

Spectroscopic Evidence of Jet-Cooled *p*-Chloro- α -Methylbenzyl Radical in Corona Excitation

Chang Soon Huh, Young Wook Yoon, and Sang Kuk Lee*

Department of Chemistry and The Chemistry Institute of Functional Materials, Pusan National University, Pusan 609-735, Korea

*E-mail: sklee@pusan.ac.kr

Received April 20, 2012, Accepted June 8, 2012

We report the first spectroscopic evidence of the jet-cooled *p*-chloro- α -methylbenzyl radical. The visible vibronic emission spectrum was recorded from the corona discharge of precursor *p*-chloro-ethylbenzene seeded in a large amount of inert carrier gas helium using a pinhole-type glass nozzle coupled with a technique of corona excited supersonic expansion. From the comparison with the vibronic spectrum of the *p*-chlorobenzyl radical, we identified the evidence of formation of the jet-cooled *p*-chloro- α -methylbenzyl radical in the corona discharge of precursor *p*-chloro-ethylbenzene.

Key Words : Spectroscopy, *p*-Chloro- α -methylbenzyl radical, Corona discharge

Introduction

Benzyl radical,¹ a prototypical aromatic free radical, has been believed to be one of the fundamental reaction intermediates in aromatic chain reactions and has been the subject of the numerous spectroscopic studies. Although the spectroscopic observation of benzyl radical has been carried out using a variety of experimental techniques, substituted benzyl radicals have attracted less attention due to the difficulties associated with the identification of the species and possible rearrangements at the transition state.

Among substituted benzyl radicals, methyl and fluorine substituted benzyl radicals have been extensively examined because they emit strong fluorescence in the visible region. Since the first observation of the vibronic emission spectra of the xylyl radicals from the electric discharge of the xylenes by Bindley *et al.*,² many papers have been published for the vibronic assignments of xylyl radicals using different experimental techniques. Selco and Carrick³ provided the complete assignments of many vibronic bands of three isomers of xylyl radicals with a technique of electric discharge. Recently, Lee group⁴⁻⁶ reported the spectroscopic observation of multi-methyl substituted benzyl radicals.

The spectroscopic study of fluorobenzyl radicals was initiated by Bindley *et al.*⁷ using an electric discharge of corresponding fluorotoluenes, in which the vibronic structure of all three isomeric fluorobenzyl radicals were definitely determined from the analysis of the emission spectra. Further assignments of multi-fluorine substituted benzyl radicals were obtained with a technique of corona discharge.⁸ Recently, the evidence of new type of benzyl-type radical was tested to detect the *p*-fluoro- α -methylbenzyl radical⁹ from the analysis of the vibronic spectrum observed in the corona discharge of *p*-fluoro-ethylbenzene.

Although halobenzyl radicals are of considerable interest for understanding the stability of benzyl-type radicals, the chlorine-substituted species are much more difficult to iden-

tify, because they emit at an extremely weak fluorescence in the visible region. Nevertheless, all three isomers of chlorobenzyl radicals have been clearly identified using techniques of laser induced fluorescence (LIF)¹⁰ and electric DC discharge.¹¹⁻¹³ However, the 2,6-dichlorobenzyl radical¹⁴ is the only multi-chlorine substituted benzyl radical observed so far. Recently, the spectroscopic evidence of the jet-cooled *o*-chloro- α -methylbenzyl radical¹⁵ was reported using a precursor *o*-chloro-ethylbenzene that may produce benzyl-type radicals by dissociation of methyl C-CH₃ or methyl C-H bond.

