adjusted for the maximum emission intensity and believed to be about 1% in the gas mixture. The gas mixture was expanded through the pinhole type nozzle made of the thick walled quartz tube of 12.7 mm outer diameter and 200 mm length and narrowed one end to a capillary by flame heating. The nozzle was terminated abruptly on the vacuum side for the free expansion by grinding the one end until the nozzle opening of the appropriate dimension is formed. Two different pinhole size of nozzles have been employed in this work.

The anode made of a sharpened stainless steel rod of 1.5 mm in diameter and 300 mm in length was inserted into the nozzle and firmly fixed in the center of the pinhole using a couple of teflon holder. In the original nozzle system developed by Engelking,¹⁰ the electrode sits just behind the nozzle opening on the high pressure side which leads to excitation before expansion, causing a problem of nozzle clogging when large organic compounds were used for the precursor. Thus, we have made the tip of the anode be located inside the nozzle throat since the corona discharge of the *p*-fluorotoluene produces heavy soot deposits clogging the pinhole. Although the length of the metal tip positioned inside the nozzle throat was shorter than 1.0 mm, it significantly improved the clogging problem of the nozzle by allowing excitation after expansion.

The anode was connected to a 3.0 kV high voltage dc

power supply and the discharge was stabilized by using a 150 k Ω current limiting ballast resistor. The typical discharge current was 5 mA at the 2.0 kV dc potential. The cathode made of copper rod of 100 mm long and 1.5 mm in diameter was placed to be parallel with the jet direction under the expansion chamber to reduce the arching noise.

The Pyrex expansion chamber of six-way cross type was evacuated by two 800 L/min mechanical vacuum pumps, resulting in the pressure range of 0.5-1.0 Torr during the expansion with 2.0 atm of backing pressure.

A blue colored jet was the evidence of existence of the *p*-fluorobenzyl radical in the jet. The light emanating from the downstream jet area 5 mm away from the nozzle opening was collimated by a quartz lens placed inside the expansion chamber and focussed onto the slit of the monochromator (Jobin Yvon U1000) containing two 1800 groove/mm grating and detected by photon counter with a cooled Hamamatsu R649 photomultiplier tube. During the scans, the slits were set to 0.200 mm, providing an effective resolution of 2.0 cm⁻¹ at the visible region. The spectral region from 18000 to 28000 cm⁻¹ was scanned at the step of 0.2 cm⁻¹ over 1 hr. to obtain the final spectra. For the vibronic emission spectra exhibiting the bandshapes, a high resolution FT spectrometer (Bruker IFS-120HR) has been used at the 0.5 cm⁻¹ resolution and integrated for 2.0 hrs with appropriate optical filters. The frequency of the spectrum was calibrated using the He atomic lines²¹ observed at the same frequency region as the *p*-fluorobenzyl radical and is believed to be accurate within 0.2 cm⁻¹.

Results and Discussion

A portion of the vibronic emission spectra of the D₁→D₀ transition of the *p*-fluorobenzyl radical generated in a large size of nozzle ($\phi=0.5$ mm) with carrier gases He and Ar are shown in Figures 1 and 2, respectively. From the comparison, it is shown that the He gas is more suitable for the generation of *p*-fluorobenzyl radical from the *p*-fluorotoluene in a corona excited supersonic expansion while the Ar gas produces lots of small fragments C₂. In Figure 2, the bands marked by asterisks belong to the swan bands (³Π_g→³Σ_u⁺)²² of the C₂. Most of the vibronic bands belonging to the *p*-fluorobenzyl radical are found in the region of 19000-22000 cm⁻¹. It consists of a strong origin

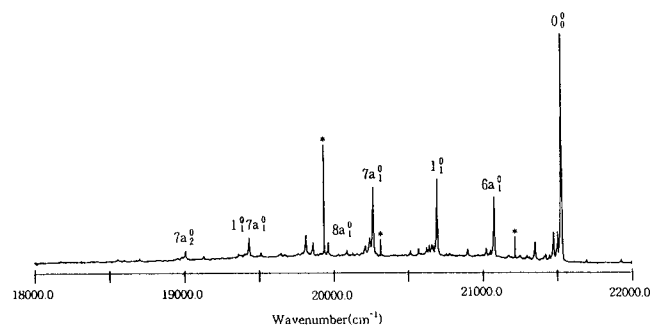


Figure 1. A portion of vibronic emission spectrum in the D₁→D₀ transition of the *p*-fluorobenzyl radical generated from the *p*-fluorotoluene with a large size of nozzle ($\phi=0.5$ mm) and a carrier gas He in a corona excited supersonic expansion. The peaks marked with an asterisk indicate the He atomic lines.

