

## SPECTROSCOPY STUDY OF BENZYL-TYPE RADICAL MOLECULE

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### ABSTRACT

The vibronic emission spectrums of the jet-cooled methyl-substituted benzyl radicals in the  $D_1 \rightarrow D_0$  transition have been observed and analyzed to obtain accurate vibrational frequencies in the ground electronic state by comparing with those of methyl substituted toluene as well as those from the *ab-initio* calculation using HF and B3LYP methods.

**Keywords:** Benzyl radical, Corona discharge, *ab initio* calculation.

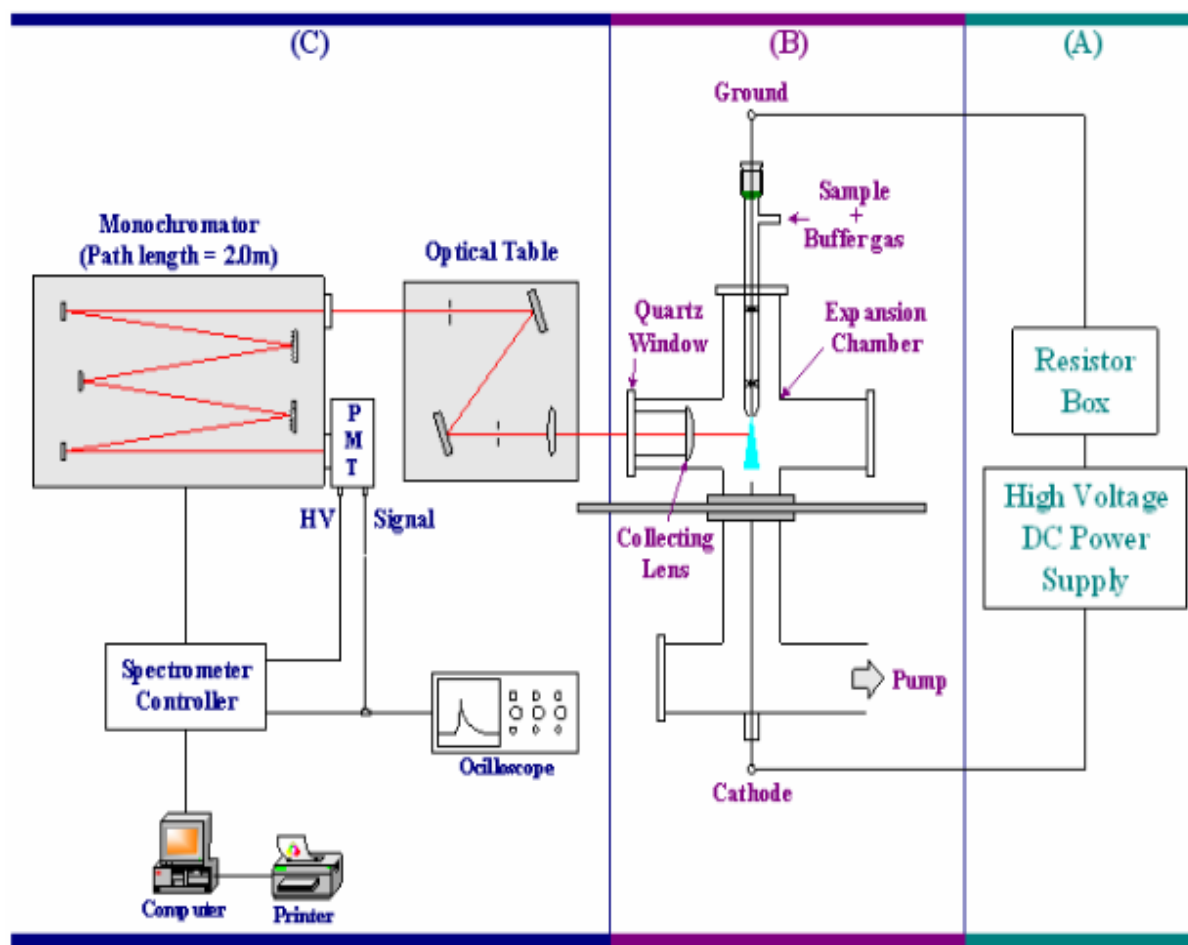
### INTRODUCTION

Supersonic jet expansion has been recognized as a powerful spectroscopic technique for observing molecular spectra in the gas phase [1]. 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 [2,3] which has been widely employed for observation of the vibronic emission spectra of transient species [4]. This has been applied to the observation of the vibronic emission spectra of many jet-cooled benzyl-type radicals in the gas phase [5-7].

