

## SPECTROSCOPIC STUDY OF 2,4,5-TRIMETHYLBENZENE

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### ABSTRACT

Multi-substituted benzyl radicals is generated in the jet with a large amount of carrier gas (He) and vibronically cooled electronic emission spectra are observed in a corona excited supersonic expansion(CESE) apparatus. The spectra are analyzed in terms of progressions of the fundamental vibrational modes and molecular structures of multi-substituted benzyl radicals are calculated and compared with experimental data and precursors. For the first time the 2,4,5-trimethylbenzene radicals are generated in a jet and the vibronic emission spectra in the  $D_1 \rightarrow D(0)$  transition have been recorded.

**Keywords:** 2,4,5-trimethylbenzene, Corona discharge, *ab initio* calculation.

### INTRODUCTION

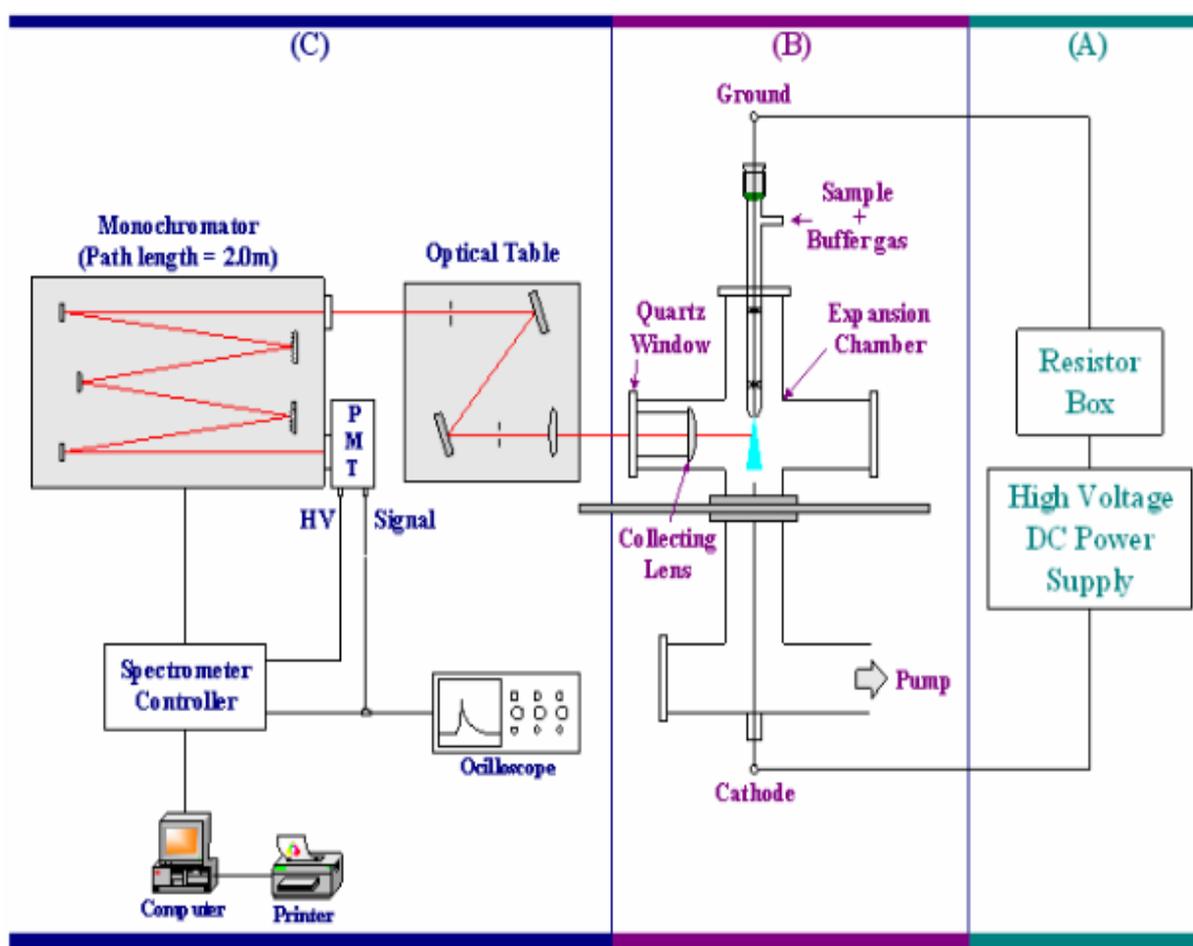
Charlton and Thrush [1] have observed the laser induced fluorescence (LIF) spectra of alkyl substituted benzyl radicals and have measured the lifetime in the excited vibronic states. Recently, our molecular spectroscopy group[2-5] have extended the assignments of vibrational modes of xylyl radicals from the vibronic emission spectra. The controversial assignments of p-xylyl radicals have been confirmed by the bandshape analysis of the vibronic bands from high resolution emission spectra [6]. The torsional barrier of the internal methyl group has been calculated for the xylyl radicals by Lin and Miller [13] from an analysis of the laser induced fluorescence excitation and dispersed emission spectra. Although the exact mechanism for generation and excitation of benzyl-type radicals in a corona discharge is not known, the analysis of vibronic spectrum observed provides the species produced with the spectroscopic evidence for identification.

