

## Vibronic Assignments of Isomeric Trimethylbenzyl Radicals : Revisited<sup>†</sup>

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The vibronic emission spectra of isomeric trimethylbenzyl radicals were reassigned based on substituent effect on electronic transition energy as well as *ab initio* calculation of the benzyl radical. The electronic transition energy of three isomeric jet-cooled trimethylbenzyl radicals produced by corona discharge of 1,2,3,5-tetramethylbenzene were analyzed using the empirical data of three isomeric methylbenzyl radicals. Calculated data were obtained by summing up the shifts measured from methylbenzyl radicals as well as taking the position and alignment of substituents on the benzene ring into account. The revised assignments show better agreement with observation, and rationalize the validity of the model developed to explain the substituent effect on electronic transition energy of benzyl radicals.

**Key Words** : Spectroscopy, Trimethylbenzyl radicals, Vibronic spectrum, Substituent effect

### Introduction

Transient species such as molecular ions and radicals have long been believed to play a crucial role as intermediates in chemical reactions and to determine reaction pathways *via* transition state. For those interested in the fundamental issues of reaction dynamics, the study of transient species provides a possible way of describing the nature of chemical reactivity.<sup>1</sup>

Benzyl radical, the prototype aromatic free radical, is one of the most fundamental reaction intermediates in aromatic chemistry and has been the subject of numerous spectroscopic studies.<sup>2,3</sup> On the other hand, substituted benzyl radicals have attracted less attention due to the difficulties associated with production of species. The majority of studies on methyl substituted benzyl radicals have focused on mono-substitution, and as a result, multi-substituted benzyl radicals have received little attention, probably due to the production of isomers during corona discharge of polymethylbenzenes.

Spectroscopic study of benzyl-type radicals was initiated by Schüler *et al.*<sup>4</sup> and Walker and Barrow<sup>5</sup> in the visible region. Bindley and Walker<sup>6</sup> assigned several strong bands in the visible vibronic emission spectra of isomeric methylbenzyl radicals produced from xylenes by corona discharge. Charlton and Thrush<sup>7</sup> confirmed the vibronic assignments using the technique of laser-induced fluorescence. In addition, torsional analysis of the methyl rotor in methylbenzyl radicals was carried out by Lin and Miller.<sup>8</sup> Selco and Carrick<sup>3,9</sup> used corona discharge to perform vibronic assignments for benzyl and methylbenzyl radicals.

Lee and coworkers began spectroscopic work on multi-substituted methylbenzyl radicals using a pinhole-type glass

nozzle which generates jet-cooled but vibronically excited benzyl-type radicals from polymethylbenzenes, and identified six isomeric jet-cooled dimethylbenzyl radicals<sup>10-12</sup> by analyzing vibronic emission spectra observed from the corona discharge of trimethylbenzenes. Recently, the vibronic assignment of dimethylbenzyl radicals for the D<sub>1</sub> → D<sub>0</sub> transition was performed using dimethylbenzyl chlorides as a precursor.<sup>11</sup> Furthermore, the vibronic spectra of jet-cooled trimethylbenzyl radicals<sup>13,14</sup> were also observed from corona discharge of tetramethylbenzenes, from which the electronic transition of each isomer was assigned based on the identification of trimethylbenzyl radicals<sup>15</sup> in the solid state.

Petruska<sup>16</sup> applied first- and second-order perturbation theory to describe the red-shift of the electronic transition of aromatic compounds upon methyl substitution into benzene ring. Branciard-Larcher *et al.*<sup>15</sup> tried to assign the electronic emission spectra of multi-methyl-substituted benzyl radicals produced at liquid nitrogen temperature using a simple molecular orbital calculation. However, the limited resolution of the solid state spectra obtained prevented the satisfactory resolution of species in the mixed spectrum obtained after the photolysis of 1,2,3,5-tetramethylbenzene.

In this work, we analyzed the effect of methyl substitution on the electronic transition energy of trimethylbenzyl radicals using the substituent effect, which has been well developed to describe the red shift of the origin bands of substituted benzyl radicals. The calculation performed showed better agreement with the observation for the assignments of electronic transition of isomeric trimethylbenzyl radicals with respect to the D<sub>1</sub> → D<sub>0</sub> transition.