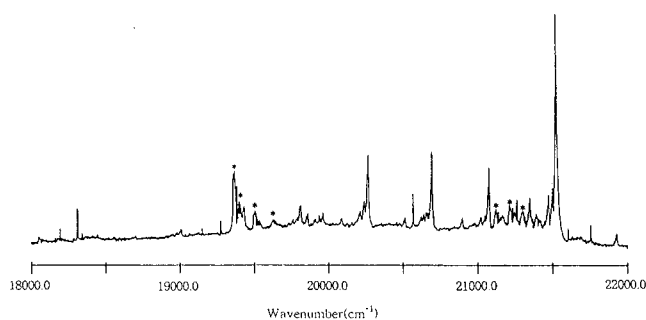


Figure 2. A portion of vibronic emission spectrum in the $D_1 \rightarrow D_0$ transition of the *p*-fluorobenzyl radical generated from the *p*-fluorotoluene with a large size of nozzle ($\phi=0.5$ mm) and a carrier gas Ar in a corona excited supersonic expansion. The peaks marked with an asterisk belong to the Swan bands (${}^3\Pi_g \rightarrow {}^3\Sigma_u^+$) of the C_2 .

band of the $A(1^2A_2) \rightarrow X(1^2B_2)$ transition at 21530.1 cm^{-1} (in air), followed to lower energies by a series of vibronic bands. But no band with observable intensity has been found to the blue of the origin band. The assignments of the vibronic bands are given in the previous work.²³ The weak bands observed at 21928.7 and 21695.2 cm^{-1} are the origin bands of the *o*- and *m*-fluorobenzyl radicals, respectively, which were generated from the small amount of impurity, *o*- and *m*-fluorotoluenes in the sample.

Although the exact excitation mechanism is not known for the emission source in a corona excited supersonic expansion, it is generally accepted that the molecules initially excited by electronic collision to a wide range of vibrational levels of the excited electronic state undergo the collisional relaxation to the vibrationless state at the nozzle throat as the evidence in the spectra observed. Thus, the intensity of hot bands are greatly reduced, confirming extensive vibrational cooling at the nozzle opening.

Besides the strong vibronic bands, several weak low frequency sequence bands have been observed at the interval of approximately -14 , -27 , -54 , and -179 cm^{-1} from the every strong vibronic band, which could not be resolved in the laser dispersed fluorescence spectra.⁸ The regularity of the sequence bands observed in this work is clearly shown in Figure 3, in which the low frequency sequence bands are plotted with reference to the strong vibronic band already assigned. Recently, Fukushima and Obi⁸ have also observed the several weak bands in the vicinity of the strong bands from the laser excitation spectra and attributed them as belonging to the van der Waals molecules. However, from Figures 1 and 2, it seems unlikely that these bands could belong to dimers or van der Waals molecules since the same bands were observed with different carrier gases.

In the room temperature spectra of toluene using an electric discharge, Kahane-Palius and Leach²⁴ observed the low frequency sequence bands and attributed those to combination or hot bands originating from the vibrationally excited S_1 states of toluene. In the present work, however, no observation of any bands belonging to *p*-fluorobenzyl radical beyond the origin band strongly excludes the possibility of the hot bands. This also confirms extensive vibrational cooling of the D_1 state, resulting in insufficient populations at the vibrationally excited states.

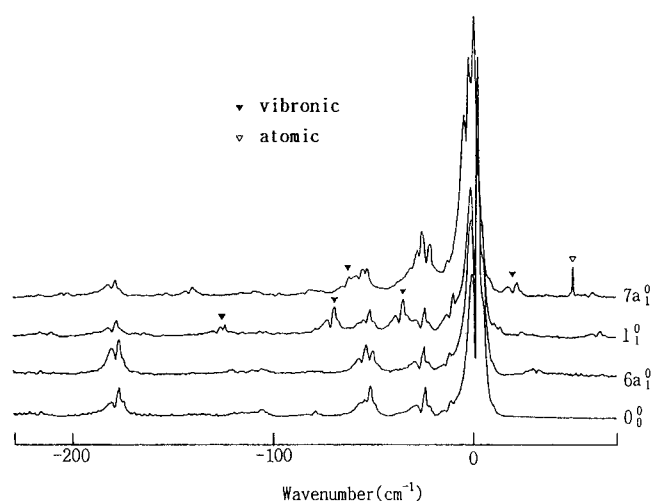


Figure 3. The regularity of the low frequency sequence bands observed with the strong vibronic bands. The sequence bands were plotted with reference to the strong vibronic bands whose assignments were also indicated.

