

Ab initio and spectroscopic study of dimethylbenzyl radicals in a corona excited supersonic expansion

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Abstract— We report the spectroscopic and ab initio and spectroscopic evidence of the 2, 3- and 2, 6-dimethylbenzyl radical in corona excitation. The electronically hot but jet-cooled 2, 3- and 2,6-dimethylbenzyl radical has been produced from precursor 1, 2, 3-trimethylbenzene seeded in large amount inert carrier gas helium by using the technique of corona excited supersonic expansion (CESE) with a pinhole-type glass nozzle. The vibronic emission spectrum of the 2, 3- and 2, 6-dimethylbenzyl radicals were recorded with a long path monochromator in the $D_1 \rightarrow D_0$ electronic transition in the visible region. Ab initio calculation of the ground-state benzyl radical have been carried out with density functional method and the complete basis set model. The observed spectrum is consistent with the result of vibrational frequencies of the ab initio calculation and the benzyl radical ground state reaction mechanism through the hydrogen migration is presented. Furthermore, the ab initio calculation explains the benzyl radical generation mechanism in the excited state through the anti-bonding energy surface. By Additional help of the substitution effect of methyl substituted benzyl radicals, we could identify the jet-cooled 2, 3- and 2, 6-dimethylbenzyl radicals formed in corona discharge of 1, 2, 3-trimethylbenzene.

Index Terms— Dimethylbenzyl radical, Corona Excited Supersonic Expansion (CESE), Vibronic Emission Spectrum, Ab initio Calculation

I. INTRODUCTION

Benzyl radical, 1^2A_2 and 1^2B_1 transition, provides a well-known, typical example of the aromatic hydrocarbons. Since the first work on, benzyl radical done by Schuler [1], the excited-state vibronic coupling, the ground electronic structure of benzyl radical and its derivatives have attracted much attention in the experimental aspects. Cossart-Magos and Leach [2] has studied the D_1 - D_0 transition by a discharge in the visible region. Lin and Miller [3] has observed methyl substituted benzyl radicals produced by a laser induced fluorescence technique and analyzed the methyl torsional levels in the D_1 and D_0 state. Recently, S. K. Lee [4]-[10] have studied the analysis of the vibronic emission spectra of many benzyl-type radicals substituted by fluorine, chlorine and methyl groups by applying the technique of corona excited supersonic expansion. However, the analysis of methyl substituted benzyl radicals has not been much studied because not only vibronic structure but also the torsional structure of methyl groups make it complicated in analysis of the corona excited supersonic expansion (CESE) spectrum. The CESE was set up by Engelking and has been known to a powerful technique for analyzing of emission spectra of jet-cooled transient species [11] without laser systems. The

expansion of an inert carrier gas through the pinhole type nozzle make spectral simplification of the transient species. By using the corona discharge, continuous fluorescence intensity from the excited state to the ground state has been measured [12] [13], which making it possible to obtain the spectra with good signal to noise(S/N). In the corona discharge, the mechanism of the benzyl radical generation has not been established, the analysis of such vibronic spectra observed provides spectroscopic evidence for identification of the transient species produced and generation mechanism of benzyl radical in a corona excited supersonic expansion.

In this work, we report the formation of the 2,3-dimethylbenzyl radical which is competition reaction with 2,6-dimethylbenzyl radical from 1,2,3-trimethylbenzene in a corona excited supersonic expansion. From the analysis of spectrum observed, the spectroscopic data of electronic transition and vibrational mode frequencies were accurately determined by comparing with those of *ab initio* calculation as well as those of precursor. Also, the generation of two geometric isomers produced was discussed with complete basis model of CBS-QB3 and DFT calculation to explain the weaker intensity of 2, 3-dimethylbenzyl radical than 2, 6-dimethylbenzyl radical. Furthermore, benzyl radical producing mechanism was suggested by a TD-DFT calculation.