Corona excited supersonic expansion(CESE) has been recognized as a useful spectroscopic technique for observing molecular spectra in the gas phase [7]. The spectral simplification and transient molecular stabilization associated with expansion of inert carrier gas cannot be achieved in any other ways. Combination of technique of supersonic jet expansion with emission spectroscopy has had an enormous impact on the repertoire of spectroscopic studies of transient molecular species. Of the emission sources utilizing these combination, the one providing enough continuous photon intensity for high resolution studies of weak transition is the pinhole-type glass nozzle which has been widely employed for observation of the vibronic emission spectra of transient species [8-10]. This has been applied to the observation of the vibronic emission spectra of many jet-cooled benzyl-type radicals in the gas phase [11-13].

### EXPERIMENTAL AND THEORETICAL METHODS

Figure 1 shows the schematic diagram of the corona excited supersonic jet system used in this work, which is mainly divided into three parts; (a) energy source, (b) electric discharge and

supersonic system and (c) spectrometer and acquisition system. For the generation of transient molecules in a jet from the precursor molecules, we have employed a conventional corona discharge system which is similar to that developed by Engelking [8]. A conventional corona discharge [9] coupled with a supersonic expansion is consisted of a thin metal rod, terminated with a sharp point, mounted inside an insulating and inert tube. Forming a supersonic nozzle. The metal tip is placed very close to the exit hole and a high positive voltage is applied to the rod. Thus, the nozzle body, in this work, was formed from a thick-walled quartz tube of 12mm outer diameter, 2mm thickness, and 250mm length, narrowed by flame heating at one end to a capillary of the desired pinhole size. The nozzle was connected to threaded adaptor (Ace glass model 5027-05). A long and sharpened anode, made of a 1.6mm diameter stainless steel rod was inserted through a rubber o-ring into the quartz nozzle for the generation and excitation of transient molecules. The o-ring was tightened by a teflon bushing with a hole in center through which the anode was connected to the high voltage electric dc power supply (Bertan model 210-05R).

