Spectroscopic Identification of Isomeric 2,3- and 2,6-Dimethylbenzyl Radicals in Corona Discharge

Young Wook Yoon and Sang Kuk Lee[*]

Department of Chemistry, Pusan National University, Pusan 609-735, Korea. [*]E-mail: sklee@pusan.ac.kr
Received October 8, 2012, Accepted December 8, 2012

We resolved the controversial assignments of the visible vibronic bands observed from corona discharge of 1,2,3-trimethylbenzene. The vibronic bands belonging to the jet-cooled 2,6-dimethylbenzyl radical were clearly identified from the spectrum observed from corona discharge of 2,6-dimethylbenzyl chloride. After subtracting the bands of the 2,6-isomer from the spectrum observed from corona discharge of 1,2,3-trimethylbenzene, the vibronic bands of the 2,3-isomer were also identified. By comparing data with the known vibrational data of 1,2,3-trimethylbenzene and the results of *ab initio* calculations, we determined the electronic energies of the $D_1 \rightarrow D_0$ transitions and vibrational mode frequencies in the ground electronic states of the 2,3- and 2,6-dimethylbenzyl radicals.

Key Words : Spectroscopy, Vibronic spectrum, Dimethylbenzyl radicals, 1,2,3-Trimethylbenzene, Corona discharge

Introduction

As key reaction intermediates that are created in a single step and rapidly destroyed in subsequent reactions, free radicals have been long believed to play important roles in the dynamics of reactions.[1] However, transient natures of free radicals have added considerably to the difficulties of performing spectroscopic studies in free jets. On the other hand, once the challenges to radical generation are able to be overcome, spectroscopy in free jets offers an attractive means of investigating the characteristics of free radicals in the gas phase.

Whereas benzyl radical, a prototypical aromatic free radical, has attracted much attention and been the subject of many spectroscopic works,[2] multi-methyl-substituted benzyl radicals have been far less studied, due to possible formation of isomers from polymethylbenzenes and difficulties associated with analyzing spectra.

Spectroscopic work on the xylyl radicals was initiated in the visible region by Schüler *et al.*[3] and by Walker and Barrow.[4] Bindley *et al.*[5] could assign several vibronic bands of the emission spectra of three isomeric xylyl radicals produced by passing an electric discharge through the corresponding xylenes. Charlton and Thrush[6] applied laser-induced fluorescence to confirm vibronic assignments and measure the lifetimes of xylyl radicals. Fukushima and Obi[2] investigated vibronic coupling between the two lowest excited electronic states of the *p*-xylyl radical. Controversial vibronic assignments of the *p*-xylyl radical[7] were clearly resolved by rotational contour analysis of its high resolution visible vibronic spectrum.

Hiratsuka *et al.*[8] determined the energies and symmetry of close-lying doublet electronic states in benzyl-type radicals to explain vibronic coupling between excited electronic states. Cossart-Magos *et al.*[9] obtained the electronic transition di-

pole moments by analyzing the rotational contours of *o*-xylyl radicals. Lin and Miller[10] completed torsional analysis of the methyl rotor in xylyl radicals, and Selco and Carrick[11] extended the vibronic assignment of xylyl radicals by observing vibronic emission spectra produced by a corona discharge through xylenes.

For dimethylbenzyl radicals, Branciard-Larcher *et al.*[12] reported the assignments of the electronic transitions of isomeric dimethylbenzyl radicals using a matrix isolation technique at liquid N_2 temperatures. Of the six possible isomeric dimethylbenzyl radicals, Yoon and Lee recently confirmed the vibronic assignments of three isomeric dimethylbenzyl radicals from the corona discharge of 1,2,4-trimethylbenzene and dimethylbenzyl chlorides as precursors.[13] Although a few papers[14,15] have been published on the assignments of the visible vibronic bands observed from corona discharge of 1,2,3-trimethylbenzene, the ambiguous assignments have not been confirmed.

In this study, we present the assignments of the vibronic bands observed from corona discharge of 1,2,3-trimethylbenzene which produces the 2,3- and 2,6-dimethylbenzyl radicals simultaneously. By analyzing the spectrum observed from a different precursor, we revised the previous assignments of the vibronic bands and determined the electronic energy in the $D_1 \rightarrow D_0$ transition as well as vibrational mode frequencies in the ground electronic state of the jet-cooled 2,3- and 2,6-isomers. This completes the vibronic assignments of dimethylbenzyl radicals in the gas phase.

