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Spectroscopic evidence of α-methylbenzyl radical in the gas phase

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ABSTRACT

We report the observation of the spectroscopic evidence of the α-methylbenzyl radical in a corona excited supersonic expansion using a pinhole-type glass nozzle for the first time. The precursors, toluene, ethylbenzene, and isopropylbenzene, seeded in a large amount of inert carrier gas helium, were electrically discharged to produce benzyl-type radicals as a result of the breaking off of a C–H or a C–C bond from the alkyl chain. The vibronic emission spectra, obtained in the visible region from the precursors, were compared to identify the species generated in the corona discharge of the precursors, from which we found the spectroscopic evidence of the α-methylbenzyl radical.

1. Introduction

The benzyl radical, a prototypical aromatic free radical, has attracted much attention from spectroscopists. Earlier work on benzyl radicals in the visible region have been reported by Schuler et al. [1] and Walker and Barrow [2]. Bindley et al. [3,4] made the first assignments of the vibronic bands from an analysis of the emission spectra of the xylyl radicals produced by an electric discharge of xylenes.

Charlton and Thrush [5] have applied the technique of laser-induced fluorescence (LIF) to the observation of the vibronic emission spectra of benzyl-type radicals as well as to measurements of the lifetime in the excited vibronic states. Recently, Lee group [6–12] extended the assignments of the vibrational modes of benzyl-type radicals by employing the technique of corona-excited supersonic expansion, from which the vibronic emission spectra of many benzyl-type radicals having substituents in the benzene ring have been observed with better resolution and S/N.

The technique of corona excited supersonic expansion (CESE) has been recognized as a powerful spectroscopic technique for observation of vibronic emission spectra of jet-cooled transient species [13]. The spectral simplification and molecular stabilization associated with the expansion of an inert carrier gas cannot be achieved in any other way. The combination of supersonic expansion with the emission spectroscopy has greatly expanded the repertoire of spectroscopic studies of transient molecular species. Of the emission sources utilizing this combination, the one providing enough continuous photon intensity for high resolution studies of the weak transition is the pinhole-type glass nozzle [14,15], which has been widely employed to observe the vibronic emission spectra of transient species. Accordingly, this nozzle has been applied to the observation of the vibronic emission spectra of jet-cooled benzyl-type radicals in the gas phase. Although the mechanism for generation and excitation of benzyl-type radicals in a corona discharge is not exactly understood, the analysis of such vibronic spectra observed provides spectroscopic evidence for the identification the transient species produced.

In this study, we report the first spectroscopic evidence of the α-methylbenzyl radical, which has been believed to play an important role as a reaction intermediate in the chain reaction of alkylbenzenes. From a comparison of the vibronic emission spectra obtained from the different precursors in the corona discharge, the formation of the α-methylbenzyl radical could be confirmed.

2. Experimental

The corona discharge of precursors toluene, ethylbenzene, and isopropylbenzene was carried out using the CESE technique, of which the experimental apparatus is similar to those described elsewhere [16].

Electronically excited but jet-cooled benzyl-type radicals were produced from the corona discharge of the precursors (Aldrich, reagent grade), which were seeded in a large amount of carrier gas helium. The concentration of the precursor in 3 bar of carrier gas was adjusted by opening a by-pass valve for the maximum emission intensity monitored from the strongest band, and was believed to be less than 1% in the mixture. The gas mixture was expanded through the 0.3 mm diameter of the pinhole-type glass nozzle fabricated in this laboratory according to the method described previously [17]. A sharpened long tungsten rod, acting as an anode, was connected to a high-voltage dc power supply in the negative polarity, in which the axial discharging current was 5 mA at a 1500 V dc potential and stabilized using a 150 kΩ current-limiting ballast resister. The Pyrex expansion chamber was evacuated by a 800 l/min mechanical rotary vacuum pump, resulting in a pressure of 2.0 mbar during continuous expansion, with 3.0 bar of backing pressure.

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A weak blue-green colored jet provides the evidence for the formation of the benzyl-type radicals in the $D_1 \rightarrow D_0$ transition. The light emanating from the downstream jet area 5 mm from the nozzle opening was collimated using a quartz lens (d = 3.8 cm, f = 5.0 cm) placed inside the chamber and focused onto the slit of the monochromator (Jobin Yvon U1000, path length = 2.0 m) containing two 1800 lines/mm gratings, and detected with a cooled photomultiplier tube (Hamamatsu R649) and a photon counting system. During the scans, the slits were set to 0.100 mm, providing an effective resolution of about 2 cm^{-1} in the visible region. The spectral region from 18000 to 22000 cm^{-1} was scanned in 2.0 cm^{-1} increment over 2 h to record the spectra shown in Fig. 1. The wavenumber of the spectrum was calibrated using the He atomic lines [18] observed in the same spectral region as the benzyl-type radicals, and is believed to be accurate within ±1.0 cm^{-1}.

3. Results and discussion

It has been demonstrated that a well-controlled corona discharge of substituted toluene seeded in a large amount of inert carrier gas predominantly produces corresponding benzyl-type radicals in the excited vibronic state. Although the mechanism for generation and excitation of benzyl-type radicals was not exactly established, it has been suggested that the metastable He atom produced in a corona discharge transfers its excess energy to the precursor through a collisional process, which generates corresponding benzyl-type radicals by extracting a hydrogen atom from the methyl group rather than the benzene ring. The molecular radicals produced undergo collisional relaxation to lose vibrational energy in the excited electronic states, and eventually emit a fluorescence corresponding to the energy difference between the two vibronic states.