The technique of CESE, Corona Excited Supersonic Expansion, originally invented by Engelking^{16,17} has been recognized to be a useful laser-free spectroscopic tool for observation of vibronic emission spectra of jet-cooled transient species, especially for benzyl-type radicals. The stabilization of transient species and simplification of spectrum associated with the expansion of an inert carrier gas cannot be obtained in any other way. Among the emission sources developed for this purpose, the only one providing sufficient continuous fluorescence intensity for weak transitions is the pinhole-type glass nozzle which was well designed in the laboratory¹⁸ to improve the longer stability of corona discharge of heavy aromatic precursors that produce soot deposit clogging the nozzle throat, thus making it possible to detect the transient molecules emitting very weak fluorescence in the visible region.

In this paper, we report the first spectroscopic evidence of the *p*-chloro- α -methylbenzyl radical produced from the corona discharge of precursor, *p*-chloro-ethylbenzene seeded in a large amount of an inert carrier gas He using a pinhole-type glass nozzle in conjunction with the technique of CESE.

Experimental Details

The experimental setup employed in this work is similar to

those described elsewhere.¹⁹ Briefly, it employed a pinhole-type glass nozzle coupled with the technique of CESE for the generation of vibronically excited but jet-cooled benzyl-type radicals from precursor, from which the vibronic emission spectrum of benzyl-type radicals was recorded with a long-path monochromator in the visible region.

The precursor *p*-chloro-ethylbenzene (reagent grade, Sigma-Aldrich) was purchased and used without further purification. The precursor was vaporized at room temperature inside the vaporizing vessel of 2.0 bar of carrier gas He. The concentration of the precursor in the carrier gas was controlled by adjusting the bypass valve of the carrier gas to achieve the maximum emission intensity monitored from the strongest band, and was believed to be less than 1%.

To improve the stability of the corona discharge, we employed a modified pinhole-type glass nozzle with an orifice diameter of 0.3 mm made in this laboratory. The modified nozzle significantly reduced the amount of soot deposit clogging the orifice of the nozzle during the corona discharge of the precursor. The size of nozzle throat was further reduced by partially insertion of a sharpened anode. A sharpened stainless steel rod, acting as an anode inside the nozzle cavity, was electrically connected to a high voltage DC power supply of the negative polarity, in which the axial discharging current was about 5 mA at a DC potential of 2000 V and stabilized using a 150 k Ω current-limiting ballast resistor.

Since the generation of benzyl-type radicals is highly sensitive to the chamber pressure, we optimized the pumping capacity of the 800 L/min mechanical vacuum pump, maintaining a chamber pressure of 3.0 mbar during continuous jet expansion, with a backing pressure of 3.0 bar. The backing pressure was limited by the tolerance of the glassware used for the nozzle. The weak blue-green colored jet was the evidence of the presence of the benzyl-type radicals.

The light emanating from the downstream jet area 5 mm below the nozzle opening, was collimated using a collecting quartz lens ($d = 3.8$ cm, $f = 5.0$ cm) placed inside the chamber and focused on the slit of the long-path monochromator (Jobin Yvon U1000, path length = 2.0 m) equipped with two 1800 lines/mm gratings, and detected with a cooled photomultiplier tube (Hamamatsu R649) and a photon counting system. During the scans, the slit width was set to 100 μm , providing an effective resolution of about 2 cm^{-1} in the visible region. The spectral region from 19000 to 22000 cm^{-1} was singly scanned in 2.0 cm^{-1} increment over a period of 2 hrs to record the spectrum shown in Figure 2. The wavenumber of the spectrum was calibrated using the He atomic lines²⁰ observed in the same spectral region as the benzyl-type radicals, and is believed to be accurate to within ± 1.0 cm^{-1} .

Since the vibrational mode assignments of the *p*-chloro- α -methylbenzyl radical have not been completely accomplished, *ab initio* calculations on the ground electronic states (D_0) of the radicals were carried out to assist the spectral assignments. Calculations were performed using a personal computer equipped with an Intel(R) Core(TM) 2 Duo CPU of 3.0 GHz

processor with 2.0GB RAM using the standard methods included in the Gaussian03 program for windows package. Geometric optimization and vibrational frequency calculations were performed at the B3LYP level, and the 6-311G* basis set was employed in all calculations.

