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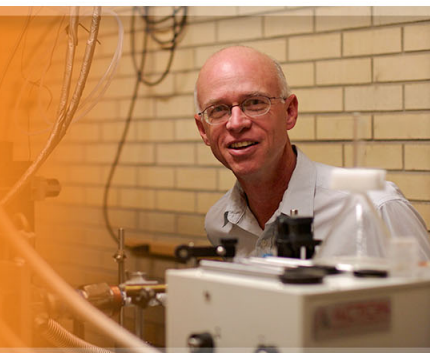
Excited-state decay of hydrocarbon radicals, investigated by femtosecond time-resolved photoionization: Ethyl, propargyl, and benzyl

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The excited state decay of the hydrocarbon radicals ethyl, C_2H_5; propargyl, C_3H_3; and benzyl, C_7H_7 was investigated by femtosecond time-resolved photoionization. Radicals were generated by flash pyrolysis of *n*-propyl nitrite, propargyl bromide, and toluene, respectively. It is shown that the $2\,^2A'$ ($3s$) Rydberg state of ethyl excited at 250 nm decays with a time constant of 20 fs. No residual signal was observed at longer delay times. For the $3\,^2B_1$ state of propargyl excited at 255 nm a slower decay with a time constant 50 ± 10 fs was determined. The $4\,^2B_2$ state of benzyl excited at 255 nm decays within 150 ± 30 fs. © *2005 American Institute of Physics.*
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I. INTRODUCTION

The unimolecular dissociation of hydrocarbon radicals is of considerable interest for the chemistry of reactive environments, in particular, combustion engines[1] or interstellar space.[2] To characterize the reactions of isolated radicals in the laboratory, a well-defined amount of energy can be deposited in the radical by UV-laser radiation. The resulting electronic excitation is typically converted into vibrational energy by internal conversion (IC) and subsequently leads to dissociation. The unimolecular dissociation can be monitored either by photofragment Doppler spectroscopy[3–5] or by translational energy spectroscopy.[6] The interpretation of such data often assumes a fast redistribution of energy within the molecule, including a fast nonradiative decay of the photoexcited state to the electronic ground state. For most hydrocarbon radicals those primary photophysical processes are not understood and the assumption of rapid IC is solely based on the observation of broad and unstructured absorption spectra. Time-resolved pump-probe spectroscopy[7] allows the direct observation of the primary photophysical processes and can address this issue. This was demonstrated for the allyl radical (C_3H_5), where time-resolved photoelectron spectroscopy showed that the electronically excited radicals return to the ground state surface within 20 ps or less by internal conversion in a two-step process.[8,9] Allyl subsequently dissociates, preferentially to allene+H, following a mechanism appropriately modeled by statistical reaction theories.[10]

In alkyl radicals on the other hand it is questionable whether purely statistical models can explain the observed dissociation rates: An investigation of the hydrogen atom loss from ethyl radical (C_2H_5) upon excitation into the $2\,^2A'$

state, nominally the $3s$ Rydberg state, yielded a rate constant more than four orders of magnitude slower than expected from simple RRKM calculations.[11] In similar experiments on *t*-butyl radical (C_4H_9), a dissociation rate in agreement with statistical theories was measured at excitation wavelengths above 330 nm, however, the rate dropped by an order of magnitude upon changing the excitation wavelength to 325 nm.[12] It is an open question, whether the discrepancy between theoretical expectations and experimental observations might be attributed to slow IC processes. For this reason we investigated the dynamics of the initially excited $2\,^2A'$ state in ethyl by femtosecond time-resolved photoionization. Due to its detection sensitivity and mass selectivity this method is perfectly suited to examine reactive species.

Compared to alkyl radicals, the photodissociation dynamics of the unsaturated 2-propynyl radical (C_3H_3, commonly termed propargyl) is better understood and, like allyl radical, can be well described by statistical models. Here, photofragment Doppler spectroscopy showed cyclopropenylidene (*c*-C_3H_2) to be the major reaction product at low excess energies, formed on a nanosecond time scale.[13] We nevertheless decided to characterize the time scale and mechanism of the internal conversion after optical excitation to obtain a complete picture of the propargyl photochemistry. The additional data should help to decide whether there exists a fundamental difference in the photophysics of conjugated hydrocarbon radicals with a π-electron system versus nonconjugated radicals.