II. EXPERIMENTAL DETAILS

The experimental condition of this work was accomplished with the apparatus described elsewhere [14]. In brief, we employed the different precursor and conditions that play a important role in the favorable generation of substituted benzyl radicals in a corona excitation. The precursor 1, 2, 3-trimethylbenzene of reagent grade was used without further purification purchasing from Sigma-Aldrich.

The concentration of the precursor was believed to be less than 1% in the mixture of the He carrier gas at ambient temperature. The gas mixture was expanded through the glass nozzle [15] with the 0.2 to 0.3 mm diameter connected with a vacuum chamber pumped by 800 l/min mechanical rotary pump. The high voltage which is 5 mA at 2000 V was applied to a stainless steel rod that ran the length of the glass tube to within almost 0.5 mm of the opening. After corona discharge was induced at the nozzle orifice, a blue-green colored jet could be seen by the benzyl-type radicals in the $D_1 \rightarrow D_0$ transition. The 5 mm light jet area from the nozzle opening was collimated and focused on the slit of the 2m monochromator containing two 1800 lines/mm gratings, and detected with a cooled Hamamatsu R649 photomultiplier tube and a photon counting system. During the scans, the monochromator slit were typically set to 100 to 200 μm , providing resolution of about 2 cm^{-1} . The spectrum from

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18000 to 21500 cm^{-1} was acquired in 2.0 cm^{-1} increment over 2 hours. The Helium (He) atomic lines [16] were used as calibration points, observed in the same spectral region of the Benzyl - type radicals.

Ab initio calculations were carried out to study the lowest doublet potential energy surfaces using the density functional method and the complete basis set (CBS) model [17]-[19]. Geometries of ground and transition states were optimized at the hybrid density functional Becke, three-parameter, Lee-Yang-Parr (B3LYP) levels using the 6-31G* basis set as the initial guesses. B3LYP Time-dependent Density functional theory (TD-DFT) was employed to obtain excited state energies and structures of benzyl-type radicals with 6-31G* basis set [20]. The vibrational frequencies of the benzyl-type radicals were computed to analyze vibronic structures and characterize the stationary points with a scaling factor 0.98. To acquire the transition-state structure, the synchronous transit-guided quasi-Newton method was applied with starting and product structures. The complete basis set models were employed to perform more accurate and reliable results of benzyl radical system. *Ab initio* calculations were executed on Intel i5-3570 CPU processor and 8.0 gigabyte (GB) RAM using GAUSSIAN 09 system for windows [21].

III. RESULTS AND DISCUSSION

The electric discharge technique CESE was invented by Engelking [12] and the CESE system became more general for generation of jet-cooled large radicals such as benzyl-type radicals, which cannot be observed in any other way because of its transient species stabilization and spectral simplification as well. For these purposes of the emission sources, pinhole-type glass nozzle was adopted to provide continuous photon intensity and high resolution spectrum.

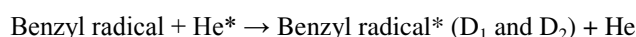
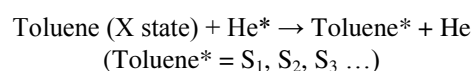
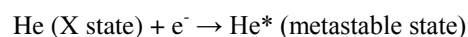
The visible CESE emission from benzyl-type radicals is supposed to occur from transitions of the 1^2B_2 (D_0) ground state from the D_2 and D_1 excited electronic states [20], in which the two electronically excited states could be associated by vibronic coupling, and ring substitution is also assumed to affect the structures and energies of the ground and excited states differently. The 1^2A_2 electronic state is the lowest excited electronic state of the benzyl-type radicals. By the vibronic coupling between D_2 and D_1 states, Rapid collisional relaxation transfers most of the population from the D_2 to the D_1 state so the transitions from the D_1 to D_0 state is observable mainly.