A possible explanation of these low frequency bands may be attributed to the combination bands associated with the strong vibronic bands since the intensity of the sequence bands is proportional to that of the vibronic bands, as shown in Figures 1 and 3. Cossart-Magos and Cossart⁶ have observed the similar weak satellite bands near the origin band by the room temperature electric discharge and assigned as the $16a_1^1 11_1^0$, $18b_1^1$, 11_1^1 , and $10b_1^1$ bands for the bands at -11.3 , $+7.1$, -27.2 , and -54.8 cm^{-1} , respectively, from the comparison with the analogous vibrations in the substituted benzene derivatives. If the bands observed in this work belong to the combination bands associated with the strong vibronic band, another bands should be observed with comparable intensity for the transitions which have a common upper state but different lower states since the Franck-Condon factor which determine the emission intensity in the spectra²⁵ should be similar between the neighboring lower vibrational states. However, no observation of any bands to the blue of the origin band strongly excludes this possibility.

In order to further identify the initial state, we have employed a small size of nozzle ($\phi=0.2$ mm) to observe the vibronic emission spectra of the colder *p*-fluorobenzyl radical with a He carrier gas as shown in Figure 4. From the comparison between Figures 1 and 4, it is obvious that the smaller size of nozzle generates the colder spectrum, giving reduced emission intensity of He atomic lines and weaker background radiation. The comparison of the sequence bands associated with the origin band is shown in Figure 5, in which the intensity of sequence bands was normalized with respect to the origin band. From the comparison, it is clear that the sequence bands show reducing intensity of different ratio and different bandshapes upon cooling. The band at -27 cm^{-1} shows much weaker intensity upon cooling. The bandshape can be easily obtained from the calculation using appropriate rotational constants and temperature. Recently Lee *et al.*²⁶ have produced the simulated spectrum of *p*-xylyl radical at different rotational temperature. The change in bandshape is due to the difference in

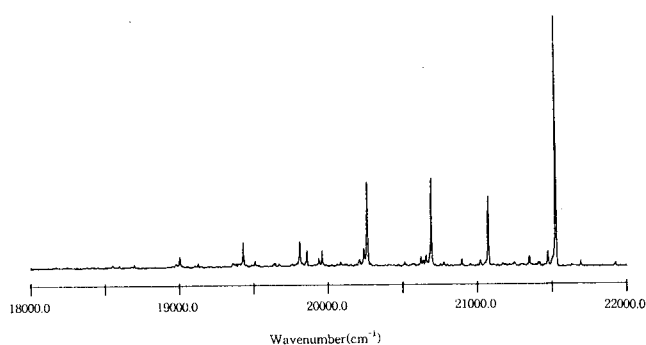


Figure 4. A portion of vibronic emission spectrum in the $D_1 \rightarrow D_0$ transition of the colder *p*-fluorobenzyl radical generated from the *p*-fluorotoluene with a small size of nozzle ($\phi = 0.2$ mm) and a carrier gas He in a corona excited supersonic expansion. The intensity of the He atomic lines was substantially reduced in comparison with Figure 1.

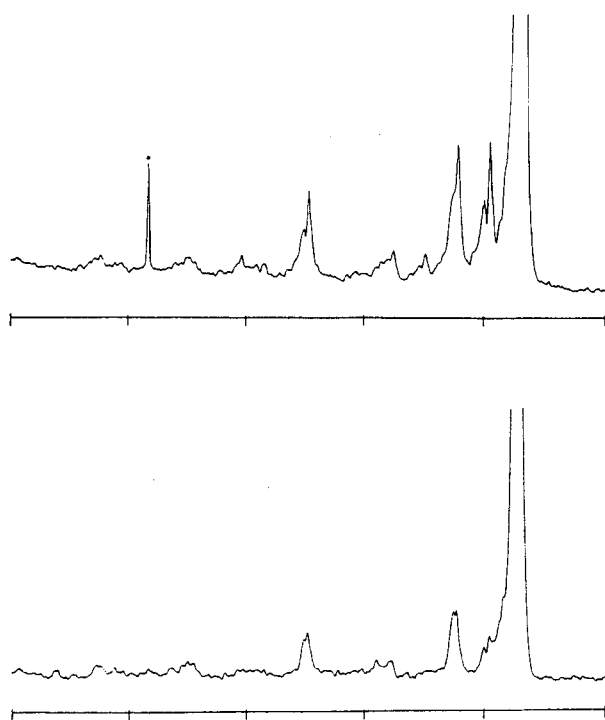


Figure 5. An enlarged view of the low frequency sequence bands associated with the origin band. The upper and lower spectra were taken from the Figures 1 and 4, respectively.

rotational temperature at a given state. Thus, we may conclude the initial state of the sequence bands is not the vibrationally excited states because some of the sequence bands maintains the emission intensity upon cooling.

