

Spectroscopic Evidence of Vibronic Relaxation in Methyl Substituted Benzyl Radicals

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Energy transfer and redistribution processes are believed to play important roles in explaining the reaction dynamics of large aromatic compounds, and have been studied for many decades.¹ The benzyl radical² is known to have close-lying $2^2B_2(D_2)$ and $1^2A_2(D_1)$ excited electronic states separated by about $22,000\text{ cm}^{-1}$ from the $1^2B_2(D_0)$ ground electronic state. Ring substitution is also expected to affect the energies of the two excited electronic states differently, which could be mixed by vibronic coupling.³ In methyl-substituted benzyl radicals, the electronic interaction between the methyl group and the benzene ring is undoubtedly of the second-order compared to that between the methylene group and the benzene ring, since the molecule has a planar structure of 7 delocalized π electrons in which the CH_2 group contributes an electron.

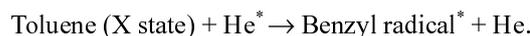
The weak visible emission from benzyl-type radicals⁴⁻⁶ is believed to arise from transitions from the close-lying D_2 and D_1 excited electronic states to the D_0 ground state. Since the vibronic coupling between the two excited electronic states is believed to be very efficient in benzyl-type radicals,⁷ it might not be possible to directly observe the transition from the D_2 state except for the *p*-chlorobenzyl radical,⁸ in which the energy separation between the two excited states is only 95.2 cm^{-1} .

In this paper, we report for the first time the observation of the transition arising from the D_2 state of methyl substituted benzyl radicals and the spectroscopic evidence that the efficiency of vibronic relaxation is related to the energy difference between the two excited electronic states to be coupled as well as the vibrational mode frequencies of benzyl-type radicals.

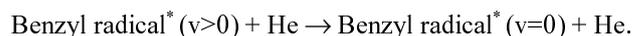
Vibronically excited but jet-cooled methyl substituted benzyl radicals were generated using a technique of corona excited supersonic expansion (CESE)⁹ using a pinhole-type glass nozzle described elsewhere. For observation of the visible vibronic emission spectra of the methyl substituted benzyl radicals, the precursors (reagent grade from the Sigma-Aldrich) toluene, 1,2,3-trimethylbenzene, and 1,2,4-trimethylbenzene were used to produce benzyl, 2,6-dimethylbenzyl, and 3,4-dimethylbenzyl radicals, respectively. The spectral region from 20000 to 23000 cm^{-1} was scanned at increments of 2.0 cm^{-1} over 2 hrs for the vibronic emission spectra in Figure 1. The wavenumber of the spectra was calibrated using the He atomic lines¹⁰ observed in the same spectral region, and is believed to be accurate within $\pm 1.0\text{ cm}^{-1}$.

Although the mechanism for generation and excitation of

benzyl-type radicals is not exactly known, it is quite possible that electrons in a corona discharge excite the most abundant species present, the inert carrier gas He, and subsequently the excited atoms collide with the precursor, resulting in the formation of the radical over a wide range of vibronic states by extracting a hydrogen atom from the methyl group. The processes could be summarized for the case of the benzyl radical as follows:



The mechanism of *o*-xylyl radical formation in solution was discussed in terms of the photodissociation of *o*-xylene.¹¹ The complication of emission spectra at the room-temperature gas phase was illustrated for the *p*-xylyl and *p*-fluorobenzyl radicals.¹² However, the inert carrier gases also quench vibrational fluorescence through a collisional process. The vibrational quenching of the benzyl radical in the D_1 and D_2 states in collision with carrier gas He can be described as follows:



Since there are a great number of collisions inside the nozzle throat prior to the expansion, it is possible to experience collisional relaxation of vibrational energy. Thus, the spectrum exhibits increasing intensity for the transitions from the vibrationless state, resulting in vibrational mode structures in the ground electronic state, which is a result similar to that obtained from the dispersed fluorescence spectra while pumping the origin band of the electronic transition.²

The vibronic coupling between the D_2 and D_1 states plays an important role in observing the transition from the D_2 state, in which coupling the energy difference between the two excited electronic states determines the rate of the relaxation process from the D_2 state to the D_1 state. For the fast relaxation process to occur, the vibrational mode frequencies of benzyl-type radicals should be comparable to the energy difference of the two excited electronic states.

