Vibronic Spectroscopy of Jet-Cooled Benzyl-type Radicals Produced from 2-Fluoro-4-Chlorotoluene by Corona Discharge

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A home-made pinhole-type glass nozzle was employed to generate vibronically excited but jet-cooled benzyl-type radicals from precursor 2-fluoro-4-chlorotoluene with a large amount of carrier gas He, from which the visible vibronic emission spectrum was recorded with a long-path monochromator. From an analysis of the spectrum observed, it was found that two benzyl-type radicals, 2-fluorobenzyl and 2-fluoro-4-chlorobenzyl radicals, were formed from the precursor in corona discharge. The possible pathway for the production of benzyl-type radicals that can explain the spectroscopic observation is herein proposed. In addition, the electronic energy of the $D_1 \rightarrow D_0$ transition and the vibrational mode frequencies in the D_0 state of the 2-fluoro-4-chlorobenzyl radical were determined for the first time.

Key Words : Spectroscopy, Corona discharge, 2-Fluoro-4-chlorobenzyl radical, Reaction mechanism, Benzyl-type radical

Introduction

Transient species have long been believed to play a key role as reaction intermediates in many chemical reactions. For those interested in the fundamental issues of chemical reaction, the structure and characteristics of reaction intermediates should provide at least to define the nature of chemical reactivity in reaction dynamics.[1]

Although it is extremely difficult to observe the spectrum of transient species due to the short lifetime and low concentration in the gas phase medium, the structural information can provide important clues to an understanding of the reaction mechanism undergoing at the transition state. Thus, the spectroscopic study has been recognized to be an indispensable tool for identification of transient species.

Benzyl radical, a prototypical aromatic free radical and reaction intermediate in aromatic chain reactions, has been the subject of numerous spectroscopic studies.[2] On the other hand, halogen-substituted benzyl radicals have been relatively less studied owning to the difficulties associated with the possible rearrangement to another species and spectroscopic analysis of the spectrum.

Bindley *et al.*[3] reported the first electronic emission spectra of three fluorobenzyl radicals generated by an electric discharge of corresponding fluorotoluenes. Since then, many papers have been published using a variety of experimental techniques. Lloyd and Wood[4] assigned the vibronic bands of fluorobenzyl radicals in the solid state. Charlton and Thrush[5] used laser excitation technique to confirm vibronic assignments and lifetimes. Lee group[6-8] extended the vibronic assignments from the vibronic emission spectra of fluorobenzyl radicals formed by corona discharge of fluorotoluenes. Of three isomeric fluorobenzyl radicals, the *p*-isomer has been more studied compared to other isomers due to its symmetry

character. Hiratsuka *et al.*[9] determined the symmetries and energies of the excited electronic states of *p*-fluorobenzyl radical. The rotational constants of *p*-fluorobenzyl radical were obtained by Cossart-Magos and Cossart[10] from simulation of the rotational contour of the origin band of observed at room temperature. Fukushima and Obi[2] confirmed the vibronic assignments using laser excitation technique.

Although chlorine substituted benzyl radicals were known to emit weak fluorescence in the visible region, the *p*-chlorobenzyl radical was detected in a laser excitation experiment.[11] Subsequently, Tokumura *et al.*[12] identified the characteristics of excited electronic states and Hamatani *et al.*[13] carried out the vibronic assignments and lifetime measurement by using a technique of laser induced fluorescence. Lee group used a discharge source to excite emission from jet-cooled chlorobenzyl radicals to extend the vibronic assignments.[14-16]

The spectroscopy of hetero-halogen bi-substituted benzyl radicals is believed to be useful for characterizing bond dissociation in corona excitation. Recently, the corona discharge[17] of 2-chloro-4-fluorotoluene has been reported, in which the identification of the spectra observed offers the evidence of reaction pathway through bond dissociation process.

In this work, we present the observation of visible vibronic emission spectrum from the corona discharge of precursor 2-fluoro-4-chlorotoluene using a pinhole-type glass nozzle to examine the role of halogen substituents in the dissociation dynamics of precursor molecules. From the analysis of the spectrum observed, we obtain the electronic energy of the $D_1 \rightarrow D_0$ transition and vibrational mode frequencies in the D_0 state of the 2-fluoro-4-chlorobenzyl radical for the first time.

