

Vibronic Emission Spectra of Jet-Cooled *o*-Cyanobenzyl Radical

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Benzyl radical is a prototypical aromatic free radical that has been the subject of numerous spectroscopic studies.¹ It has been well known that this radical emits weak fluorescence in the visible region, arising from the transition to the ground electronic state from the lowest excited electronic state.² Also, many vibrational modes of molecule with similar frequencies make it more difficult to identify mode frequencies without observing high quality spectra.

The electronic structure of benzyl-type radicals is expected to depend on substitution to the benzene ring and molecular symmetry³ that is one of the most important factors for the analysis of spectra, together with the transition intensity. Of many benzyl-type radicals, the assignments of vibronic bands of xylyl radicals have been extensively carried out to determine the vibrational mode frequencies in the ground electronic state.^{4,5} The torsional contribution of the methyl rotor has been obtained from simulation of the rotational contours of the high resolution Fourier transform emission spectra.⁶

As for halogen-substituted benzyl-type radicals, many vibrational modes of fluorobenzyl radicals in the ground electronic state have been determined using different spectroscopic techniques.⁷⁻¹¹ Weakly emitting chlorobenzyl radicals have been recently identified from the vibronic emission spectra, in which the sequence of electronic energy of the lowest excited electronic state exhibits similar tendency to those of chlorotoluenes.¹²⁻¹⁶

Cyanobenzyl radicals are also interesting species in spectroscopy due to the electron-rich substituent. The analysis of the vibronic bandshape of the *p*-cyanobenzyl radical has revealed that the lowest excited electronic state is ²B₂ which is different from other types of benzyl radicals.¹⁷ The vibrational modes in the ground electronic state have been determined from the analysis of vibronic emission spectrum.¹⁸ Very recently, the visible vibronic emission spectrum of *m*-cyanobenzyl radical has been observed in this laboratory for the first time.¹⁹

In this study we report the vibronic emission spectrum of the jet-cooled *o*-cyanobenzyl radical in the D₁ → D₀ transition, which is the first observation in any spectral region. The origin band of the radical has been identified by comparing with that of tolunitriles and chlorobenzyl radicals.

It has been reported that the well-controlled corona

discharge of substituted toluenes seeded in a large amount of inert carrier gas produces corresponding benzyl-type radicals in the excited vibronic states.⁴ The metastable He atoms produced in a corona discharge transfer the excitation energy to the precursor through collisional process to form benzyl-type radicals by breaking off α -hydrogen bond of methyl group.

The supersonic free jet expansion has been proven to be a powerful spectroscopic tool for observation of molecular spectra in the gas phase. The spectral simplification associated with cooling by expansion of inert buffer gas cannot be usually obtained in any other ways. The combination of jet expansion technique with the emission spectroscopy has had an enormous impact on the repertoire of spectroscopic studies of molecular species that cannot be carried out.²⁰

Among many emission sources developed so far for these purposes, the only one giving enough continuous photon intensity for high resolution studies of weak transition is a pinhole-type glass nozzle which has been widely employed for the observation of vibronic emission spectra of transient molecules.²¹⁻²³ This has been also applied to the observation of vibronic emission spectra of jet-cooled benzyl-type radicals in the gas phase.

The technique of corona excited supersonic expansion (CESE) well-developed in this laboratory has been applied to generate the *o*-cyanobenzyl radical from *o*-tolunitrile, in which the experimental setup is very similar to those described previously.²⁴ The *o*-cyanobenzyl radical was produced in a jet from *o*-tolunitrile (reagent grade, Aldrich) and vibronically excited with a large amount of inert carrier gas He in a CESE. The vapors of the precursor at room temperature were entrained in a carrier gas of 2.0 atm of He, although another inert gas Ar was also tried in several experiment. The concentration of vapor in a carrier gas was adjusted for the maximum emission intensity monitored from the strongest band by controlling sample temperature and opening the by-pass valve of the carrier gas. The gas mixture was expanded through the 0.3 mm diameter of pinhole-type glass nozzle.

