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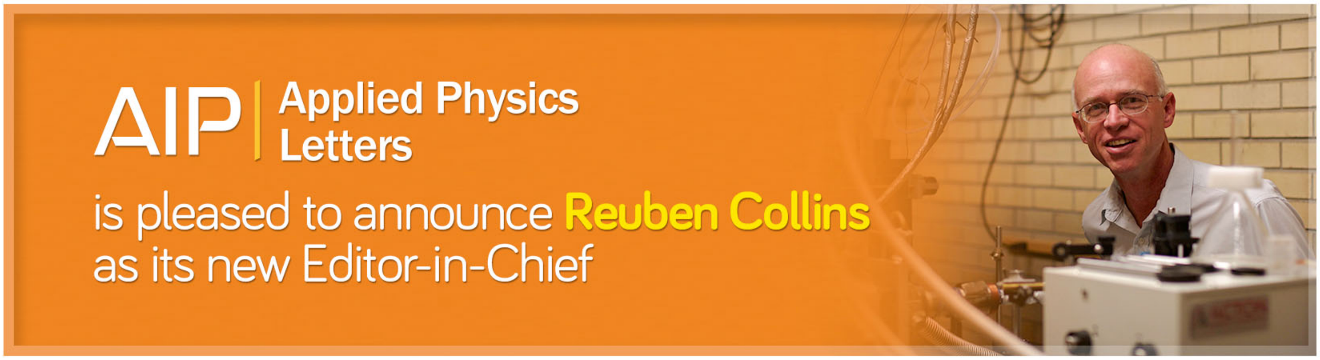

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Time- and frequency-resolved photoionization of the C $^2A_2$ state of the benzyl radical, C_7H_7

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The structure and dynamics of the C $^2A_2$ electronically excited state of the benzyl radical, C_7H_7, were investigated by nanosecond and femtosecond pump-probe photoionization. A free jet of benzyl radicals was generated by flash pyrolysis from the precursors 2-phenylethyl nitrite and toluene. Nanosecond multiphoton ionization spectra show a number of vibronic bands that are excited in the wavelength range of 290–310 nm. At excitation wavelengths of 305, 301, and 298 nm, rapid biexponential decay of the excited states was observed. Lifetimes at the C-state origin (305 nm excitation) are 400 fs and 4.5 ps. The lifetimes decrease with increasing excitation energy. The dynamics can be understood within a two-step internal conversion to the electronic ground state. © *2010 American Institute of Physics*. [doi:10.1063/1.3469787]

I. INTRODUCTION

In this manuscript we describe a combined time- and frequency-resolved spectroscopic investigation of the C $^2A_2$ state of the benzyl radical (C_7H_7). The work is part of our research program aimed at understanding the photochemistry, photophysics, and photodissociation dynamics of reactive intermediates.[1] To characterize the photodissociation of isolated radicals in the laboratory, it is convenient to deposit a well-defined amount of energy in the radical by UV-laser excitation.[2] In most hydrocarbon radicals the electronic energy is rapidly converted into vibrational energy by internal conversion (IC) processes. The resulting vibrationally excited radicals may have enough energy to overcome the barrier to fragmentation. This unimolecular dissociation can be monitored by spectroscopic methods such as photofragment Doppler spectroscopy[2,3] or translational energy spectroscopy.[4] The interpretation of such data within the framework of statistical theories relies on a fast energy redistribution within the molecule and is based on the assumption of a fast nonradiative decay of the photoexcited state to the electronic ground state. However, the primary photophysical processes are in most cases not understood and rapid IC is often assumed, based only on broad and unstructured absorption spectra. Time-resolved pump-probe spectroscopy with short laser pulses allows the direct observation of the primary photophysical processes[5,6] and can address this issue. We demonstrated this approach in the past for a number of hydrocarbon radicals,[7–9] as well as for carbenes.[10,11]