Experimental Section

The experimental setup employed in this work is similar to

those described previously.[18] A home-made glass nozzle has been employed to produce vibronically excited but jet-cooled benzyl-type radicals in a technique of corona excited supersonic expansion (CESE). The visible vibronic emission spectra were recorded with a long-path monochromator.

The precursor 2-fluoro-4-chlorotoluene (reagent grade) was purchased from Aldrich and used without further purification. It was vaporized inside a vaporizing vessel of carrier gas He at 2 bar. The concentration of precursor in the carrier gas was optimized for the maximum emission intensity as monitored from the strongest band in the spectrum, and was calculated to be less than 1% by mole fraction from the vapor pressure of precursor at room temperature.

For the generation of vibronically excited but jet-cooled benzyl-type radicals, we adapted a modified nozzle[18] that can significantly reduce the formation of soot deposits clogging the nozzle throat during corona discharge and improve a long period stability of corona discharge by allowing excitation to occur after expansion. The round bottom surface of the glass nozzle greatly reduces the soot deposition compared to the original Engelking nozzle[19] of grinded flat surface. A minimum discharging voltage was applied to minimize the cleavage of benzene ring, which produces C_2 emitting strong fluorescence in the same spectral region as benzyl radical. A corona discharge was obtained at 1.8 kV with 5 mA and stabilized by a 150 kΩ current-limiting ballast resister. However, it should be noted that the formation of C_2 molecule cannot be completely avoided from the corona discharge, especially using chlorine-containing precursors.

The Pyrex expansion chamber was evacuated using a 800 L/min mechanical vacuum pump, maintaining 2.0 mbar of chamber pressure during continuous jet expansion with 2.0 bar of backing pressure through the nozzle of a 0.3 mm throat diameter. The backing pressure was mainly limited by the pressure tolerance of the glassware used for the nozzle. Also, we controlled the capacity of the vacuum pump to obtain the brightest emission from benzyl-type radicals, in which the production is highly sensitive to the chamber pressure.

A blue-green colored jet indicates the evidence of formation of benzyl-type radicals from the corona discharge of precursor. The emission was collected using a quartz lens (D=38 mm, F=50 mm) positioned inside the chamber arm to view the emission point 5 mm below the nozzle throat and focused onto the slit of the long-path monochromator (Jobin Yvon U1000) with a cooled photomultiplier tube (Hamamatsu R649). The vibronic emission spectrum was recorded over 1 h by singly scanning from 20000 to 22000 cm^{-1} in increments of 2.0 cm^{-1} with a slit width of 200 μm. The spectral wavenumber was calibrated with the He atomic lines observed at the same spectral region and was believed to be accurate within ± 1.0 cm^{-1}.[20]

For the vibrational-mode assignments of the 2-fluoro-4-chlorobenzyl radical, an *ab initio* calculation was carried out on the ground electronic state. The calculations were executed on a personal computer equipped with an Intel Pentium IV 1.2 GHz CPU processor and 2048MB RAM, in accordance with the standard methods included in the Gaussian04 for Windows packages. Geometry optimization and vibrational mode frequencies were obtained at the DFT level, and a 6-311G* basis set was employed in the calculations. Each vibrational mode was visualized from the output of the calculation using the HyperChem program.

Results and Discussion

Although benzyl chloride[21] has been used as a precursor for production of benzyl radical by laser irradiation, a well-controlled corona discharge of toluene[22] seeded in a large amount of carrier gas He preferrentially produces the vibronically excited benzyl radicals. It has been suggested that the metastable He atom in the 1s2s $^3S_1$ state, about 19.82 eV above the ground state that is initially excited by corona discharge,[23] transfers its excess energy to the precursor through a collisional process. The energy transfer *via* collisional process from the metastable He atom to other species is a well-known technique in the excitation of Ne atoms of the HeNe laser. With collisional excitation, the methyl C-H bond of toluene is dissociated to produce benzyl radical because the benzylic C-H bond (bond energy = 356 kJ/mol) is the weakest one in the precursor molecule. The explanation in terms of bond dissociation energy seems to be reasonable for the observation of the radicals in this work. However, the plasma chemistry will not often follow simple thermochemical rules if excited electronic states are involved. The mechanism for photodissociation[24] of the methyl C-H bond has been closely examined in a time-resolved experiment of *o*-xylene, in which the excitation of molecule from the S_0 to the S_1 state can loosen the methyl C-H bond and subsequently produce the *o*-xylyl radical by dissociation.