A blue-green color was the evidence of the presence of the *o*-cyanobenzyl radicals in the jet. The light emanating from the downstream jet area 5 mm away from the nozzle opening was collimated by a 3.8 cm diameter of quartz lens ($f = 5.0$ cm) placed inside the expansion chamber and focussed using a concave mirror onto the emission port of a Fourier transform spectrometer (Bruker IFS-120HR). The instrument was operated with a Quartz-vis beam splitter, a

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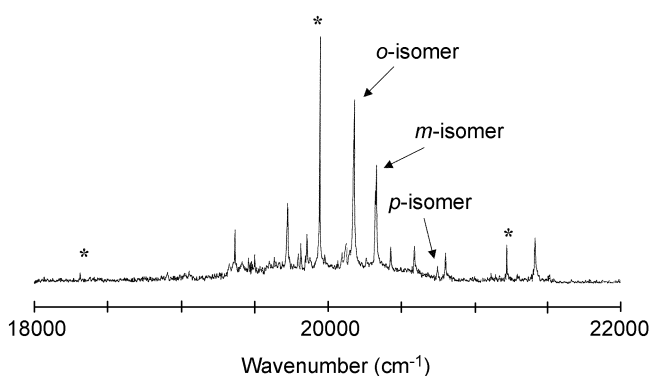


Figure 1. A portion of the visible vibronic emission spectrum of the jet-cooled *o*-cyanobenzyl radical in the $D_1 \rightarrow D_0$ transition recorded with a Fourier transform spectrometer. The origin bands of other isomers have been also observed with weak intensity due to the very low concentration in the sample. The peaks marked with an asterisk in the spectrum indicate the He atomic transitions.

preamplifier (EG&G 113) and a photomultiplier tube (Hamamatsu R106UH) for photon detection.

Survey scans were obtained at low resolution of 2.0 cm^{-1} . Subsequently, after the conditions were optimized, we have obtained higher resolution scans at 0.5 cm^{-1} . The ratio of signal to noise was mainly limited by the source noise, *i.e.*, the fluctuations in the discharge intensity. Thus, a total of 150 scans over 2 hrs were averaged to obtain the final spectra shown in Figure 1. The wavenumber of the spectrum was calibrated using the He atomic lines observed at the same spectral region as the *o*-cyanobenzyl radical and is believed to be accurate within $\pm 0.05 \text{ cm}^{-1}$.²⁵

In cyanobenzyl radicals, the electronic interaction between the CN group and aromatic ring is undoubtedly of second-order compared to the interaction between the methylene group and the ring since the molecule has a planar structure with 7 delocalized π electrons. Thus, *o*-cyanobenzyl radical should exhibit a close relation to those of the benzyl radical of 7 delocalized π electrons and one may be able to relate the two lowest lying electronic states of *o*-cyanobenzyl radical to parent benzyl $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states.

Figure 1 shows a portion of the vibronic emission spectrum of the *o*-cyanobenzyl radical in the $D_1 \rightarrow D_0$ transition. Most of bands are observed with weak intensity in the region $19000\text{--}22000 \text{ cm}^{-1}$. The origin bands of *m*- and *p*-isomers are also observed at the frequencies reported previously, that are believed to be generated from the small amount of isomer impurity in the sample.

With a pinhole-type nozzle in a CESE, vibrational cooling is so efficient at the excited electronic state that no band with noticeable intensity could be observed to the blue of the origin, as in many benzyl-type radicals.²⁶ Thus the vibronic emission spectra observed is similar to the dispersed fluorescence (DF) spectra obtained by exciting the origin band of the electronic transition, in which the spacing of the vibronic bands from the origin band in the spectra represents the vibrational mode frequencies at the ground electronic state.

The origin band of the *o*-cyanobenzyl radical have been determined by comparing with the sequence of origin bands

of tolunitriles, which has been reported to be 35764 , 35812 , and 36222 cm^{-1} for *o*-, *m*-, and *p*- isomers, respectively.²⁷ Chlorotoluenes²⁸ also exhibit similar sequence of origin bands to chlorobenzyl radicals whose origin bands have been observed at 21040 , 21194 , and 21645 cm^{-1} for *o*-, *m*-, and *p*-isomers, respectively. Thus, the strong band at 20171.87 cm^{-1} in this spectrum was assigned to be the origin band of the *o*-cyanobenzyl radical. By comparing with the neighboring origin band of *m*-isomer, it has been found that the emission intensity of *o*-isomer is much weaker than that of *m*-isomer.

In summary, the jet-cooled *o*-cyanobenzyl radical was generated from *o*-tolunitrile seeded in a large amount of carrier gas He using a pinhole-type glass nozzle in a corona excited supersonic expansion (CESE). Vibronically well-resolved visible emission spectra of the *o*-cyanobenzyl radical in the $D_1 \rightarrow D_0$ transition were recorded with a high resolution FT spectrometer, in which the origin band has been determined. Also the possible origin of vibronic bands to the blue of the origin band has been described.

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