

## SPECTROSCOPIC ANALYSIS OF 2,3-DIFLUOROBENZYL RADICAL

**Chang Soon Huh**

Applied Chemistry Major, Division of  
Chemical and Environmental  
Engineering, College of Engineering  
/Dong-eui University  
South Korea  
0411black@deu.ac.kr

### ABSTRACT

The vibronically cooled electronic emission spectra of the 2,3-difluorobenzyl radical was observed in a corona excited supersonic expansion (CESE) apparatus. Several fundamental modes of methyl- and trimethylbenzene were assigned on the basis of previous infrared and Raman values of the precursor and calculation. The spectrum was analyzed in terms of progressions of the fundamental vibrational modes and molecular structures of 2,3-difluorobenzyl and 2,6-difluorobenzyl were calculated and compared with experimental data. The fluoro-substitution effect is first suggested by this group. The substitution effect is that each fluoro substituted position of benzyl radical affect the energy level and also the band shape of the benzyl radical independently. We have generated for the first time the 2,3-difluorobenzyl radical in a jet from which the vibronic emission spectra in the  $D_1 \rightarrow D_0$  transition have been recorded.

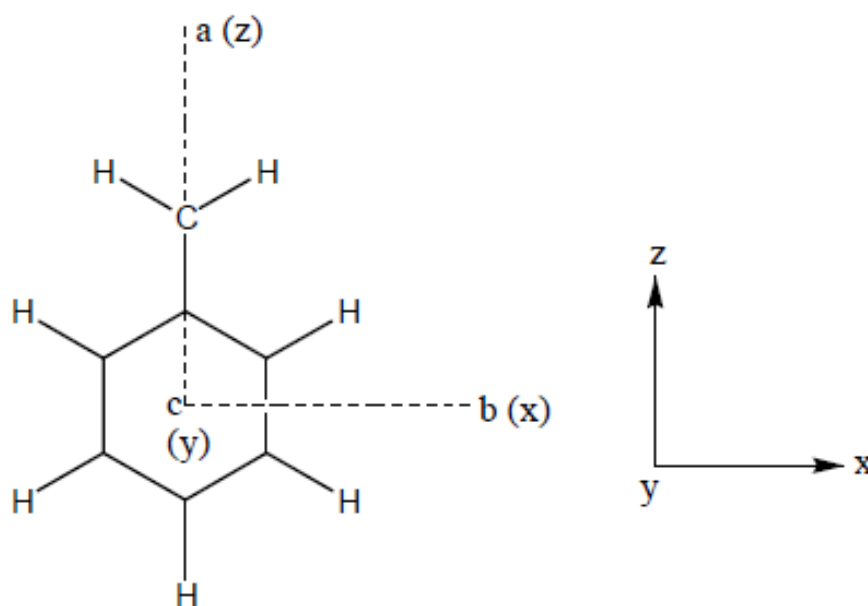
**Keywords:** 2,3-difluorobenzyl, 2,6-difluorobenzyl, CESE, *ab initio* calculation.

### INTRODUCTION

Free radicals are a group of chemical species that is highly reactive, short-lived, and characterized by one or more unpaired electrons. The first measurement of a radical species was obtained in the emission spectrum of a Bunsen flame by Wollaston in 1802 and then again by Swan in 1857 [1]. Then thank for the advances in the molecular spectroscopy, the more general study of radicals gain prominence significantly in the early part of the 20th century [2-4]. The chemical detection and identification of molecular free radicals in the gas phase was first explained in the classic thermal decomposition experiments by Paneth and Hofeditz in 1929 [5], establishing the incorporation of radicals into the mechanism of chemical reactions [6]. Subsequently, the study by Gerhard Herzberg gained particular prominence [7], with his pioneering investigations. His work helped stimulate a resurgence of investigations into the chemical reactions of gases. Today, radicals are understood as important species in the chemical processes in both the laboratory as well as industry.