Finally, we investigated benzyl (C_7H_7), a relatively stable aromatic radical that attracts considerable interest in spectroscopy and kinetics because of its role in the combustion of aromatic molecules. Internally hot benzyl is often prepared by electronic excitation,[14,15] again assuming fast IC, however, the excited state dynamics has not yet been studied.

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II. EXPERIMENT

All experiments were carried out in a differentially pumped standard molecular beam apparatus, equipped with a Wiley–McLaren time-of-flight mass spectrometer. A suitable radical precursor seeded in 1.5 bar helium employed as a carrier gas was expanded through a pulsed solenoid valve (General Valve, series 9), operated at 100 Hz with an electrically heated SiC tube mounted at the exit. The radicals were generated by supersonic jet flash pyrolysis, a method known to produce an intense and clean molecular beam of internally cold radicals. The details of the design of the pyrolysis source are described in the literature.[16] Ethyl iodide, commercially obtained from Aldrich, and *n*-propylnitrite synthesized following the literature procedure[17] served as precursors for ethyl radicals, propargyl bromide, C_3H_3Br (Aldrich) for propargyl, and toluene (Aldrich) for benzyl. While ethyl iodide and toluene were employed without further purification, commercial propargyl bromide contains 20% toluene as a stabilizer which was distilled off before use. Nevertheless residual toluene was detected in the experiment.

The molecular beam entered the interaction region after passing a 1 mm skimmer. Here it was crossed by two laser beams for molecular excitation and ionization. The laser beams were generated from a commercial Ti:sapphire oscillator (Spectra Physics TSUNAMI), regeneratively amplified to millijoule levels at 1 kHz (Spectra Physics SPITFIRE). For excitation we used the frequency mixed and doubled output of an optical parametric generator (Light Conversion TOPAS, model $4/800/f$) giving $0.5-1$ μJ light at 250 and 255 nm. For ionization we used either the frequency mixed and doubled output of a second optical parametric generator with $1-2$ μJ at 280 nm (Light Conversion TOPAS, model $4/800/f$) or part of the amplified 800 nm fundamental. While the 250 and 800 nm beams were overlapped collinearly, the 250 and 280 nm beams were overlapped at a small angle ($<0.5°$). To optimize the pump-probe contrast, the laser beams were attenuated by factors of 3–30, using neutral density filters. The two beams were focused by a 300 mm lens to spot sizes of $\leqslant100$ μm. The temporal characteristics of the laser pulses were determined by measuring the laser cross correlation (cc) within the spectrometer. We found a Gaussian cc with a $130-140$ fs full width at half maximum (FWHM). To obtain time-dependent ion signals, a translation stage with submicrometer resolution was used to delay the probe beam. To obtain a time-resolved pump-probe spectrum, the delay line was scanned 12 times across the pump-probe delays of interest with data being taken every 25 fs. At each delay time, the ion signal was acquired for 200 laser shots. Typically three such experiments were averaged to obtain the decay traces shown below.

III. RESULTS AND DISCUSSION

A. Ethyl, C_2H_5

As mentioned in the Introduction, the photophysics and photochemistry of the ethyl radical are not well understood. The lowest electronically excited state is the $2\,^2A'$ state, nominally the 3*s* Rydberg state, the corresponding absorption band with a maximum at 246 nm being broad and unstructured.[18,19] If this state decays by IC to the electronic ground state as suggested, the subsequent dissociation to $C_2H_4 + H$ is expected to proceed within some picoseconds, as calculated by statistical theories[20,21] based on a heat of reaction, $\Delta_R H° = 159$ kJ/mol and a reverse barrier of around 10 kJ/mol. However, time-resolved detection of the H-atom photofragment[11] yielded a rate constant on the order of 10^7 s^{-1}. H-atom loss occurred exclusively on the methyl group.[11,22] In their Rydberg time-of-flight spectra Amaral, Xu, and Zhang[23] observed slow H atoms with a translational energy distribution similar to the earlier experiments,[11] but also a fast component assigned to direct excited state dissociation. Electronic structure computations suggested the latter process to proceed via a bridged intermediate.[24] First femtosecond time-resolved experiments[25] reported three decay times with time constants of 40 fs, 370 fs, and 6.6 ps. In this study, the radicals were generated photolytically from ethyl iodide by absorption of one pump photon. The authors assigned the three decay times to the excited-state lifetimes of ethyl iodide, excited-state dissociation of ethyl, and to the time for unimolecular dissociation of ground-state ethyl radicals. The time-dependent signal thus represents a convolution of various time-dependent processes in the radical and the precursor molecule that are not easily separated.