Benzyl is an aromatic radical that is stabilized by a delocalized π-system.[12,13] This radical attracts considerable interest in spectroscopy and kinetics[14–16] because of its role in the combustion of aromatic molecules.[17–19] The relevant electronic states are shown in Fig. 1. The lowest electronically excited states A $^2A_2$ and B $^2B_2$ have been studied in some detail by laser-induced fluorescence and multiphoton ionization.[4,20–22] Rotational resolution was achieved, indicating a long lifetime. Less is known about the higher-lying states. For the D $^2B_2$ state, a lifetime of approximately 150 fs was determined in a previous study.[8] Information on the C $^2A_2$ state is available from an absorption spectrum of photolytically generated benzyl, recorded in a gas cell,[23] and from an emission spectrum in a 77 K cyclohexane matrix.[24] In the present work we probed the excited state by photoion-

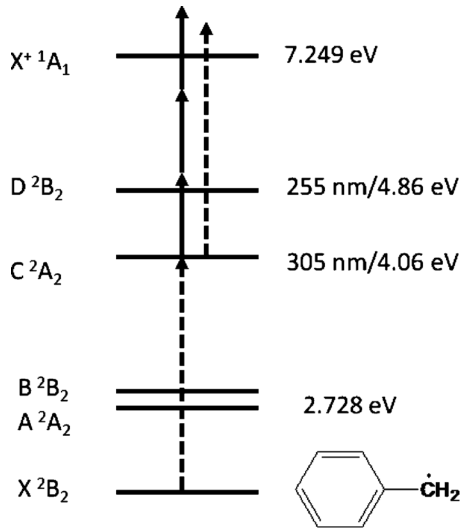

FIG. 1. The electronic states of the benzyl radical. In our nanosecond multiphoton ionization experiments we used a [1+1] excitation-ionization scheme (dashed arrows); in the femtosecond experiments, the excited states were probed by a multiphoton ionization scheme (solid arrows). Energies are taken from Ref. 38.

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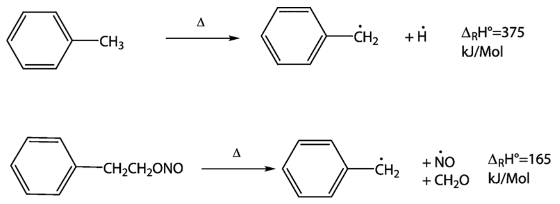

FIG. 2. Two pyrolytic pathways for the generation of benzyl radical from the precursors toluene and 2-phenylethyl nitrite. The heat of reaction for generation from toluene is based on literature values (Ref. 38), the one for generation from 2-phenylethyl nitrite was computed by density functional theory, using the B3LYP functional and a $6\text{-}311G^{****+}$ basis set.

ization, which allows mass-selective detection of radical signals with high sensitivity. The ionization energy of benzyl is reported as 7.249 eV.[25]

II. EXPERIMENTAL

Benzyl was generated by flash pyrolysis, a technique successfully applied in the study of numerous reactive intermediates.[26] As depicted in Fig. 2, the two precursors 2-phenylethyl nitrite and toluene were employed. Toluene was acquired from Aldrich and used without further purification; 2-phenylethyl nitrite was synthesized following the literature procedure.[27] The precursors were seeded in 2 bar of helium and expanded through a pulsed solenoid valve (General Valve, series 9) with an electrically heated SiC pyrolysis tube mounted at the valve orifice. The valve was water cooled to achieve stable operation at high pyrolysis temperatures. It was operated at 100 Hz in the femtosecond experiments and at 10 Hz in the nanosecond experiments.