Results and Discussion

Although the benzyl radical can be generated by the laser irradiation of benzyl halides,²¹ it has been demonstrated²² that the corona discharge of toluene generates the benzyl radical more effectively in a CESE system using a pinhole-type glass nozzle with a large amount of the inert carrier gas helium. Although the exact mechanism for the generation and excitation of benzyl radical has not been established in a CESE system using a pinhole-type glass nozzle, it has been suggested that the metastable He atom in the $1s2s\ ^3S_1$ state, about 19.82 eV above the ground state produced by a corona discharge,²³ transfers its excess energy to toluene *via* a collisional process. The vibronically excited toluene then decomposes to form benzyl radicals by cleavage of methyl C-H bond, the weakest bond in the precursor molecule. Similarly, ring-substituted toluenes should undergo the same excitation process to form the corresponding benzyl-type radicals in the gas phase.

The collisional energy transfer using metastable He atoms is a well known process in the excitation of Ne atoms of the HeNe laser. In the plasma chemistry using corona discharge, the bond dissociation energy plays a crucial role in producing benzyl-type radicals because the weaker bonds are preferentially dissociated. However, it is usually not true that the discharge chemistry will obey simple thermochemical rules, if the excited electronic states are involved.

Although it has been reported that a diradical²⁴ was produced in the matrix isolation of 1,3,5-trimethylbenzene (mesitylene) due to the abstraction of a hydrogen atom from each of the two methyl groups rather than from the benzene ring, no one has ever observed a diradical in the gas phase, because of their extremely short lifetimes and low concentrations in the gas phase medium. Thus, we believe that the benzyl-type radicals generated in this work belong to monoradicals only.

In benzyl-type radicals that have a planar structure, the electronic interaction between the substituents and the benzene ring should be undoubtedly of second-order compared with that between the methylene group and the benzene ring, to which the methylene group contributes one π electron to make 7 delocalized π electronic systems, leading to the significant lowering of the excited electronic energy to the visible region. Thus, the π electronic structure of the benzyl-type radicals should be similar to that of the parental benzyl radical, regardless of the nature of the substituents. However, ring substitution is expected to affect the energies of the two excited electronic states differently. Generally, the substituent effect on electronic energy is to reduce the energy of the excited electronic states by extending the space for delocalizing π electrons. Table 1 lists the electronic energy

Table 1. Origin Bands in the D₁ → D₀ Transition of Benzyl-type Radicals^a

Molecules	Origin band	Shift ^h
benzyl ^b	22002	0
<i>o</i> -chlorobenzyl ^c	21040	962
<i>m</i> -chlorobenzyl ^c	21194	808
<i>p</i> -chlorobenzyl ^c	21645	357
2,6-dichlorobenzyl ^d	20153	1849
<i>o</i> -chloro- α -methylbenzyl ^e	21180	822
<i>p</i> -chloro- α -methylbenzyl ^f	21140	862
<i>p</i> -fluoro- α -methylbenzyl ^g	20854	1148

^aMeasured in vacuum (cm⁻¹). ^bRef 22. ^cRefs 11-13. ^dRef 14. ^eRef 27. ^fThis work. ^gRef 9. ^hWith respect to the origin band of the benzyl radical (22002 cm⁻¹)

in the D₁ → D₀ transition of the benzyl-type radicals related to chlorine-substituted benzyl radicals. The origin bands of the substituted benzyl radicals always show the shift to red region compared to that of parental benzyl radical. For multi-substituted benzyl radicals, the substitution shows a synergic effect, giving almost twice shift for the 2,6-dichlorobenzyl radical compared to that of the 2-chlorobenzyl radical.