In our experiments, we may also expect unpyrolyzed precursor to be photolytically cleaved to generate radicals with an unknown, but probably significant internal energy distribution. To control such effects in the experiments discussed below, we used two different precursors: ethyl iodide and *n*-propyl nitrite (n-C_3H_7ONO). We found negligible photolytic generation of ethyl from the latter. Therefore, we will concentrate on the results obtained by pyrolysis of *n*-propyl nitrite. However, our experiments using pyrolysis of ethyl iodide as a radical source yielded data qualitatively very similar to those obtained with *n*-propyl nitrite, indicating only a small contribution from photolytically generated ethyl. The cold beam of ethyl radicals was then excited to the $2\,^2A'$ (3*s*) state at 250 and 255 nm, and subsequently ionized either in a $[1+1']$ process with a 280 nm probe photon, or by multiphoton ionization using the 800 nm fundamental. Both ionization schemes gave identical results and in the following we will show the results for 800 nm multiphoton ionization because of the better signal-to-noise ratio. The mass spectra recorded at the zero in time, $t=0$ with the pyrolysis on (upper trace) and off (lower trace) are presented in Fig. 1. No one-color background signal from pump or probe laser is present in either spectrum. The mass spectrum without pyrolysis (lower trace) shows that photolysis of *n*-propyl nitrite at 250 nm leads predominantly to *n*-propyl ($m/z=43$)+NO_2, thus the background of photolytically produced ethyl is negligibly small. Upon pyrolysis (upper trace) the ethyl signal increases by more than an order of magnitude. The precursor is cleaved according to

$$n\text{-}C_3H_7ONO \rightarrow C_2H_5 + CH_2O + NO,$$

thus nitric oxide and formaldehyde are formed as side products, both with $m/z=30$. From the 3*s* state, ethyl radicals with some internal energy can barely be ionized by two
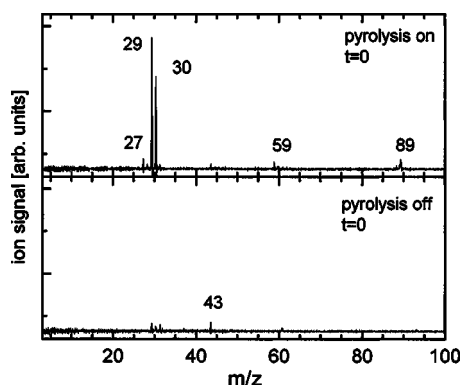
FIG. 1. Typical mass spectra of n-propyl nitrite, recorded at the zero in time, using 250 nm pump and 800 nm probe. Without pyrolysis (lower trace) only a negligible amount of ethyl is visible. When the pyrolysis is turned on (upper trace) intense signals at $m/z=29$ (ethyl) and 30 (NO, CH_2O) appear.

800 nm photons,[26,27] but since Franck–Condon factors are small at threshold due to a large geometry change from C_s to C_{2v} symmetry, ionization by at least three photons is more likely.