Especially, benzyl radical as shown in figure 1 is a prototype of aromatic radical and researchers have attention to the benzyl radical. But as large aromatic radicals, halogen substituted benzyl radicals have been less studied [8,9]. Bindley et al. studied the first vibronic emission spectrum of fluorobenzyl radicals generated from an electric discharge of fluorotoluenes [10]. Since then, many researches are reported about the fluorobenzyl radicals and spectroscopic techniques to measure target molecules [11–26]. The study of rotational contours of *p*-fluorobenzyl radical were performed in the high temperature condition by Cossart-Magos and Cossart and rotational constants were obtained [27]. Fukushima and Obi studied with LIF excitation and dispersed fluorescence spectra and assigned first full

vibrational modes in the ground electronic state [11]. Also, by Miller et al, [12] accurate rotational constants have been obtained in the analysis of high-resolution LIF spectra coupled in a supersonic-jet expansion. Recently, Lee et al. has investigated the vibrational mode analysis in the vibronic spectra of the jetcooled chloro substituted benzyl [13-16] radicals in a corona excited supersonic expansion. Lee et al. also obtained vibronic emission spectra of mono-fluorobenzyl [17-19], difluorobenzyl [20] and pentafluorobenzyl [21] radicals using corona excited supersonic expansion. Still many spectroscopic data have been reported for mono-substituted fluorobenzyl radicals, the multi-substituted halogen benzyl radicals have not been less studied spectroscopically.



**Figure 1.** Molecular fixed-axis system of benzyl radical.

## EXPERIMENTAL AND THEORETICAL METHODS

Figure 2 shows the schematic diagram of the corona excited supersonic jet system used in this work. This system contains discharge source, vacuum chamber, supersonic system and spectrometer and acquisition system. From the precursor molecule, transient molecule is generated in a jet using conventional corona discharge system which is analogous with Engelking's conventional corona discharge [29].

The electronically excited multi-substituted benzyl radical is generated from multi-substituted toluene derivatives by corona excited supersonic expansion with helium buffer gas. The multi-substituted toluene is vaporized at room temperature inside the vaporizing vessel made of thick Pyrex glass bottle under 1.0 atm of He gas.

The concentration of the precursor in the carrier gas is adjusted for the maximum emission intensity and believed to be about 1% in the gas mixture. By controlling the temperature of sample vessel or valve of gas tube, the concentration of the precursor in a carrier gas can be adjusted.

The radicals are formed by electron dissociative attachment from neutral multi-substituted toluene precursors by a corona discharge (2.0 kV, 5.0 mA) localized vacuum chamber which is six-way cross pyrex tube of 50 mm inner diameter. The high voltage dc power supply is discharging source which is connected to anode and coupled with a 200 k $\Omega$  ballast resistor. The high voltage electric dc power supply has a maximum 5 kV and 40 mA capacity.

