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Observation of the Vibronic Emission Spectra of Pentafluorobenzyl Radical Generated in a Jet

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Free radicals exist only transiently as reaction intermediates, created in one step and quickly consumed in a subsequent step of a complex chain reactions.[1] For those interested in fundamental issue of chemistry, the structure and characteristics of radicals serve at least to define the nature of chemical reactivity.[2] The benzyl-type radicals are one of the most important species in chemical reaction of aromatic compounds, so they have been subjects of numerous spectroscopic studies by the method of both experiment[3-7] and theory.[8] Lee and coworkers[9-13] have produced many benzyl-type radicals by subtracting a hydrogen atom from the substituted toluene compounds in a corona excited supersonic expansion. Thrush group[3,4] has published interesting papers for the vibronic assignments of the substituted benzyl radicals using laser induced fluorescence technique. Also Cossart and coworkers[14] have determined the symmetry of the excited electronic state from the analysis of rotational contour of vibronic bands observed by emission spectroscopy. The rotational constants of substituted benzyl radicals have been accurately determined from the high resolution rovibronic spectra[15,16] as well as the rotational contour analysis of the spectra.[14,17] Although fluorine substituted benzyl radicals are the most suitable candidates for spectroscopic experiments, only monofluorobenzyl radicals have been so far investigated.

In this study, we have observed for the first time to the best of our knowledge the vibronic emission spectra of pentafluorobenzyl radical in the gas phase with a technique of corona excited supersonic expansion. The provisional vibronic assignments of the radical have been made from the spectra.

The experimental setup employed in this work is similar to those described previously.[18] Briefly, the pentafluorobenzyl radical was generated in a jet with He as a carrier gas in a corona excited supersonic expansion from pentafluorotoluene(Aldrich, reagent grade) and used without further purification. The precursor was vaporized at room temperature inside the vaporizing vessel made of thick Pyrex glass bottle under 2.0 atm of He gas. The concentration of the precursor in the gas mixture was adjusted for the maximum emission intensity and believed to be about 1% in the gas mixture. Since the corona discharge of the precursor compound produces heavy soot deposits clogging the nozzle throat, we have employed a modified Engelking type nozzle of 0.5 mm pinhole diameter developed in this laboratory[19] which substantially reduces the clogging by inducing the excitation after expansion of the molecules. The new nozzle was also effective for improving the quality of the spectra by reducing the arching noise limiting the signal to noise ratio of the spectrum. The typical discharge condition was 5 mA at the 2000 V dc potential through 150 kΩ current limiting ballast resister. The discharge voltage was adjusted for the maximun total fluorescence from the origin band using the narrow band optical interference filter.

The chamber was evacuated by a mechanical vacuum pump of 800 L/min capacity, obtaining the chamber pressure of 1.5 Torr during the expansion with 2.0 atm of backing pressure. With electric discharge of the precursor, the pentafluorobenzyl radical was generated in the downstream of the green jet. The downstream jet area of 4 mm in diameter below the nozzle throat was collected through the quartz lens of 38 mm diameter and 50 mm focal length placed inside the expansion chamber and focussed onto the double monochromator (Jobin Yvon U1000) equipped with a cooled PMT (Hamamatsu model R649). The visible emission spectra were obtained by scanning from 19000 to 23000 cm^{-1} at the step of 0.2 cm^{-1} with 100 μm of slit width over 30 min. The frequency of spectrometer was calibrated with the He atomic transitions recorded with the spectra and believed to be accurate within ± 0.5 cm^{-1}.

The corona excited supersonic expansion using an Engelking type nozzle has been well-known as a simple and inexpensive way of producing transient molecules[20,21] and widely used for producing a large fraction of benzyl-type radicals in excited electronic state from which emission to the ground state can be observed with spectrometers.[22-25] The vibronic emission spectra of benzyl-type radicals and substituted toluenes used as a precursor are observable in the visible and uv region, respectively.[24-26]

The weak visible emission spectrum of the benzyl radical is believed to arise from transitions from the close-lying 2^2B_2 and 1^2A_2 excited states to the 1^2B_2 ground state.[27] Two excited electronic states are mixed by vibronic coupling via the 6a, 6b, and 18b vibrational modes.[16] Ring substitution is expected to affect the energies of the 2^2B_2 and 1^2A_2 excited states differently. For *p*-fluorobenzyl radicals, the lowest excited electronic state is the 1^2A_2 state like the benzyl radical, thus giving the B type bandshape for the pure electronic transition between the 1^2A_2 and 1^2B_2 states.[27] Theory[8] predicts that the 2^2B_2 state lies some 1400 cm^{-1} above the 1^2A_2 state and that its oscillator strength is ten times smaller than that of the 1^2A_2 state. However, the transition from the second excited state to the ground state has not been observed yet. Figure 1 shows a portion of the vibronic emission spectra of the pentafluorobenzyl radical generated in this work. Most of the bands are observed in the region of 20500-22000 cm^{-1}. Since the collisional vibrational cooling is very effective with the Engelking type nozzle in a corona excited supersonic expansion, the vibronic emission spectra should be similar to the dispersed fluorescence spectra obtained by pumping the origin band.[13] In the spectrum, the most intensive band is found at 21857 cm^{-1} which is believed to be the origin band of the $1^2A_2 \rightarrow 1^2B_2$ transition. Also, the absence of the band having observable intensity beyond the origin band supports the assignment. For comparison, *o*-, *m*-, and *p*-fluorobenzyls show the origin band at 21929, 21695, and 21532 cm^{-1}, respectively,[4,28] while the origin band of benzyl radical[16] locates at 22002 cm^{-1}. The origin band in the emission spectrum can be easily confirmed by mirror image relationship with the absorption spectra. Since the pentafluorobenzyl radical belongs to the C_{2v} symmetry, the band should exhibit A or B type bandshape depending on the vibrational modes.[29] From the comparison with the simulated spectrum of the *p*-fluorobenzyl,[14] the origin band exhibits B type transition, suggesting the excited state belong to the A type symmetry. The strong band at 21581(276) cm^{-1} exhibits different bandshape from the origin band, indicating the mixing of vibrational mode with different symmetry. The number in the parenthesis represents the spacing from the origin band in units of cm^{-1}. From the bandshape and the vibrational data on the precursor, the band is tentatively assigned as the $9a_1^0$ transition. The frequency of vibrational mode 9a of the precursor is 269 cm^{-1} in the ground electronic state. The strong bands observed at 21454(403) and 21307(550) cm^{-1} with the same bandshape as the origin band are assigned as the $10a_1^0$ and 1_1^0 transitions, respectively. The precursor gives 389 and 556 cm^{-1} for the vibrational modes 10a and 1, respectively.[29] The sharp peaks are from the He atomic transitions[30] which are represented by asterisks. Besides these strong bands, many weak bands are also observable in a relatively broad form for this molecules. More reliable assignments should be made using a technique of laser induced fluorescence and precise calculation for transition intensity.