All experiments were carried out in a differentially pumped molecular beam apparatus. After passing a skimmer with 1 mm open diameter, the molecular beam entered the interaction region of a Wiley–McLaren time-of-flight mass spectrometer. Femtosecond experiments were performed in the application laboratory of the Max-Born-Institute in Berlin. A commercial Ti:sapphire oscillator with 60 fs pulse duration was regeneratively amplified to millijoule power levels at 1 kHz. The experimental repetition rate was limited by the pulsed valve and only one out of ten laser shots was used for the spectroscopy. For the pump beam, we employed the frequency mixed and frequency doubled output of an optical parametric generator giving 0.2–1.8 μJ light in a wavelength range of 298–305 nm. For the probe beam, a small part of the amplified 800 nm fundamental was utilized. At least three 800 nm photons are required to ionize benzyl. To optimize the pump-probe contrast of the photoexcitation-ionization process, the laser beams were attenuated by factors of 3–30 using neutral density filters. The two beams were focused with a 750 mm spherical mirror to spot sizes greater than 100 μm. The laser cross-correlation of 140 fs full width at half maximum (FWHM) and the zero in time were determined inside the spectrometer by measuring time dependent signals of calibration molecules. A translation stage with submicrometer resolution was used to delay the probe beam. At each delay time, the ion signal was acquired for at least 200 shots.

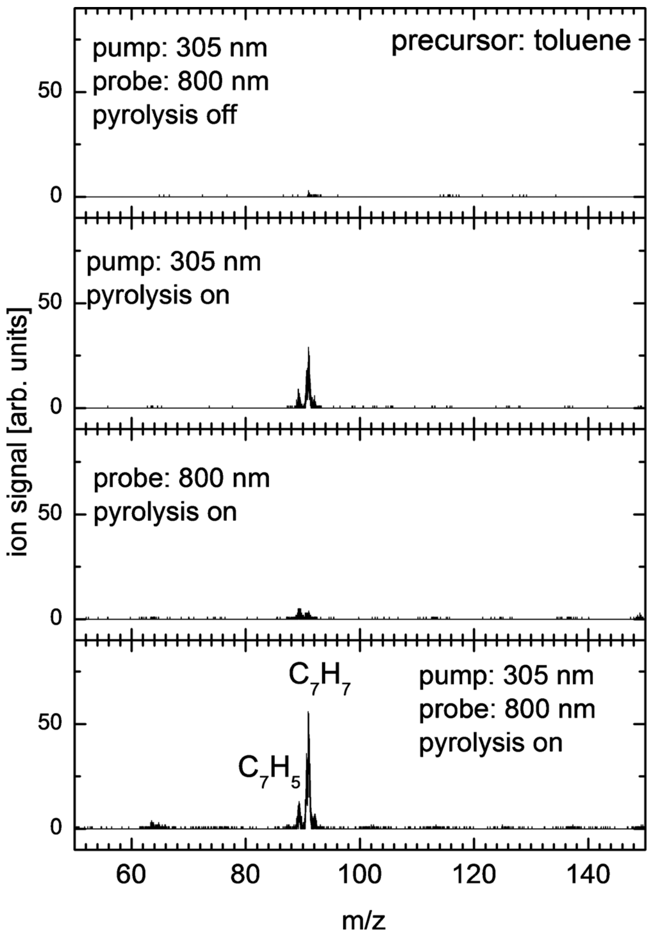

FIG. 3. Typical mass spectra of pyrolyzed toluene, photoionized by 305 nm pump and 800 nm probe pulses at the zero in time. Without pyrolysis (top trace), no signal is observed. With pyrolysis, a benzyl signal at $m/z=91$ appears in the pump-only and probe-only signals (center traces) and the pump-probe signal (bottom trace).The pyrolysis of 2-phenylethyl nitrite gave comparable yields of benzyl radical.

Nanosecond one-color resonance-enhanced multiphoton ionization (REMPI) experiments were carried out in a similar apparatus that has been described in detail before.[28] The frequency-doubled output of a nanosecond-dye laser, pumped by the second harmonic of a Nd:yttrium aluminum garnet laser, produced laser pulses in the wavelength range of 290–307 nm. Unfocused pulses with a typical energy of 1.5 mJ were used for photoexcitation and ionization in a one-color process.