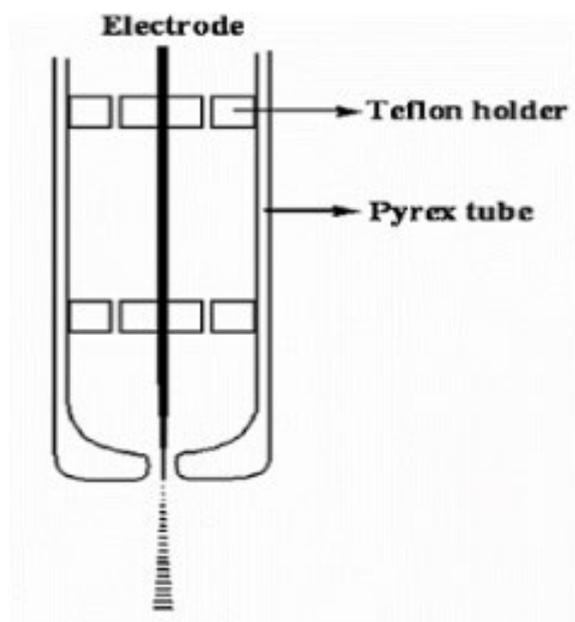


**Figure 1.** The schematic diagram of the CESE system.

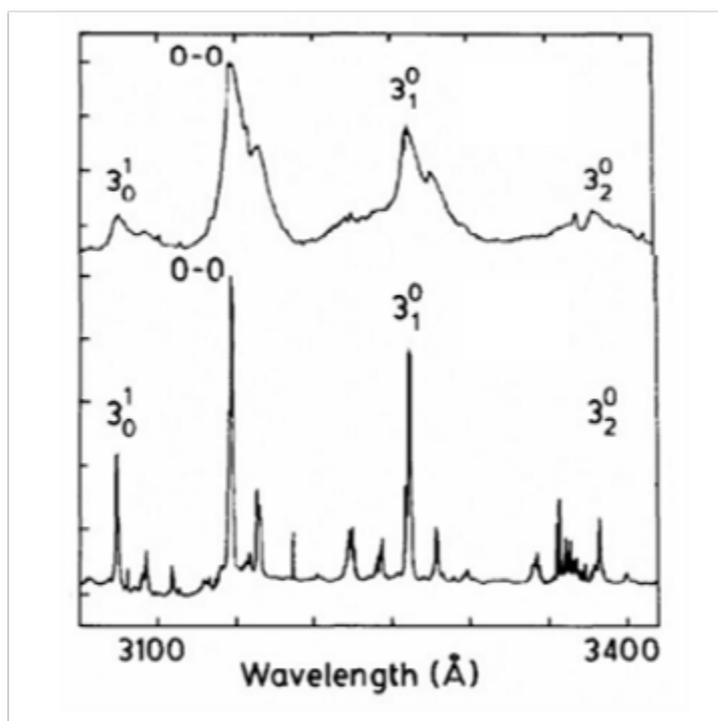
The position of the metal tip used for the anode has been proven to be critical for the stability of the discharge over a long period. For example, in Engelking type corona discharge the metal tip is located inside the nozzle and the molecules are excited before expansion, which substantially reduces the stability of the discharge when heavy organic compounds are used as precursors, the messy fragments generated by an electric discharge of the organic precursor easily block the narrow hole of the nozzle. Thus, in this design we put the metal tip outside the

nozzle. Even though the length of the metal tip exposed outside the nozzle is less than 0.5mm, it changes the mechanism, leading to excitation after expansion. However, it is very important to let the metal tip be centered at the hole for the straightly downstream beam. The anode was firmly fixed into the center of nozzle by using teflon holders inside the nozzle. The teflon holder made of 3mm thickness of teflon disk of whose diameter is exactly same as the inner diameter of the nozzle has a center hole for the anode and several small holes for the gas flow.

The nozzle was positioned into the expansion chamber via a Cajon fit attached to the stainless steel flange. The cathode was located at under the chamber supporter made by an acrylic plate to avoid seeing the arching by the spectrometer during the discharge. The arching was more severe when the surface of the cathode was contaminated by foreign compounds. When a dilute mixture of a precursor molecule in a rare gas was expanded through the orifice, an electrical discharge produced not only molecular fragments but also vibronically excited molecules. The details of the nozzle system is shown in Figure 2. The anode was connected via a 200k $\Omega$  ballast resistor to the high voltage electric dc power supply which has a maximum 5kV and 40mA capacity.



**Figure 2.** The details of the nozzle structure.



Comparison of spectrum bandshape of transition with nozzle (below) and without nozzle (above).

The expansion gas is supplied from 2 atm rare gas reservoir seeded with a small quantity of stable precursor molecules vaporized inside the vaporizing vessel. The concentration of the precursor in a carrier gas can be controlled by immersing the sample in a temperature-controllable water bath. Since the discharge occurs in the high pressure region of the nozzle, molecules undergo collisional relaxation into the vibrational ground level of the electronic excited state before they emit. Thus, it has an advantage of observing the transitions from a single vibronic state.