The visible emission of benzyl-type radicals is believed to arise from transitions to the D₀(1²B₂) ground state from the close-lying D₂(2²B₂) and D₁(1²A₂) excited electronic states which could be mixed through vibronic coupling, transferring the population from the D₂ to D₁ states. Thus, it is difficult to observe the transition from the D₂ to D₀ states for benzyl-type radicals because of the efficient relaxation of the population from the D₂ to D₁ states. The only exception is the moderate observation of the D₂ → D₀ transition of the *p*-chlorobenzyl radical,¹⁰ which might be due to the very small energy difference of 94 cm⁻¹ between the two excited electronic states compared to those of the vibrational modes, making the vibronic relaxation be less efficient.

In addition to vibronic relaxation, the molecular radicals produced in corona excitation also experience collisional relaxation with the He atoms, the process of losing their rotational and vibrational energies in the D₁ state during the supersonic jet expansion producing electronically excited but rovibrationally cold species. The simulation of rotational contour²⁵ showed that the rotational temperature of about 40 K, which is relatively high for supersonic jet expansion, because the system adopted electric high voltage DC discharge, continuous jet expansion, and low backing pressure in CESE system.

The vibronic emission spectrum observed with CESE using a pinhole-type glass nozzle is similar to the LIF-DF spectrum observed while exciting the origin band of the D₁ ← D₀ electronic transition, which exhibits the origin band with the strongest intensity at the highest wavenumber. Thus, the spacing from the origin band to the observed vibronic bands provides the vibrational mode frequencies in the D₀ state, as shown in Table 2.

Figure 1 shows the possible formation of benzyl-type radicals from the corona discharge of the precursor, *p*-

Table 2. List of the Observed Vibronic Bands and Their Assignments^a

Position	Intensity	Spacing ^b	Assignments ^{c,d}
21736	m		origin (1) D ₂ -D ₀
21644	s		origin (1) D ₁ -D ₀
21386	vw	258	15 ₁ ⁰ (1)
21300	m		α (2)
21262	m	382	7a ₁ ⁰ (1)
21250	m	394	16a ₁ ⁰ (1)
21217	m		He atomic
21178	s	-38	α (2)
21168	w	-28	α (2)
21140	vs	0	origin (2)
21122	s	18	α (2)
21086	m	54	α (2)
21014	vs	630	12 ₁ ⁰ (1)
21008	m	636	6b ₁ ⁰ (1)
20920	w	724	4 ₁ ⁰ (1)
20820	s	824	6a ₁ ⁰ (1)
20782	m	358	7a ₁ ⁰ (2)
20766	w	878	10a ₁ ⁰ (1)
20570	vs		H atomic
20502	m	638	10 ₁ ⁰ (2)
20390	w	750	7a ₂ ⁰ (1)
20376	m	1268	14 ₁ ⁰ (1)
20354	m	786	6a ₁ ⁰ (2)
20332	m	1312	3 ₁ ⁰ (1)
20316	m		He atomic
20194	m	1450	6a ₁ ⁰ 12 ₁ ⁰ (1)
20114	m	1530	8b ₁ ⁰ (1)
20072	vw	1068	1 ₁ ⁰ (2)
20000	w	1644	6a ₂ ⁰ (1)
19938	s		He atomic
19718	w	1422	6a ₁ ⁰ 12 ₁ ⁰ (2)
19646	vw	1494	19b ₁ ⁰ (2)
19610	w	1530	19a ₁ ⁰ (2)
19586	vw	1554	8b ₁ ⁰ (2)
19556	vw	1584	8a ₁ ⁰ (2)

^aMeasured in vacuum (cm⁻¹). ^bSpacing from the origin bands at 21644 and 21140 cm⁻¹ for the *p*-chlorobenzyl and *p*-chloro- α -methylbenzyl radicals, respectively. ^cGreek letters indicate the sequence bands associated with the strong vibronic bands. ^dThe numbers 1 and 2 indicate the *p*-chlorobenzyl and *p*-chloro- α -methylbenzyl radicals, respectively.

chloro-ethylbenzene seeded in a large amount of inert carrier gas helium. We expect two types of benzyl-type radicals from the dissociation process. The bond cleavage of the C-H and C-CH₃ at the α -position of the ethyl group of the precursor would generate the *p*-chloro- α -methylbenzyl and *p*-chlorobenzyl radicals, respectively. Thus, the spectrum should show two series of vibronic structures of benzyl-type radicals, including the observation of the strong origin bands at the highest wavenumber of each vibronic series.

