

Observation of Vibronic Emission Spectrum of the Jet-Cooled 2,6-Difluorobenzyl Radical

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The jet-cooled 2,6-difluorobenzyl radical was generated and vibronically excited in a corona excited supersonic expansion from the gas mixture of 2,6-difluorotoluene and a buffer gas He. The vibronically resolved emission spectra of the jet-cooled 2,6-difluorobenzyl radical have been recorded with a long path monochromator in the visible region and analyzed to give accurate electronic transition and vibrational mode frequencies in the ground electronic state by comparing with those of 2,6-difluorotoluene as well as those from an ab initio calculation.

Introduction

As reaction intermediates, created in one step and quickly consumed in a subsequent step of chain reactions,¹ free radicals have been long believed to play an important role in the reaction dynamics. For those interested in the fundamental issue of chemical reaction, the structure and characteristics of radicals serve at least to define the nature of chemical reactivity.²

Benzyl radical is one of the most important transient species in the aromatic chemical reaction and the subject of numerous spectroscopic studies.^{3–7} For the generation of free radicals in the gas phase, a number of discharge techniques have been applied to the supersonic nozzles. Several groups have attempted to produce metastable molecular beams with an electric discharge in the high-pressure region of the expansion.^{8,9} A corona excited supersonic expansion was demonstrated as being a useful technique for the production of benzyl-type radicals.¹⁰ Recently, Lee and co-workers^{11–13} have further improved the efficiency of radical generation using a modified Engelking type nozzle¹³ for the laser-free spectroscopy.

The first fluorine substituted benzyl radicals were generated by Bindley et al. from electric discharge of the corresponding toluenes.¹⁴ The benzyl-type radicals were also produced from the corresponding substituted toluenes by means of hydrogen abstraction reaction¹⁵ using fluorine atom for the laser excitation spectra. The high-temperature gas phase *p*-fluorobenzyl radical was formed by Cossart–Magos and Cossart for the rotational contour analysis.¹⁶ Recently, Lee and Baek have obtained the jet cooled *p*-fluorobenzyl¹⁷ and pentafluorobenzyl¹⁸ radicals in a corona excited supersonic expansion for the vibronic analysis. Although fluorine substituted benzyl radicals are supposed to be suitable candidates for spectroscopic observation, only a few fluorobenzyl radicals have been identified by spectroscopic technique.

In this paper, we present for the first time the observation of visible vibronic emission spectra of the jet-cooled 2,6-difluorobenzyl radical using a modified Engelking type nozzle in a corona excited supersonic expansion.

Experimental Section

The experimental setup employed in this work is similar to those described elsewhere.^{11,17} Briefly, it consists of a pinhole

type quartz nozzle coupled with corona discharge, a high vacuum expansion chamber, and a spectrometer for the observation of emission spectrum. The jet-cooled 2,6-difluorobenzyl radical was generated from the gas mixture of 2,6-difluorotoluene and a large amount of He in a corona excited supersonic expansion using a modified Engelking type nozzle. Reagent grade 2,6-difluorotoluene was purchased from the Aldrich and used without further purification. The precursor was vaporized at 25 °C 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 produces heavy soot deposits clogging the nozzle throat, we have used a modified Engelking type nozzle of 0.3 mm diameter developed in this laboratory which substantially improves the clogging problem by allowing the excitation to occur after the expansion.¹³ The discharging voltage between the cathode and the anode located inside the nozzle was adjusted to be about 1.0 kV for the maximum intensity of fluorescence from the origin band.

The expansion chamber was evacuated by a mechanical vacuum pump of 800L/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 2,6-difluorobenzyl radical was generated in the downstream blue-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 focused onto the slit of the monochromator (Jobin Yvon U1000) equipped with a cooled PMT (Hamamatsu R649). The visible emission spectra were obtained by scanning from 18000 to 22500 cm⁻¹ at the step of 1.0 cm⁻¹ with 200 μm of slit width over 1 h. The frequency of spectrometer was calibrated by the He atomic transitions recorded with the spectra and believed to be accurate within ±0.5 cm⁻¹.