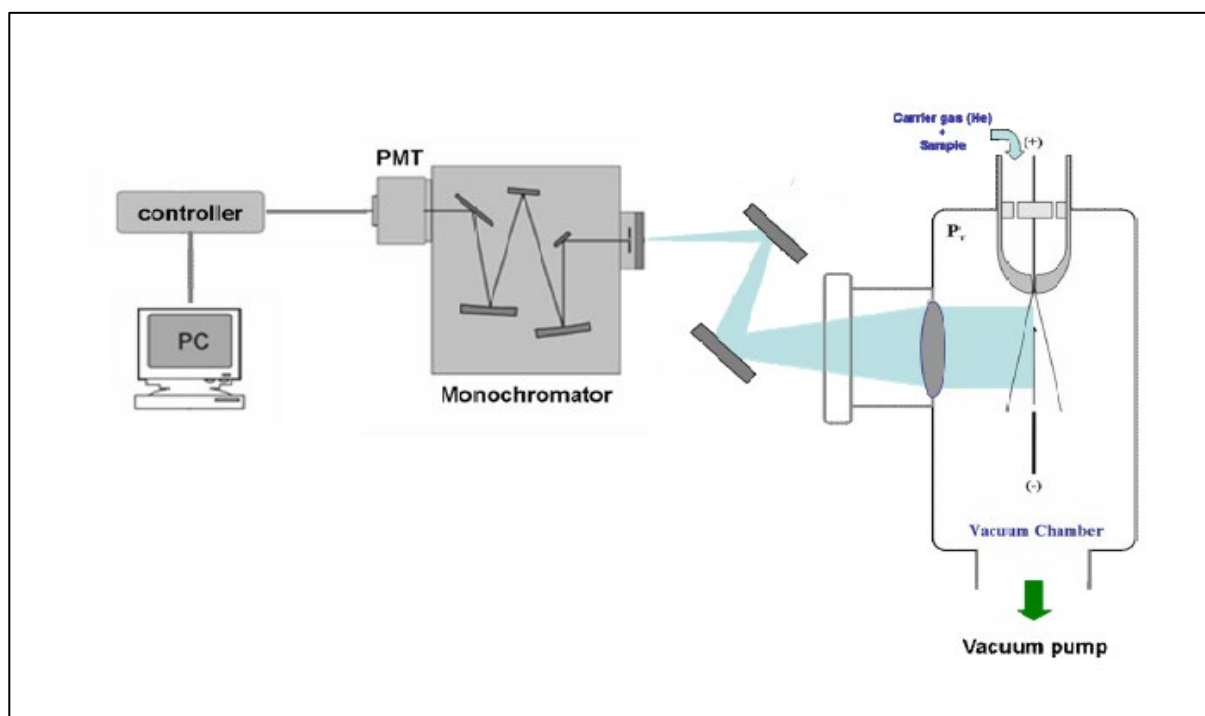
An 800L/min mechanical vacuum pump (WS Automa model W2V80) is connected to the chamber, resulting in the pressure range of 10<sup>-3</sup> Torr during the operation. A blue color of jet is an evidence of existence of the multi-substituted benzyl radical in the CESE. The light from the downstream jet area 5 mm away from the nozzle orifice is collimated by a quartz lens placed inside the expansion chamber and focused onto the slit of the monochromator (Jobin Yvon U1000) and detected with a photomultiplier tube (Hamamatsu R649) and a photon counting system.

During the scan, the slits are set to 0.200 mm, providing resolution of 2 cm<sup>-1</sup> at the visible region. Double type monochromator (Jobin Yvon model U-1000) is effective 2.0m path length using 3 mirrors and 2 gratings of 1800 groves/mm. double type monochromator is effective 2.0m path length using 3 mirrors and 2 gratings of 1800 groves/mm.

The spectrometer scan range is from 11,500 cm<sup>-1</sup> to 32,000 cm<sup>-1</sup>, with a maximum resolving power of 0.15 cm<sup>-1</sup> at 17,000 cm<sup>-1</sup> which is good enough to observe the rotational contour of the vibronic band of large molecules in a jet. The output of the PMT is transferred to the spectrometer control box via the preamplifier. The spectrometer is controlled by using a software SPECTRAMAX [30] with a personal computer.

From 19000 to 22000 cm<sup>-1</sup>, the spectrum is scanned in about 1 hr in 2.0 cm<sup>-1</sup> steps to obtain the benzyl-type radical spectrum. The frequency of the spectrum is calibrated using the He atomic lines observed at the same frequency region as the halogen-substituted benzyl radicals are observed and is believed to be accurate within  $\pm 0.2$  cm<sup>-1</sup>.

Since the precursor and multi-substituted benzyl radical have many vibrational modes and the assignments have not been completed, assignment of radical spectrum is performed with *ab initio* calculations using the GAUSSIAN 09 for Windows package. Geometry optimizations is computed at the B3LYP method for the multi-substituted benzyl radical. The calculations are executed with a personal computer equipped with an Intel Pentium VI, 3 GHz processor and 1 GMB RAM.