Figure 2 shows the time-dependent ion signal in the mass channels $m/z=29$ (open circles) and 30. The $m/z=30$ signal is fitted by a Gaussian with a FWHM of 127 fs, indicating a nonresonant ionization. We assume that both NO and CH_2O contribute to this signal. While NO does not have excited electronic states below 227 nm, formaldehyde absorbs weakly around 250 nm. Since the integrated oscillator strength of the $n\pi^*$ transition[28] is only around 10^{-4}, resonant processes are not expected to play an important role. Thus the $m/z=30$ signal conveniently provides an instrument response function (irf) and an accurate zero in time for each pump-probe spectrum. Inspection of the ethyl signal shows that the curve maximum is shifted to positive delay times. A satisfactory fit of the ethyl signal was only obtained by convoluting the irf with a monoexponential decay with a time
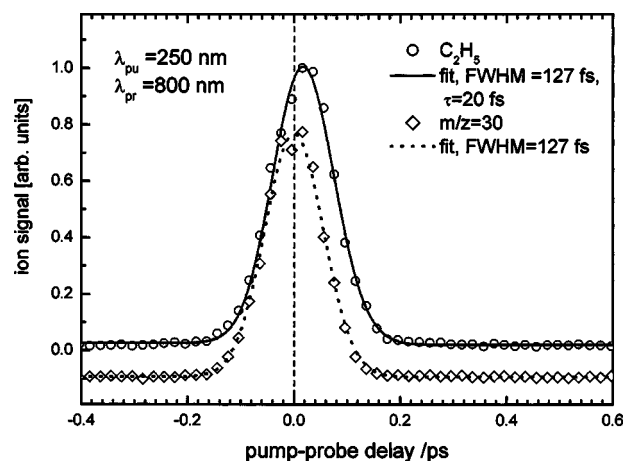

FIG. 2. Time-dependent ion signal of ethyl, $m/z=29$ (open circles) and $m/z=30$ (NO, CH_2O, open diamonds, shifted by 0.1 arb. units for ease of viewing). Positive delay times correspond to the pump pulse preceding the probe pulse. The $m/z=30$ signal was fitted by a Gaussian with a FWHM$=127$ fs (dotted line) and provided an instrument response function (irf) as well as a zero in time. An accurate fit of the ethyl signal (full line) was only possible when the irf was convoluted with a monoexponential decay of $\tau=20$ fs.

constant $\tau=20\pm3$ fs. We assigned this time constant to the lifetime of the ethyl $3s$ Rydberg state. Note that a deconvolution of such a small lifetime is only possible because the zero in time was determined independently within the same experiment.

The data recorded using $\lambda_{pr}=280$ nm gave similar results. The $m/z=30$ signal was fitted well by a Gaussian, in this case with a FWHM$=140$ fs. At this wavelength, the $m/z=30$ signal is predominantly due to NO, which can be ionized in a $[1+1']$ process, but not CH_2O, which would require a $[1+2']$ process. A good fit to the ethyl data required again inclusion of an additional exponential decay function with $\tau=20\pm10$ fs. The larger error bars in this case are due to the inferior signal-to-noise ratio. Identical lifetimes were observed for excitation with 250 and 255 nm. Absorption of five photons at 800 nm should lead to dissociative ionization,[29] forming vinyl cation, $C_2H_3^++H_2$. A small signal at $m/z=27$ is indeed visible in the upper trace of Fig. 1. It can be described by the same time dependence as ethyl, thus confirming the occurrence of dissociative ionization. On the other hand, the small size of the signal indicates that this high-order process is only a minor channel within our experimental conditions.

Secondary pyrolysis of the formaldehyde generated from the precursor can produce formyl radical, HCO, another important combustion intermediate that also appears at $m/z=29$, like ethyl. However, contributions of HCO to the time-dependent signal can be ruled out for two reasons: First, experiments using C_2H_5I as a precursor yielded qualitatively similar results. Second, the $B\,^2A' \leftarrow X\,^2A'$ system of formyl around 250 nm shows a structured spectrum with well resolved vibronic bands and even a partial rotational resolution,[30,31] implying an excited-state lifetime that is longer by several orders of magnitude.