The ground state electronic configuration[25] of benzyl radical of seven π electrons is $(1b_2)^2(2b_2)^2(1a_2)^2(3b_2)^1$. There are two possible isoenergetic ways of promoting one electron to form a degenerate pair of lowest excited $^2A_2$ states. Only slightly higher in energy is a comparable pair of degenerate $^2B_2$ states. Configuration interaction between states of the same symmetry causes mutual repulsion, leaving a single $^2A_2$ state and $^2B_2$ state as candidate for the terminus of the lowest electronic excitation at 450 nm. It is now widely accepted that the lowest excited state is the D_1 ($^2A_2$), which has weak oscillator strength connecting it to the D_0 ($^2B_2$) state. Less than 1000 cm^{-1} above the D_1 ($^2A_2$) state lies the D_2 ($^2B_2$) state and, thus, there is strong vibronic coupling[26] between levels of these two states, leading to rapidly transfer the population to the D_1 state. Substitutions into benzene ring affect the energies of the D_2 and D_1 states differently, in which the electronic energy, vibrational mode frequencies, and transition intensity depend on the nature, the position, and the number of substituents on the benzene ring.

In benzyl-type radicals, the electronic interaction between the substituent(s) and the ring is undoubtedly of second order compared to the interaction between the CH_2 group and the ring because the molecule has a planar structure with

seven delocalized π electrons. Thus, the electronic configuration of benzyl-type radicals should be similar to that of the benzyl radical. Two lowest excited D_1 and D_2 states could be mixed *via* vibronic coupling,[26] which increases significantly the relaxation rate of the population from the D_2 to D_1 states, resulting in almost negligible emission intensity of the $D_2 \rightarrow D_0$ transition while strong intensity of the $D_1 \rightarrow D_0$ transition.

In addition, the vibrational relaxation shifts the population to the vibrationless state (v=0) in the D_1 state during supersonic jet expansion. Hence, the typical vibronic emission spectrum of benzyl-type radical observed with a pinhole-type nozzle in CESE system is similar to the LIF-DF spectrum while pumping the origin band of the $D_1 \leftarrow D_0$ transition, exhibiting the origin band of the $D_1 \rightarrow D_0$ transition with strongest intensity at the highest wavenumber in the vibronic emission spectrum. The spacing between the origin band and the other vibronic bands observed represents the vibrational mode frequencies in the D_0 state.

Figure 1 represents the possible benzyl-type radicals obtainable in a CESE system from the corona discharge of the precursor 2-fluoro-4-chlorotoluene. The 2-fluoro-4-chlorobenzyl radical[1] can be formed by simple dissociation of the methyl C-H bond of the precursor, as described above. On the other hand, the 2-fluorobenzyl[2] and 4-chlorobenzyl[3] radicals are obtained by the replacement of the Cl and F atoms at the 4- and 2-positions by an H atom, respectively, along with the dissociation of the methyl C-H bond.

Figure 2 exhibits a portion of the vibronic emission spectrum observed from the corona discharge of the precursor. It consists of a strong origin band in the $D_1 \rightarrow D_0$ transition of the 2-fluorobenzyl radical at 21924 cm^{-1}, followed by a series of vibronic bands with observable intensity in the lower frequency region, which show excellent agreement with those reported previously.[6] A weak complicate features in the spectral region of 21150-21400 cm^{-1} are attributed to the swan system of C_2 molecules[27] generated from the precursor. Generally, the production of C_2 molecules rapidly increases with the voltage beyond the threshold limit, especially for the precursor containing Cl atom(s). However, we could not detect the bands belonging to the 4-chlorobenzyl radical, the origin band of which was reported at 21040 cm^{-1} previously.[16]

After subtraction of the bands belonging to the 2-fluorobenzyl radical from the observed spectrum, we tried to assign the vibronic bands observed in this work. The assignment of the origin band is straightforward because there is no band of
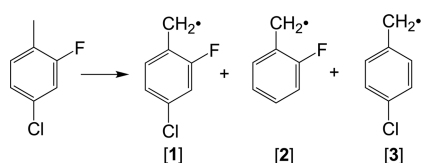