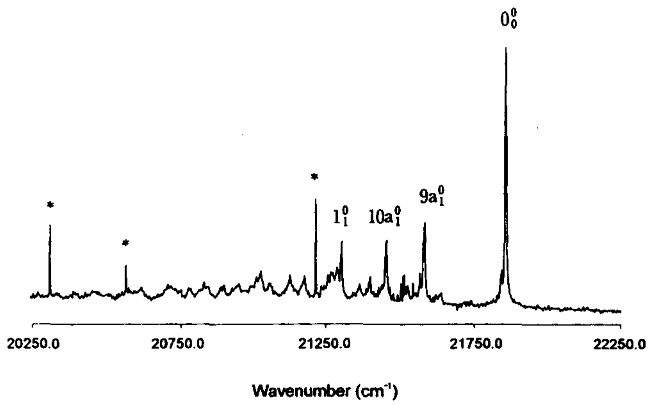

Figure 1. A portion of vibronic emission spectrum of the pentafluorobenzyl radical in the $1^2A_2 \rightarrow 1^2B_2$ transition generated in a corona excited supersonic expansion. The He atomic lines are indicated by asterisks.

In summary, we have generated the pentafluorobenzyl radical in a jet from which the vibronic emission spectra in the $1^2A_2 \rightarrow 1^2B_2$ transition have been recorded for the first time. By comparing the bandshape and spacing from the origin band with those from the pentafluorotoluene, we are able to make provisional assignments for the vibrational modes in the ground electronic state.

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Phenylpropanedione; A New Visible Light Photosensitizer for Dental Composite Resin with Higher Efficiency than Camphorquinone

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Chemical or light induced polymerization resin system has been used as an esthetic and permanent restorative dental composite resin in dentistry.[1] Light induced polymerization system is more widely used than chemical resin system because it has many advantages[2] such as higher color versatility, better color stability, less bubble generation, and one paste system.

The light induced polymerization system has been used for the preparation of dental composite resin, denture, dental adhesives, and impression material. It can be divided into two types based on the light source; UV or visible light. Recently, visible light is mostly used to avoid harmful effects of UV light. Camphorquinone (CQ) is the most widely used photosensitizer for the visible light cured composite resin,[3] but it has some drawbacks such as low polymerization efficiency and toxicity. Low polymerization efficiency of camphrquinone results in low mechanical properties of the composite resin and toxic effects to the human body because of the residual monomers. To overcome these drawbacks, a photosensitizer with high polymerization efficiency is necessary. However, only a few studies have been done to replace camphorquinone.[4,5]

In the previous study,[6] we reported on the visible light-cured restorative dental composite resin with low water absorption. The present paper deals with the properties of diacetyl (DA) and phenylpropanedione (PD) as a new photosensitizer for dental composite resin and those of dental composite resin containing them.

Physical state of DA and PD is yellow liquid and that of CQ is solid at room temperature. Figure 2 shows UV absorption spectra (Model V-550, Jasco, Japan) of three photosensitizers. The λ_{max} of CQ, DA, and PD in ethyl alcohol is 468, 418.5, 393 nm and ε_{max} is 80, 50, 20 respectively. The ε_{max} values of 20-80 and blue shift of absorption maximum with increasing solvent polarity indicate (n-π^*) transitions.

Photopolymerization efficiency of the resin was studied by the IR absorption spectroscopy. A mixture of 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy]phenyl propane (bis-GMA, 1.0 g),[7] N-dimethylaminoethyl methacrylate (DAEM, 0.001 g), and 2.0 wt% of photosensitizer based on bis-

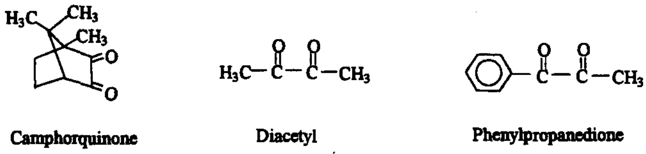

Figure 1. Photosensitizers used in this experiment.