### Model of Substituent Effects

Conjugated double bonded organic molecules are excellent candidates<sup>17</sup> for testing free electron molecular orbital theory of  $\pi$  electronic states using 'particle in a box' eigen-

<sup>†</sup>This paper is to commemorate Professor Myung Soo Kim's honourable retirement.

functions. The theory assumes that  $\pi$  electrons in a conjugated molecule can be separated from  $\sigma$  electrons and that the  $\sigma$  frame is frozen. In addition, all interelectronic interactions are neglected and the effective potential acting on each  $\pi$  electron is assumed to be given by ‘a particle in-a-box’ potential.

For linear or nearly linear molecules, the box can be taken to be one dimensional. Alternatively, a two dimensional box, where the area of the box is the same as the cross-sectional area of molecules, can be applied to planar molecules, like benzene. The wave function and energy of a particle in a 2-dimensional rectangular box with sides  $a$  and  $b$  is given by:

$$\Psi(x,y) = \sqrt{\frac{4}{ab}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \quad (1)$$

$$E_{n_x, n_y} = \frac{\hbar^2}{8m^2} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} \right) \quad (2)$$

For methyl-substituted benzyl radicals, conjugation between the methyl group with the  $\pi$  electrons of the aromatic system can be approached using the concept of hyperconjugation, that is, the methyl group is conjugated to the rest of the  $\pi$  system *via* two electrons and two orbitals, one being a  $p$  orbital on the carbon atom of the methyl group and the other a pseudo  $p$  orbital that is a linear combination of the hydrogen 1s orbitals. Thus, the energies of  $\pi$  electrons are dependent on area and shape of the substituted benzene ring including methyl substituents, as shown in Table 1. Also, it can be suggested that the conjugation is broken, if the nodal point, the zero amplitude of  $\pi$  electrons, is located at the other side of the conjugation. The position of nodal point depends on the symmetry of the upper electronic state, from which molecules emit radiation.

For dimethylbenzyl radicals, we assume that the area of the molecular plane available for delocalized  $\pi$  electrons is constant irrespective of substitution position. However, the shape of the molecular plane should be sensitive to the positions of methyl groups. For example, the anti-parallel alignments of two methyl groups in 2,5-dimethylbenzyl radical elongate the plane than parallel alignments of two methyl groups in 2,3-dimethylbenzyl radical, which lowers the translational energy of  $\pi$  electrons in benzyl-type radicals, as has been already confirmed from the energy of a particle in a 2-dimensional box and causes larger substituent effects on the electronic transition energy.

For the assignments of electronic transition energy and vibrational modes in the ground electronic state, density functional calculations were carried out on the ground ( $D_0$ ) and lowest excited ( $D_1$ ) electronic states of isomeric trimethylbenzyl radicals. Geometry optimization, vibrational frequency, electronic transition energy, and oscillator strength calculations were obtained at the time-dependent density functional theory (TDDFT/B3LYP) level, and the 6-311G\* basis set in all calculations. The calculations were executed with a personal computer equipped with an Intel Pentium IV CPU 2.80 GHz processor with 2.0GB RAM, according to

**Table 1.** Shift of the Origin Bands of Methyl-Substituted Benzyl Radicals in the  $D_1 \rightarrow D_0$  Transition<sup>a</sup>

Molecules	Origin band	Shift <sup>j</sup>
benzyl <sup>b</sup>	22002	0
<i>o</i> -methylbenzyl <sup>c</sup>	21345	657
<i>m</i> -methylbenzyl <sup>c</sup>	21485	517
<i>p</i> -methylbenzyl <sup>c</sup>	21700	302
2,3-dimethylbenzyl <sup>d</sup>	21164	838
2,4-dimethylbenzyl <sup>e</sup>	21306	696
2,5-dimethylbenzyl <sup>e</sup>	20558	1444
2,6-dimethylbenzyl <sup>d</sup>	20616	1386
3,4-dimethylbenzyl <sup>e</sup>	21592	410
3,5-dimethylbenzyl <sup>f</sup>	20842	1160
2,4,5-trimethylbenzyl <sup>g</sup>	20832	1170
2,3,4-trimethylbenzyl <sup>h</sup>	20844	1158
2,3,6-trimethylbenzyl <sup>i</sup>	19796	2206
2,4,6-trimethylbenzyl <sup>h</sup>	20800	1202
3,4,5-trimethylbenzyl <sup>i</sup>	20836	1166
2,3,5-trimethylbenzyl <sup>i</sup>	20352	1650