In substituted benzyl-type radicals, the electronic interaction between the substituents and the benzene ring is undoubtedly of the second-order compared with that between the methylene group and the benzene ring, since the molecule has a planar structure with 7 delocalized π electrons, in which the methylene group contributes an electron. Thus, the electronic structure of substituted benzyl-type radicals should exhibit a close relationship to that of the benzyl radical, and one might be able to closely relate the two lowest-lying electronic states of such benzyl-type radicals to the parental benzyl $2^2B_2(D_2)$ and $1^2A_2(D_1)$ states.

The weak visible emission from benzyl-type radicals is believed to arise from transitions to the $1^2B_2(D_0)$ ground state from the close-lying D_2 and D_1 excited electronic states [19], in which the two excited states could be mixed by vibronic coupling [20], and ring substitution is also expected to affect the energies of the excited states differently. Most of the benzyl-type radicals have the lowest excited electronic state of 1^2A_2 [21]. The rapid collisional relaxation from the D_2 and D_1 states transfers most of the population to the D_1 state, thereby rendering observable only the transitions from the D_1 to D_0 state.

Fig. 1 shows a portion of the vibronic emission spectra observed from the transient species formed in the corona discharge of the precursors, (a) toluene, (b) ethylbenzene, and (c) isopropylbenzene in the visible region, with a large amount of inert carrier gas helium, in which spectrum 1(a) is in exact agreement with the vibronic emission spectra of the benzyl radical reported previously [22,23]. The strong $6b_1^0$ and $6a_1^0$ bands and the weak origin band are the characteristics of the benzyl radical, because the corona discharge of toluene produces only the product, benzyl radical, by breaking off of the C–H bond of the methyl group, as illustrated in Fig. 2a. Spectrum 1(b) observed from the corona discharge of ethylbenzene shows the strong vibronic structure of the benzyl radical as well as the weak band at 21778 cm^{-1}, which we assume

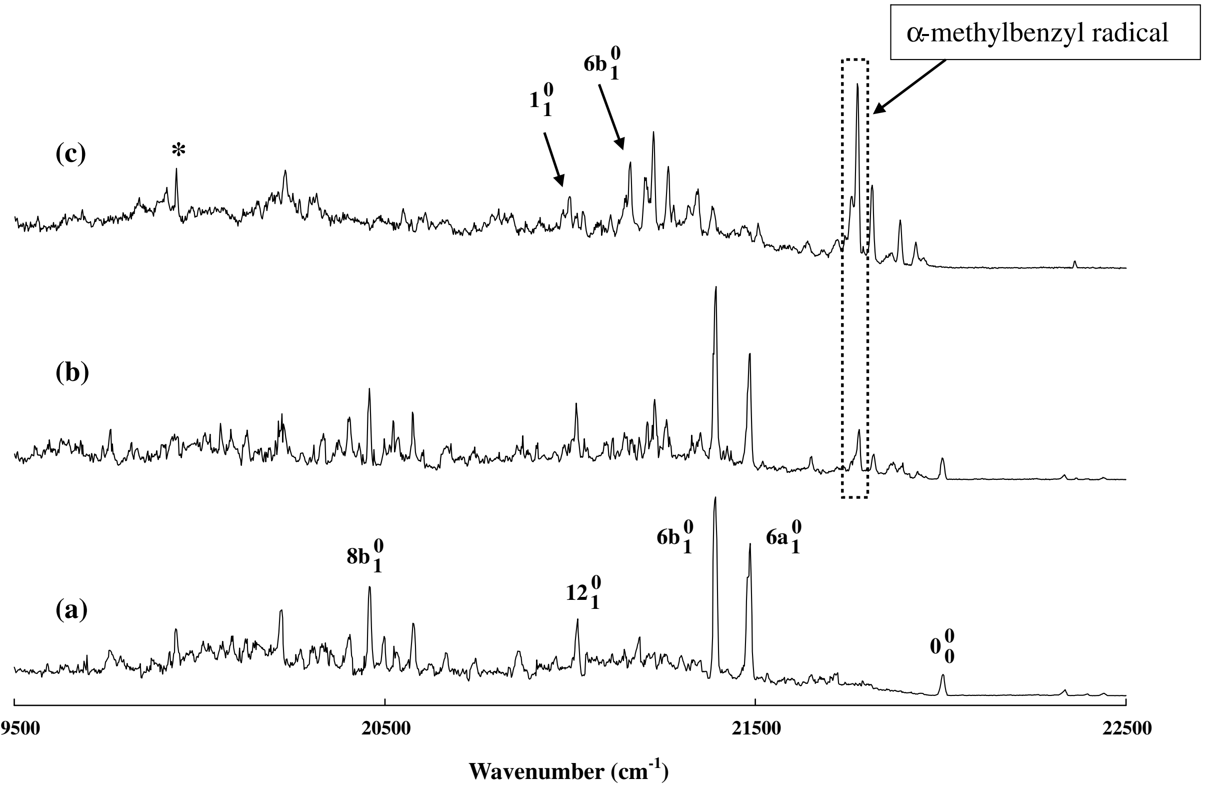

Fig. 1. A portion of the visible vibronic emission spectra in the $D_1 \rightarrow D_0$ transition observed from the corona discharge, using a pinhole-type glass nozzle in a CESE scheme, of the precursors, (a) toluene, (b) ethylbenzene, and (c) isopropylbenzene, seeded in a large amount of inert carrier gas helium. The peak marked by an asterisk in spectrum (c) indicates the He atomic transition.