III. RESULTS AND DISCUSSION

A. Mass spectra

Figure 3 presents the mass spectra of unpyrolized and pyrolized toluene, ionized at the zero in time using femtosecond 305 nm pump pulses and 800 nm multiphoton probe pulses. The pump beam and probe beam were both attenuated to minimize one-color signals. The mass spectrum without pyrolysis (top trace) shows only a weak benzyl signal originating from photolysis or dissociative ionization. When the pyrolysis is turned on, an intense benzyl signal appears at $m/z=91$. A significant pump-only signal due to resonant two-photon ionization with 305 nm is visible, but the probe-

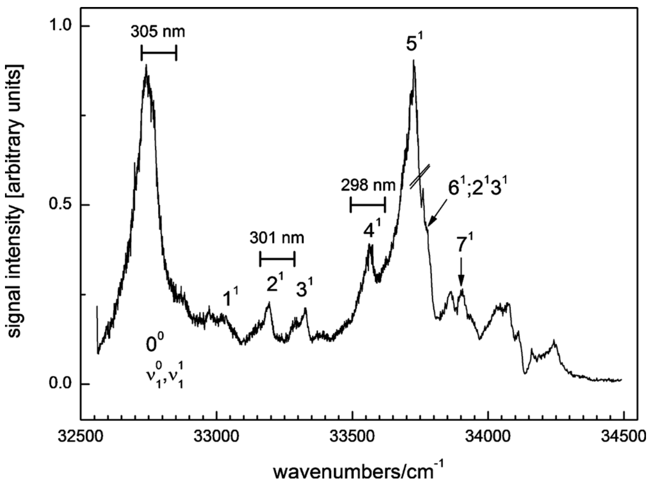

FIG. 4. [1+1] REMPI spectrum of the C $^2A_2 \leftarrow X\ ^2B_2$ transition in benzyl (trace is composed of three separate scans). A high resolution scan of the origin (not shown) shows partially resolved hot and sequence bands.

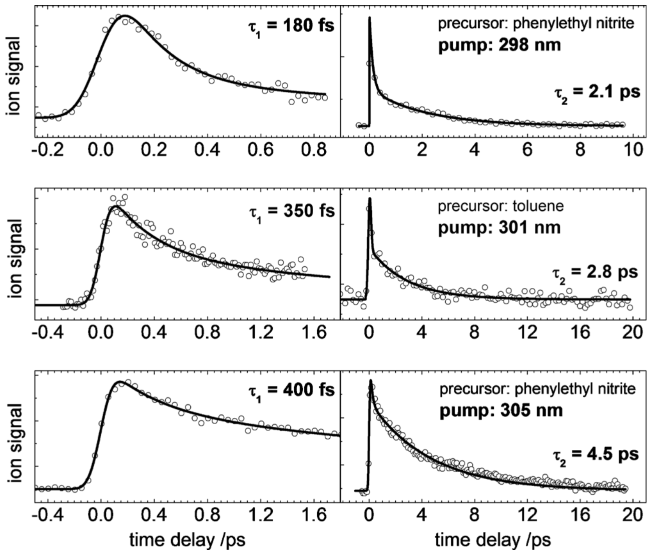

FIG. 5. Time-resolved ion signals of benzyl at three different excitation wavelengths. A biexponential decay with subpicosecond lifetime τ_1 and picosecond lifetime τ_2 is observed in all cases.

only signal is negligible. The two-color pump-probe signal is larger than one-color signals by a factor of approximately 3. A small signal at m/z=89 is noticeable, but is missing in corresponding mass spectra recorded using the 2-phenylethyl nitrite precursor, which otherwise looks very similar. The origin of this signal will be discussed below. Note that toluene does not absorb at 305 nm and thus does not appear in the spectra. A small signal at m/e=92 is due to the ^{13}C isotopomere of benzyl and shows the same excited state lifetimes.