For the rotational cooling, the supersonic expansion chamber was made of six-way cross pyrex tube of 50mm inner diameter. The chamber was evacuated by a 800L/min mechanical vacuum pump (WS Automa model W2V80), resulting in the pressure range of 1.5-1.8 Torr during the operation with 2.0 atm of backing pressure. The emitting light from the downstream jet was collected through a collecting quartz lens of 38mm diameter and 50mm focal length placed at focal length from the tip of the nozzle, and focused onto the slit of the double-type monochromator using a combination of two mirrors and a lens.

For the spectrometer, we have employed the double type monochromator (Jobin Yvon model U-1000) which has effective path length of 2.0m using 3 mirrors and 2 gratings of 1800 groves/mm. The scanning range of the spectrometer is from 11,500  $\text{cm}^{-1}$  to 32,000  $\text{cm}^{-1}$ , with a maximum resolving power of 0.15  $\text{cm}^{-1}$  at 17,000  $\text{cm}^{-1}$  which is good enough to observe the rotational contour of the vibronic band of large molecules in a jet. For the photon counting, a head-on photomultiplier tube (Hamamatsu model R649) was employed. The output of the PMT was fed to the spectrometer control box via the preamplifier. The spectrometer was fully operated using a software SPECTRAMAX [14] by a personal computer.

**Figure 1. The schematic diagram of the CESE system.**

The methyl-substituted toluene of the reagent grade was obtained commercially from Aldrich and used without further purification. For the CESE experiment, the electronically excited methyl-substituted benzyl radical was generated from methyl-substituted toluene by corona discharge in a supersonic expansion with helium buffer gas. The methyl-substituted toluene was vaporized at room temperature inside the vaporizing vessel made of thick Pyrex glass bottle under 2.0 atm of He gas. The concentration of the precursor in the carrier gas was adjusted for the maximum emission intensity and believed to be about 1% in the gas mixture. Since the precursor and methyl-substituted benzyl radical have many vibrational modes and the assignments have not been completed, we performed to assist assignment of their spectrum. *Ab initio* calculations were carried out using the GAUSSIAN 09 for Windows package. Geometry optimizations were performed at the RHF and B3LYP method for the methyl-substituted toluene and also UHF and B3LYP method for the methyl-substituted benzyl radical. The calculations were executed with a personal computer equipped with an Intel Pentium VI, 3 GHz processor and 2 GMB RAM.

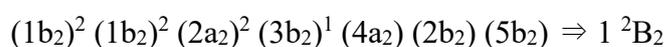
**RESULTS**

It is well known that the high voltage electric discharge of the toluene with a large amount of inert carrier gas produces the benzyl radical at the excited states. Benzyl radical is a planar structure of  $C_{2v}$  symmetry as shown in the Figure 3. The weak visible emission spectrum of benzyl radicals with  $C_{2v}$  symmetry is believed to arise from transitions from the close-lying  $2^2B_2$  and  $1^2A_2$  excited states to the  $1^2B_2$  ground state. Two excited electronic states can be combined by vibronic coupling. [24] Also, ring substitution is expected to affect the energies of the  $2^2B_2$  and  $1^2A_2$  excited states differently. [15]

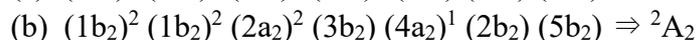
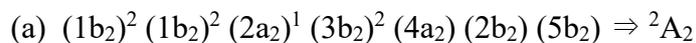
Assigning the observed  $D_1 \rightarrow D_0$  spectra implies identification of the observed CESE measurements in terms of the ground state normal mode vibrations and determination of the compositions of these bands in terms of quantum numbers for the ground states. Spectra were assigned by considering (1) gas phase infrared absorption frequencies and intensity of precursor; and in a few cases also the calculated infrared intensities of the fundamentals (2) the observed band frequencies and their intensities in the CESE measurements of this work; (3) the calculated *ab initio* frequencies of this work.