**Figure 2. Simple schematics of Corona Excited Supersonic Expansion system.**

## RESULTS AND DISCUSSION

By corona discharge of 2,3-difluorotoluene, the spectrum, figure 3, is obtained and it shows a portion of the visible vibronic emission spectrum of the jet-cooled 2,3-difluorobenzyl radical, in which most of the bands are observed with intensity in the region of  $19000 \sim 22000 \text{ cm}^{-1}$ .

From similar experiments [22] the rotational temperature of 50 K was proved in the jet expansion with corona by a low backing pressure in a supersonic jet expansion and collisional relaxation in the D1 state is so efficient by help of a pinhole-type glass nozzle in a corona excited supersonic expansion that the CESE spectra are similar to the dispersed fluorescence spectra observed by pumping the origin band of the electronic state [12].

Thus, the shift of the observed vibronic bands from the origin band represents the vibrational mode frequencies in the ground electronic state. And by collisional relaxation, the population in the vibrationless state of the lowest excited electronic state increases. The band of the strongest intensity at  $21338 \text{ cm}^{-1}$  is believed to be the origin band of the 2,3-difluorobenzyl radical in the  $D1 \rightarrow D0$  transition and followed band of lower frequency from origin band are series of vibronic bands. There are no strong bands in the blue of the origin band, since the enough vibronic relaxation process occurs in the D1 and D2 state of the benzyl-type radicals.

The shift of the frequency of origin band from the benzyl radical  $22002 \text{ cm}^{-1}$  shows the substitution effect to the electronic energy of benzyl-type radical. The 2,6-difluoro benzyl radical shows the origin band at  $21774 \text{ cm}^{-1}$  [20], shifted by  $228 \text{ cm}^{-1}$  from the transition energy of benzyl radical and it is almost twice the shift of *o*-fluoro benzyl radical [17]. In the 2,6-dichloro [16] and 2,6-dimethylbenzyl [23] radicals, a similar characteristic is observed.

For assigning the vibronic bands, *ab initio* calculation and the known vibrational frequencies of the 2,6-difluorobenzyl radical are used, since the molecules are subjected to the isodynamic approximation rule. This rule has already been applied to the vibrational mode assignment of

many benzyl-type radicals [13–26].

Low frequency sequence bands with  $50\text{ cm}^{-1}$  and  $70\text{ cm}^{-1}$  in the vicinity of the origin band is observed. From the origin band, the value is less than  $150\text{ cm}^{-1}$ . Cossart-Magos and Cossart [27] have observed several weak low frequency sequence bands near the origin band of the *p*-fluorobenzyl radical, and assigned them as combination bands. Thus, it is strongly believed that owing to the incomplete collisional relaxation in the excited electronic state induces the sequence bands near the origin.

The band at  $290\text{ cm}^{-1}$  from the origin band is assigned to mode 15 vibration. As showed in table 1, mode 15 of C–H bending motion is accord well with *ab initio* value,  $288\text{ cm}^{-1}$ . Very weak band at  $474\text{ cm}^{-1}$  is assigned to mode 6a and strong band at  $498\text{ cm}^{-1}$  is assigned to 6b of ring deformation, these two bands are one of the most prominent modes in benzyl-type radical derivatives [13-26]. Mode 6a is degenerate with mode 6b in benzene with a mode frequency of  $606\text{ cm}^{-1}$ .

In the vibronic emission spectrum of the 2,6- difluorobenzyl radical [20] of  $C_{2v}$  symmetry, mode 6a is observed with a strong intensity, whereas mode 6b was barely detected with a very weak intensity. Table 2 shows the vibronic assignment of 2,6-difluorobenzyl radical with B3LYP/cc-pvdz *ab initio* calculation using the data from the Reference [20].

