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Mass resolved excitation spectroscopy of radicals: Benzyl and phenylnitrene

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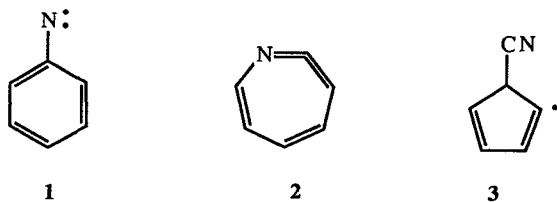
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Two-color mass resolved excitation spectra are obtained for the benzyl and "phenylnitrene" radicals. The spectrum previously assigned to the benzyl radical is generated by a species with mass 91 amu. This finding is consistent with the proposed $C_6H_5\dot{C}H_2$ benzyl radical structure. The origin of this $1^2A_2 \leftarrow 1^2A_1$ transition lies at $21\,997\text{ cm}^{-1}$. The ionization energy for the benzyl radical is $\sim 7.236\text{ eV}$. The phenylnitrene radical spectrum is associated with a species of 90 amu. The phenylnitrene designation is not appropriate for this mass number: the suggested cyanocyclopentadienyl radical species (C_5H_4CN) is consistent with this mass. This radical has an ionization threshold of $\sim 9.05\text{ eV}$. Lifetimes are reported for a number of the vibronic states of both radicals.

I. INTRODUCTION

Identification and spectroscopic study of reaction intermediates and highly reactive molecules have always been of considerable interest because of the central role these species play in reaction mechanisms and dynamics. Radicals have been studied in the gas phase^{1,2} and in low temperature inert matrices³ in order to suppress their high reactivity and build up their concentration. The two radicals discussed in this report, benzyl^{1,4,5} and "phenylnitrene,"^{1,6-8} have been well studied in the past and are prototypic aromatic organic radicals. Benzyl is suggested to be a doublet π radical while phenylnitrene has been suggested to be triplet π radical. In this brief report we present three experimental observations concerning these two species: (1) the first observed mass resolved excitation spectra of benzyl and phenylnitrene radicals; (2) the ionization potentials of both radicals; and (3) the lifetimes of various vibronic excited states as detected by mass resolved excitation spectroscopy. Each of these measurements is important for the identification of these radicals and contributes to their characterization.

Ever since the first observation of the electronic spectrum of gas phase phenylnitrene, concerns have been voiced over the nature of the carrier of the spectrum. Suggestions have included triplet phenylnitrene (1),^{7,8} 1-aza-1, 2, 4, 6-cycloheptatetraene (2)⁹ and cyanocyclopentadienyl (3).^{6,7(b)} These various possibilities have been extensively reviewed in the recent literature.⁶



The possibilities 1, 2, and 3 can be distinguished in principle by high resolution rotationally resolved optical spectroscopy. Moreover, 3 can be distinguished from 1 and 2 by

two-color mass resolved excitation spectroscopy (two-color MRES) since 1 and 2 have a mass of 91 amu while 3 has a mass of 90 amu. Thus, some aspects of the question of the carrier of the so-called phenylnitrene radical spectrum can be addressed by two-color MRES.

Studies of the benzyl radical (4) and related compounds¹⁻⁵ seem to be on a much firmer footing in terms of spectral carrier. The general agreement seems to be that the observed visible absorption and emission spectra are carried by 4, although other possibilities (e.g., the tropyli radical 5) have been suggested.⁹ In particular, the photolysis process employed to generate the radical produces many products of different mass, only a few of which are readily identifiable. Thus not only can rearranged radicals be responsible for some of the observed spectra, but other species (e.g., photo-fragments) may contribute as well. Two-color MRES can be employed to distinguish between some possible spectral carriers, but 4 and 5 have the same mass (91 amu). Nonetheless, even for this case, two-color MRES can be fruitfully employed to study the benzyl radical and ionization potentials can also be obtained by this approach. No mass detected spectrum of either of these radicals has been previously reported to the best of our knowledge.



II. EXPERIMENTAL PROCEDURES

Supersonic jet expansion and two-color mass resolved and fluorescence excitation spectroscopy of radicals differ little from comparable experiments on closed shell molecular systems.¹⁰ The only differences are identification of appropriate precursor systems and photolytic generation of radicals during the expansion process.