Experimental Section

The vibronic emission spectra of jet-cooled dimethylbenzyl radicals were observed using an experimental setup, which been previously described in detail.[16] A technique of corona excited supersonic expansion (CESE) using a pinhole-type

glass nozzle was used to generate vibronically excited but jet-cooled benzyl-type radicals. The visible vibronic emission spectra of radicals were recorded using a long-path monochromator.

Although the benzyl radical can be formed by removing Cl atom from benzyl chloride,[2] it has been well demonstrated that toluene is much more effective precursor for production of benzyl radicals in a CESE system,[17] because it produces almost pure benzyl radicals free of C_2, which emits strong fluorescence in the same spectral region as the benzyl radical. Thus, isomeric dimethylbenzyl radicals were produced by corona discharges of trimethylbenzenes.

The precursor 1,2,3-trimethylbenzene (reagent grade) was purchased from Aldrich and used without further purification. The concentration of 1,2,3-trimethylbenzene in carrier gas He was adjusted to produce maximum emission intensity by monitoring the strongest band at 20614 cm^{-1}, and was believed to be less than 1% in the gas mixture. The vibronically excited but jet-cooled dimethylbenzyl radicals were produced from the precursor using a pinhole-type glass nozzle with an orifice diameter of 0.3 mm, in which a sharpened long stainless steel rod acting as an anode was connected to a high voltage DC power supply. The axial discharging current was 5 mA at 1.8 kV and it was further stabilized by a 150 kΩ current-limiting ballast resister. A long copper rod of cathode was positioned under the expansion chamber to prevent 'arc noise' from the corona discharge reaching the spectrometer. The discharging voltage was optimized to maximize the production of benzyl-type radicals without producing C_2, as shown in Figure 1. The production of C_2 molecules from precursor rapidly increases with increasing discharging voltage beyond 2.0 kV.

The Pyrex expansion chamber made of thick-walled glass tubes of 50 mm diameter was evacuated using a 800 L/min mechanical vacuum pump to maintain 2.0 mbar of chamber pressure during continuous expansion at backing pressure of 2.0 bar. The backing pressure was mainly limited by the pressure tolerance of the glassware used for the nozzle.

A blue-green colored jet indicates the presence of dimethyl-benzyl radicals. The light emanating from the downstream jet area 5 mm in front of the nozzle opening was collimated
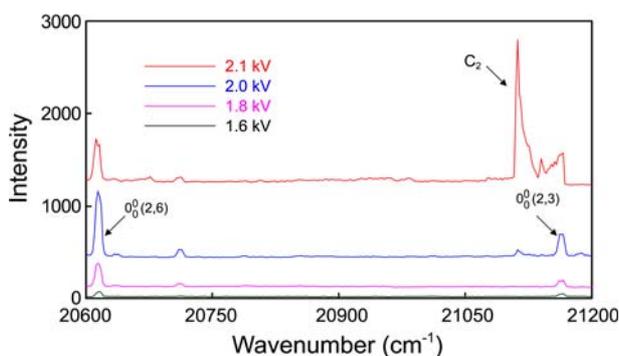
Figure 1. Intensity variation of the origin bands of the 2,3- and 2,6-dimethylbenzyl radicals at 21166 and 20614 cm^{-1}, respectively, with discharging voltage. The production of C_2 rapidly increases with discharging voltage beyond 2.0 kV.
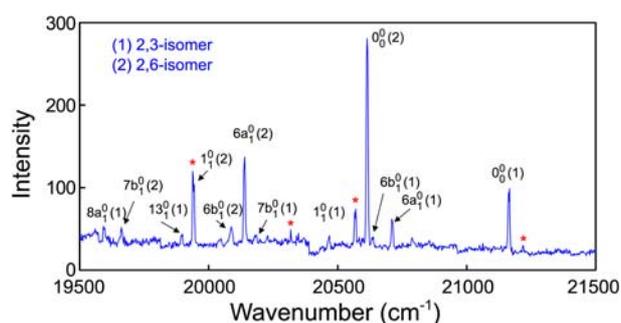
Figure 2. A portion of the vibronic emission spectrum observed from the corona discharge of 1,2,3-trimethylbenzene. The bands at 21166 and 20614 cm^{-1} are the origin bands of the 2,3- and 2,6-dimethylbenzyl radicals, respectively. The H and He atomic transition lines are indicated by an asterisk.