The benzyl radical is the most well-known aromatic species and has been observed by a variety of experimental techniques. Although the theoretical calculation¹³ predicted that the D_2 state is located about 800 cm^{-1} above the D_1 state, as listed in Table 1, and though the D_2 - D_0 transition has comparable oscillator strength to the D_1 - D_0 , we did not

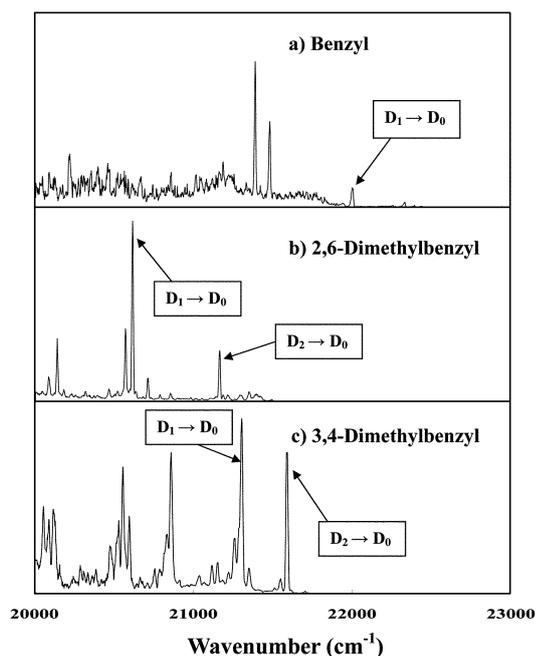


Figure 1. Visible vibronic emission spectrum of (a) benzyl, (b) 2,6-dimethylbenzyl, and (c) 3,4-dimethylbenzyl radicals in the region of the origin band of the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions observed with a technique of corona excited supersonic expansion.

observe any transition from the D_2 state in the emission spectrum. Thus, it is quite possible that the radicals being formed in the D_2 state could cross to the D_1 state via strong vibronic coupling between the two electronic states during expansion, as shown in Figure 2(a).

Although the origin band of the 2,6-dimethylbenzyl radical¹⁴ has recently been reported to be located at 21164 cm^{-1} in the vibronic emission spectrum, the bandshapes exhibit that the bands at 20616 and 21164 cm^{-1} should be reassigned as the origin band of the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions, respectively, because the same vibrational structure in the ground electronic state was observed to the red region of the origin band in both transitions. Thus, we determined and report here, for the first time, that the energy difference between the D_1 and D_2 states is 548 cm^{-1} in the 2,6-dimethylbenzyl radical, which is not sufficient to have efficient vibronic coupling, as shown in Figure 2(b).

The 3,4-dimethylbenzyl radical¹⁵ has recently been identi-

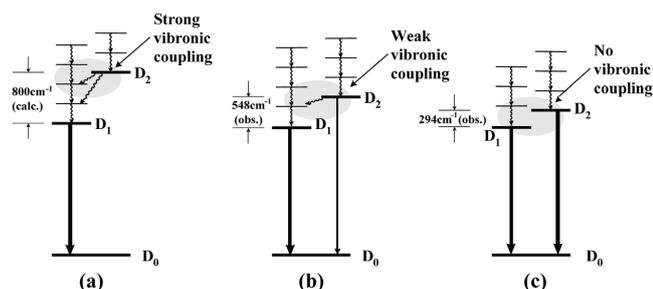


Figure 2. Comparison of the vibronic coupling and the relaxation efficiency among (a) benzyl, (b) 2,6-dimethylbenzyl, and (c) 3,4-dimethylbenzyl radicals.

Table 1. Origin band intensity ratio of the $D_2 \rightarrow D_0$ to the $D_1 \rightarrow D_0$ transitions

Molecules	Difference ^a	Intensity Ratio
Benzyl	800^b	0
2,6-Dimethylbenzyl	548^c	0.28
3,4-Dimethylbenzyl	294^c	0.93

^aEnergy difference between the D_2 and the D_1 states in units of cm^{-1} (in air). ^bTheoretical prediction. ^cObservation.

fied from the emission spectra obtained by the corona discharge of 1,2,4-trimethylbenzene in the visible region. The vibronic spectrum consists of two series of vibronic bands starting from the bands at 21306 and 21600 cm^{-1} , which are the origin bands of the $D_1 \rightarrow D_0$ and $D_2 \rightarrow D_0$ transitions, respectively, followed to lower energies by a series of vibronic bands. The observation of comparable intensity from the transitions between $D_2 \rightarrow D_0$ and $D_1 \rightarrow D_0$ can confirm that vibronic coupling cannot be obtained between the two excited electronic states as shown in Figure 2(c) because the energy difference is too small to have vibronic coupling, as observed in the *p*-chlorobenzyl radical.⁸

In summary, we observed the visible vibronic emission spectra of the benzyl, 2,6-dimethylbenzyl, and 3,4-dimethylbenzyl radicals by a technique of corona excited supersonic expansion using a pinhole-type nozzle. From the comparison of the intensity ratio of the origin bands, it is suggested that the efficiency of vibronic coupling is related to the energy difference between the D_2 and D_1 electronic states as well as the vibrational mode frequencies of methyl substituted benzyl radicals.

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