A critical step of the procedure was to establish the ground state vibrational modes. This was mostly based upon the identification of the strongest bands in the  $\Delta v=0$  regions in the jet-cooled emission spectra. It was presumed that the vibrational modes, of which the observed bands were composed, retained most of their character upon the transition between the two electronic states. We denoted corresponding modes of the ground states.

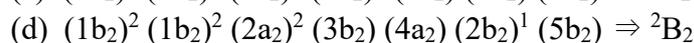
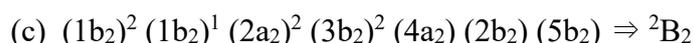
The general electronic structure of the benzyl-type radical can be simply described by the Huckel theory. The seven  $\pi$ -molecular orbitals can be written in terms of the seven  $p$ -atomic orbitals. For the  $\pi$ -electron system, there exist single nonbonding orbital and pairs of bonding and antibonding orbitals located with equal energy differences below and above the nonbonding orbitals. The seven molecular orbitals of benzyl-type radical would give rise to the following ground-state configuration in  $C_{2v}$  symmetry.



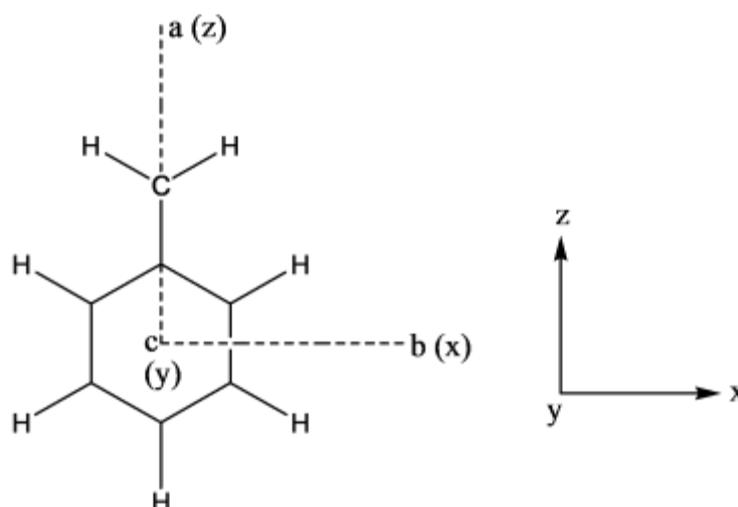
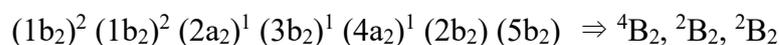
The lowest three orbitals are bonding, the  $3b_2$  orbital nonbonding, and the three highest orbitals antibonding with the based upon the pairing theorem, for excited electronic states, there are two possible isoenergetic ways of promoting an electron involving  $a_2$  MOs, resulting in two electron configurations of  $A_2$  symmetry.



These two promoting ways are shown as paths (a) and (b). Similarly, there are also two isoenergetic one electron promotions as paths (c) and (d) involving  $b_2$  MOs. These give rise to two electron configurations of  $B_2$  symmetry in Figure 4. [16]



There is also the excited configuration



**Figure 3. Molecular fixed-axis system of benzyl radical.**

In the oneelectron approximation, we would have as the lowest excited electronic states a degenerate pair of  ${}^2A_2$  states with another degenerate pair of  ${}^2B_2$  states only slightly higher in energy. However, in the presence of configuration interaction (CI), the two degenerate pairs of zeroth order electronic states of the same symmetry interact and repel very strongly, splitting widely the initially degenerate pairs. In the case of the  ${}^2B_2$  states the lower frequency state, i.e.  $2^2B_2$ , is the antisymmetric linear combination of mixed state and carries a small oscillator strength, due to cancellation of transition moments calculated from the single configurations [17]. For the same reason, the lower of the  ${}^2A_2$  states, i.e.  $1^2A_2$ , lies in the same energy region and also has a low oscillator strength.