In substituted benzyl-type radicals, the substituents give the second-order effect on the geometric and electronic structure of the benzyl-type radical compared with the first-order factor of the methylene group in the benzyl radical. Since the methylene group provides an additional π electron to the benzene ring, the molecule has a planar structure with 7 delocalized π electrons. Thus, the geometric and electronic structure of substituted benzyl-type radicals should be analogous to that of the benzyl radical, which is closely relate to the two lowest-lying excited electronic states of $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states.

3.1 Analysis of Dissociation Dynamics

It has been well elucidated that the corona excitation of substituted toluenes in a large amount of helium carrier gas generates corresponding benzyl-type radicals. However the

generation mechanism of benzyl-type radicals was not exactly provided. So it has been proposed that the excess energy of metastable He by a corona discharge is transferred to the precursor through collisional process in the pin-hole type nozzle. The benzyl-type radicals are then produced by extracting a hydrogen atom from the benzylic hydrogen rather than the phenyl hydrogen according to the bond dissociation energy (BDE) of benzyl-H, 89.7 kcal per mole which is lower than the BDE of phenyl-H, 112 kcal per mole [22] [23]. For the further study of the benzyl radical formation mechanism, TD-DFT calculation is introduced and the formation processes are suggested in detail. The processes could be summarized for the generation of benzyl radical from toluene.



The toluene initially excited to the S_1 , S_2 and higher electronic state by collision with metastable He. The dissociation of benzyl-H bond can occurred in the S_{17} state which is anti-bonding state of benzyl and hydrogen from TD-DFT calculation and the S_{17} state has 9.14 eV higher energy state than ground state which energy is half of the metastable He 19.82 eV. The TD-DFT potential energy surface of toluene is depicted in Fig. 1.

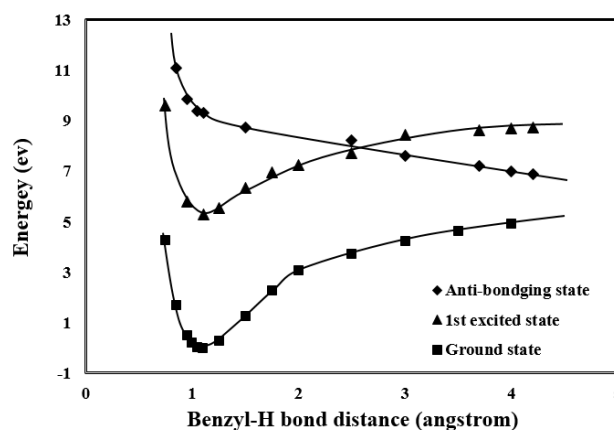


Fig. 1. The TDDFT potential energy curve along the coordinate of the benzyl-H bond in the ground, first excited and anti-bonding state

The potential energy surface of anti-bonding state is computed based on the first excited state optimized geometry using TD-B3LYP/6-31g* theory. It is believed that the ground state benzyl-type radicals produced continuously undergo collisional excitation with metastable helium and emit fluorescence corresponding to the energy difference between D_2 , D_1 and D_0 states, until benzyl-type radicals pass through the pin-hole type nozzle.

Fig. 2 explains that the species generated from precursor 1, 2, 3-trimethylbenzene in corona discharge are 2, 3-dimethylbenzyl and 2,6-dimethylbenzyl radicals, which are

same reaction mechanism with benzyl radical producing; the cleavage of C1-H bond generates the 2, 6-dimethylbenzyl radical while the breaking off the C1-H and C3-H bond produce the 2, 3-dimethylbenzyl radical. In the anti-bonding state of 1, 2, 3-trimethylbenzene which is 9.89 eV higher than ground state induced by collision with metastable He, the C-H bonds of benzylic positions in the 1, 2, 3-trimethylbenzene are dissociated to the dimethylbenzyl radical on the anti-bonding potential surface.