The time-dependent ion signal decayed to zero within some hundred femtoseconds. Neither a second decay constant nor a residual population was observed. One thus might be tempted to interpret the data as confirming earlier suggestions that the $3s$ state of ethyl decays very fast by IC to the electronic ground state. However, upon ionization the geometry of ethyl changes from a classical C_s geometry to a nonclassical bridged C_{2v} structure.[27,32,33] Therefore the Franck–Condon factors for ionization of ethyl ($v''=0$) into the vibronic ground state of the cation are negligibly small at threshold. Since on the other hand, vibrationally hot ground state ethyl radicals are expected to have a reasonable ionization probability, the absence of any residual signal at long delay times is surprising. In an earlier paper on t-butyl, we suggested the coupling to an unidentified dark state to be responsible for the decreasing dissociation rate. This suggestion was based on computations on ethyl[34] that indicate an interaction, possibly a conical intersection, between the $2\,^2A'$ ($3s$) and the $3\,^2A'$ state, nominally one of the $3p$-Rydberg states. The experiments described here do not provide any evidence for the existence of such a dark state. If it exists, the partial cross section for ionization to the cationic ground state must be vanishingly small.

Zyubin, Mebel, and Lin suggested a direct excited state dissociation into ethene$+$H, proceeding via a bridged
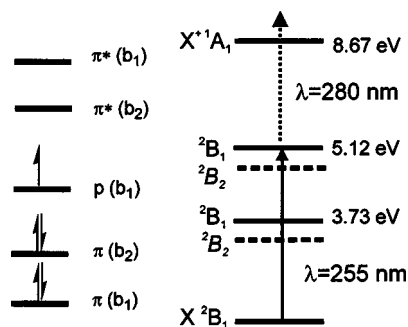
FIG. 3. The relevant electronic states of the propargyl radical. The $^2B_1$ $\rightarrow$ $^2B_1$ transition excited by 255 nm radiation is associated with a $\pi(b_2)$ $\rightarrow$ $\pi^*(b_2)$ excitation. The energies of the $^2B_2$ states are only known from computations (Ref. 39).
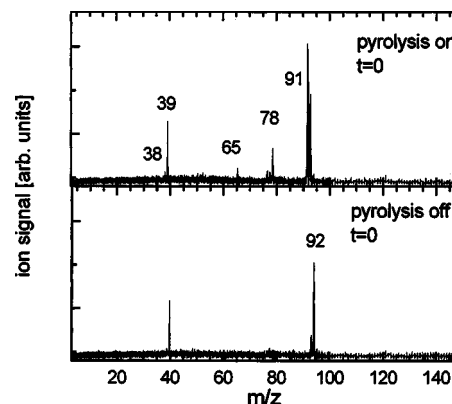

FIG. 4. Typical mass spectra of propargyl bromide, recorded at the zero in time, using 255 nm pump and 280 nm probe. Without pyrolysis (lower trace), the largest signal at $m/z = 92$, corresponds to toluene and a substantial amount of propargyl ($m/z = 39$) is present due to photolysis or dissociative photoionization of the precursor. The former is added as a stabilizer to commercial C_3H_3Br and can be resonantly excited at 255 nm. When the pyrolysis is turned on (upper trace) the major part of the propargyl signal is due to pyrolyzed precursor. An additional signal at $m/z = 91$ can be assigned to benzyl, originating from pyrolysis of toluene.

intermediate.[24] Amaral, Xu, and Zhang interpreted this process as the source of their fast H atoms.[23] Due to its ionization energy of 10.513 eV (Ref. 35) ethene is difficult to observe in the experiments described above. We only observed a small signal around $t=0$ presumably due to ethene formed by secondary reactions in the pyrolysis nozzle. Upon increasing the 800 nm energy to 160 μJ, a time-independent one-color background signal due to ethene appeared, but no additional time-dependent signal was visible at longer delay times. Therefore we found no evidence for a fast excited-state dissociation channel. As a more sensitive method to investigate the possible existence or absence of this pathway, we suggest resonant ionization of H atoms[36] or ethene[37] as the probe step, because otherwise small product yields might remain undetected.