<sup>a</sup>Measured in vacuum ( $\text{cm}^{-1}$ ). <sup>b</sup>Reference 3. <sup>c</sup>Reference 9. <sup>d</sup>Reference 12. <sup>e</sup>Reference 11. <sup>f</sup>Reference 10. <sup>g</sup>Reference 20. <sup>h</sup>Reference 13. <sup>i</sup>This work. <sup>j</sup>With respect to the origin band of benzyl radical at  $22002 \text{ cm}^{-1}$ .

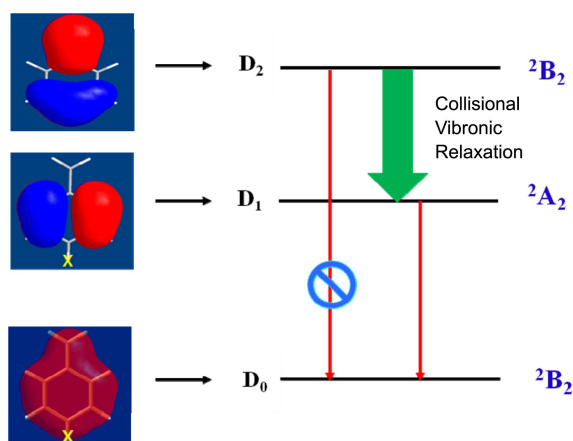
the standard method in the Gaussian 09 program<sup>18</sup> for Window package. The atomic motion of each mode was visualized using the HyperChem program and the calculation.

## Results and Discussion

The visible emission of methyl-substituted benzyl radicals<sup>19</sup> is believed to be due to transition from the close-lying  $2^2B_2(D_2)$  and  $1^2A_2(D_1)$  excited states to the  $1^2B_2(D_0)$  ground state. Ring substitution is also expected to change the energies of the two excited electronic states differently, which depend on the nature, position, and number of substituents on the benzene ring. However, the strong vibronic coupling between the two excited electronic states rapidly transfers the population from the  $D_2$  state to the  $D_1$  state, and vibrational relaxation in the  $D_1$  state, during supersonic jet expansion, causes an accumulation of the vibrationless state ( $v=0$ ), leading to the strongest observation of the origin band of the  $D_1 \rightarrow D_0$  transition. Thus, the energy of the  $D_1 \rightarrow D_0$  transition could be identified from observed spectra because of the absence of bands with observable intensity to blue region, as shown in Figure 4.

It has been found that the effect of substituents on the electronic transition energies of benzyl radicals strongly depends on the nature, number, and position of substituents. For methylbenzyl radicals, 2-, 3-, and 4- substitutions<sup>9</sup> shift the origin bands to the red by 657, 517 and 302  $\text{cm}^{-1}$  from that of the benzyl radical at  $22002 \text{ cm}^{-1}$ , as listed in Table 1. These shifts are attributed to the lowering translational energies of delocalized  $\pi$  electrons. The electron density of each carbon atom in the benzene ring is related to the magnitude of the conjugation of the delocalized electronic system.

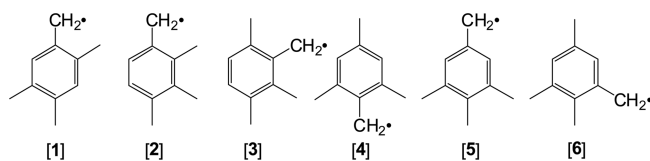
Regarding the substituent effects of dimethylbenzyl radicals,



**Figure 1.** Hückel's molecular orbital of the benzyl radical in the ground ( $D_0$ ) and first ( $D_1$ ) and second ( $D_2$ ) excited electronic states. Due to vibronic coupling between the  $D_1$  and  $D_2$  states, the population relaxes to the  $D_1$  state, preventing observation of the transition from the  $D_2$  to  $D_0$  state. X indicates a substituent at the 4-position (the nodal point).