B. Nanosecond REMPI spectrum

The one-color REMPI spectrum for the C $^2A_2 \leftarrow X\ ^2B_2$ transition is depicted in Fig. 4. The spectrum shows several broad vibronic bands which reproduce the band positions reported in the absorption spectra by Ward.[23] The matrix emission spectra by Grajcar and Leach[24] yield ground-state vibrational frequencies. The nomenclature and the vibrational band assignments in these papers are based on a comparison with the spectrum of toluene[24] and will be followed here. The most intense bands can be assigned to the C-state origin at 32 760 cm^{-1}, and the ν_5 fundamental (C–C valence mode "1" in toluene) at 33 691 cm^{-1}. A scan of the origin band at higher resolution (not shown) revealed several subbands that can be assigned to hot- or sequence-band transitions also reported in the absorption spectrum. Several other bands correspond to fundamentals of the ν_2 and ν_3 modes (the "6a" and "6b" ring deformation modes in toluene), as well as the ν_4 mode (C–C mode "12" in toluene). Further bands were observed by Ward and tentatively assigned to combination bands. They are indicated in Fig. 4 where applicable. The FWHM of the absorption bands is hard to estimate from the published photo plates, but Ward reported a FWHM of 20 cm^{-1} for most bands. In our data, the FWHM for the ν_2 and ν_3 modes agrees with the value from Ward, but other bands seem to be broader due to an overlap between neighboring bands. This might indicate unusually warm conditions in our pyrolytic experiment, but the print quality of the published photo plates makes a detailed comparison of the bandwidths difficult.

There is a second C_7H_7 isomer, the tropyl radical, with D_7h symmetry. The heat of formation for tropyl lies ≈70 kJ/mol higher than that of benzyl radical.[29] Nevertheless, one might worry about a possible isomerization in the pyrolysis nozzle. UV/IR hole burning spectra of photolytically produced benzyl were recorded at 305 nm by Satink *et al.*[30] The resulting infrared spectrum of isolated benzyl proved the assignment of the 305 nm transition to benzyl. The vibrational frequencies of several modes are similar to the ones observed in the absorption spectra of Ward and the REMPI spectra reported here. Note that the electronic spectroscopy of tropyl has been investigated as well,[31] yielding quite different results. We can therefore assign all our data to the benzyl radical and exclude any contribution from the tropyl radical.

C. Time-resolved traces

The excited state lifetimes were studied at three different excitation wavelengths of 305, 301, and 298 nm, corresponding to the C-state origin, and the ν_2 and ν_4 fundamental modes. Due to the large bandwidths of the femtosecond pulse, neighboring bands may be excited to some extent. The estimated spectral FWHM of the excitation pulses of 150–200 cm^{-1} is indicated by the bars in Fig. 4. The delay traces of the benzyl mass channel are summarized in Fig. 5. The observed excited state decay is biexponential at all three excitation wavelengths and the two-color signal decays to nearly zero within a delay of 10–20 ps. We therefore carried out short scans with closely spaced data points (left hand side) to extract the fast time constant τ_1 and longer scans (right hand side) to extract the longer time constant τ_2. Both time constants decrease with increasing excitation energy: at the C-state origin (305 nm) we observe values of τ_1 =400 fs and τ_2=4.5 ps, but with 298 nm excitation the values are reduced by more than a factor of 2 to $\tau_1=180$ fs and $\tau_2=2.1$ ps, respectively. The radical precursor employed in each case is indicated in the spectra. At 305 nm, the dynamics were investigated with both precursors and gave similar results. The measured decay times τ_1 at 305 and 301 nm are in agreement with the width of the bands observed in absorption and REMPI spectra. At 298 nm this agreement is less obvious because the 4^1 and 5^1 bands overlap in the REMPI spectrum. The time constant τ_1 therefore reflects the depopulation of the initially excited state. We assign the decay to an IC, most likely to excited vibrational states of the strongly coupled A/B states. The decreasing τ_1 lifetime with increasing excitation energy may reflect the increasing density of vibronic A/B states. In particular, the excitation of ring deformation modes may lead to enhanced overlap between electronic states of different symmetry and thereby accelerate the nonradiative decay in aromatic molecules. This has been shown for several heteroaromatic systems and DNA bases.[32,33] The time constant τ_2 would then correspond to a second IC from the A/B state to the electronic ground state, leading to highly vibrationally excited benzyl. Thus, we assume a stepwise deactivation of benzyl. Note that parallel processes $C \rightarrow A/B$, $C \rightarrow X$ would result in a single time constant. The interpretation of a stepwise deactivation agrees with the work of Troe, Hippler, and co-workers, who studied bimolecular reactions of internally hot benzyl radicals,[15,34] produced by direct photoexcitation of benzyl. With the second IC, the ion signal decays to almost zero. This is common in time-resolved spectra after IC to the ground state, because the Franck–Condon factors between the vibrationally excited ground-state levels and low ionic states are generally poor. In our earlier work on the D $^2B_2$ state[8] we observed a time constant of 150 fs for deactivation at 255 nm. A residual signal was also present, but the scan lengths and the signal-to-noise ratio were insufficient to determine a second time constant or deduce information on the final state. The dynamics of the D-state observed before thus fits the picture outlined here.