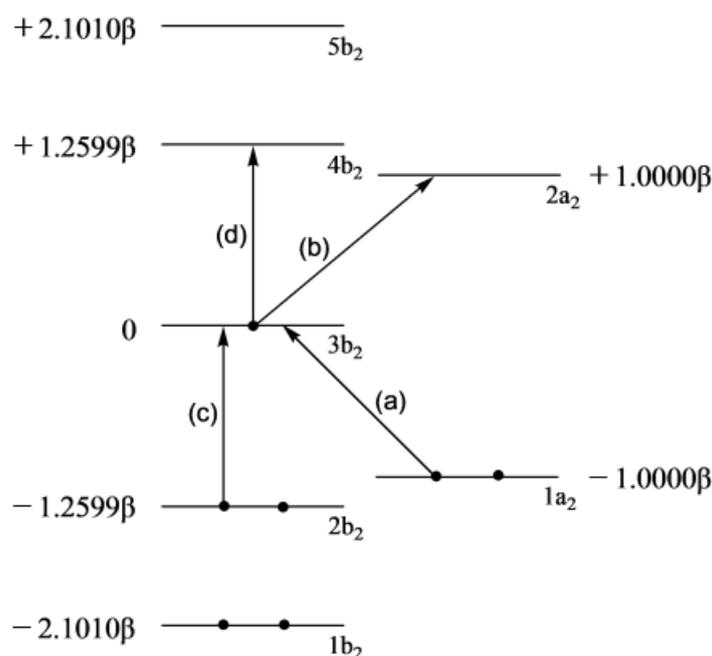


Figure 4. Huckel molecular orbital energy level scheme of benzyl radical.

## DISCUSSION

When the current and voltage of the CESE power supply were adjusted to obtain a green jet (using 1,2,4,5-tetramethylbenzene as the solide), the fluorescence spectrum of the 2,4,5-trimethylbenzyl radical was observed.

The weak visible emission spectrum of benzyl-type radicals is believed to arise from transitions from the close-lying  $3^2A''_2$  and  $2^2A''_2$  excited states to the  $1^2A''_2$  ground state like benzyl radical. [18] Two excited electronic states are mixed through vibronic coupling. [19] Ring substitution is also expected to affect the energies of the  $2^2A''_2$  and  $1^2A''_2$  excited states differently. The transition from the second excited state to the ground state has not been observed due to the rapid collisional relaxation process.

Figure 5 exhibits a portion of the vibronic emission spectrum of the 2,4,5- trimethylbenzyl radical generated in this work. Most of the bands are observed in the region of  $19000-21000\text{ cm}^{-1}$ . As shown in Figure 6, the spectrum exhibits one kind of bandshapes. The strong band at  $20836\text{ cm}^{-1}$  shows the bandshape of Figure 7(a) and also the other strong bands represent the same character in the spectrum.

In the spectrum, the most intensive band is found at  $20836\text{ cm}^{-1}$  which is believed to be the origin band of the  $D_1(2^2A''_2) \rightarrow D_0(1^2A''_2)$  transition, followed to lowed energies by a series of vibronic band. Also, the absence of the band with noticeable intensity beyond the origin band supports the assignment. For comparison, *o*-, *m*-, and *p*-methylbenzyl show the origin band at  $21345$ ,  $21485$  and  $21700\text{ cm}^{-1}$ , respectively and the origin band of benzyl radical [19] locates at  $22002\text{ cm}^{-1}$ . It seems that *o*-, *m*-, and *p*-methyl-substitution affect independently the energy of the benzyl radical. We suggest that substituted-methyl group subtract the energy of benzyl radical. for example, 2,4,5-trimethylbenzyl radical has three substituted methyl groups of ortho, meta and para. So we would predict the energy of origin of 2,4,5-trimethylbenzyl radical like  $22002 - (302 + 517 + 657) = 20526\text{ cm}^{-1}$ . Comparing with experimental value, this substitution effect is reasonable.

The vibronic bands observed in this work were provisionally assigned with the help of the known vibrational mode frequencies of the precursor, 1,2,4,5-tetramethylbenzene since both molecules are subjected to the isodynamic approximation[20,21] which states the correspondence of vibrational mode frequencies and intensity. This has been already applied to the vibrational mode assignments of many benzyl-type radicals.