Another possibility is the torsional coupled with electronic transition because, unlike most skeletal vibrations, an internal rotation around benzene ring has typically large amplitude and low frequency.²⁷ Information on the torsional dynamics is easily provided by spectroscopic experiments at higher frequency in the visible/uv regions of the electromagnetic spectrum. This is because the properties of the potential energy surface along the torsional coordinate often change upon electronic excitation. Also, the coupling of torsional with the vibrational motion changes the torsional barrier,

giving slightly different torsional energy levels for each vibrational mode, which correspond to the regularity shown in Figure 3. On the other hand, since the torsional energy levels are not far away from the ground vibrational state, the cooling effect is reflected to a certain extent in the emission spectrum, which agrees well with the experimental results.

Although the torsional motion of methyl group in *p*-fluorotoluene has been well established,²⁸ there was, as far as we are concerned, no study about the torsional motion of $-\text{CH}_2$ group directly connected to the benzene ring. Since the benzyl radical which was much studied by many optical spectroscopy does not show any evidence of torsional motion at room temperature, it is hard to believe that the $-\text{CH}_2$ group has free internal rotation around the benzene ring. But, the shift of electron density by the halogen atom attached to the benzene ring may allow for the hindered internal rotation.²⁹ However, the theoretical background of the torsional motion of substituted benzyl radicals has not been established.

Summary

We have observed the vibronic emission spectra in the transition of $D_1 \rightarrow D_0$ of the *p*-fluorobenzyl radical which was generated from the *p*-fluorotoluene and vibronically excited in a corona excited supersonic expansion. The low frequency sequence bands observed in the vicinity of the every strong vibronic band have been investigated by varying the experimental conditions such as carrier gas and nozzle size to identify the origin of the transition in the spectra. The results shows strong evidence for the possibility of the torsional transition coupled with vibronic transition.

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A Study on the Sulfur-Resistant Catalysts for Water Gas Shift Reaction I. TPR Studies of Mo/ γ -Al₂O₃ Catalysts

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Mo/ γ -Al₂O₃ catalysts were prepared by impregnation method in various conditions to identify the states of surface Mo species. TPR (Temperature-Programmed Reduction) and Raman spectroscopy were applied to analyze the surface Mo species. TPR analysis revealed that MoO₃ was reduced to Mo through MoO₂, the intermediate state and the increase of Mo loading enhanced the reducibility of Mo oxide till the formation of monolayer coverage. High temperature calcination induced oxygen defects in MoO₃ giving their unstable states for easier reduction. Raman spectroscopy analysis showed that the increase of Mo loading induced the polymeric Mo oxide.

Introduction

Metal oxides which are supported on stable supports such as γ -Al₂O₃ and SiO₂ are widely used as catalysts for various chemical reactions. Supported metal oxides show different reduction behavior from unsupported ones. The difference of reduction property plays an important role in catalysis. The reduction of supported metal oxides could be hindered or promoted depending on the interaction between metal oxide and support. Nowak and Koros¹ reported that supported NiO has higher oxidation state than unsupported one. Holm and Clark² reported the formation of metal aluminate or metal silicate in supported metal oxide systems. The shape of supported metal oxides could be fine metal oxide form or metal oxide island form distributed homogeneously. In case

of metal oxide island form, the reduction behavior is similar to that of unsupported metal oxide, and the support acts as dispersing agent and promotes the reduction of the oxide. In this condition, the rate equation of reduction is same as in unsupported metal oxide.

Metal atom or fine crystallite is mobile on the support.³ The reduction of homogeneously supported metal oxide is proceeded by restructuring fine crystallites after the reduction of each metal ion or cluster resulting in the formation of large metal crystallites. This fine metal crystallite could promote the reduction by autocatalytic reaction. In case of Pt/ γ -Al₂O₃, hydrogen spillover happens above 600 K.⁴ If activated hydrogen atoms produced by autocatalytic reaction lose their mobility, the effect of autocatalytic reaction could be lost. There is possibility of inhibition to nuclei growth by the loss of metal mobility due to the strong interaction between metal and support.

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