the shifts can be easily estimated by adding up the shifts of each substituent in methylbenzyl radicals. For example, the shift of the origin band of 2,6-dimethylbenzyl radical<sup>12</sup> is  $1386\text{ cm}^{-1}$ , which is almost twice that ( $657\text{ cm}^{-1}$ ) of the 2-methylbenzyl radical, because it has two methyl groups at the 2 and 6-positions. Furthermore, the 3,5-dimethylbenzyl radical<sup>10</sup> shows a very similar effect. In addition, we found that a substituent at the 4-position makes negligible contribution to the shift, because the nodal points, zero amplitude of  $\pi$  electrons, are located at the 1 and 4 position in the  $D_1$  state of  $A_2$  symmetry, as shown in Figure 1. After excluding the effect of the 4-position, the empirical calculations exhibited excellent agreement with the observation for 2,4- and 3,4-dimethylbenzyl radicals.<sup>11</sup> On the other hand, the mutual alignment of two substituents is predicted to strongly affect shift, that is, the anti-parallel orientation of two substituents of the 2,5-isomer has a larger shift than the parallel orientation of the 2,3-isomer, because it changes the shape of the delocalized  $\pi$  electron plane. The energy difference between the two alignments was estimated to be about  $500\text{ cm}^{-1}$  for methyl substitution.

There are six possible isomers of trimethylbenzyl radicals, that is, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6-, and 3,4,5-, as shown in Figure 2. Of these isomers, the 2,4,5-isomer was generated by corona discharge of 1,2,4,5-tetramethylbenzene (durene), in which the four methyl groups are equivalent. Thus, the position of the origin band of the 2,4,5-isomer can be easily confirmed from its vibronic emission spectrum.<sup>20</sup> On the other hand, the 2,3,4- and 2,3,6-isomers can be simultaneously generated by corona discharge of 1,2,3,4-tetramethylbenzene (prehnitene) by dissociation of methyl C-H bonds at the 1 and 2-positions, respectively.<sup>13</sup> The shift of both isomers is easily predicted by adding up the contributions of substituents. The 2,3,6-isomer has two methyl groups at ortho positions and one methyl group at a meta position. In addition, the two methyl groups at the 3-

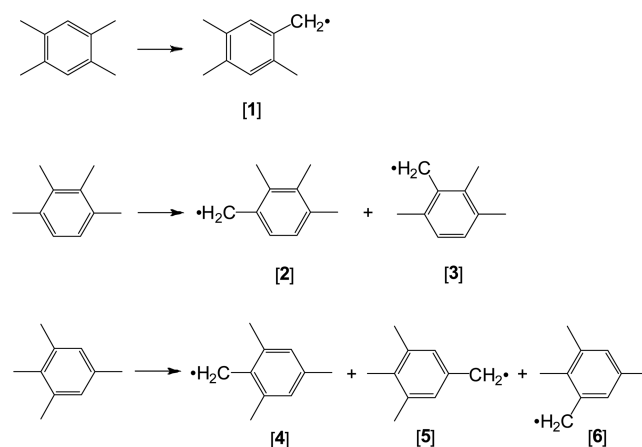


**Figure 2.** Structures of the six possible isomeric trimethylbenzyl radicals. The numbers 1,2,3,4,5, and 6 represent 2,4,5-, 2,3,4-, 2,3,6-, 2,4,6-, 3,4,5-, and 2,3,5-trimethylbenzyl radicals, respectively.