Figure 1. Three possible benzyl-type radicals obtainable from the corona discharge of precursor 2-fluoro-4-chlorotoluene in CESE system. The numbers 1, 2, and 3 in the brackets show the 2-fluoro-4-chlorobenzyl, 2-fluorobenzyl, and 4-chlorobenzyl radicals, respectively.
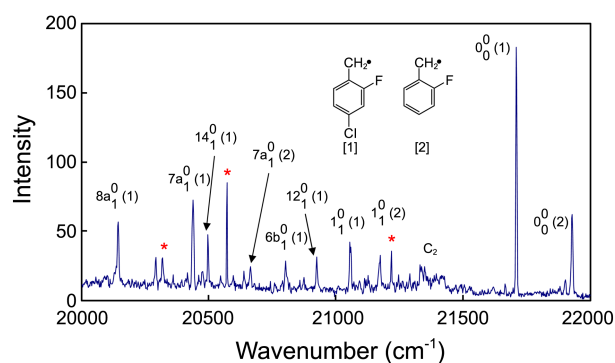

Figure 2. A portion of vibronic emission spectrum observed in CESE system from the corona discharge of precursor 2-fluoro-4-chlorotoluene seeded in a large amount of carrier gas He. The numbers 1 and 2 in the parentheses of the notations of the transition quantum numbers represent the bands belonging to the 2-fluoro-4-chlorobenzyl and 2-fluorobenzyl radicals, respectively. The atomic lines of He and H are marked by an asterisk.

observable intensity to blue region, as already described above. Thus, the strongest band at 21708 cm^{-1} was assigned to the origin band of the 2-fluoro-4-chlorobenzyl radical in the $D_1 \rightarrow D_0$ transition. The red-shift of the origin band from the benzyl radical at 22002 cm^{-1} can be explained by the conjugation of the p orbital of methyl group with the π electrons of the aromatic system. Thus, the shift of bi-substitutions can be estimated by summing up that of each substituent. Table 1 lists the shift of benzyl-type radicals related to 2-fluoro-4-chlorobenzyl radical. The shift of 294 cm^{-1} of 2-fluoro-4-chlorobenzyl radical is similar to that of 2,4-difluorobenzyl radical rather than 2,4-dichlorobenzyl radical, suggesting that the Cl at the 4-position has negligible contribution to substituent effect of 2-fluoro-4-chlorobenzyl radical, which confirms the recent discovery[17] of nodal point on substituent effect. The position nodal points, zero amplitude of delocalized π electrons are located at the 1- and 4-positions at the D_1 state of $^2B_2$ symmetry and disconnect the conjugation of π electrons to substituents.

The vibronic bands belonging to the 2-fluoro-4-chlorobenzyl radical were assigned by comparing the observation with the known vibrational data[28] of the precursor and *ab initio* calculations. For the benzene derivatives,[28] the most well-known vibrational modes are mode 1 of ring-breathing vibration and modes 6a and 6b of in-plane ring deformation vibration. The moderate band, red-shifted by 654 cm^{-1} from the origin band, was assigned to mode 1 because the wave-

Table 1. Red-shift of Origin Bands in the $D_1 \rightarrow D_0$ Transition of Benzyl-type Radicals[a]

Molecules	Origin band	Shift[b]
benzyl[c]	22002	0
2-fluorobenzyl[d]	21924	78
4-chlorobenzyl[e]	21645	357
2-fluoro-4-chlorobenzyl[f]	21708	294

[a]Measured in vacuum (cm^{-1}). [b]With respect to the origin band of benzyl radical (22002 cm^{-1}). [c]Ref 22. [d]Ref 8. [e]Ref 16. [f]This work.

number of this mode should be consistent with that (654 cm^{-1}) of the precursor. The moderate band at 906 cm^{-1} was assigned to mode 6b, because the calculation yields the only a' symmetry band within ± 70 cm^{-1} of the observation. Modes 6a and 6b are degenerate at 606 cm^{-1} in benzene, but split with asymmetric substitutions. The splitting increases with the increasing size of substituents. Mode 6b is a vibration along the axis of the F atom, whereas mode 6a is a vibration perpendicular to mode 6b, along the axis of the Cl atom. In this study, we could not observe mode 6a, as inactive in 1,2,4-trisubstitution. Our calculation predicted this mode to be 547 cm^{-1} and agreed with the precursor (551 cm^{-1}). Mode 7 of in-plane C-X stretching vibration split into modes 7a and 7b with substitution, in which mode 7a always shows stronger intensity in substituted benzyl radicals with higher frequency. Mode 7a was assigned to the strong band at 1270 cm^{-1}, which has a large amplitude in 1,2,4-trisubstitution. Mode 7b was weakly detected at 462 cm^{-1}. The observation agrees well with the calculation and precursor for these modes. Modes 12 of in-plane ring deformation and 14 of in-plane ring stretching were assigned to the bands with moderate intensity at 784 and 1212 cm^{-1} because the observation