using a quartz lens (F = 5.0 cm, D = 3.8 cm) placed inside the chamber and focused on the slit of a long-path double monochromator (Jobin Yvon U1000) with two 1800 lines/mm gratings, and detected using a photomultiplier tube (Hamamatsu R649) and a photon counting system. During scans, the slits were set at 100 μm, which provided an effective resolution of ~2 cm^{-1} in the visible region. The spectral region from 19500 to 21500 cm^{-1} was singly scanned in 2.0 cm^{-1} increments over 1 hr to obtain the spectra in Figure 2. The wavenumber of the spectra observed was calibrated using H and He atomic lines[18] observed in the same spectral region as the radicals, and is believed to be accurate to within ± 1.0 cm^{-1}.

To identify the vibronic bands belonging to individual isomer generated by the corona discharge of 1,2,3-trimethyl-benzene, we employed 2,6-dimethylbenzyl chloride as a precursor. In the corona discharge of 2,6-dimethylbenzyl chloride, rather strong blue emission was detected due to the presence of C_2.

Since the vibrational modes of the 2,3- and 2,6-dimethyl-benzyl radicals have not been previously analyzed, we carried out an *ab initio* calculation on the ground electronic states of two isomers to assist vibrational mode assignments. Calculation was performed on a personal computer equipped with an Intel(R) Core(TM) 2 Duo CPU 3.0 GHz processor and 2.0 GB of RAM, using the standard methods included in the Gaussian04 program for Windows. Geometric optimization and vibrational frequency calculations were performed at the DFT level, and the 6-311G** basis set was employed for all calculations.

Results and Discussion

It has been well demonstrated that benzyl radical can be generated more effectively by the corona discharge of toluene than of benzyl chloride in a CESE system with a pinhole-type glass nozzle[19] because C_2 production is lower. Although the mechanism responsible for the generation and excitation of benzyl radical in a corona discharge has not been established, it has been suggested that He atoms in carrier are excited by corona discharge to a metastable state
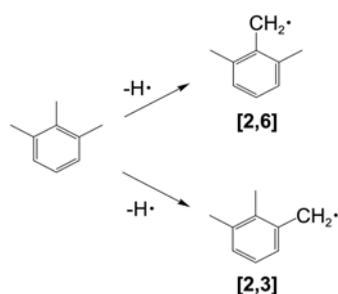
Figure 3. Formation of the two isomeric dimethylbenzyl radicals by corona discharge of 1,2,3-trimethylbenzene. The 2,3- and 2,6-isomers were generated by removing a H atom from methyl groups at positions 1 and 2, respectively.

(1s2s $^3S_1$) 19.98 eV above the ground state[20] and that this excess energy is transferred to precursor molecules by collisional process, resulting in the removal of a H atom from the methyl group of toluene to form benzyl radical. Energy transfer by collision from metastable He is a well-known process in the HeNe laser system. Similarly, we believe that isomeric dimethylbenzyl radicals were generated from trimethylbenzenes by the removal of a H atom from different methyl groups of precursor.

Although it has been reported that a diradical[21] was produced in the matrix isolation of 1,3,5-trimethylbenzene (mesitylene) due to the abstraction of a H atom from each of the two methyl groups rather than from the benzene ring, no diradical has ever been reported in the gas phase. Thus, we believe the species formed in the CESE system was a monoradical despite the use of trimethylbenzenes as a precursor.
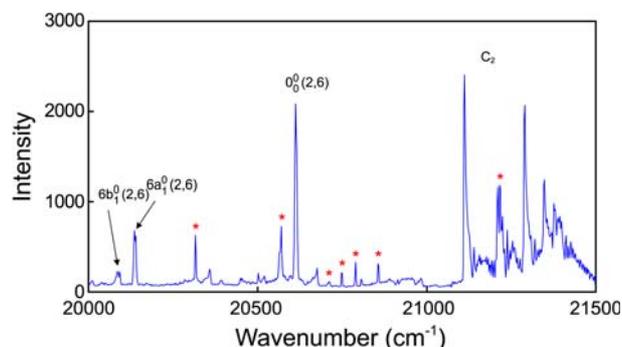
During the corona discharge of 1,2,3-trimethylbenzene, two isomeric radicals, namely, 2,3- and 2,6-dimethylbenzyl radicals are produced due to the removal of a H atom from the methyl groups at the 1- and 2- positions, respectively, as shown in Figure 3.