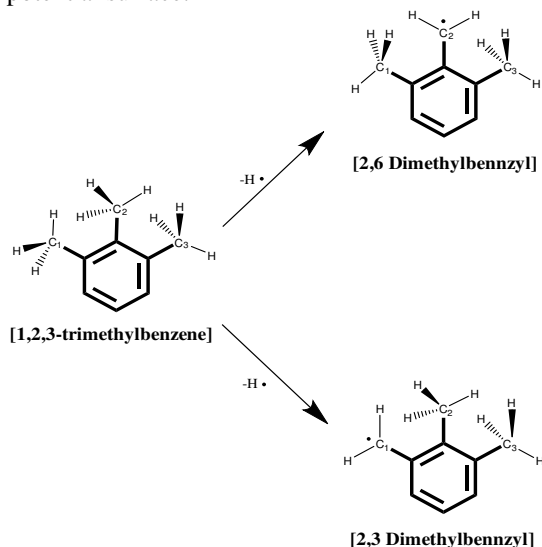


Fig. 2. Formation of the two isomeric dimethylbenzyl radicals by corona discharge of 1, 2, 3-trimethylbenzene. The 2, 3- and 2, 6-isomers were generated by removing H atom from methyl groups at positions 1 and 2, respectively

Fig. 3 illustrates the schematic diagrams for the pathway of the 1, 2, 3-trimethylbenzene reaction on the lowest D_0 potential energy surface. The diagrams display typical hydrogen migration reaction mechanism. After collision with metastable He and 1, 2, 3-trimethylbenzene, produced dimethylbenzyl radicals form isomerization by the hydrogen migration reaction. Dimethylbenzyl radicals undergoes the five-membered transition state through the H-migration from one methyl group to the methylene group leading to the formation of another dimethylbenzyl radical. The barrier height from 2, 6-dimethylbenzyl to 2, 3-dimethylbenzyl is estimated to be 55.9 kcal/mol, which is higher than the typically known range of 20 to 40 kcal/mol for the hydrogen migration process. Until passing the pin hole type nozzle, hydrogen migration reaction is important process in the collisional condition. By energetic comparison, the hydrogen migration is believed to be the one of the main reaction process in the corona discharge because the hydrogen migration energy is lower than that of benzyl D_1 excitation 62 kcal/mol and toluene anti-bonding excitation 228 kcal/mol. Thus, the generation of 2, 6-dimethylbenzyl is a preferential than 2, 3-dimethylbenzyl in terms of the bond dissociation energy by *ab initio* calculation. Table 1 shows that *ab initio* calculation value of C2-H bond dissociation energy from 1,2,3-trimethylbenzene is 1.2 to 1.8 kcal/mol lower than that of C1-H and C3-H bond dissociation energy with DFT and CBS. Although 2, 3-dimethylbenzyl radical which is dissociated from two hydrogen atoms at C1 or C3 has more statistical weights compared to 2, 6-dimethylbenzyl radical

generated from one C2-H group, the more favorable product is believed to be the 2, 6-dimethylbenzyl radical than 2, 3-dimethylbenzyl radical by thermodynamic reaction energies and hydrogen migration in the CESE system.

Table 1. Benzyl-H Bond Dissociation energy D_0 (kcal/mol) for the methyl-substituted toluene

Reaction	B3LPY/CBS7	CBS-Q	CBS-Q B3
Toluene $\rightarrow$ benzyl	85.81	84.75	89.45
<i>o</i> -xylene $\rightarrow$ <i>o</i> -xylyl	85.68	86.88	89.35
<i>m</i> -xylene $\rightarrow$ <i>m</i> -xylyl	85.93	85.82	89.38
<i>p</i> -xylene $\rightarrow$ <i>p</i> -xylyl	85.40	87.17	89.18
1,2,3-trimethylbenzene (C1-H or C3-H) $\rightarrow$ 2,3-dimethylbenzyl	85.84	86.83	89.53
1,2,3-trimethylbenzene (C2-H) $\rightarrow$ 2,6-dimethylbenzyl	84.57	85.01	88.15
1,3,5-trimethylbenzene $\rightarrow$ 3,5-dimethylbenzyl	85.62	90.43	89.04

^a Measured in vacuum (cm^{-1})

