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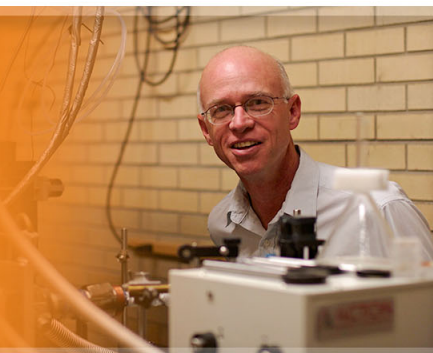
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# The nonradiative decay of the allyl radical excited $B^2A_1$ state studied by picosecond time-resolved photoelectron spectroscopy

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The nonradiative decay rates of the vibrational ground state and the  $\nu_7$  fundamental in the electronically excited  $B^2A_1$  state of the allyl radical,  $C_3H_5$ , are studied by picosecond time-resolved pump-probe photoelectron spectroscopy. The states decay by internal conversion with a time constant of 20 and 16 ps, respectively. © 1997 American Institute of Physics.

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In this paper we report the lifetime of low-lying vibrational levels in the electronically excited  $B^2A_1$  state of the allyl radical,  $C_3H_5$ , as revealed by picosecond time-resolved pump-probe photoelectron spectroscopy.

As the simplest conjugated  $\pi$ -radical allyl is an interesting model system. Being a relatively stable radical it also constitutes an important intermediate in reactive environments. Its photochemistry upon UV excitation is thus of considerable relevance for tropospheric chemistry and combustion. The UV band system, starting at 250 nm and observed first in absorption,<sup>1</sup> was studied by resonant multiphoton ionization (MPI),<sup>2–5</sup> allowing the identification of a large number of vibronic bands and their assignment to the electronic  $B$ ,  $C$ , and  $D$  states, which are strongly coupled with each other. Resonance Raman spectra from these states were also recorded,<sup>6</sup> but no fluorescence has been observed, despite the large oscillator strength calculated for the  $C \leftarrow X$  transition,<sup>7</sup> indicating short lifetimes. MPI experiments on the other hand revealed a partially resolved rotational  $K_a$  structure<sup>4</sup> for several vibronic bands with a linewidth of  $1 \text{ cm}^{-1}$ , posing a lower limit of 5 ps on the lifetime of the low-lying vibronic states. Recently, we reported the hydrogen loss from hot  $C_3H_5$  upon UV excitation on a nanosecond time scale and showed that a reaction forming allene is in agreement with a statistical analysis of the data.<sup>8</sup> Here we will concentrate on the primary photophysical processes which occur directly after the initial excitation of the  $B^2A_1$  state. From the MPI spectra<sup>5</sup> it was concluded that the  $B$  state, a perturbed  $3s$  Rydberg state, is slightly nonplanar and the CCC angle significantly reduced as compared to the ground state of both neutral and cation. As the ground state is of  $A_2$  symmetry the transition into the  $B$ -state origin is two-photon allowed. Earlier [2+2] MPI studies<sup>3</sup> revealed a strong dependence of the appearance of the spectrum on the laser power which was explained by an accidental resonance on the three-photon level. Thus a [2+1'] experiment using two different colors for pump and probe is advantageous.

Like allyl, many organic radicals do not possess long-lived excited states that permit fluorescence detection. Due to the fast relaxation, the application of the established high-resolution methods is often not appropriate to gain insight

into the photochemistry of these systems. On the other hand, time-domain methods employing short laser pulses are well suited for this kind of research.<sup>9–11</sup> In particular, time-resolved photoionization with short-pulse lasers has proven to be a powerful method to study the photophysics and photochemistry of molecular systems for which no fluorescing electronic states are known.<sup>9,10,12</sup> As shown within the last couple of years, a particularly high amount of information can be extracted when the energy of the photoelectron, and thus the ion internal energy, is analyzed.<sup>13–25</sup> The photoelectron spectrum might evolve in time even when the total ion yield is almost constant, i.e., population flow between electronic states can be monitored by final state analysis. Techniques based on the detection of photoelectrons are also background free, allowing one to discriminate against time-independent ionization signals from the pump or probe laser alone.

In order to reduce intensity effects, short-pulse experiments have to be carried out at relatively low fluences as compared to nanosecond experiments. As reactive intermediates can only be produced in small number densities a very efficient detection scheme is needed. Time-of-flight photoelectron spectroscopy in a magnetic bottle is a probe method that combines a high collection efficiency of more than 30% with the possibility of a final state energy analysis, and is thus well suited for short-pulse experiments as shown in several studies on stable molecules,<sup>18</sup> and, just recently, on mass-selected anionic clusters.<sup>26</sup> Due to the number density problems mentioned above only a few radicals, like  $NO_2$ ,<sup>27</sup> have been studied in the time domain with subnanosecond laser pulses. In the present paper we show that time-resolved photoelectron spectroscopy is also well suited to study the photophysics of medium-sized hydrocarbon radicals.