B. Propargyl, C₃H₃

The propargyl radical is one of the most important intermediates in soot formation, because two radicals can form benzene or phenyl radicals in one bimolecular step.[38] This leads to great interest in the reaction dynamics of this species. The relevant molecular orbitals and energy levels are depicted in Fig. 3. In contrast to ethyl, propargyl is excited into a higher-lying excited state by 255 nm light (full arrow), corresponding to a $^2B_1 \rightarrow {}^2B_1$, $\pi(b_2) \rightarrow \pi^*(b_2)$ transition.[39] The available absorption spectra[13,39] show the absorption maximum for this band at 242 nm. We therefore excite the radical on the red edge of the absorption band. The absorption cross section at 255 nm was measured[39] to be around 1.9×10^{-18} cm². A lower-lying transition between 290 and 345 nm (Ref. 40) corresponds to the $^2B_1 \rightarrow {}^2B_1$, $\pi(b_1) \rightarrow np(b_1)$ excitation. In addition, two other electronic excited states are expected to lie in the energy range of interest, corresponding to the $\pi(b_2) \rightarrow np(b_1)$ excitation and $np(b_1) \rightarrow \pi^*(b_2)$ excitation. Both transitions are of the $^2B_1 \rightarrow {}^2B_2$ type, and thus optically forbidden in C_{2v} symmetry. The $^2B_2$ states are indicated in Fig. 3 by dashed lines. Note that in general there are no low-lying quartet states in hydrocarbon radicals.

The excited propargyl radicals are ionized by a 280 nm probe photon (dotted line). The ionization energy was determined by conventional[41] and high-resolution photoelectron spectroscopy.[42] The geometry of the ionic ground state is

known to be similar to the neutral ground state, because a nonbonding electron is removed upon ionization.[42–44] The mass spectra with and without pyrolysis are shown in Fig. 4 and demonstrate that some propargyl is generated without pyrolysis (lower trace). This is presumably due to photolysis of the precursor molecule C_3H_3Br at 255 nm, but dissociative photoionization $[AE \ (C_3H_3^+, C_3H_3Br) = 10.88$ eV (Ref. 45)] cannot be ruled out. A large peak at $m/z = 92$ corresponds to residual toluene, which is added to commercial propargyl bromide as a stabilizer and was only incompletely removed by distillation prior to the experiment. Toluene is resonantly excited at 255 nm and thus appears with high intensity. Only very small signals from propargyl bromide or bromine atoms are visible. Note that the $[1+2']$ process necessary for ionization of C_3H_3Br [IE = 10.48 eV (Ref. 45)] already permits dissociative photoionization. When the pyrolysis source is turned on (upper trace) the intensity of the propargyl peak increases slightly. We chose pyrolysis conditions known to result in optimal conversion from earlier one-photon ionization experiments. Interestingly the intensity of the $m/z = 92$ peak also increases significantly and a peak at $m/z = 91$ appears that can be assigned to benzyl radical formed in the pyrolysis (see below). In addition several smaller peaks appear in the mass spectrum, in particular, $m/z = 78$ and 77. They are due to benzene and phenyl radical, formed by a bimolecular reaction in the pyrolysis nozzle. Both species are known to be formed by the dimerization of two propargyl radicals (see above) and appear in the spectra due to efficient resonant excitation. Control experiments demonstrated that neither propargyl nor any of the C_6H_x species are formed upon pyrolysis or photolysis of toluene.

The time-dependent ion signal of propargyl is given in Fig. 5. The fit to the experimental data points (open circles) was obtained by convoluting a Gaussian instrument response function (FWHM = 130 fs) with an exponential decay with $\tau = 43$ fs that corresponds to the lifetime of the $\pi(b_2) \rightarrow \pi^*(b_2)$ excited electronic $^2B_1$ state. Since neither the accu-
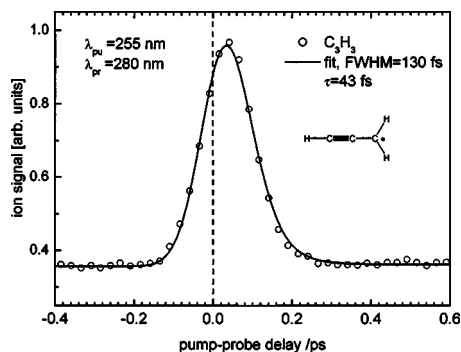
FIG. 5. The time-dependent ion signal of propargyl (open circles) is fitted (solid line) by a convolution of a Gaussian (FWHM=130 fs) with a monoexponential decay of $\tau=43$ fs. A small residual signal at large delay times is visible.
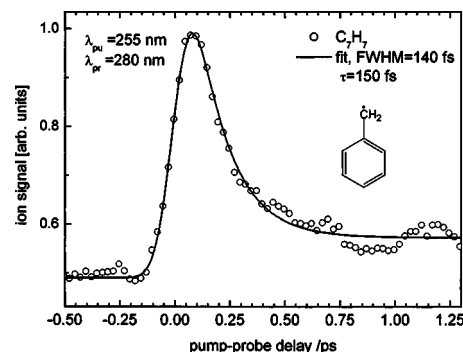