^b Spacing from the origin band at 21846 cm^{-1}

^c Greek letters indicate the sequence bands associated with the strong vibronic band

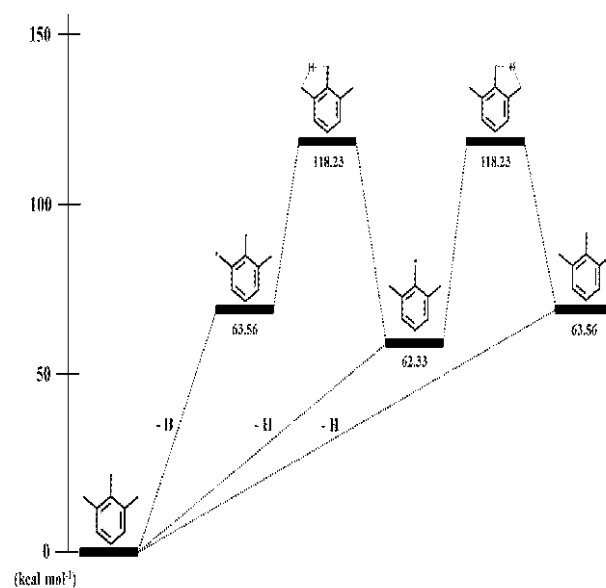


Fig. 3. Schematic energy diagram of the potential energy surface for the reaction of 2, 3- and 2, 6-dimethylbenzyl radical and its rearrangement at the CBS-QB3 level of theory (kcal mol^{-1})

3.2 Analysis of vibronic spectrum

Fig. 4(a, b) shows a portion of the visible vibronic emission spectrum observed in the corona discharge of the precursor, 1,2,3-trimethylbenzene in the region of 18000 to 21300 cm^{-1} . The benzyl radical has the origin band with weak intensity at 22002 cm^{-1} . As the benzyl radical is substituted into the benzene ring, the origin band shifts to the lower wavenumber. The origin band of the *o*-, *m*-, and *p*-methylbenzyl [3] radicals is observed at 21345 cm^{-1} , 21485 cm^{-1} , and 21700 cm^{-1} ,

shifted by 657 cm^{-1} , 517 cm^{-1} , and 302 cm^{-1} from benzyl radical, respectively. The 2, 6-dimethylbenzyl [5], 3, 5-dimethylbenzyl⁷ radicals are reported to have the origin bands at 20616 cm^{-1} and 20842 cm^{-1} . In the previous study, the origin band $D_1 \rightarrow D_0$ electronic transition of 2, 6-dimethylbenzyl radical has been observed with strong intensity at 20616 cm^{-1} as shown at Figure 4(a). Also many vibronic bands belonging to 2, 6-dimethylbenzyl radical were found at the same wavenumber with similar intensity. The strong vibronic bands at 20140 cm^{-1} , shift by 476 cm^{-1} from the origin band is the 6a band of 2,6-dimethylbenzyl radical which is very important vibrational mode of C-C-C angle deformation, degenerate in benzene at about 606 cm^{-1} . The splitting between 6a and 6b increases with increasing mass of the substituents. The splitting is 12 cm^{-1} for 2,6-dimethylbenzyl only, while 28 cm^{-1} and 32 cm^{-1} for 2,6-difluorobenzyl and 2,6-dichlorobenzyl radicals respectively. The strong band at 19940 cm^{-1} was assigned to 1 of ring breathing vibration which is consistent with that of the precursor. After assignment of bands belonging to 2, 6-dimethylbenzyl radical from the spectrum observed, we found a series of vibronic bands which are similar band shape with the meta-substituted methyl benzyl-type radicals as shown at Figure 4(b). The strongest band at 19386 cm^{-1} was assigned to the origin band of 2, 3-dimethylbenzyl radical. In the corona excitation spectra of benzyl-type radicals, the origin band always has the strongest intensity at highest wavenumber. The band at 18912 cm^{-1} , shift by 474 cm^{-1} from the origin band were assigned to 6a vibrational mode. Another important vibrational mode in benzyl-type radicals, mode 1 of ring breathing vibration was assigned to the band at 18814 cm^{-1} , a shift of 672 cm^{-1} because the vibrational mode 1 should be high sensitive vibration in benzyl-type radicals. Table 2 lists the vibronic bands observed and their assignments.