Since the 2,6-difluorobenzyl radical has many vibrational modes and the assignments have not been completed, ab initio calculations on the ground electronic state were also performed to assist the assignments of vibronic emission spectra. The calculations were executed with a personal computer equipped with an Intel Pentium 300 MHz processor and 32 MB RAM,

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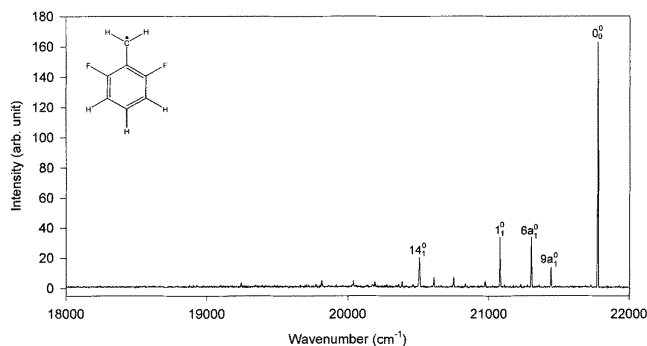


Figure 1. A portion of vibronic emission spectrum of the jet-cooled 2,6-difluorobenzyl radical in the $D_1(^2A_2) \rightarrow D_0(^2B_2)$ transition which was generated from 2,6-difluorotoluene with a carrier gas He in a corona excited supersonic expansion.

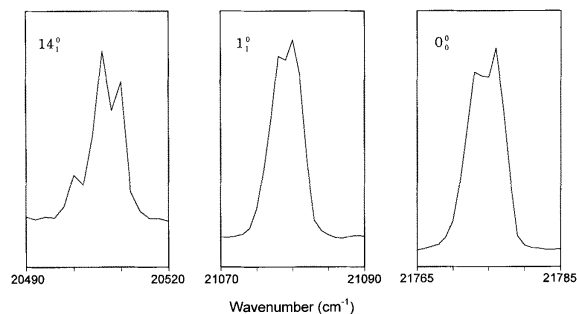


Figure 2. Enlarged view of the band shape. The band assigned as the mode 1 has similar band shape to the origin band with the characteristic of doublet, while the band assigned as the mode 14 has triplet band shape.

and with the standard methods included in the GAUSSIAN 94 for Windows program package. The geometry optimization and vibrational frequency calculations were performed at the UHF level and 6-31 g^{**} basis set was employed in all calculations.

Results and Discussion

The weak visible emission spectrum of benzyl-type radicals 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.¹⁹ Two excited electronic states are mixed through vibronic coupling.²⁰ Ring substitution is also expected to affect the energies of the 2^2B_2 and 1^2A_2 excited states differently.²¹ For the *p*-fluorobenzyl radical, the lowest excited electronic state is the 1^2A_2 state like the benzyl radical, giving the B type band shape for the electronic transition between the 1^2A_2 and 1^2B_2 states.¹⁷ However, the transition from the second excited state to the ground state has not been observed due to the rapid collisional relaxation process. Since the 2,6-difluorobenzyl radical belongs to the C_{2v} point group, the vibronic bands should exhibit A or B type band shape depending on the vibrational modes.

Figure 1 shows a portion of the visible vibronic emission spectrum of the jet-cooled 2,6-difluorobenzyl radical generated in this work. Most of the bands are observed in the region of 19000–22000 cm^{-1} . As shown in Figure 2, the spectrum exhibits two kinds of band shapes according to the vibrational modes of the transition; doublet and triplet band shapes. The strong band at 20506 cm^{-1} shows the triplet while the other strong bands represent the doublet character in the spectrum. Thus, the wavenumber of each band was measured at the minimum intensity between the doublet, while the band of triplet type was measured at the maximum intensity of the band, which are believed to be close to the band origin in comparison with

the simulated spectra at 50 K of the B and A types of transitions.²²

Since it is well-known for the benzyl-type radicals that the collisional vibrational relaxation is very effective at the excited electronic state 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 exciting the origin band.¹⁷ In the spectrum, the most intensive band is found at 21774 cm^{-1} (in air), believed to be the origin band of the $1^2A_2 \rightarrow 1^2B_2$ transition, followed at lower energies by a series of vibronic bands. Also, the absence of the band with noticeable intensity to the blue of the origin band strongly supports this assignment. For comparison, *o*-, *m*-, and *p*-fluorobenzyls shows the origin band at 21929, 21695, and 21532 cm^{-1} , respectively,¹⁵ while the origin band of benzyl radical²⁰ is located at 22002 cm^{-1} . In contrast, the lowest electronic transitions of substituted toluenes^{23–26} are observed in the region of 36000–38000 cm^{-1} .