FIG. 6. The time-dependent ion signal of benzyl (C_7H_7, open circles) is fitted (solid line) by a convolution of a Gaussian (FWHM=140 fs) with a monoexponential decay of $\tau=150$ fs.

racy of the zero in time nor the signal/noise ratio was comparable to the ethyl experiments described above, a range of lifetimes between 40 and 60 fs were extracted from a number of different experiments. The time-dependent ion signal of propargyl recorded with the pyrolysis source turned off looked qualitatively similar. Since absorption of an additional 250 nm photon for photolytic generation of the radical is necessary for its appearance, the signal-to-noise ratio of the decay traces is inferior and prohibits the extraction of reliable lifetimes. A careful inspection of the data shows that a small residual propargyl signal is present at longer delay times. The measured lifetime thus corresponds presumably to an internal conversion into a lower-lying excited state. Since a pump- and probe-only background signal accounted for roughly 30% of the signal at $t=0$, a reliable decay constant for the second process could not be extracted.

C. Benzyl, C_7H_7

As discussed above a peak at $m/z=91$ appeared in the pyrolysis of propargyl bromide. Control experiments on pure toluene confirmed that it originates from the pyrolysis of toluene (C_7H_8) which is present as a stabilizer in commercial propargyl bromide. The peak can be assigned to benzyl radical, which is known to be formed in the pyrolysis of alkyl benzenes.[46] Since the temporal behavior differed from that of the $m/z=92$ peak, dissociative photoionization of toluene can be ruled out as the origin of the signal. A heat of reaction $\Delta_R H°=375$ kJ/mol is computed for the formation of benzyl from toluene.[47] For the second isomer of the same mass, tropyl radical, the heat of formation is higher by roughly 70 kJ/mol.[48–50] Tropyl will thus not be generated in significant concentration. Benzyl itself is a relatively stable radical because of resonance stabilization due to interactions with the aromatic ring system.[51,52] Therefore it can accumulate in combustion processes and is involved in the synthesis of polycyclic aromatic hydrocarbons.[53,54] Bimolecular reactions of benzyl radicals thus receive considerable attention in chemical kinetics.

At 255 nm we excite a strong absorption band of benzyl centered at 253 nm, which can be assigned to the $X\,^2B_2 \rightarrow 4\,^2B_2$ transition.[55–57] Due to its large extinction coefficient, the 253 nm band often serves as a marker for benzyl in ki-

netics experiments.[14,15] A fast decay by internal conversion is generally assumed, but the dynamics has not yet been investigated. Since the IE was determined by high-resolution photoelectron spectroscopy to be 7.249 eV (Ref. 58) the radical is easily ionized in a $[1+1']$ process using $\lambda_{pr}=280$ nm. The time-dependent ion signal of benzyl is given in Fig. 6. The signal-to-noise ratio is lower than in both the ethyl and propargyl experiments because of the lower number of averaged scans. A fit to the experimental data was obtained by convoluting a Gaussian instrument response function (FWHM =140 fs) with an exponential decay with $\tau=150\pm30$ fs. As visible the signal does not decay to zero and residual final state population from a lower electronic state, presumably the electronic ground state, is detected. Since only little information on the geometry and the electronic character of the $4\,^2B_2$ state is available, it is not clear whether this state of benzyl decays directly to the electronic ground state or in a multistep process via the intermediate electronic states.