In dimethylbenzyl radicals, electronic interactions between the benzene ring and the methyl groups are undoubtedly of second order as compared with interactions between the benzene ring and the methylene group because the molecule possesses a planar structure with seven delocalized π electrons. Thus, the electronic configuration of dimethylbenzyl radicals should be similar to that of benzyl radical, and indeed, the two lowest lying excited electronic states of dimethylbenzyl radicals should resemble the $2^2B_2(D_2)$ and $1^2A_2(D_1)$ of benzyl radical. Thus, the weak visible emission of dimethylbenzyl radicals is believed to be due to transitions from the quasi-degenerate D_2 and D_1 excited states to the $1^2B_2(D_0)$ ground electronic state. However, strong vibronic coupling due to small energy gap between the D_2 and D_1 electronic states facilitates non-radiative transfer of the molecules from D_2 to D_1, which results in almost negligible emission intensity for the $D_2 \rightarrow D_0$ transition.

In addition, vibrational relaxation in the D_1 state during supersonic jet expansion increases the population in the vibrationless D_1 state. Thus, the emission spectra observed in the CESE system using a pinhole-type glass nozzle are similar to the laser excited dispersed fluorescence (DF)

spectra obtained while pumping the origin band of the electronic transition, which exhibit the origin band of the $D_1 \rightarrow D_0$ transition at the highest wavenumber with strongest intensity. Also, the spacings of vibronic bands from the origin band provide vibrational mode frequencies in the ground electronic states for many benzyl-type radicals.

Figure 2 shows a portion of the vibronic emission spectrum observed from the corona discharge of 1,2,3-trimethylbenzene, in which several strong bands were observed in the 19500-21500 cm^{-1} region. The strong band at 21166 cm^{-1} could be assigned to the origin band of the one of the two isomers because no band with observable intensity was detected to the blue of this band. To confirm the origin of this band, we obtained the vibronic emission spectrum of the corona discharge of 2,6-dimethylbenzyl chloride in the region from 20000 to 21500 cm^{-1}, as shown in Figure 4. This spectrum consisted of the strong C_2 bands of the swan system $(A^3\Pi_g \rightarrow X'^3\Pi_u)^{22}$ at around 21300 cm^{-1}, H, He, and Cl atomic lines,[18] and a few vibronic bands belonging to the 2,6-dimethylbenzyl radical. Again, a strong band at 20614 cm^{-1} was observed from the precursor 2,6-dimethylbenzyl chloride, confirming that this is the origin band of the 2,6-dimethylbenzyl radical in the $D_1 \rightarrow D_0$ transition. Thus, we assigned the strong bands at 21166 and 20614 cm^{-1} as the origin bands of the $D_1 \rightarrow D_0$ transitions of the 2,3- and 2,6-dimethylbenzyl radicals, respectively. The other vibronic bands belonging to the 2,6-dimethylbenzyl radical were clearly identified by comparing the spectrum (Fig. 4) of 2,6-dimethylbenzyl chloride with that of 1,2,3-trimethylbenzene. Table 1 compares the origin bands of the two isomeric dimethylbenzyl radicals of the $D_1 \rightarrow D_0$ transition observed in this work with the previous observations. Although the TDDFT calculation is believed to be accurate with respect to the predictions of the electronic energies of small molecules, it fails to predict the energies of the excited electronic states of large aromatic molecules, like benzyl-type radicals. While the observation showed the 2,3-isomer had a higher wavenumber than the 2,6-isomer, the TDDFT calculation suggested an opposite trend. In addition, previous assignments[12] of solid state observations based on a Hückel molecular orbital

Figure 4. A portion of the vibronic emission spectrum observed from the corona discharge of 2,6-dimethylbenzyl chloride. The bands belonging to the 2,6-isomer were observed together with the swan system of C_2 in the 21100-21500 cm^{-1} region. The H, He, and Cl atomic transition lines are indicated by an asterisk.