Precursors for benzyl radical generation are α -chlorotoluene, toluene, and benzylmethyl ether. Precursors for the phenylnitrene radical are 2-chloroaniline and phenyl iso-

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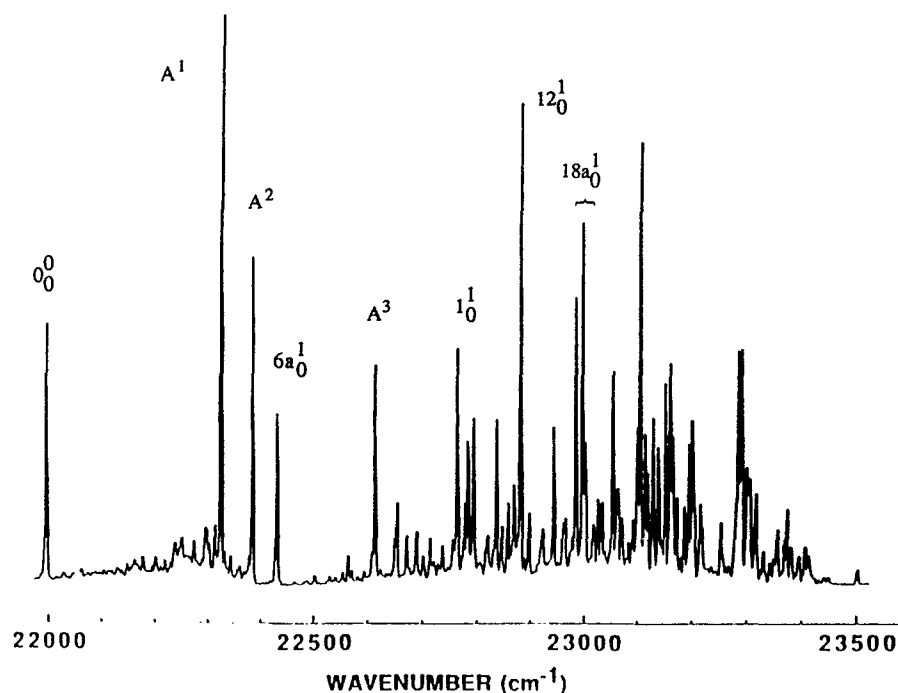


FIG. 1. Two-color mass resolved excitation spectrum of the benzyl radical. The mass channel is 91 amu and the 0_0^0 transition is at $21\,997\text{ cm}^{-1}$. Assignments for some of the possible excited state vibrations are given in the figure.

cyanate. All compounds are purchased from Aldrich and used as supplied. Both radicals are generated at the nozzle throat of a pulsed nozzle by a 100 mJ/pulse, 193 nm beam from an ArF excimer laser. The photolysis beam intersects the molecular jet expansion at the nozzle orifice at $\sim 45^\circ$ angle. Identical spectra are obtained for each radical independent of the precursor employed to generate it.

Timing of the four events of this experiment is accomplished through a series of delay generators and pulse generators. After the valve is triggered the excimer laser is fired

$\sim 7\text{ }\mu\text{s}$ before the Nd:YAG laser in the fluorescence experiment and $\sim 80\text{ }\mu\text{s}$ before the Nd:YAG lasers in the two-color MRES experiment.

Benzyl spectra are obtained with C460 and C440 coumarin dyes in the excitation dye laser and R590 dye in the ionization dye laser. The R590 output is doubled to generate the ionization beam.

Phenylnitrene spectra are obtained with R548 dye in both dye lasers. The output of the excitation laser is mixed with residual $1.064\text{ }\mu\text{m}$ radiation from the pump Nd:YAG laser and the output of the ionization laser is doubled and mixed with residual $1.064\text{ }\mu\text{m}$ radiation from its Nd:YAG pump laser.

In all other respects the experiments follow procedures outlined in our previous publications for two-color mass resolved and fluorescence excitation spectroscopy.¹⁰ Lifetimes are measured in fluorescence excitation studies employing a transient digitizer to generate a time base.

Careful calibration of the time of flight mass spectrometer is achieved with compounds of known mass, spectra, and ionization potential. For the radicals of interest here, toluene (92 amu) and aniline (93 amu) are employed as calibration species.