Table 2. List of Vibronic Bands Observed in This Work and Their Assignments

Position[a]	Intensity	Spacing[b]	Assignments[c]
21924	s	0	origin of 2-fluorobenzyl(2)
21902	w	22	α(2)
21880	vw	44	β(2)
21708	vs	0	origin of 2-fluoro-4-chlorobenzyl(1)
21664	w	44	α(1)
21618	vw	90	β(1)
21348	w	576	$6a_1^0$ (2)
21330	w	378	$9b_1^0$ (1)
21246	vw	462	$7b_1^0$ (1)
21218	m		He atomic
21168	m	756	1_1^0 (2)
21054	m	654	1_1^0 (1)
20924	m	784	12_1^0 (1)
20802	m	906	$6b_1^0$ (1)
20660	w	1264	$7a_1^0$ (2)
20638	w	1286	14_1^0 (2)
20596	w	1112	$7b_1^0 1_1^0$ (1)
20570	s		H atomic
20546	w	1162	$9b_1^0 12_1^0$ (1)
20496	m	1212	14_1^0 (1)
20460	w	1248	$7b_1^0 12_1^0$ (1)
20438	s	1270	$7a_1^0$ (1)
20354	vw	1570	$8a_1^0$ (2)
20316	m		He atomic
20292	m	1416	$19a_1^0$ (1)
20144	s	1564	$8a_1^0$ (1)

[a]Measured in vacuum (cm^{-1}). [b]The spacing from the origin band of each benzyl-type radical. [c]The numbers 1 and 2 represent the 2-fluoro-4-chlorobenzyl and 2-fluorobenzyl radicals, respectively. The Greek letters indicate the low frequency sequence bands associated with the strong bands

agrees well with the precursor and calculation for these modes. Mode 19a of in-plane ring stretch and deformation vibration was assigned to the moderate band at 1416 cm^{-1} because of the excellent agreement with the precursor. Finally, the strong band at 1564 cm^{-1} from the origin band was assigned to mode 8a of C-C stretching vibration. Table 2 lists the vibronic bands observed in this work together with their assignments and the origin of the species. Table 3 lists the ground state vibrational frequencies of the 2-fluoro-4-chlorobenzyl radical for the comparison with the *ab initio* calculations and the known vibrational data of the precursor. In this work, the modes with a' symmetry of in-plane vibration were observed. The vibrational modes with strong intensity listed above are active in combination bands, in which the modes with the same symmetry combine.

Besides the fundamental bands, we also observed very weak bands in the vicinity of the strong origin bands of the 2-fluorobenzyl and 4-chloro-2-fluorobenzyl radicals. The band at 21902 cm^{-1}, red-shifted by 22 cm^{-1} from the origin band, was not detected in the previous observation[6] of 2-fluorobenzyl radical. We believe these bands may attribute to the hot bands originating from the excited vibrational levels at the D$_1$ state because the dissociation process moves the molecules into excited states easily. However, we cannot assign these bands at this moment due to the lack of information at the D$_1$ state.

Of three possible benzyl-type radicals, the 2-fluorobenzyl and 4-chlorobenzyl radicals should be formed by the replacement of the Cl and F atoms at the 4- and 2-positions by an H atom, respectively, along with the dissociation of the methyl C-H bond. However, we could not see any evidence of the formation of the 4-chlorobenzyl radical, whose origin band in the D$_1$ → D$_0$ transition was reported previously[16] to locate at 21040 cm^{-1} in the vibronic spectrum.