With regard to the bond dissociation energies²⁶ of benzylic C-H (356 kJ/mol) and C-CH₃ (305 kJ/mol), the breaking of the C-CH₃ bond could be the preferential pathway in the parallel reaction, yielding the *p*-chlorobenzyl radical as the major product. However, the two H atoms at the α -position

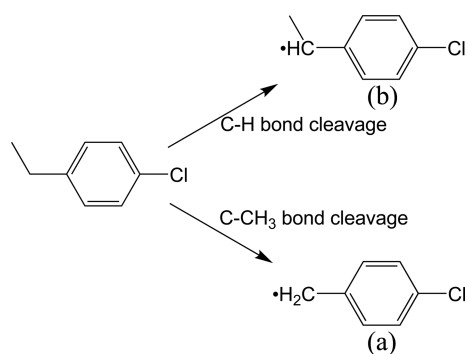


Figure 1. Possible formation of the (a) *p*-chlorobenzyl and (b) *p*-chloro- α -methylbenzyl radicals from the precursor, *p*-chloroethylbenzene. The cleavage of the C-CH₃ and C-H bonds at the α -position of the ethyl group generates the *p*-chlorobenzyl and *p*-chloro- α -methylbenzyl radicals, respectively.

should have more statistical weight than one -CH₃ group.

In the vibronic emission spectrum observed from the corona discharge of the precursor ethylbenzene, the α -methylbenzyl radical²⁷ was weakly detected in the bush of the benzyl radical, indicating that the bond dissociation energy played a key role in the kinetics of the parallel reaction. However, the α -methylbenzyl radical was obtained in the larger portion from the corona discharge of the isopropylbenzene which cannot produce benzyl radical because of the absence of C-H bond in the isopropyl group.

For halogen substituted benzyl-type radicals, the *p*-fluoro- α -methylbenzyl radical⁹ was found with very weak intensity among the strong vibronic bands of the *p*-fluorobenzyl radical. On the other hand, the *o*-chloro- α -methylbenzyl radical¹⁵ was observed with stronger intensity compared to the *o*-chlorobenzyl radical from the precursor *o*-chloroethylbenzene.

Although the identification of large transient molecules should be obtained by analyzing the high resolution spectrum, the observation of a series of vibronic structures, including the strongest origin band of the electronic transition and a few vibronic bands of the well-known vibrational modes, may provide reliable evidence for the identification of the benzyl-type radicals generated in the corona discharge. Thus, we attempted to obtain the evidence of each benzyl-type radical produced by comparing the observation with the calculation for the electronic transition and vibrational modes because of the limited resolution of the spectrum observed in this work.

Figures 2(a) and 2(b) exhibit the vibronic emission spectra observed with CESE system from the corona discharge of precursors, *p*-chlorotoluene and *p*-chloroethylbenzene seeded in a large amount of carrier gas helium, respectively, at the almost same experimental conditions. It was reported that the corona discharge of *p*-chlorotoluene produces only the *p*-chlorobenzyl radical¹² whose vibronic assignments were established previously. However, the spectrum in Figure 2(b) shows many bands at the same frequency in Figure 2(a), confirming that the corona discharge of *p*-chloroethylbenzene produces not only the *p*-chloro- α -methylbenzyl radical but also the *p*-chlorobenzyl radical. The vibronic bands