### 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 12 mm outer diameter, 2 mm thickness, and 250 mm 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 1.6 mm 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).



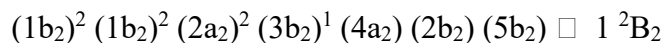
**Figure 1. The schematic diagram of the CESE system.**

The 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.

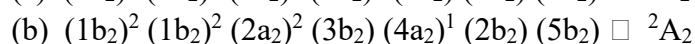
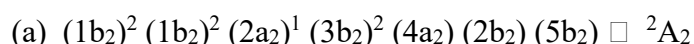
## RESULTS

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

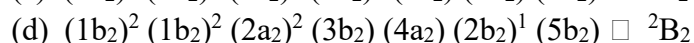
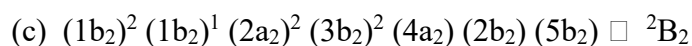
orbitals. For the  $\pi$ -electron system, there exist single nonbonding orbital and pairs of bonding and antibonding orbitals located with equal energy differences below and above the nonbonding orbitals. The seven molecular orbitals of benzyl-type radical would give rise to the following ground-state configuration in  $C_{2v}$  symmetry.



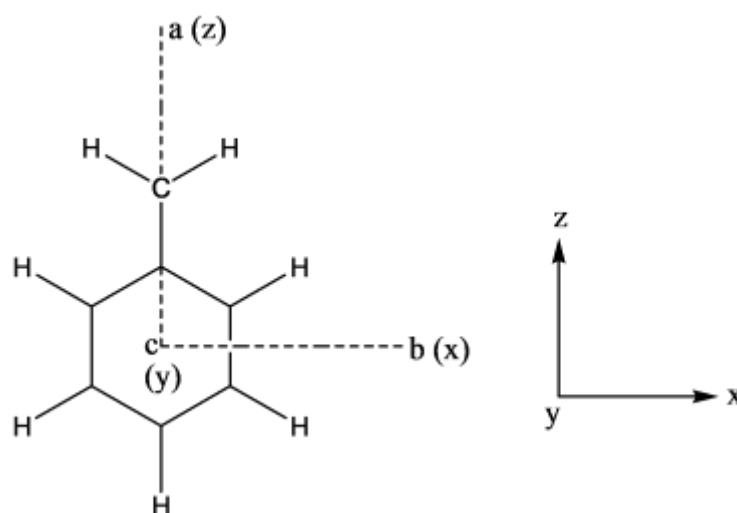
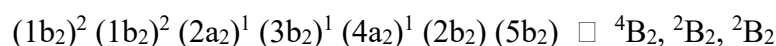
The lowest three orbitals are bonding, the  $3b_2$  orbital nonbonding, and the three highest orbitals antibonding with the based upon the pairing theorem, for excited electronic states, there are two possible isoenergetic ways of promoting an electron involving  $a_2$  MOs, resulting in two electron 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. [10]