D. Other species

Careful inspection of the mass spectra presented above shows the presence of several other reactive species, although at rather small intensity. The observation of mass $m/z=43$ in Fig. 1, for example, indicates that n-propyl is formed upon photolysis of n-propyl nitrite. From the steady-state UV spectrum recorded in our laboratory we conclude that n-propyl is generated by 250 nm excitation of n-propyl nitrite. It is then excited by a second 250 nm photon to the $3s$ state,[18,19] the lifetime of which is probed by either 280 nm or 800 nm ionization. Since the radical was produced by photolysis in the ionization region, again only a limited analysis of the data is possible. However, the lifetime is significantly shorter than the 127 fs instrument response function, and most likely in the same range as the lifetime of the ethyl $3s$ state.

In the experiments on propargyl we also observed a small amount of C_3H_2 ($m/z=38$ in Fig. 4). The time dependence of this signal indicates an inverted process with excitation by the 280 nm pulse and subsequent ionization by 250 nm. From time-resolved spectra we derived a decay constant of $\tau=32$ fs. The signal is thus not due to dissociative ionization of propargyl and we assume that a small amount of C_3H_2 is formed in the pyrolysis source. However, there

are three different isomers of this composition: propadienylidene with a high ionization potential IE=10.43 eV is not detectable by $[1+1']$ ionization in our experiment;[59] the IEs of the two other isomers, cyclopropenylidene [IE =9.15 eV (Ref. 59)] and propargylene [IE≈8.96 eV (Ref. 60)] are low enough to allow detection. The latter isomer can easily be formed by loss of HBr from the precursor and is thus a likely carrier of the signal. We intend to carry out experiments on more suitable precursors in the future to investigate the dynamics of the C_3H_2 isomers.

E. Discussion and conclusion

We determined lifetimes for the decay of the initially excited state in a number of radical species. For the $3s$ state of ethyl we found a lifetime of 20 ± 3 fs, for the $3\,^2B_1$ state of propargyl we determined a lifetime of 50 ± 10 fs, for the $4\,^2B_2$ state of benzyl a lifetime of 150 ± 30 fs. All investigated radicals thus show ultrafast excited state relaxation. This was expected for the propargyl radical, where subsequent dissociation into cyclopropenylidene+H is well described as a statistical fragmentation in the ground state. For ethyl radical, this result is somewhat surprising: Here statistical theory predicts subsequent dissociation into C_2H_4+H to proceed with a rate of $\sim10^{-12}$ s^{-1}, in stark contrast to the observed dissociation rate of 10^{-7} s^{-1}. Our experiments demonstrate that this discrepancy between expected and observed fragmentation rate cannot be explained by a long lifetime of the optically excited state. Since the time-dependent ion signal decays to zero within a few hundred femtoseconds, no information about the final state of the nonradiative decay can be extracted. We thus want to discuss briefly how additional information might be obtained.

An interesting aspect of the time-resolved photoionization of propargyl becomes evident from an inspection of Fig. 3. At least in a picture describing the excited states by a single determinant, the molecular orbital occupancy of the initially excited state, $\pi(b_1)^2\pi(b_2)np(b_1)\pi^*(b_2)$, does not correlate with the electron configuration of the cationic electronic ground state, $\pi(b_1)^2\pi(b_2)^2$. The same holds for the lower-lying state of B_1 symmetry. As discussed previously in the literature small partial ionization probabilities are expected under these conditions.[61] However, ionization to excited electronic states of the cation can be very efficient due to better correlation of the molecular orbital configuration.[62] Partial ionization cross sections can be measured by time-resolved photoelectron spectroscopy, which allows to distinguish contributions of the various lower-lying electronic states.[63] In ethyl we face a similar situation. Preliminary electronic structure calculations indicate a conical intersection between the initially excited $3s$ state, corresponding to excitation of the electron from the singly occupied $p(7a')$ orbital and the higher-lying $3\,^2A'$ state, which has contributions of electron excitation from the $\sigma(6a')$ molecular orbital. Again this state does not correlate with the electronic ground state of the cation, but with an electronically excited state. If this state was to play a role, it might be revealed by time-resolved experiments using excited ionic states as a template. Since in radical experiments often more than one

species is present, a measurement of the photoelectron spectrum in coincidence with the mass spectrum might be the ideal method to convey additional information on the intermediate state dynamics.[64,65]

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