Ionization Potential of Benzyl Radical

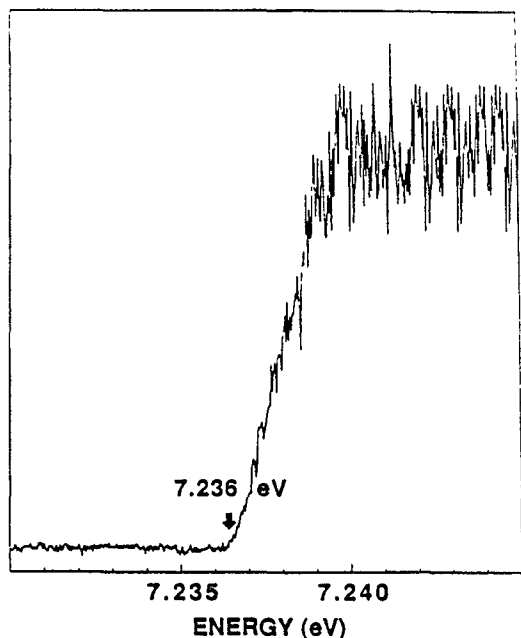


FIG. 2. Photoionization threshold spectrum of the benzyl radical.

III. RESULTS AND DISCUSSION

A. Benzyl radical

The two-color MRES spectrum of the benzyl radical is displayed in Fig. 1. This spectrum is identical with our fluorescence spectrum and published^{1,4,5} spectra with regard to peak positions. The intensities of a number of peaks are different in the mass detected and fluorescence detected spectra, however. In particular, the intensity of the 0_0^0 band of the $1^2A_2 \leftarrow 1^2A_1$ ($D_1 \leftarrow D_0$) transition is much larger in the mass detected than in the fluorescence detected spectrum. This can be due to the Franck-Condon factors for the

Two-Color MRES of the Phenylnitrene Radical

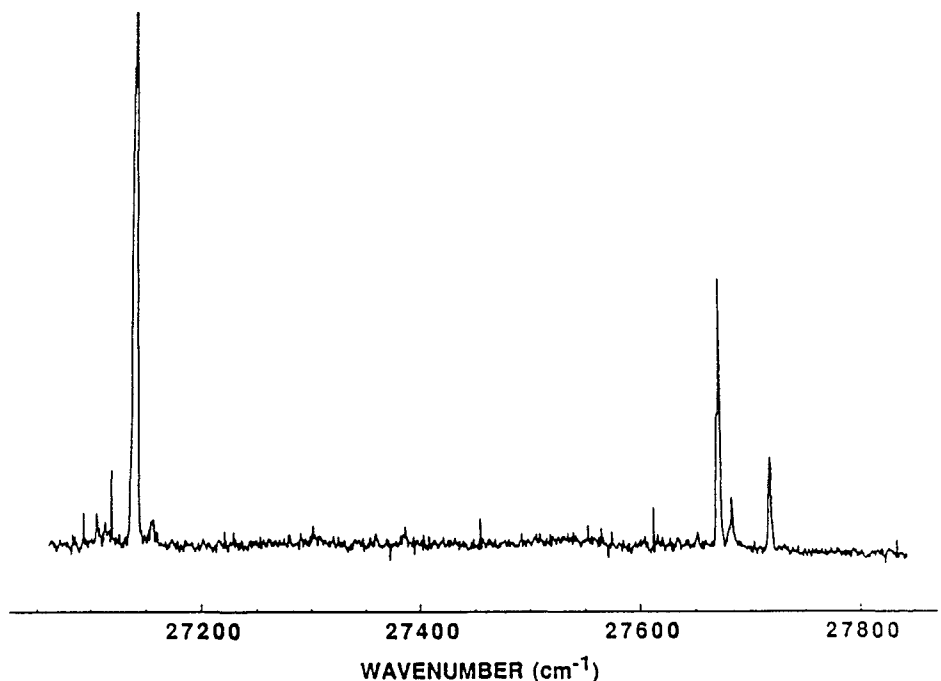


FIG. 3. Two-color mass resolved excitation spectrum of the phenylnitrene radical. The spectrum is detected only in mass channel 90 amu. The 0_0^0 transition is at $27\,142\text{ cm}^{-1}$.