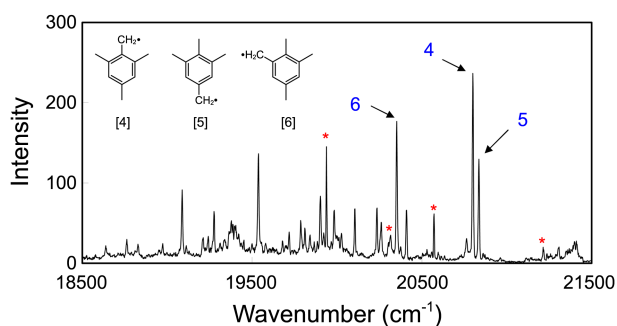
and 6-positions have anti-parallel alignments, and thus, contribute an additional of  $\sim 270\text{ cm}^{-1}$ , as shown for dimethylbenzyl radicals in Table 1. Thus, the substituent effect is  $657 \times 2 + 517 + 270 = 2101\text{ cm}^{-1}$ , which agrees well with the observation ( $2206\text{ cm}^{-1}$ ). The 2,3,4-isomer has three methyl groups, at ortho, meta, and para-positions. The group at the 4-position makes zero contribution to the shift because of the locations of nodal points in the  $D_1$  state of  $A_2$  symmetry. Thus, we have  $657 + 517 = 1174\text{ cm}^{-1}$  for the shift of the 2,3,4-trimethylbenzyl radical, which also agrees with that observed for the 2,3-dimethylbenzyl radical ( $1345\text{ cm}^{-1}$ ). These two isomers exhibit large and different spectral shifts, which makes it possible to identify them clearly.

Regarding the assignments of isomers generated from 1,2,3,5-tetramethylbenzene (isodurene), three possible isomers, 2,3,5-, 2,4,6-, and 3,4,5-trimethylbenzyl radicals<sup>14</sup> can be generated by the dissociation of the methyl C-H bond at the 1-, 2-, and 5-positions, respectively, as shown in Figure 3. Thus, we would expect three isomers to be produced by the corona discharge of 1,2,3,5-tetramethylbenzene.

Figure 4 shows the mixed spectrum of the three isomers. The strong band at  $20836\text{ cm}^{-1}$  can be assigned to the origin band of one isomer because of the absence of bands to the blue region, as described above. In addition, the neighboring strongest band at  $20800\text{ cm}^{-1}$  could be the origin band of



**Figure 3.** Possible production of trimethylbenzyl radicals from the corona discharge of precursor tetramethylbenzenes produced by dissociation of a methyl C-H bond. Only one isomer can be generated from 1,2,4,5-tetramethylbenzene (durene) because the four methyl groups are equivalent. Two isomers are possible from 1,2,3,4-tetramethylbenzene (prehnitene), and three possible isomers from 1,2,3,5-tetramethylbenzene (isodurene).



**Figure 4.** Vibronic emission spectrum observed from the corona discharge of the precursor 1,2,3,5-tetramethylbenzene in a large amount of He carrier gas in CESE. The numbers 4, 5, and 6 indicate the origin bands of the 2,4,6-, 3,4,5-, and 2,3,5-trimethylbenzyl radicals, respectively. H and He atomic lines are marked by asterisks.

another isomer because of its strong intensity and the absence of a vibrational mode of  $36\text{ cm}^{-1}$ . Previous solid state observations<sup>15</sup> could not resolve these two nearby bands and assigned to the origin band of the 2,4,6-isomer.

According to substituent effects, the 2,4,6- and 3,4,5-isomers should exhibit smaller shifts than the 2,3,5-isomer because of the presence of a methyl group at the 4-position. Calculation gave shift of  $1314$  and  $1034\text{ cm}^{-1}$  for the 2,4,6- and 3,4,5-isomers, respectively, which agreed well with observation for the 2,6- ( $1386\text{ cm}^{-1}$ ) and 3,5-dimethylbenzyl ( $1160\text{ cm}^{-1}$ ) radicals. Thus, we were able to assign the two strong bands at  $20836$  and  $20800\text{ cm}^{-1}$  to the origin bands of the 3,4,5- and 2,4,6-isomers, respectively. Differences between observation and calculation were  $\sim 100\text{ cm}^{-1}$  for these two isomers. The assignment of the remaining 2,3,5-isomer was more complicated than expected because several strong

**Table 2.** Comparison of the Observed with the Calculated Shift of Methyl-Substituted Benzyl Radicals<sup>a</sup>

Molecules	This work	Previous work <sup>c</sup>	TDDFT <sup>f</sup>	Shift		Calc <sup>i</sup>	Diff <sup>j</sup>
				Obs. <sup>g</sup>	TDDFT <sup>h</sup>		
benzyl	22002	22002	25988	0	0	0	
2,4,5-trimethyl <sup>b</sup>	20832	20832	24272	1170	1716	1174	-4
2,3,4-trimethyl <sup>c</sup>	20844	20844	23845	1158	2143	1174	-16
2,3,6-trimethyl <sup>c</sup>	19796	19796	22365	2206	3623	2104	102
3,4,5-trimethyl <sup>d</sup>	20836	20800	24704	1166	1284	1034	132
2,4,6-trimethyl <sup>d</sup>	20800	20836	23906	1202	2082	1314	-112
2,3,5-trimethyl <sup>d</sup>	20352	19536	22674	1650	3314	1691	-41