Table 1. Transition Energy of Dimethylbenzyl Radicals in the $D_1 \rightarrow D_0$ Transition[a]

Molecules	This work		Previous work	
	obs.[b]	calc.[c]	solid state[d]	gas phase[e]
2,3-dimethylbenzyl	21166	23584	20243	-
2,6-dimethylbenzyl	20614	24177	20324	20616

[a]Measured in vacuum (cm^{-1}). [b]This observation. [c]TDDFT calculation. [d]Reference 12. [e]Reference 25.

calculation should be revised.

The origin bands of substituted benzyl radicals always shift to the red because the space available for delocalized π electrons is extended by substituents, which lowers the energies of excited electronic states. Whereas the benzyl radical shows an origin band of the $D_1 \rightarrow D_0$ transition at 22002 cm^{-1}, xylyl radicals[15] have red-shifted origin bands, due to substitution into the benzene ring. The *o*-, *m*-, and *p*-xylyl radicals[11] were observed to have the origin bands at 21345, 21485, and 21700 cm^{-1}, respectively, which represent shifts of 657, 517, and 302 cm^{-1} with respect to the benzyl radical. For dimethylbenzyl radicals, the shifts are expected to increase by existence of two methyl groups, except for the 2,4- and 3,4-dimethylbenzyl radicals which show the shifts comparable to the 2- and 3-xylyl radicals, respectively. For example, the 2,6- and 3,5-dimethylbenzyl radicals, in which the two substituents are located at symmetric equivalent positions on the benzene ring, exhibit approximately twice the shifts of the 2- and 3-xylyl radicals, respectively. Table 2 lists the substituent effects of dimethylbenzyl radicals on the energy of the $D_1 \rightarrow D_0$ transition. The substituent effect of the 2,6-isomers is estimated by additive of each substituent to be 1314 cm^{-1} which agrees very well with the observation of 1388 cm^{-1}. The same phenomenon is applied to the 3,5-dimethylbenzyl radical. However, for dimethylbenzyl radicals (2,3- and 2,5-isomers) of non-symmetric substitutions into benzene ring, the observation shows a large deviation from the simple additives of each substituent.

The smaller shifts of the 2,4- and 3,4-isomers as compared with the other isomers are attributed to the negligible contribution through π electrons made by substituents at the 4-position, that is, the position of the nodal point in the D_1 state

Table 2. Substituent Effect of Dimethylbenzyl Radicals on Energy of the $D_1 \rightarrow D_0$ Transition[a]

Molecules	Origin band	Shift[b]
benzyl[c]	22002	0
2,4-dimethylbenzyl[d]	21306	696
3,4-dimethylbenzyl[d]	21592	410
2,5-dimethylbenzyl[d]	20558	1444
3,5-dimethylbenzyl[e]	20842	1160
2,6-dimethylbenzyl[f]	20614	1388
2,3-dimethylbenzyl[f]	21166	836

[a]Measured in vacuum (cm^{-1}). [b]With respect to the origin band of benzyl radical (22002 cm^{-1}). [c]Reference 15. [d]Reference 13. [e]Reference 26. [f]This work.

Table 3. List of the Vibronic Bands Observed in This Work and Their Assignment[a]

Position[b]	Intensity	Species[c]	Spacing[d]	Assignments
21218	w			He atomic
21166	s	2,3	0	origin
20710	m	2,3	456	$6a_1^0$
20638	w	2,3	528	$6b_1^0$
20614	vs	2,6	0	origin
20570	m			H atomic
20468	m	2,3	698	1_1^0
20316	w			He atomic
20182	w	2,3	984	$7b_1^0$
20140	s	2,6	474	$6a_1^0$
20088	m	2,6	526	$6b_1^0$
19944	s	2,6	670	1_1^0
19938	s			He atomic
19898	w	2,3	1268	13_1^0
19662	w	2,6	952	$7b_1^0$
19592	w	2,3	1574	$8a_1^0$

[a]Measured in vacuum (cm^{-1}). [b]Observed in this work. [c]2,3 and 2,6 indicate the 2,3- and 2,6-dimethylbenzyl radicals, respectively. [d]Shift from the origin band of each isomer.

with A_2 symmetry. The substituent effect on electronic transition energy in the $D_1 \rightarrow D_0$ transition has been well explained for benzyl-type radical using a Hückel molecular orbital theory.[23]

Given the above determinations of the origin bands of the two isomers, we attempted to assign vibronic bands to each isomer by comparing with the vibrational data predicted by an *ab initio* calculation and those of 1,2,3-trimethybenzene.[24] Table 3 lists the vibronic bands observed in this work, the isomers, and their assignments.