It has been generally accepted that the calculation using GAUSSIAN 09 program calculation method predicts the vibrational mode frequencies within +10% from the experimental values. From the calculation on the 2,4,5-trimethylbenzyl radical, a total of 63 vibrational mode frequencies have been obtained. Table 1 lists the frequencies of the transitions observed, together with the relative intensities of the peaks measured in this work and Table 2 shows the comparison of calculation with precursor data. The numbers in the parenthesis represent the spacing from the origin band in units of wavenumber. The strong band at 20406(430)  $\text{cm}^{-1}$  was assigned to the 6b transition according to the similarity to the precursor(445  $\text{cm}^{-1}$ ). The slight discrepancy from the precursor reflects the change of  $-\text{CH}_3$  to  $-\text{CH}_2$ .

In the vibronic emission spectrum of benzyl-type radicals with  $C_{2v}$  symmetry, the mode 6a of ring deformation was observable with fairly strong intensity while the mode 6b was detected with much weak intensity.[29] But in this work, 2,3,4-trimethylbenzyl radical is  $C_s$  symmetry and the mode 6b of ring deformation was observed. In benzene Both modes 6a and 6b are degenerate. In *p*-methylbenzyl radical, the frequency of modes 6a and 6b was measured to be 458 and 637  $\text{cm}^{-1}$ , respectively.

The strong band at 20106(730)  $\text{cm}^{-1}$  was assigned to the  $1^0$  transition because the mode 1 of ring breathing should be consistent with that of the precursor(735  $\text{cm}^{-1}$ ) and also the calculation value support the 1 mode in the Table 7. Moreover, as shown in Figure 7, the band of mode 1 also exhibits the similar bandshape to the origin band, indicating that the vibrational mode comes from 2,4,5-trimethylbenzyl radical.

Although the several weak bands observed in this work and the peaks may be the combination bands and overtone transitions, but we exclude to assign these bands to the other vibrational modes. Because it does not have enough proofs to explain vibrational mode like a bandshape.