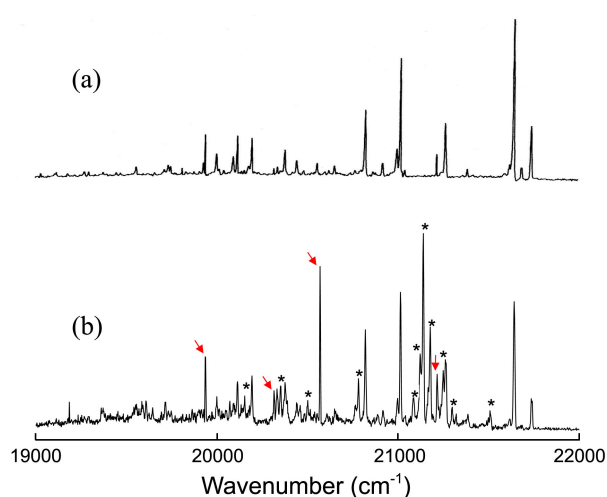


Figure 2. A comparison of the vibronic emission spectrum of the (a) *p*-chlorobenzyl radical with (b) that observed from the corona discharge of the precursor, *p*-chloroethylbenzene, with a large amount of inert carrier gas, He. The bands belonging to the *p*-chloro- α -methylbenzyl radical in the D₁ → D₀ electronic transition are marked by an asterisk in the spectrum. The atomic lines are indicated by an arrow.

observed in Figure 2(b) are listed in Table 2, together with the assignments.

Since the origin band of the benzyl-type radicals should show the strongest intensity at highest frequency, the band at 21140 cm⁻¹, shifted by 862 cm⁻¹ from that of the benzyl radical, was assigned to the origin band in the D₁ → D₀ transition of the *p*-chloro- α -methylbenzyl which was red shifted by 504 cm⁻¹ from that of the *p*-chlorobenzyl radical. The red shift of the origin band with the methyl group at the α -position can be explained by the extension of the space for delocalized π electrons. Other substituted α -methylbenzyl radicals also show the red shift of the origin band. The shift of the origin band is comparable to that of the *o*-chloro- α -methylbenzyl radical even though there is large difference in the position of the origin band of between *o*- and *p*-chlorobenzyl radicals. The *p*-fluoro- α -methylbenzyl radical shows a shift of 1148 cm⁻¹, as in Table 1. Although chlorine and fluorine belong to the electron withdrawing group to benzene ring, their substituent effect is quite different. The strongest effect was observed for the *o*-chlorine substitution, but for *p*-fluorine substitution in benzyl-type radicals, which could explain the large difference in red-shift of the chlorine and fluorine-substituted benzyl radicals.

With the assignment of the origin band, the band at 20782 cm⁻¹ was assigned to the mode 7a of the C-Cl stretching vibration, one of the most distinct modes in substituted benzyl-type radicals. The *p*-chlorobenzyl radical also shows a similar frequency for this mode. Mode 12 of the radial skeletal vibration was assigned to the band at 20502 cm⁻¹, a shift of 638 cm⁻¹ from the origin band because the calculation gives the only a' symmetry mode within ± 100 cm⁻¹. The *p*-chlorobenzyl radical gives a similar frequency of 630 cm⁻¹ for this mode. The band at 20354 cm⁻¹ with medium intensity, a shift of 786 cm⁻¹ from the origin band, was