The *ab initio* calculation predicts the observed frequencies very well. Mode 18b of C–H bending motion is assigned at  $550\text{ cm}^{-1}$ . The ring breathing vibration mode 1 is assigned at  $686\text{ cm}^{-1}$ . The calculation ( $699\text{ cm}^{-1}$ ) agreed well with the observation value. The mode 17b of C–H bending vibration band is assigned at  $786\text{ cm}^{-1}$ . Because the calculation value gives a very accurate prediction  $789\text{ cm}^{-1}$ . The medium band at  $828\text{ cm}^{-1}$  is assigned as a mode 12 of in-plane ring deformation vibration. The calculation  $830\text{ cm}^{-1}$  agrees well with the observed value.

The medium band at  $1046\text{ cm}^{-1}$  is assigned as a mode 7b of C–H stretching vibration since the calculation and the observation are accord as well as *ab initio* value. The strong intensity band at  $1284\text{ cm}^{-1}$  is assigned to mode 20a of in-plane C–F ring stretching vibration. Finally, mode 8a of C–H in-plane stretching vibration is assigned to band at  $1574\text{ cm}^{-1}$  from the origin and  $1594\text{ cm}^{-1}$  for 8a mode of isomer 2,6-difluorobenzyl radical is analogous with 8a band of 2,3-difluorobenzyl radical.

In table 1, the observed vibrational mode frequencies, *ab initio* calculation are compared with frequencies of the precursor, together with the symmetry and intensity. All six isomers of difluorobenzyl radicals can be classified into three different classes: 1,2,3-substitutions, 1,2,4-substitution and 1,3,5-substitution. 1,2,3-substitution group contains 2,6- and 2,3-difluorobenzyl radicals with  $C_{2v}$  and  $C_s$  symmetry. 1,2,4-substitution group consists 2,4-, 2,5-, and 3,4-difluorobenzyl radicals of  $C_s$  symmetry.

Finally, 3,5-difluorobenzyl radical of  $C_{2v}$  symmetry belongs to 1,3,5-substitution. The vibronic emission spectrum of 2,3-difluorobenzyl radical is compared with that of 2,6-difluorobenzyl in figure 4, in which both spectra show similar vibronic structure in the ground state. While the 6b mode is very weak and 6a is strong intensive mode in the spectrum of 2,6- difluorobenzyl radical, the 6b mode is observed with strong intensity in 2,3-difluorobenzyl radical but 6a is weak. These characteristics has been measured in many benzyl-type radicals of  $C_s$  and  $C_{2v}$  point groups.