<sup>a</sup>Measured in vacuum ( $\text{cm}^{-1}$ ). <sup>b</sup>Reference 20. <sup>c</sup>Reference 13. <sup>d</sup>This work. <sup>e</sup>Reference 14. <sup>f</sup>B3LYP/6-311G\*. <sup>g</sup>Shift from the origin band of benzyl at  $22002\text{ cm}^{-1}$ . <sup>h</sup>Calculated shift from the origin band of benzyl at  $25988\text{ cm}^{-1}$ . <sup>i</sup>Empirical data based on methylbenzyl radicals. <sup>j</sup>Difference between observation and empirical data.

**Table 3.** Vibrational Mode Frequencies of Trimethylbenzyl Radicals from 1,2,3,5-Tetramethylbenzene<sup>a</sup>

Mode <sup>b</sup>	This work (D <sub>0</sub> )	Previous work <sup>c</sup> (D <sub>0</sub> )	<i>Ab initio</i> <sup>d</sup> DFT/6-311G* (D <sub>0</sub> )	Precursor		Symmetry (C <sub>s</sub> )
				1,2,3,5-Tetramethylbenzene <sup>e</sup> (S <sub>0</sub> )		
2,3,5-Trimethyl (C <sub>s</sub> )						
origin	20352	19536				
3	324		322	328		a'
6b	450		452	453		a'
1	566	574	597	573		a'
14	1264		1261	1294		a'
2,4,6-Trimethyl (C <sub>2v</sub> )						
origin	20800	20836				
6a	426	450	457	453		a <sub>1</sub>
7b	994		985	958		b <sub>2</sub>
1	574	564	592	573		a <sub>1</sub>
12	732		714	734		b <sub>2</sub>
14	1256		1267	1294		b <sub>2</sub>
3,4,5-Trimethyl (C <sub>2v</sub> )						
origin	20836	20800				
6a	424	448	454	453		a <sub>1</sub>
7b	988		991	958		b <sub>2</sub>
1	564	564	592	573		a <sub>1</sub>
14	1262		1263	1294		b <sub>2</sub>

<sup>a</sup>Measured in vacuum ( $\text{cm}^{-1}$ ). <sup>b</sup>Reference 22. <sup>c</sup>Reference 14. <sup>d</sup>Not scaled. <sup>e</sup>Reference 21.

vibronic bands appeared to red region of the origin band of other two isomers in the spectrum.

Although analyses of high resolution spectra showing rotational fine structure should provide the most trustworthy identification of large aromatic molecules with similar structures, observation of the origin band of an electronic transition and a few vibronic bands of well-known vibrational modes, could provide a reliable means of assigning benzyl-type radicals generated by a corona discharge. In this study, we attempted to obtain evidence of each isomer produced by comparing the observed vibronic bands with the calculated bands for the electronic transitions and vibrational modes of isomer, because the spectra observed in this work showed a limited resolution.

To assign vibronic bands belonging to each isomer, a series of vibrational structures of modes 6a, 6b, and 1 were checked in the spectrum, because these are well-known in benzyl-type radicals. In-plane C-C ring deformation vibrational modes 6a and 6b are degenerate at 606  $\text{cm}^{-1}$  in benzene.<sup>21</sup> With substitution on the benzene ring, these modes were split, providing lower and higher vibrational frequencies for modes 6a and 6b, respectively, for  $C_{2v}$  symmetry