In the experiments described here a picosecond Ti:sapphire laser system was employed, regeneratively amplified at 10 Hz to approximately 5–6 mJ. The pulse duration for the fundamental around 820–830 nm was measured to be 2.5 ps. The light was frequency doubled and mixed in KDP crystals to access the UV region. In order to obtain pump pulses around 500 nm the second harmonic was Raman shifted in 15–20 bar of hydrogen, producing radiation Stokes shifted by  $4155 \text{ cm}^{-1}$ . The details of the setup, and a characterization of the stimulated Raman scattering process were given

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in an earlier publication.<sup>28</sup> The frequency mixed output around 275 nm served as the probe pulse. The two beams were recombined and focused collinearly by means of a 500 mm quartz lens into the ionization region of a magnetic bottle photoelectron spectrometer with a 50 cm flight tube. Typically a pump energy of 20  $\mu\text{J}$  was used, while the probe energy was attenuated to around 5  $\mu\text{J}$ . The time delay between the two laser pulses was adjusted by a computer controlled stepper motor. Typically 100–200 data points were averaged for each delay. The allyl radicals were produced by supersonic jet flash pyrolysis<sup>29</sup> of 1,5 hexadiene,  $\text{C}_6\text{H}_{10}$ , seeded in 1.5 bar of helium. The skimmed molecular beam enters the ionization region of the magnetic bottle where it crosses the laser beam at a right angle. The details of the radical source<sup>30</sup> and of the spectrometer<sup>31,32</sup> have already been described elsewhere.

A magnetic bottle spectrometer can, in principle, be operated as a mass spectrometer albeit with low detection efficiency and limited mass resolution. It was not possible to record mass spectra under the same conditions as photoelectron spectra. However, when the pump laser was tightly focused, a time-independent mass signal of  $m/e=41$  was observed, with a small peak at  $m/e=39$  showing up with 10% of the intensity and likely being due to fragmentation in the ion. The peaks disappeared when the heat for the pyrolysis source was turned off, confirming that the signal is due to pyrolytic and not photolytic cleavage of the precursor. We did detect hexadiene only in trace quantities, although its ionization potential of 9.29 eV is energetically accessible in the  $[2+1']$  process studied here, indicating that no resonance of hexadiene exists in the range of pump energies used.

We will now concentrate on the time-resolved photoelectron spectrum obtained for the  $B\ 0_0^0$  band of the allyl radical pumped with two photons at 499.5 nm (2.48 eV), and probed with one photon at 275.8 nm (4.5 eV). With the bandwidth of our pump photons of  $\delta\omega=16\ \text{cm}^{-1}$  a large part of the rotational envelope of the vibronic state is excited, meaning that our results constitute an average over many rotational states. For comparison, the full width at half-maximum of the bands reported in the  $[2+2]$  MPI spectra<sup>5</sup> lies around  $40\ \text{cm}^{-1}$ . In Fig. 1 the photoelectron spectrum at pump–probe delays of  $t=-10\ \text{ps}$  and  $t=0\ \text{ps}$  is given. The time-dependent signal can be well separated from the time-independent signal, which is due to  $[2+2]$  MPI by the pump–laser alone, showing the ability of photoelectron spectroscopy to detect the time-dependent signal in a background-free fashion. From the flight times, one can also deduce that the time-dependent signal is indeed due to the  $B$  state via a  $[2+1']$  process. An alternative process would be the competing  $[3+1']$  route, suggested by Sappey and Weishaar<sup>3</sup> to explain the unusual power dependence in their MPI spectra. The formation of ions with little internal energy would create much faster electrons (time-of-flight  $\approx 450\ \text{ns}$ ) that would also appear earlier in time than the pump-only signal. We want to point out that it would not be possible to distinguish between the two processes if only the total ion signal were measured.

In Fig. 2, a three-dimensional representation is given,

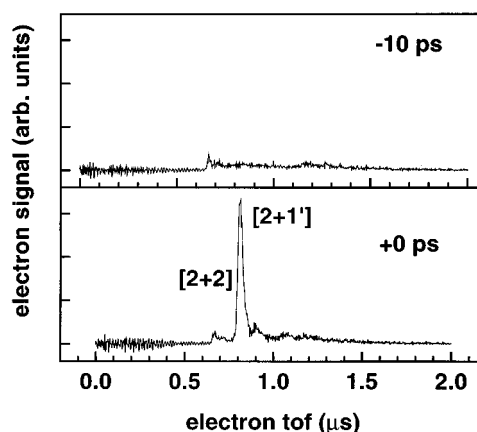


FIG. 1. Photoelectron time-of-flight spectrum obtained at  $-10\ \text{ps}$  (upper trace) and  $0\ \text{ps}$  (lower trace). The  $[2+1']$  pump–probe signal can be easily distinguished from the time-independent  $[2+2]$  background. Note that the order of the process can be readily deduced from the flight times. Both traces were obtained from the complete spectrum given in Fig. 2.

which shows the evolution of the complete pump–probe photoelectron spectrum of the  $B\ 0_0^0$  band over a range of more than 100 ps. Figure 2 illustrates the multiplex advantage of photoelectron detection, where all energetically accessible final states are recorded at the same time for a given pump–probe delay. The rise and decay of the pump–probe signal is clearly visible. As can be seen from Figs. 1 and 2 the pump–probe signal, as well as the pump-only signal, shows some vibrational structure on the low energy side, due to vibrational excitation in the ion. This structure is due to the difference in geometry between the planar ion and the nonplanar  $B$  state with its smaller CCC bond angle. The decay of the time-dependent signal is shown in Fig. 3, which illustrates the temporal evolution of the major pump–probe peak. It was obtained from the photoelectron spectrum given in Fig. 2 by integrating over the main peak from 0.78 to 0.87  $\mu\text{s}$  and plotting the integral as a function of the delay time.