Since, as described above, the spectrum observed in this work is similar to the single vibrational level dispersed fluorescence spectrum¹⁷ obtained by exciting the origin band of the electronic transition, the spacing of the vibronic bands from the origin band represents the vibrational mode frequencies at the ground electronic state.

The vibronic bands observed in this work were provisionally assigned with the help of an ab initio calculation as well as the known vibrational mode frequencies of the precursor,²⁷ 2,6-difluorotoluene since both molecules are subjected to the isodynamic approximation which states the correspondence of vibrational mode frequencies and intensity. This has been already applied to the vibrational mode assignment of many benzyl-type radicals.^{17,18,21}

The strong band at -332 cm^{-1} from the origin band in Figure 1 was assigned to the $9a_1^0$ transition since the frequency of mode 9a agrees well with the precursor (328 cm^{-1}). The calculation (331 cm^{-1}) predicts an excellent agreement for this mode. The $9a_1^0$ transition was also observed with strong intensity in the vibronic emission spectra of pentafluorobenzyl radical.¹⁸ The strong band at -470 cm^{-1} was assigned to the $6a_1^0$ transition according to the similarity to the precursor (484 cm^{-1}) and the calculation (472 cm^{-1}). The slight discrepancy from the precursor reflects the change of $-CH_3$ to $-CH_2$. In the vibronic emission spectrum of benzyl-type radicals with C_{2v} symmetry, the mode 6a of ring deformation was observable with fairly strong intensity while the mode 6b was detected with much weak intensity.²⁸ Both modes 6a and 6b are degenerate in benzene. In *p*-fluorobenzyl radical,¹⁷ the frequencies of modes 6a and 6b were measured to be 453 and 632 cm^{-1} , respectively. The strong band at -696 cm^{-1} was assigned to the 1_1^0 transition because the mode 1 of ring breathing should be consistent with that of the precursor (699 cm^{-1}). The calculation (672 cm^{-1}) gives a slightly lower wavenumber for this mode. But this is, in the calculation, the only a_1 symmetry mode in the range of 500–900 cm^{-1} . The *p*-fluorobenzyl radical¹⁷ shows the similar prediction for this mode. As shown in Figure 2, the band also exhibits the similar band shape to the origin band, indicating the vibrational mode has a_1 symmetry. The mode 14 of the C–C stretching with b_2 symmetry was assigned to the strong triplet band at -1268 cm^{-1} since the frequency of this mode is insensitive to the substitution to the benzene ring. The observation agrees well with the calculation (1276 cm^{-1}) and the precursor (1277 cm^{-1}) for this vibrational mode. This band has a different band shape from the shapes of other strong bands observed in the spectrum, confirming the different vibrational

TABLE 1: Vibrational Frequencies (cm⁻¹) of 2,6-Difluorobenzyl Radical

mode ^a	this work (D ₀)	ab initio ^b		symmetry (C _{2v})
		UHF/6-31 g** (D ₀)	2,6-difluoro- toluene ^c (S ₀)	
9a	332	331	328	a ₁
6a	470	472	484	a ₁
1	696	672	699	a ₁
14	1268	1276	1277	b ₂

^a Reference 29. ^b Multiplied by a scaling factor of 0.945. ^c Reference 27.

symmetry. The strong observation of the bands with a₁ symmetry is in accordance with the other fluorine substituted benzyl radical. The vibrational mode frequencies obtained in this work are listed and compared with those of an ab initio calculation and the precursor together with the mode symmetry in Table 1.