**Table 4.** List of the Vibronic Bands Observed and Their Assignments

Position <sup>a</sup>	Intensity	Spacing <sup>b</sup>	Assignments <sup>c</sup>
21217	w		He atomic
20836	s		origin of 2,4,6-[4]
20800	vs		origin of 3,4,5-[5]
20764	w		
20572	m		H atomic
20410	m	426	6a <sub>1</sub> <sup>0</sup> [4]
20376	vw	424	6a <sub>1</sub> <sup>0</sup> [5]
20352	vs	0	origin of 2,3,5-[6]
20316	w		He atomic
20262	m	574	1 <sub>1</sub> <sup>0</sup> [4]
20236	m	564	1 <sub>1</sub> <sup>0</sup> [5]
20106	m	732	12 <sub>1</sub> <sup>0</sup> [4]
20028	w	324	3 <sub>1</sub> <sup>0</sup> [6]
19984	m	852	6a <sub>2</sub> <sup>0</sup> [5]
19938	s		He atomic
19902	m	450	6a <sub>1</sub> <sup>0</sup> [6]
19842	w	994	7b <sub>1</sub> <sup>0</sup> [4]
19812	w	988	7b <sub>1</sub> <sup>0</sup> [5]
19786	m	566	1 <sub>1</sub> <sup>0</sup> [6]
19718	m	1118	1 <sub>2</sub> <sup>0</sup> [2]
19582	vw	1256	14 <sub>1</sub> <sup>0</sup> [4]
19536	s	1262	14 <sub>1</sub> <sup>0</sup> [5]
19378	w		
19276	m	1560	1 <sub>1</sub> <sup>0</sup> 7b <sub>1</sub> <sup>0</sup> [4]
19242	w	1558	1 <sub>1</sub> <sup>0</sup> 7b <sub>1</sub> <sup>0</sup> [5]
19212	w		
19088	s	1264	14 <sub>1</sub> <sup>0</sup> [6]

<sup>a</sup>Measured in vacuum ( $\text{cm}^{-1}$ ). <sup>b</sup>Spacing from the origin band in the  $D_1 \rightarrow D_0$  transition of each species. <sup>c</sup>The numbers 4, 5, and 6 in parentheses indicate the bands belonging to the  $D_1 \rightarrow D_0$  transition of the 2,4,6-, 3,4,5-, and 2,3,5-trimethylbenzyl radicals, respectively.

species, while the trend was reversed for  $C_s$  symmetry. Furthermore, splitting between these two modes is increased by increasing the sizes of the substituents on the benzene ring. The precursor 1,2,3,5-tetramethylbenzene has the bands at 453 and 514  $\text{cm}^{-1}$  for modes 6a and 6b, respectively. Other tetramethylbenzenes also exhibit similar splitting between the two modes. Mode 1 of ring breathing provides most reliable evidence for the identification of aromatic compounds and is less sensitive to substitution. Thus, all isomers should show similar to the precursor for this mode.

The second strongest band at 20352  $\text{cm}^{-1}$  was assigned to the origin band of the 2,3,5-isomer rather than the vibronic band belonging to the 3,4,5- or 2,4,6-isomer, because the spacing (484 or 448  $\text{cm}^{-1}$ ) from the origin band of the other isomers did not match well with the *ab initio* calculation of mode 6a, as detailed in Table 3.

After determining the origin bands of each isomer, the assignments of other vibronic bands were obtained for each species by comparing with the calculated values and those of the precursor. From these assignments, the vibrational modes 1, 6a, 7b, and 14 were observed in the emission spectrum for the 2,4,6- and 3,4,5-isomers of  $C_{2v}$  symmetry. Furthermore, these observations were in excellent agreement with the calculations without scaling. The modes listed above were also active in combination bands. The vibrational mode frequencies obtained in this work are listed in Table 4, together with the identification of the isomers. In addition to the vibronic bands assigned, we observed a few weak bands in the regions ( $\sim 36 \text{ cm}^{-1}$ ) of strong vibronic band, which indicates that these belonged to torsional transitions of the methyl group during jet expansion.

## Conclusion

In summary, the visible vibronic emission spectrum of the corona discharge of 1,2,3,5-tetramethylbenzene was analyzed for assignments of the  $D_1 \rightarrow D_0$  transition and vibrational modes in the ground ( $D_0$ ) electronic state by *ab initio* calculation and by using the methyl substituent effect on electronic transition energy. The new assignments show better agreement with the observation and confirm the utility of the substituent effect for the discrimination of multi-methyl benzyl radicals. Furthermore, the method adopted can be applied to benzyl radicals with substituents other than methyl.

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