Since the bond dissociation energies[29] of benzylic C-H, phenylic C-Cl and C-F bonds are, respectively, 356, 398, and 519 kJ/mol, the weak C-Cl bond can be easily replaced by C-H bond along with dissociation of the methyl C-H bond by corona discharge. However, the replacement of the strong C-F bond by the C-H bond is thermodynamically

Table 3. Vibrational Frequencies of 2-Fluoro-4-Chlorobenzyl Radical[a]

Mode[b]	This work[c] (D$_0$)	*ab initio*[d] B3LYP/6-311G* (D$_0$)	Precursor 2-fluoro-4-chlorotoluene[e] (S$_0$)	Symmetry (C$_s$)
Origin	20708[f]	25729[f]		
9b	378	379	379	a'
7b	462	465	464	a'
1	654	656	654	a'
12	784	798	755	a'
6b	906	905	894	a'
14	1212	1231	1223	a'
7a	1270	1295	1266	a'
19a	1416	1444	1406	a'
8a	1564	1564	1584	a'

[a]Measured in vacuum (cm^{-1}). [b]Ref 31. [c]This work. [d]Not scaled from B3LYP/6-311G* calculation. [e]Ref 28. [f]TDDFT calculation

Corona Discharge of 2-Fluoro-4-Chlorotoluene

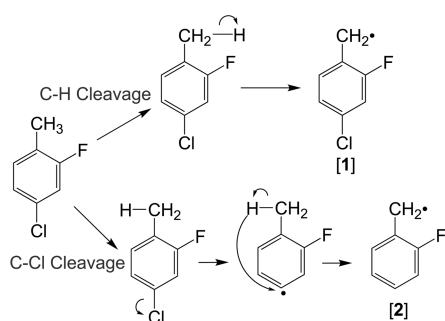*Bull. Korean Chem. Soc.* **2013**, Vol. 34, No. 12   3569

Figure 3. A proposed mechanism for the formation of the 2-fluoro-4-chlorobenzyl [1] and 2-fluorobenzyl [2] radicals from the precursor. A simple dissociation of the methyl C-H bond produces the 2-fluoro-4-chlorobenzyl radical, whereas a migration of H atom to the 4-position from the methyl group after the C-Cl bond cleavage generates the 2-fluorobenzyl radical.

much less favorable process, leading to generate the 2-fluoro-4-chlorobenzyl and 2-fluorobenzyl radicals only, which agrees with the observation in Figure 2.

Recently, we reported that the corona discharge of 2-chloro-4-fluorotoluene[17] produced the 2-chloro-4-fluorobenzyl radical as well as the 4-fluorobenzyl radical which was obtained by dissociation of phenylic C-Cl bond, along with the methyl C-H bond of the precursor. The production of 4-fluorobenzyl radical agreed very well with the prediction based on the bond dissociation energy.

As regards the formation of the 2-fluorobenzyl radical from the precursor, we suggest that it can be accomplished in three ways. The first is a two-step process whereby the Cl atom is replaced after formation of the benzyl-type radical. In order to replace the Cl atom at the 4-position by an H atom, it should collide with a free H atom liberated from the dissociation process of the methyl C-H bond. Even though benzyl-type radicals are very reactive in the excited electronic states, this process is extremely difficult to accomplish for large molecules in the gas phase, due to the very small steric factor in collision theory[30] and the low hydrogen concentration in the medium. The second possible pathway is the direct replacement of the Cl atom by a H atom of methyl group. However, the large distance between two atoms reduces the possibility of the replacement. The last possibility is the migration of H atom from methyl group to Cl position after dissociation of C-Cl bond because the C-Cl bond is very weak and dissociates easily at the excited states by corona discharge. The methyl C-H bond is already loosened by the large amplitude of vibration in the excited electronic state. The migration of Cl atom from α-carbon to benzene ring was suggested from the time-resolved experiment.[21] Figure 3 exhibits a possible mechanism for the formation of the 2-fluoro-4-chlorobenzyl as well as 2-fluorobenzyl radicals from the corona discharge of the precursor.

Conclusion

The vibronic emission spectrum of benzyl-type radicals was observed from the corona discharge of precursor 2-

fluoro-4-chlorotoluene using a pinhole-type glass nozzle in a CESE system. From an analysis of the spectrum observed, we definitely identified the formation of the 2-fluorobenzyl and 2-fluoro-4-chlorobenzyl radicals in corona discharge, for which we propose a possible mechanism to explain the observation. For the 2-fluoro-4-chlorobenzyl radical, we determine the electronic energy in the $D_1 \rightarrow D_0$ transition and the vibrational mode frequencies in the D_0 state. Additionally, the substituent effect on electronic transition energy was clearly described.

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