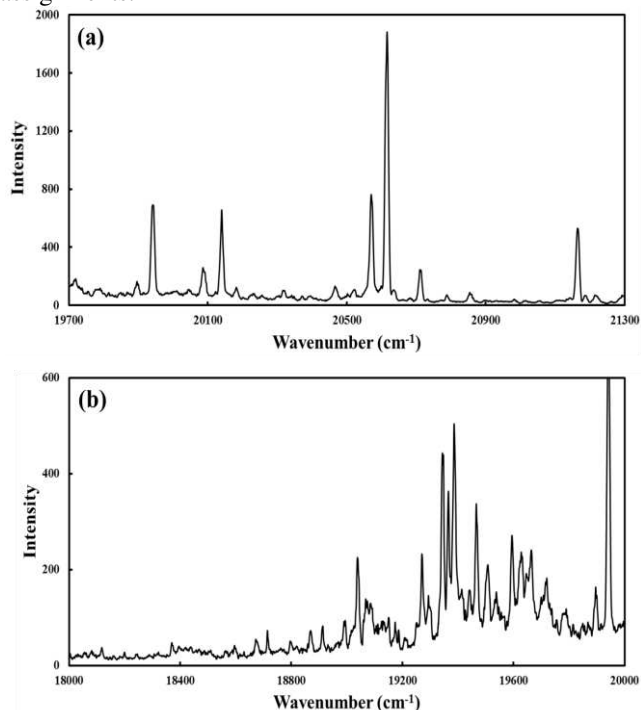


Fig. 4. A portion of the visible emission spectra observed from the corona discharge of precursor, 1, 2, 3-trimethylbenzene. (a) 2, 6-dimethylbenzyl radical at 19700 to 21300 cm^{-1} (b) 2, 3-dimethylbenzyl radical at 18000 to 20000 cm^{-1} in the $D_1 \rightarrow D_0$

It has been generally accepted that the calculation using Gaussian03 program at B3LYP level with cc-pvdz basis set predicts the vibrational mode frequencies within $\pm 10\%$ from the experimental values at worst cases. From the calculation for 2,3- and 2,6-dimethylbenzyl radicals, a total of 54 vibrational mode frequencies were obtained, of which 36 and 19 modes belong to the in-plane (a') and out-of-plane (a''), respectively. The calculated values have been multiplied by a scaling factor of 0.98 to correlate with the observed values, as in the case of 2, 3- and 2, 6-dimethylbenzyl radical. In the Table 3, the observed and calculated vibrational mode frequencies of the 2, 3- and 2, 6-dimethylbenzyl radicals are listed with the 3-fluoro-o-xylene and 2-fluoro-m-xylene as their precursor. It was found that the result of 2, 3- and 2, 6-dimethylbenzyl radicals show good agreement with the *ab initio* calculation and indicate the species generated from corona discharge of 1,2,3-trimethylbenzene is dominant in 2,6-dimethylbenzyl than 2,3-dimethylbenzyl radical.

Table 2. List of the vibronic bands observed and their assignments^a

Position	Intensity	Spacing ^b	Assignments ^c
21164	vs	547	
20710	w	94	
20616	s	0	Origin
20570	s	46	
20526	s	90	
20468	s	148	
20140	s	476	⁰ ₁ 6a
20086	m	530	
19942	w	674	⁰ ₁ 1
19900	w	716	⁰ ₁ 13
19666			
19628			
19596			
19540			
19386		0	Origin
19366			
19348			
19270			
18912			⁰ ₁ 6a
18872			
18800			
18714			⁰ ₁ 1
18674			
18596	vw	2494	⁰ ₁ 7b ⁰ ₁ 19b