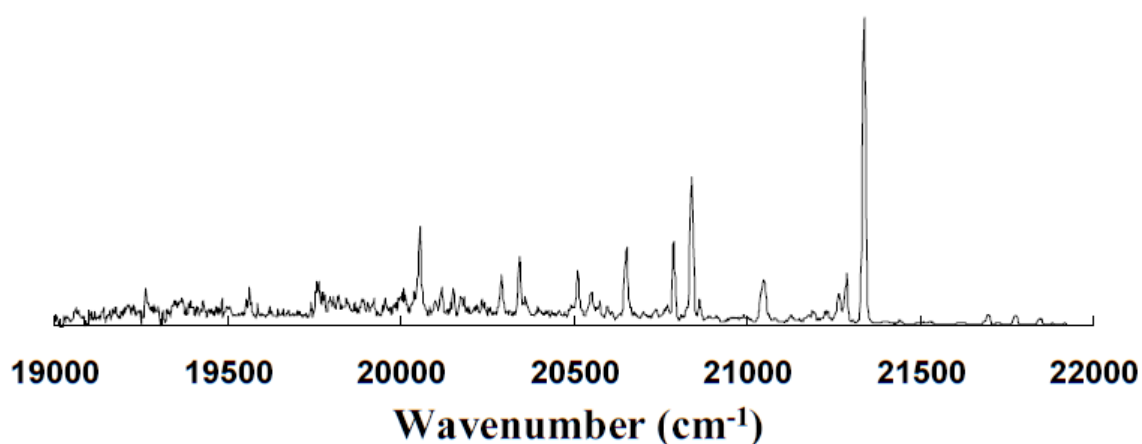


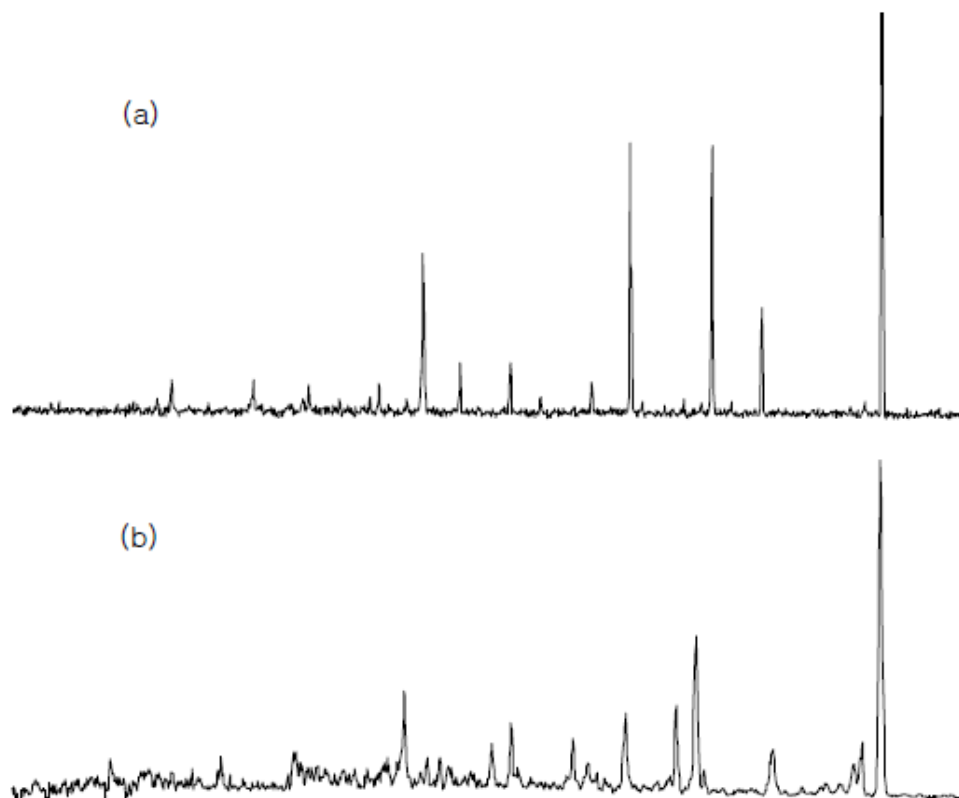
Figure 3. A portion of vibronic emission spectrum of 2,3-difluorobenzyl radical.

Table 1. Vibrational frequencies ( $\text{cm}^{-1}$ ) of the 2,3-difluorobenzyl radical.

Position	Spacing	<i>Ab initio</i> B3LYP/ cc-pvdz	Precursor <sup>a</sup> ( $S_0$ )	Mode <sup>b</sup>	Symmetry	Intensity
21338	0			Origin		vs
21288	50			$\alpha$		w
21268	78			$\beta$		w
21048	290	288	270	15	$a'$	m
20864	474	479	480	6a	$a'$	vw
20842	496	504	504	6b	$a'$	s
20788	550	554	578	18b	$a'$	s
20652	686	699	701	1	$a'$	s
20552	786	789	788	17b	$a''$	w
20510	828	830	832	12	$a'$	m
20342	992					m
20292	1046	1060	1037	7b	$a'$	m
20056	1284	1307	1330	20a	$a'$	s
19746	1574	1600	1700	8a	$a'$	w
19562	1776					w
19266	2072					w