Nevertheless, we should discuss dissociation and photochemical isomerization to tropyl as two possible alternative explanations for the second time constant. Photodissociation forming fulvenallene $(C_7H_6)+H$ is endothermic by +355 kJ/mol (3.69 eV).[35] The photoexcitation described here deposits more than 4 eV of energy in the molecule and the reaction is expected to occur in the electronic ground state, but on a nanosecond time scale. Since we do not observe any ion signals at the mass of C_7H_6 at delay times up to 20 ps, we consider a photochemical reaction from the electronically excited state unlikely. A photochemical isomerization to tropyl, on the other hand, yields ions of the same mass and cannot be completely ruled out based on our experimental results. Time-resolved photoelectron spectroscopy gives more information on the final state of the process[6,36] and might thus be a suitable method to conclusively address the issue of isomerization.

As mentioned in the discussion of the mass spectra, a signal at $m/z=89$ was detected in the experiments using toluene as a benzene precursor. This mass corresponds to a C_7H_5 species. Upon 301 nm excitation, a biexponential decay with time constants of $\tau_1=90$ fs and $\tau_2\approx 2$ ps was observed. Since the time constants are different from those observed for benzyl, dissociative photoionization can be ruled out as the origin of this mass peak. Therefore, C_7H_5 is formed as a side product in the pyrolysis and shows a distinct excited state decay. However, there are several isomers of this composition with comparably low isomerization barriers between them,[6,37] rendering a discussion of the dynamics difficult.

IV. SUMMARY AND CONCLUSION

We have determined the excited state lifetime of the C $^2A_2$ state of the benzyl radical as a function of excess energy. Time-dependent ion traces were fitted by a biexponential decay. At the origin of the C-state, excited state lifetimes of 400 fs and 4.5 ps were assigned to sequential internal conversion processes from the C-state to the A/B states and to the ground state. However, a photochemical isomerization to tropyl in the excited state cannot be ruled out. With increasing excitation, the lifetimes shorten considerably. With 301 nm excitation, mostly the ν_2 vibronic band is excited, which resembles the 6a deformation mode in toluene. Time constants of 350 fs and 2.8 ps are observed in this case. At 298 nm the time constants are 180 fs and 2.1 ps and predominately the ν_4 mode is excited, which resembles the "mode 12" in toluene. In addition we observed a decay trace for a species with the composition C_7H_5. Since several isomers of the same composition are known to exist, the carrier of the signal is not yet identified.

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