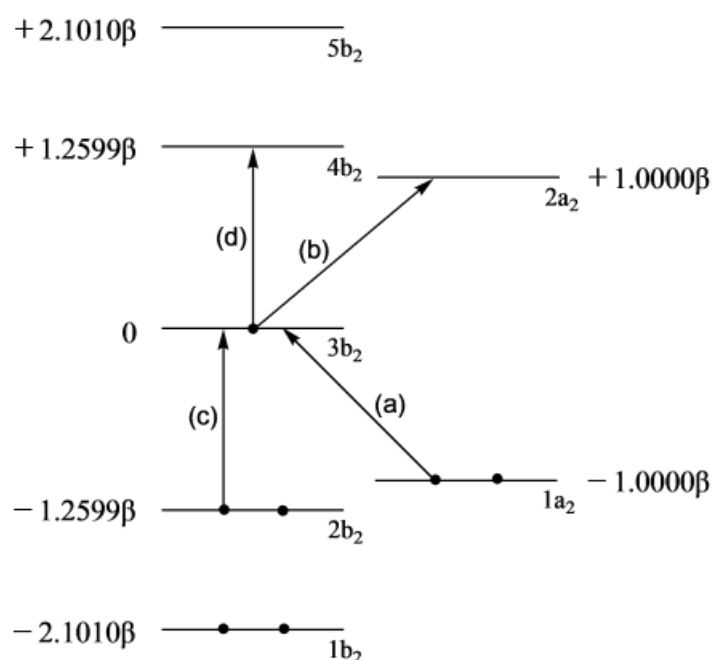
There is also the excited configuration



**Figure 2. 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

[11]. 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 3. Huckel molecular orbital energy level scheme of benzyl radical.**

## DISCUSSION

*Ab initio* calculations were carried out with the GAUSSIAN-09 package. Geometry optimizations were performed at the HF and B3LYP method and basis set ; 6-31G\*, 6-311G\*, 6-311G(df,pd), cc-pvdz. Optimized geometries were subsequently used for the calculations of the frequencies and the shapes of the respective normal modes.

In the *ab initio* calculations, it is compared with each method and basis set using benzene and toluene calculation. It is best optimization to use B3LYP/cc-pvdz. The comparison of benzene calculation is given in Table 1 and the comparison of toluene calculation is Table 2. Especially toluene has two kinds of stable structures like Figure 5 and the single point energy of these structures are compared each other. It seems that benzene molecule has the  $D_{6h}$  symmetry and toluene molecule has the  $C_s$  symmetry.

The observed vibrations were correlated with the calculated ones in most cases in the order of the decreasing frequencies, with the assumption that the ratio between the observed and the calculated frequencies was approximately uniform. Useful additional information was obtained from calculated IR absorption intensities. With an average deviation of a factor (observed/calculated), the calculated frequencies of benzene and toluene matched the experimental ones and B3LYP method for vibration assignment is better than HF method. The results of calculation are given in Table 3 and Table 4.

Table 1. Bond length comparison of calculation with experimental data of benzene.

method	single point E	C-C	C-H
experiment <sup>a)</sup>	---	1.3999	1.101
HF/6-31g*	-230.7031365	1.3865	1.0755
HF/6-31g*	-230.7431417	1.3865	1.0755
B3LYP/6-31g*	-232.2486611	1.3975	1.0875
B3LYP/6-311g*	-232.297908	1.3945	1.0865
B3LYP/6-31g(df,pd)	-232.3187926	1.3915	1.0835
B3LYP/cc-pvdz	-232.2629588	1.3985	1.0925

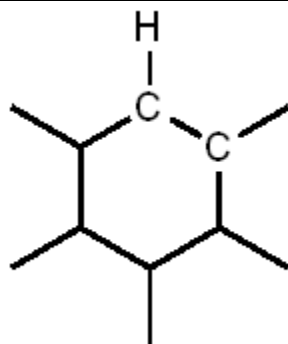


Table 2. Bond length comparison of calculation with experimental data of toluene.

method	form	single point E	$\Delta$ (cal/mol)	C <sub>1</sub> -H <sub>1</sub>	C <sub>1</sub> -C <sub>2</sub>	C <sub>3</sub> -C <sub>4</sub>	C <sub>5</sub> -H <sub>1</sub>
experiment <sup>a)</sup>			14	1.102	1.5118	1.3992	1.111
HF/6-31g*	o	-269.7401646	4.078	1.0845	1.5125	1.3855	1.0775
	p	-269.7401581		1.0858	1.5125	1.3885	1.0765
HF/6-311g*	o	-269.7864473	2.886	1.0852	1.5102	1.3855	1.0775
	p	-269.7864427		1.0848	1.5112	1.3875	1.0765
B3LYP/6-31g*	o	-271.5666505	18.947	1.0965	1.5125	1.3965	1.0885
	p	-271.5666203		1.0968	1.5125	1.3975	1.0885
B3LYP/6-311g*	o	-271.6231156	14.994	1.0945	1.5105	1.3935	1.0875
	p	-271.6230917		1.0972	1.5105	1.3945	1.0875
B3LYP/6-31g(df,pf)	o	-271.6476237	18.822	1.0928	1.5085	1.3925	1.0845
	p	-271.6476537		1.0925	1.5085	1.3905	1.0845
B3LYP/cc-pvdz	o	-271.5805644	0.753	1.1028	1.5115	1.3985	1.0945
	p	-271.5805656		1.1025	1.5115	1.3995	1.0945