assigned to mode 6a of C-C-C angle deformation, which is degenerate with 6b in benzene²⁸ at 606 cm⁻¹. The splitting between modes 6a and 6b increases with increasing size of the substituents, reaching 188 cm⁻¹ for *p*-chlorobenzyl while the separation is 59 cm⁻¹ for *o*-fluorobenzyl²⁹. With splitting, mode 6a has a higher wavenumber than mode 6b for the *o*- and *m*-isomers, but the trend is reversed for the *p*-isomer. Mode 1 of the ring breathing vibration was assigned to the very weak band at 20072 cm⁻¹, a shift of 1068 cm⁻¹, because the frequency of this mode should be insensitive to substitution.²⁸ The *p*-chlorobenzyl radical and *p*-chloro-ethylbenzene show this mode at shifts of 1086 and 1061 cm⁻¹ from the origin band, respectively. The medium intensity bands at 19610 and 19646 cm⁻¹, corresponding to the shifts of 1530 and 1494 cm⁻¹, were assigned to modes 19a and 19b of the C-Cl in-plane bending vibration, respectively, owing to the agreement with the calculation as well as the precursor. The degenerate mode 8 of the C-C stretching vibration is split by substitution into modes 8a and 8b. In the *p*-isomer, the frequency of mode 8a is higher than that of mode 8b, whereas the reverse is true in the case of the *o*- and *m*-isomers. Thus, the bands at 19556 and 19586 cm⁻¹, the shifts of 1584 and 1554 cm⁻¹ from the origin band, were assigned to modes 8a and 8b, respectively. The calculation gives similar results for these modes, which show the highest wavenumber, except for the C-H stretching vibrations at 3000 cm⁻¹. Table 3 lists the observed and calculated vibrational mode frequencies of the *p*-chloro- α -methylbenzyl radical, as well as those of *p*-chloro-ethylbenzene with the symmetry of the vibrational modes. All the bands observed in this work belong to a' symmetry of in-plane vibration that shows strong intensity in the vibronic transition of benzyl-type radicals.

Relatively short progression involving vibrational mode 7a was observed at 20390 cm⁻¹ with observable intensity. Also, the vibrational modes with strong intensity listed in Table 1 are active in the combination bands. A problem remains in identifying the origin of the low frequency

Table 3. Vibrational Frequencies of the *p*-Chloro- α -Methylbenzyl and *p*-Chlorobenzyl Radicals^a

Mode ^b	This work (D ₀)	<i>Ab initio</i> ^c B3LYP/6-311G* (D ₀)		<i>p</i> -Chloro toluene ^d (S ₀)	Symmetry C _s (C _{2v})
		<i>p</i> -chloro- α -methylbenzyl radical	<i>p</i> -chlorobenzyl radical		
origin	21140				
1	1068	1082	1094	1075	a' (a ₁)
6a	786	805	835	797	a' (a ₁)
7a	358	360	380	377	a' (a ₁)
12	638	644	645	636	a' (b ₂)
8a	1584	1599	1593	1596	a' (a ₁)
8b	1554	1567	1561	1574	a' (b ₂)
19a	1530	1503	1499	1492	a' (a ₁)
19b	1494	1462	1441	1402	a' (b ₂)

^aMeasured in vacuum (cm⁻¹). ^bRef 31. ^cNot scaled. ^dRef 28.

sequence bands in the vicinity of the origin band. Cossart-Magos and Cossart³⁰ observed several weak bands near the origin band of the *p*-fluorobenzyl radical and assigned them as combination bands coupled with the origin band. Fukushima and Obi¹ also identified weak bands in the vicinity of the strong bands and attributed them to van der Waals molecules. However, it seems unlikely that the bands observed in this work could be due to dimers or van der Waals molecules, because the same bands were observed with another carrier gas Ar, with much weaker intensity. One possible explanation for these low frequency sequence bands might be sequence bands associated with the torsional motion of the methyl group. We observed similar bands from the α -methylbenzyl radical and *p*-fluoro- α -methylbenzyl radical. However, it may not be possible at this moment to make a definitive assignment of these bands, due to the insufficient spectroscopic data on the torsional motion in the excited electronic state.

Conclusion

We obtained the spectroscopic evidence of the formation of two types of benzyl-type radicals, the *p*-chlorobenzyl and *p*-chloro- α -methylbenzyl radicals from the corona discharge of precursor, *p*-chloro-ethylbenzene, seeded in a large amount of the carrier gas He. From the analysis of the spectrum, we could assign the origin band in the D₁ → D₀ electronic transition and several vibrational modes by comparing with those of an *ab initio* calculation for the first time.