^a Measured in vacuum (cm^{-1})

^b Spacing from the origin band at 21846 cm^{-1}

^c Greek letters indicate the sequence bands associated with the strong vibronic band

Fig. 5 depicted the origin band of the methyl substituted benzyl radicals. In the previous paper, *meta*-methyl substituted benzyl radical shows strong and relatively complicated transition in the methyl torsional band. Lin and Miller reported that *m*-methylbenzyl radical represents strong

torsional bands from D_1 to D_0 using laser induced fluorescence. However, very weak methyl torsional bands has been obtained near the origin band region in the *ortho*- and *para*-methylbenzyl radicals. The phenomenon should be originated from the resonance forms of the benzylic radical. Because the neutral electron is located on the *ortho* and *para* positions of the benzene ring, but not the *meta* positions. The *m*-methylbenzyl radical can obtained intensive transition in the torsional levels of *m*-methylbenzyl radical without interaction of benzene neutral electron and the strong torsional transition is believed to be allowed in *meta*-substitutive benzyl-type radicals. As shown Figure 5(a, b, c), the *o*-, *p*-methylbenzyl and 2, 6-dimethylbenzyl radicals without meta methyl substitution shows simple and low intensity torsional bands observed in the origin region but 2, 3-dimethylbenzyl radical has several strong torsional bands in the origin band which is similar behavior with *m*-methyl and 3, 5-dimethyl benzyl radical in the Figure 5(d, e, f). The torsional band shapes strongly support that 19386 cm^{-1} band originated from 2, 3-dimethylbenzyl radical in the 1, 2, 3-trimethylbenzene corona discharge.

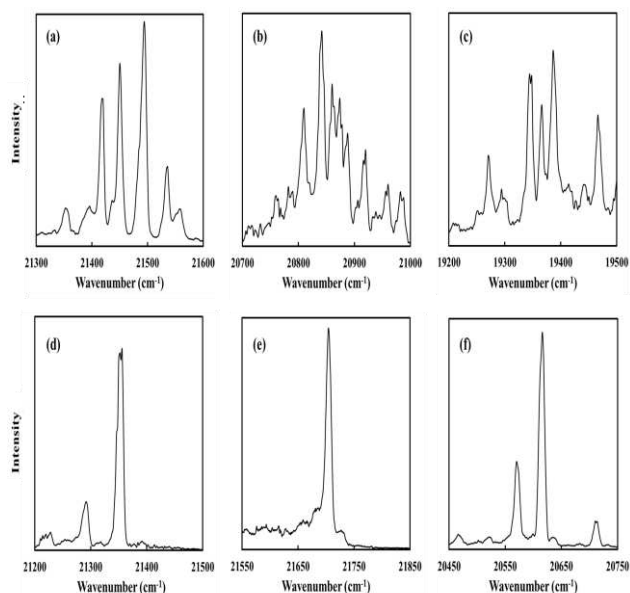


Fig. 5. Origin band shapes of the emission spectra observed from the corona discharge (a) *m*-methylbenzyl (b) 3, 5-dimethylbenzyl (c) 2, 3-dimethylbenzyl (d) *o*-methylbenzyl (e) *p*-methylbenzyl (f) 2, 6-dimethylbenzyl

IV. CONCLUSION

In summary, the vibronic emission spectra were measured in the range of 18000 to 21300 cm^{-1} by corona discharge of precursor, 1, 2, 3-trimethylbenzene. By the *ab initio* calculation, the benzyl radical generation mechanism was proposed in the benzyl-H anti-bonding state. From the analysis of the spectrum, we assigned the observed spectra of the 2, 3-dimethylbenzyl radical and 2, 6-dimethylbenzyl radical in the $D_1 \rightarrow D_0$ electronic transition. The assignment was supported by comparison with previous methyl-substituted benzyl radical and *ab initio* calculation which is computed about H-migration, bond dissociation energy and vibrational structure.

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