p : planr form

o : orthogonal form

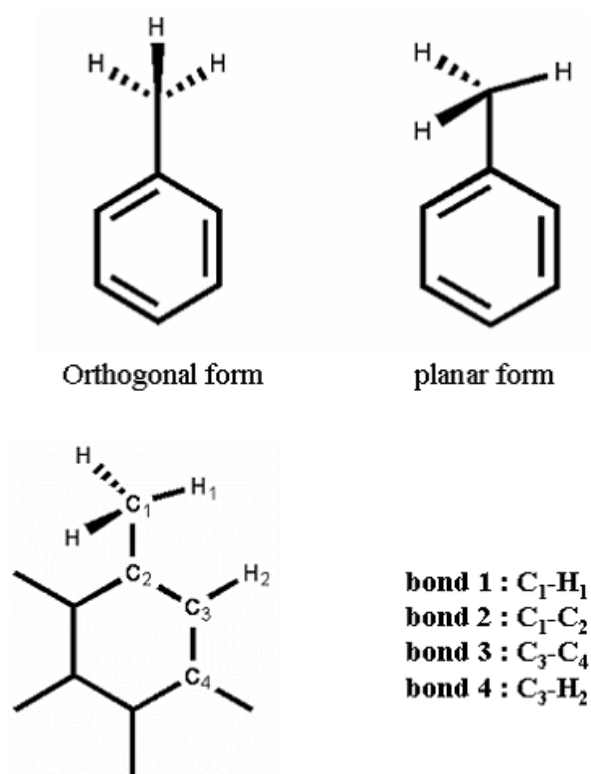


Figure 4. Two types of toluene structure.

Table 3. Comparison of calculation with experimental data of benzene vibration.

mode	experiment <sup>(1)</sup>	1	2	3	4	5	6
6	606	665	664	622	625	625	618
11	673	763	754	694	683	691	688
1	992	1083	1073	1020	1014	1015	1020
18	1038	1142	1131	1069	1061	1062	1059
19	1486	1651	1639	1532	1520	1518	1507
2	3062	3392	3369	3212	3192	3193	3205

1 : HF/6-31g\*

2 : HF/6-311g\*

3 : B3LYP/6-31g\*

4 : B3LYP/6-311g\*

5 : B3LYP/6-31g(df,pd)

6 : B3LYP/cc-pvdz

**Table 4. Comparison of calculation with experimental data of toluene vibration.**

mode	experiment <sup>(1)</sup>	1	2	3	4	5	6
6a	521	563	562	528	530	528	530
6b	623	682	681	637	639	633	639
1	784	852	848	802	800	800	801
9a	1175	1302	1294	1215	1208	1193	1206
8a	1605	1813	1800	1668	1654	1659	1651
2	3069	3385	3362	3207	3187	3198	3188

1 : HF/6-31g\*

2 : HF/6-311g\*

3 : B3LYP/6-31g\*

4 : B3LYP/6-311g\*

5 : B3LYP/6-31g(df,pd)

6 : B3LYP/cc-pvdz

## CONCLUSIONS

The methyl-substitution effect of benzyl radical is suggested for the first time by our group and the effect can be acceptable by analysing the spectrum of methyl-substituted benzyl radical.

For DFT calculation, the exchange-correlation energy function included in the Gaussian03 package was performed at the B3LYP level with high reproducibility related to chemical reactions, and the basis set used was 6-31G, which is specialized in modeling organic molecules.

In the  $D_0$  electronic state, we assigned using benzene and toluene vibrations by comparison with frequency calculations of HF and B3LYP and with the gas-phase IR absorption data of the precursor. The measured  $D_0$  vibrational frequencies matched the calculated method frequencies to within 5% using B3LYP method. The calculation method, Density Function Theory make better result than HF method. DFT is profitable to predict molecular frequencies and structure.

## ACKNOWLEDGEMENTS

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