Of the many vibrational modes of benzyl-type radicals, the most important vibrational modes are modes 6a and 6b of ring deformation and mode 1 of ring breathing vibration. The frequency of mode 1 is less sensitive to substitution, and thus, should be similar to that of the precursor.[24] The strong band at 19944 cm^{-1}, showing a 670 cm^{-1} shift from the origin band were assigned to mode 1 of the 2,6-dimethylbenzyl radical, which concurred with calculation and precursor data. Ring deformation modes 6a and 6b are degenerate at 606 cm^{-1} in benzene and 516 cm^{-1} in mesitylene and are split by non-symmetric substitution.[24] Furthermore, the splitting of these two modes increases with increasing substituent mass. In addition, after splitting, the mode 6b has a higher wavenumber than mode 6a for 1,2,3-trisubstitution, as was observed for the *p*-isomer. The bands at 20140 and 20088 cm^{-1}, which showed shifts of 474 and 526 cm^{-1} from the origin band of the 2,6-isomer, were assigned to modes 6a and 6b, respectively. Mode 6a showed stronger intensity than mode 6b for both isomers, which is similar to that observed for 2,3- and 2,6-difluorobenzyl radicals. The C-CH$_3$ stretching mode 7b was identified by analyzing the observed spectrum, and by calculation and using precursor data. Modes 7a and 7b of C-H stretching are degenerate in

Table 4. Vibrational Mode Frequencies of Isomeric Dimethylbenzyl Radicals[a]

Mode[b]	2,3-Dimethyl		2,6-Dimethyl		1,2,3-Trimethyl benzene	Symmetry[g]
	obs[c]	calc[d]	obs[c]	calc[d]	obs[f]	C_s (C_{2v})
origin	21166	23584[e]	20614	24177[e]		
6a	456	463	474	481	485	a'(a$_1$)
6b	528	537	526	538	539	a'(b$_2$)
1	698	675	670	683	659	a'(a$_1$)
7b	984	997	952	996	992	a'(b$_2$)
13	1268	1288			1193	a'
8a	1574	1587			1586	a'

[a]Measured in vacuum (cm^{-1}). [b]Reference 27. [c]This work. [d]*Ab initio* calculation using B3LYP/6-311G** without scaling. [e]TDDFT calculation. [f]Reference 24. [g]Point groups C_s and C_{2v} were applied to 2,3- and 2,6-dimethylbenzyl radicals, respectively.

benzene at 3056 cm^{-1} and split with substitution, as do modes 6a and 6b. When the substituent is a CH$_3$ group, these modes tend to move to lower frequency and show substantial splitting. All observed modes are a' symmetry of in-plane vibrational modes, which generally shows stronger intensity than a" symmetry of out-of-plane vibrational modes.

Similarly, the bands at 20710 and 20638 cm^{-1}, showing shifts of 456 and 528 cm^{-1} from the origin band of the 2,3-isomer, respectively, were assigned to modes 6b and 6a of the 2,3-isomer. The splitting between modes 6a and 6b was 72 cm^{-1}, which is slightly larger than the 52 cm^{-1} observed for the 2,6-isomer due to the less symmetric nature of the substituents on the benzene ring.

Another moderate band at 20468 cm^{-1}, showing a shift of 698 cm^{-1}, was assigned to mode 1 of the ring breathing vibration, which is similar to the shift shown by the 2,6-isomer. The weak band at 20182 cm^{-1}, showing a shift of 984 cm^{-1}, was also assigned to mode 7b. Finally, the weak bands at 19898 and 19592 cm^{-1}, showing shifts of 1268 and 1574 cm^{-1}, respectively, were assigned to mode 13 of in-plane C-CH$_3$ stretching and mode 8a of C-C stretching because of close agreement shown between observed and precursor values, and excellent agreement with the DFT calculation. Table 4 lists the vibrational mode frequencies of the observed, calculated, and precursor of the two isomers.

Because there is little difference in bond dissociation energy of C-H bond between two different methyl groups of the precursor molecule, two products should be generated in a comparable amount. But, the stronger observation of the 2,6-isomer in the emission spectrum in Figure 2 as compared with the 2,3-isomer is attributed to the oscillator strengths for the D$_1$ → D$_0$ electronic transition. The TDDFT calculation shows the oscillator strengths of the 2,3- and 2,6-isomers for the D$_1$ → D$_0$ electronic transition to be 0.0033 and 0.0068, respectively.