$I \leftarrow 1^2A_2$ transition. The mass of the carrier associated with this spectrum is 91 amu. The measured ionization potential for benzyl is $\sim 7.236\text{ eV}$ as displayed in Fig. 2. These results are obtained for 0_0^0 excitation ($21\,997\text{ cm}^{-1}$) with a $\sim 250\text{ V/cm}$ ion extraction electric field (i.e., 4000 and 3750 V on the two plates separated by $\sim 1.0\text{ cm}$). This value can be compared to that reported in Ref. 11 for a zero field measurement: under these conditions, the benzyl radical ionization potential is found to be 7.2477 eV . A difference between these two results of $\sim 80\text{ cm}^{-1}$ in the correct direction seems quite reasonable. The lifetime of the 0_0^0 state is found to have two components: $\tau_s \sim 0.5\text{ }\mu\text{s}$ and $\tau_L = \sim 1.7\text{ }\mu\text{s}$. This dual exponential behavior has been previously discussed by a number of workers.⁴ These long lifetimes are also consistent with those found for substituted benzyl radicals.⁴

Possible vibrational assignments for some of the vibronic features in Fig. 1 are presented in the figure. Bands marked with A^1 , A^2 , A^3 are reported^{4,5} to arise from vibronic coupling of $6b$, $18b$, and the 2^2B_1 excited electronic state origin which lies close to the 1^2A_2 system observed here. These assignments are suggested based on previous work and comparison with the excited state vibrational modes of toluene.

B. Phenylnitrene radical

Figure 3 depicts the two-color MRES spectrum of the phenylnitrene radical. The spectrum appears in mass channel 90 amu, supporting the argument made recently^{6,7} that the carrier of the phenylnitrene spectrum is actually the cyanocyclopentadienyl radical **3**. The ionization energy for this radical is $\sim 9.05\text{ eV}$ in an electric field of 250 V/cm (see Fig. 4). We expect that this is within 0.01 or 0.02 eV of the zero field adiabatic ionization energy based on the compar-

able results for the benzyl radical. The lifetimes of the three observed vibronic transitions are 53, 45, and 54 ns, in order of increasing energy. These lifetime trends are obtained by two-color threshold ionization and are thus representative of the specific mass channel (90 amu) monitored.

Ionization Potential of Phenylnitrene Radical

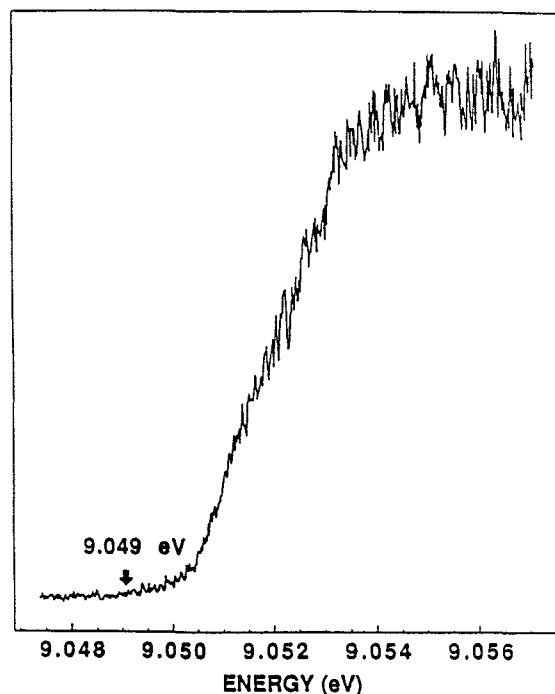


FIG. 4. Photoionization threshold spectrum of the phenylnitrene radical.

IV. CONCLUSIONS

This study has reached a number of conclusions: (1) the carrier of the phenylnitrene spectrum has a mass of 90 amu; (2) a 90 amu mass is most consistent with the previously proposed cyanocyclopentadienyl structure 3; (3) the cyanocyclopentadienyl radical has an ionization potential of ~ 9.05 eV; (4) the lifetimes of different vibronic features of both radicals are measured by two-color mass resolved threshold ionization techniques; (5) the carrier of the benzyl radical spectrum has a mass of 91 amu; (6) a 91 amu mass is consistent with the classical benzyl radical structure 4 and additionally structure 5; and (7) the benzyl radical ionization potential is ~ 7.236 eV. In future reports on these two radicals we will discuss their clusters and reactions.

ACKNOWLEDGMENTS

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