Acknowledgments. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea Government (MEST) (No. 2011-0011009).

References and Notes

- Fukushima, M.; Obi, K. *J. Chem. Phys.* **1990**, *93*, 8488.
- Bindley, T. F.; Watts, A. T.; Watts, S. *Trans. Faraday Soc.* **1962**, *58*, 849.
- Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1995**, *173*, 277.
- Yoon, Y. W.; Lee, S. K. *J. Chem. Phys.* **2011**, *135*, 214305.
- Yoon, Y. W.; Lee, S. K. *Bull. Korean Chem. Soc.* **2011**, *32*, 2751.
- Lee, G. W.; Yoon, Y. W.; Lee, S. K. *Bull. Korean Chem. Soc.* **2011**, *32*, 3389.
- Bindley, T. F.; Watts, A. T.; Watts, S. *Trans. Faraday Soc.* **1964**, *60*, 1.
- Lee, S. W.; Yoon, Y. W.; Lee, S. K. *J. Phys. Chem. A* **2010**, *114*, 9110.
- Lee, G. W.; Lee, S. K. *Chem. Phys. Lett.* **2009**, *470*, 54.
- Fukushima, M.; Obi, K. *Chem. Phys. Lett.* **1996**, *248*, 269.
- Lee, S. K.; Baek, D. Y. *Chem. Phys. Lett.* **1999**, *304*, 39.
- Lee, S. K.; Chae, S. Y. *J. Phys. Chem. A* **2001**, *105*, 5808.
- Lee, S. K.; Chae, S. Y. *J. Phys. Chem. A* **2002**, *106*, 8054.
- Lee, S. K.; Kim, S. J. *Chem. Phys. Lett.* **2005**, *412*, 88.
- Ahn, H. G.; Lee, G. W.; Lee, S. K. *J. Phys. Chem. A* **2008**, *112*, 13427.
- Engelking, P. C. *Rev. Sci. Instrum.* **1986**, *57*, 2274.
- Droegge, A. T.; Engelking, P. C. *Chem. Phys. Lett.* **1983**, *96*, 316.
- Lee, S. K. *Chem. Phys. Lett.* **2002**, *358*, 110.
- Han, M. S.; Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1996**, *17*, 991.

20. Weise, M. L.; Smith, M. W.; Glennon, B. M. *Atomic Transition Probabilities*; NSRD-NBS4; 1966.
 21. Nagano, M.; Sukuki, T.; Ichimura, T.; Okutsu, T.; Hiratsuka, H.; Kawauchi, S. *J. Phys. Chem. A* **2005**, *109*, 5825.
 22. Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1989**, *137*, 13.
 23. Banwell, C. N.; McCash, E. M. *Fundamentals of Molecular Spectroscopy*, 4th ed.; McGraw-Hill: New York, 1994.
 24. Lejeune, V.; Despres, A.; Fourmann, B.; Benoist d'Azy, O.; Migirdicyan, E. *J. Phys. Chem.* **1987**, *91*, 6620.
 25. Suh, M. H.; Lee, S. K.; Miller, T. A. *J. Mole. Spectrosc.* **1999**, *194*, 211.
 26. Sanderson, R. T. *Polar Covalence*; Academic Press: New York, 1983.
 27. Lee, G. W.; Ahn, H. G.; Kim, T. K.; Lee, S. K. *Chem. Phys. Lett.* **2008**, *465*, 193.
 28. Varsanyi, G. *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*; John Wiley & Sons: New York, 1974.
 29. Lee, S. K.; Lee, S. K. *J. Phys. Chem. A* **2001**, *105*, 3034.
 30. Cossart-Magos, C.; Cossart, D. *Mol. Phys.* **1988**, *65*, 627.
 31. Wilson, E. B. *Phys. Rev.* **1934**, *45*, 706.
-