Conclusion

In the present study, we identified the origins of the vibronic bands of dimethylbenzyl radicals generated from 1,2,3-trimethylbenzene in a CESE system using 2,6-dimethylbenzyl chloride as precursor. Based on analysis of the spectrum obtained, we determined the energy of the D$_1$ → D$_0$ electronic transition and the vibrational mode frequencies in the ground electronic state for the 2,3- and 2,6-dimethylbenzyl radicals by using the known spectroscopic data of precursor and those of an *ab initio* calculation.

References and Notes

1. Tan, X. Q.; Wright, T. G.; Miller, T. A. *Electronic Spectroscopy of Free Radicals in Supersonic Jets*: *Jet Spectroscopy and Molecular Dynamics*; Hollas, J. M., Phillips, D., Eds.; Blackie Academic & Professional: London, 1994.
2. Fukushima, M.; Obi, K. *J. Chem. Phys.* **1990**, *93*, 8488.
3. Schüler, H.; Reinebeck, L.; Köberle, A. R. *Z. Naturforsch* **1952**, *7A*, 428.
4. Walker, S.; Barrow, R. F. *Trans. Faraday Soc.* **1954**, *50*, 541.
5. Bindley, T. F.; Watts, A. T.; Walker, S. *Trans. Faraday Soc.* **1962**, *58*, 849.
6. Carlton, T. R.; Thrush, B. A. *Chem. Phys. Lett.* **1986**, *125*, 547.
7. Suh, M. H.; Lee, S. K.; Miller, T. A. *J. Mol. Spectrosc.* **1999**, *194*, 211.
8. Hiratsuka, H.; Mori, K.; Shizuka, H.; Fukushima, M.; Obi, K. *Chem. Phys. Lett.* **1989**, *157*, 35.
9. Cossart-Magos, C.; Cossart, D.; Leach, S. *Chem. Phys.* **1973**, *1*, 306.
10. Lin, T.-Y. D.; Miller, T. A. *J. Phys. Chem.* **1990**, *94*, 3554.
11. Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1995**, *173*, 277.
12. Branciard-Larcher, C.; Migirdicyan, E.; Baudet, J. *Chem. Phys.* **1973**, *2*, 95.
13. Yoon, Y. W.; Lee, S. K. *J. Chem. Phys.* **2011**, *135*, 214305.
14. Lee, S. K.; Ahn, B. U.; Lee, S. K. *J. Phys. Chem. A* **2003**, *107*, 6554.
15. Lee, G. W.; Lee, S. K. *J. Phys. Chem. A* **2006**, *110*, 2130.
16. Han, M. S.; Choi, I. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **1996**, *17*, 991.
17. Selco, J. I.; Carrick, P. G. *J. Mol. Spectrosc.* **1989**, *137*, 13.
18. Weise, M. L.; Smith, M. W.; Glennon, B. M. *Atomic Transition Probabilities*; NSRD-NBS4; NBS: Washington, DC, 1966.
19. Lee, S. K. *Chem. Phys. Lett.* **2002**, *358*, 110.
20. Banwell, C. N.; McCash, E. M. *Fundamentals of Molecular Spectroscopy*, 4th ed.; McGraw-Hill: New York, 1994.
21. Lejeune, V.; Despres, A.; Fourmann, B.; Benoist d'Azy, O.; Migirdicyan, E. *J. Phys. Chem.* **1987**, *91*, 6620.
22. Wallaart, H. L.; Pier, B.; Perrin, M.-Y.; Martin, J.-P. *Chem. Phys. Lett.* **1995**, *246*, 587.
23. Yoon, Y. W.; Lee, S. K. *J. Chem. Phys.* **2012**, *136*, 024309.
24. Varsanyi, G. *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*; John Wiley & Sons: New York, 1974.
25. Lee, G. W.; Lee, S. K. *J. Phys. Chem. A* **2006**, *110*, 2130.
26. Lee, G. W.; Lee, S. K. *J. Phys. Chem. A* **2007**, *111*, 6003.
27. Wilson, E. B. *Phys. Rev.* **1934**, *45*, 706.