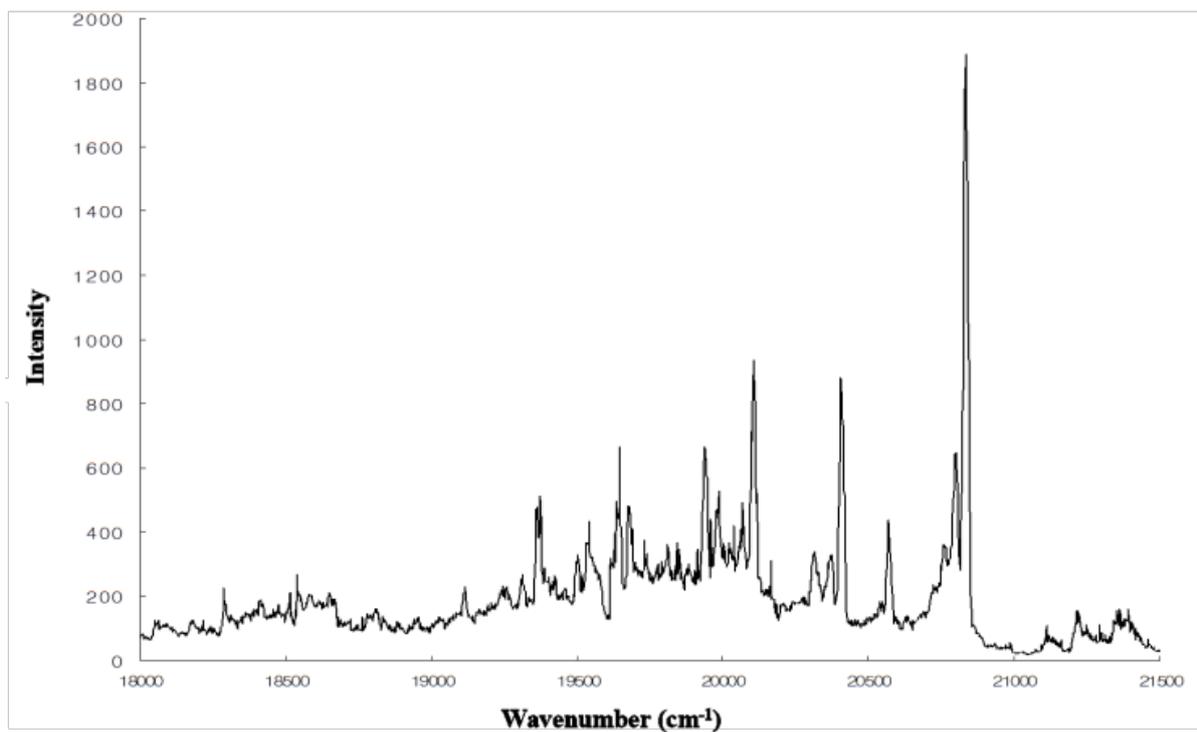


Figure 5. Vibronic emission spectrum of the 2,4,5-trimethylbenzyl radical.

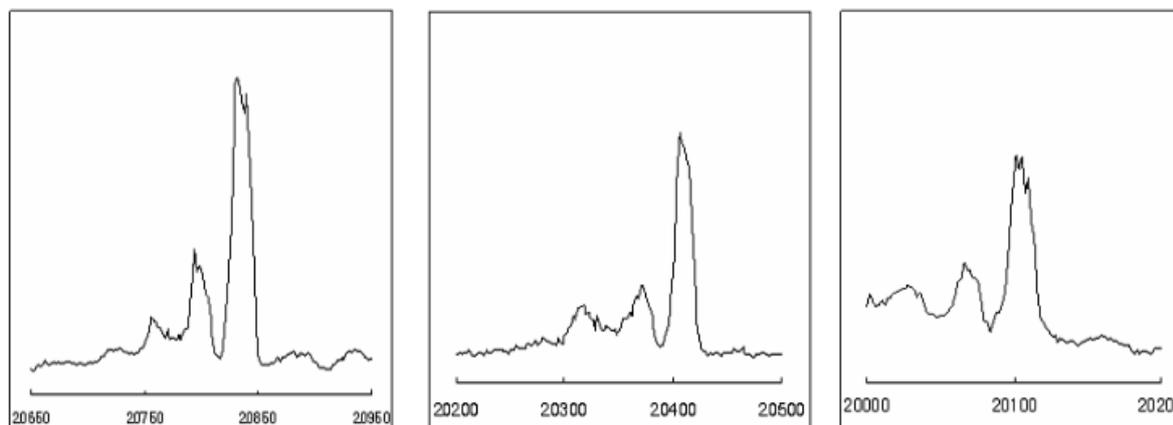


Figure 6. Enlarged bandshape of 2,4,5-trimethylbenzyl radical.

**Table 1. List of the vibronic bands observed and their assignment of 2,4,5-trimethyl benzyl radical.**

position	relative intensity	spacing from the origin	assignment
20834	VS	0	origin
20800	m	34	
20764	m	70	
20570	s	264	
20406	s	428	$6b_1^0$
20376	m	458	
20316	m	518	
20106	s	728	$1_1^0$
20068	m	766	
20030	m	804	
19986	w	848	
19940	m	894	He
19682	w	1152	
19644	w	1190	
19372	w	1462	
19314	vw	1520	
19116	vw	1718	

**Table 2. Comparison of calculation with precursor data of vibronic bands of 2,4,5-trimethylbenzyl radical.**

## CONCLUSIONS

The vibronically cooled electronic emission spectra of the 2,4,5-trimethylbenzyl radical was observed in a corona excited supersonic expansion apparatus. Several fundamental modes of tetramethyl- and trimethylbenzene were assigned on the basis of previous infrared and Raman values of the precursor and calculation. The spectrum was analyzed in terms of progressions of the fundamental vibrational modes and molecular structures of benzene, toluene and methyl-substituted toluene are calculated and compared with experimental data. The methyl-substitution effect is first suggested by this group. The substitution effect is that each methyl substituted position of benzyl radical affect the energy level and also the bandshape of the benzyl radical independently. We have generated for the first time the 2,4,5-trimethylbenzyl

radical in a jet from which the vibronic emission spectra in the  $D_1 \rightarrow D_0$  transition have been recorded.

## ACKNOWLEDGEMENTS

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