Although the several weak bands observed in this work coincides well with those of the combination bands and overtone transitions, we cannot exclude the possibilities to assign these bands to the other vibrational modes with weak intensity.

In summary, we generated the jet-cooled 2,6-difluorobenzyl radical from 2,6-difluorotoluene with a carrier gas He and vibrationally excited in a corona excited supersonic expansion, from which the vibronic emission spectrum of the 2,6-difluorobenzyl radical in the 1²A₂ → 1²B₂ transition has been obtained for the first time. The vibrational mode frequencies at the ground electronic state have been determined from the comparison with the precursor as well as with the aid of an ab initio calculation.

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References and Notes

(1) Carrington, A. *Microwave Spectroscopy of Free Radicals*; Academic Press: London, U.K., 1974.

(2) Tan, X. Q.; Wright, T. G.; Miller, T. A. *Electronic Spectroscopy of Free Radicals in Supersonic Jets: Jet Spectroscopy and Molecular Dynamics*; Hollas, J. M., Phillip, D., Eds.; Blackie Academic & Professional: London, 1994.

(3) Fukushima, M.; Obi, K. *J. Chem. Phys.* **1990**, *93*, 8488.

(4) Fukushima, M.; Obi, K. *J. Chem. Phys.* **1992**, *96*, 4224.

(5) Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1989**, *137*, 13.

(6) Langkilde, F. W.; Bajdor, K.; Wilbrandt, R.; Negri, F.; Zerbetto, F.; Orlandi, G. *J. Chem. Phys.* **1994**, *100*, 3503.

(7) Fukushima, M.; Obi, K. *Chem. Phys. Lett.* **1995**, *242*, 443.

(8) Cossart, D.; Cossart-Magos, C. *Chem. Phys. Lett.* **1996**, *250*, 128.

(9) Shen, G.; Li, X.; Chen, H.; Wang, L.; Lou, N. *Chem. Phys. Lett.* **1995**, *241*, 577.

(10) Engelking, P. *Chem. Rev.* **1991**, *91*, 399.

(11) Han, M. S.; Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1996**, *17*, 991.

(12) Ha, Y. M.; Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1997**, *18*, 692.

(13) Lee, S. K. *Bull. Korean Chem. Soc.* **1998**, *19*, 145.

(14) Bindley, T. F.; Watts, A. T.; Walker, S. *Trans. Faraday Soc.* **1964**, *60*, 1.

(15) Charton, T. R.; Thrush, B. A. *Chem. Phys. Lett.* **1986**, *125*, 547.

(16) Cossart-Magos, C.; Cossart, D. *Mol. Phys.* **1988**, *65*, 627.

(17) Lee, S. K.; Baek, D. Y. *Chem. Phys. Lett.* **1999**, *301*, 407.

(18) Lee, S. K.; Baek, D. Y. *Chem. Phys. Lett.* **1999**, *311*, 36.

(19) Hiratsu, H.; Mori, K.; Shizuka, H.; Fukushima, M.; Oki, K. *Chem. Phys. Lett.* **1989**, *157*, 35.

(20) Lin, T.-Y. D.; Tan, X.-Q.; Cerny, T. M.; Williamson, J. M.; Cullin, D. W.; Miller, T. A. *Chem. Phys.* **1992**, *167*, 203.

(21) Lee, S. K.; Baek, D. Y. *Chem. Phys. Lett.* **1999**, *304*, 39.

(22) Suh, M. H.; Lee, S. K.; Rehfuss, R. D.; Miller, T. A.; Bondybey, V. E. *J. Phys. Chem.* **1991**, *95*, 2727.

(23) Breen, P. J.; Warren, J. A.; Berstein, E. R.; Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1917.

(24) Fujii, M.; Yamaguchi, M.; Takazawa, K.; Ito, M. *Spectrochim. Acta* **1994**, *50A*, 1421.

(25) Okuyama, K.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1985**, *89*, 5617.

(26) Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1995**, *173*, 262.

(27) Baek, D. Y.; Lee, S. K. Unpublished data.

(28) Varsanyi, G. *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*; John-Wiley & Sons: New York, 1974.

(29) Wilson, E. B. *Phys. Rev.* **1934**, *45*, 706.