**Table 2. Vibrational frequencies (cm<sup>-1</sup>) of the 2,6-difluorobenzyl radical.**

Position <sup>a</sup>	Spacing	<i>Ab initio</i>		Mode <sup>c</sup>	Symmetry	Intensity
		B3LYP/ cc-pvdz	Precursor <sup>b</sup> (S <sub>0</sub> )			
21774	0			Origin		vs
21444	330	332	303	18a	a <sub>1</sub>	s
21304	470	475	480	6a	a <sub>1</sub>	s
21078	696	704	701	1	a <sub>1</sub>	s
20972	802	795	788	17b	b <sub>1</sub>	m
20832	942	952	973	5	b <sub>1</sub>	w
20748	1026	1063	1075	9a	a <sub>1</sub>	m
20610	1164	1158	1075	9b	b <sub>2</sub>	w
20510	1264	1289	1263	3	a <sub>1</sub>	s
20386	1388					w
20194	1580	1588	1665	8b	b <sub>2</sub>	w

**Figure 4. Similarity of the vibronic emission spectrum of between (a) 2,6-difluorobenzyl [20] and (b) 2,3-difluorobenzyl radicals in the D<sub>1</sub>(<sup>2</sup>A<sub>2</sub>) → D<sub>0</sub>(<sup>2</sup>B<sub>2</sub>) electronic transition.**



## CONCLUSIONS

Fluoro-substituted benzyl radicals is generated in the jet with a large amount of carrier gas (He) and vibronically cooled electronic emission spectra are observed in a corona excited supersonic expansion apparatus. The spectra are analyzed in terms of progressions of the fundamental vibrational modes and molecular structures of multi-substituted benzyl radicals are calculated and compared with experimental data and precursors. For the first time the difluorobenzyl radicals are generated in a jet and the vibronic emission spectra in the D1 → D0 transition have been recorded.

## ACKNOWLEDGEMENTS

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## REFERENCES

- [1] J. C. Whitehead, (1996) Molecular beam studies of free-radical processes: photodissociation, inelastic and reactive collisions. *Rep. Prog. Phys.* 59 993.
- [2] R. S. Mulliken, (1927) Electronic States and Band Spectrum Structure in Diatomic Molecules VI. Theory of Intensity Relations for case b Doublet States. Interpretation of CH Bands  $\lambda\lambda 3900, 4300$ . *Phys. Rev.* 30 785.
- [3] W. E. Pretty, (1928) The swan band spectrum of carbon. *Proc. Phys. Soc.* 40 71.
- [4] F. Hund, (1926) Beyond the Madelung-Klechkowski Rule of aufbau Orbital Filling Principle. *Zeitschrift für Physik* . 36 657.
- [5] F. Paneth and W. Hofeditz, (1929) Growth of Whiskers by Chemical Reactions. *Ber. Chem. Ges.* 62 1335.
- [6] F. O. Rice, (1931) The thermal decomposition of organic compounds from the standpoint of free radicals. I. Saturated hydrocarbons. *J. Am. Chem. Soc.* 53 1959.
- [7] G. Herzberg, *The Spectra and Structure of Simple Free Radicals*. (Cornell University Press, Ithaca, NY, 1971).
- [8] J. I. Selco, P. G. Carrick, (1989) Jet cooled emission spectra of toluene and the benzyl radical. *J. Mol. Spectrosc.* 137 13.
- [9] C. Cossart-Magos, S. Leach, *J. Chem. Phys.* 64 (1976) 4006.
- [10] T.F. Bindley, A.T. Watts, S. Walker, (1964) Two-mode vibronic interaction between neighboring 1 2A<sub>2</sub> and 2 2B<sub>2</sub> excited electronic states of the benzyl radical. *Trans. Faraday Soc.* 60 1.
- [11] M. Fukushima, K. Obi, *J. Chem. Phys. Lett.* 93 (1990) 8488.
- [12] T.-Y. Lin, X.-Q. Tan, T.M. Cerny, J.M. Williamson, D.W. Cullin, T.A. Miller, (1992) Jet spectroscopy and excited state dynamics of benzyl and substituted benzyl radicals. *Chem. Phys.* 167 203.
- [13] S. K. Lee, S. Y. Chae, Vibronic Emission Spectroscopy of the Jet-Cooled o-Chlorobenzyl Radical in the D1 → D0 Transition. *J. Phy. Chem. A* 106 (2002) 8054.
- [14] S. K. Lee, S. Y. Chae, (2001) Vibrational Mode Assignments of Jet-Cooled m-Chlorobenzyl Radical in the Ground Electronic State. *J. Phy. Chem. A* 105 5808.
- [15] S.K. Lee, D.Y. Baek, (1999) D1→D0 and D2→D0 transitions of the jet-cooled p-chlorobenzyl radical *Chem. Phys. Lett.* 304 39.
- [16] S.K. Lee, S. J. Kim, (2005) Vibronic emission spectrum of the jet-cooled 2, 6-dichlorobenzyl radical in a corona excited supersonic expansion. *Chem. Phys. Lett.* 412 88. *Chem. Phys*, 167 203.



- [15] T. R. Charlton, B. A. Thrush (1986) The study of substituted benzyl radicals by laser-induced fluorescence. *Chem. Phys. Lett.* 125 547.
- [16] H.C. Longuet-Higgins and J.Pople (1955) Electronic Excitations of Open Shell Systems in the Grand Canonical and Canonical Time-Dependent Hartree-Fock Models. Applications on Hydrocarbon Radical Ions. *Proc. Phys. Soc. (London)*, A68 591.
- [17] S.K. Lee, S.K. Lee, (2001) Vibronic Spectroscopy of Benzyl-Type Radicals: Jet-Cooled o-Fluorobenzyl Radical in the D1 → D0 Transition. *J. Phys. Chem. A* 105 3034.
- [18] S.K. Lee, D. Y. Baek (1999) Vibronic analysis of the jet-cooled emission spectrum of p-fluorobenzyl radical in the D1→ D0 transition. *Chem. Phys. Lett.* 301 407.
- [19] S.K. Lee, D.Y. Baek, (1999) D1→ D0 and D2→ D0 transitions of the jet-cooled p-chlorobenzyl radical. *Chem. Phys. Lett.* 302 407.
- [20] S.K. Lee, D.Y. Baek, (2000) Observation of vibronic emission spectrum of the jet-cooled 2, 6-difluorobenzyl radical. *J. Phys. Chem. A.* 104 5219.
- [21] S.K. Lee, D.Y. Baek, (1999) Visible vibronic emission spectrum of the jet-cooled pentafluorobenzyl radical. *Chem. Phys. Lett.* 311 36.
- [22] M.H. Suh, S.K. Lee, T.A. Miller, (1999) Vibronic Emission Spectrum of p-Xylyl Radical. *J. Mol. Spectrosc.* 194 211.
- [23] G.W. Lee, S.K. Lee, (2006) Vibronic structure of jet-cooled 2, 6-dimethylbenzyl radical: Revisited. *J. Phys. Chem. A* 110 2130.
- [24] G. W. Lee, S.K. Lee, (2007) Vibronic spectroscopy of benzyl-type radicals: Observation of mesityl radical in the gas phase. *J. Phys. Chem. A* 111 6003.
- [25] G. W. Lee, S.K. Lee, (2007) Observation of vibronic emission spectrum of jet-cooled duryl radical in corona excitation. *J. Chem. Phys.* 126 214308.
- [26] G. W. Lee, S.K. Lee, (2005) Observation of vibronic emission spectra of jet-cooled o-cyanobenzyl radical in the D1→ D0 transition. *Chem. Phys. Lett.* 410 6.
- [27] C. Cossart-Magos, D. Cossart, (1988) Rotational band contours of the first electronic transition origin bands of p-xylyl and p-fluorobenzyl. *Mol. Phys.* 65 627.
- [28] T. A. Miller, (1984) Chemistry and chemical intermediates in supersonic free jet expansions. *Science* 223 545.
- [29] P. C. Engelking, (1986) Corona excited supersonic expansion. *Rev. Sci. Instrum.* 57 2274.
- [30] A. T. Droege, P. C. Engelking, (1983) Supersonic expansion cooling of electronically excited OH radicals. *Chem. Phys. Lett.* 96 316.