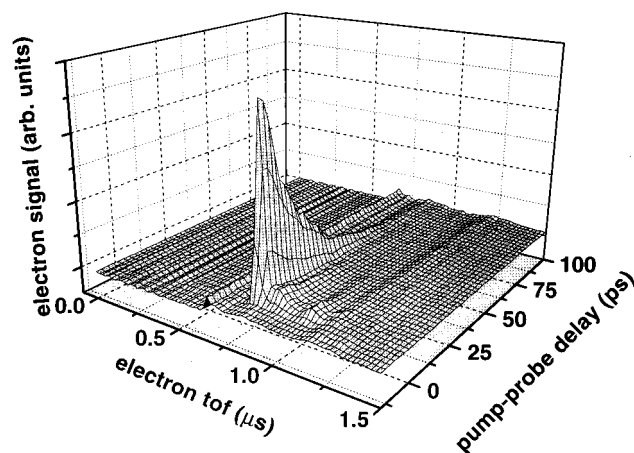


FIG. 2. Representation of the complete photoelectron spectrum over a range of more than 100 ps, demonstrating the multiplex advantage of photoelectron spectroscopy as a probe technique. The rise and decay of a time-dependent pump–probe signal is visible.

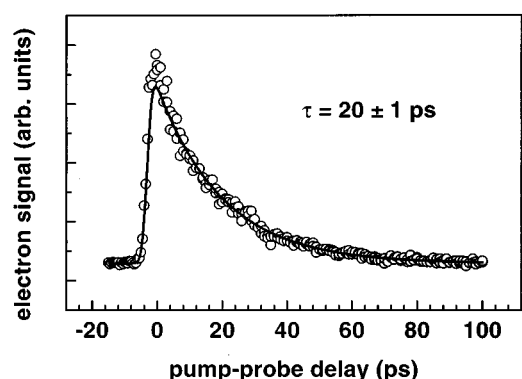


FIG. 3. Decay of the major pump-probe peak from the spectrum in Fig. 2. The time-dependent signal is fitted by a convolution of a Gaussian with a full width at half-maximum of 3 ps, representing the cross correlation of the laser pulses, and an exponential with a time constant of 20 ps.

The solid line represents a fit which was obtained by convoluting our 3 ps instrument function with an exponential decay with a time constant of  $\tau=20$  ps. The time constant  $\tau$  is accurate to within  $\pm 1$  ps. All parts of the vibrational progression in the photoelectron spectrum show the same monoexponential decay. As short-pulse experiments are inherently high-intensity experiments, we checked for intensity effects by reducing the power of the pump beam to 10  $\mu\text{J}$ , but did not observe a change in the decay of the pump-probe signal.

We will now discuss the possible decay routes for the molecule. Allyl, like most radicals, does not possess low lying electronic states of higher spin multiplicity, i.e., quartet states, which therefore excludes intersystem crossing. Another possibility would be predissociation. Indeed, we observed hydrogen loss from the  $C\ 0_0^0$  state, as reported elsewhere.<sup>8</sup> As the hydrogen loss occurs on a nanosecond time scale it is not due to dissociation directly from the UV states. All electronic states in this region are strongly coupled, so it is expected that the  $B$ - and  $C$ -state origin will behave qualitatively very similar.

This leaves internal conversion (IC) as a decay mechanism, either directly to the ground state, or via the  $A\ ^2B_1$  state. The rate of  $5 \times 10^{10}\ \text{s}^{-1}$  is unusually slow for the nonradiative decay of a second excited state. This can be explained by the large energy gaps, 1.94 eV between the  $A$  and  $B$  electronic states, and 4.96 eV between the ground and the  $B$  state, because the nonradiative transition rate is known to be an exponentially decreasing function of the energy gap.<sup>33</sup> Our earlier nanosecond experiments<sup>8</sup> indicate a reaction from the hot ground state. However, at present, we can not say conclusively whether the  $B$  state converts directly to the ground state or via the  $A$  state. Franck-Condon arguments seem to favor an initial conversion to the  $A$  state for the following reason: In *ab initio* calculations a similar geometry was calculated for the ground state and the  $A$  state,<sup>34</sup> with only the C-C bond length being slightly different ( $<0.1$  nm). This means that conversion to the ground state would result in a far higher degree of excitation in any accepting mode than conversion to the  $A$  state with subsequently much smaller Franck-Condon factors. On the other hand, the far

higher density of states,  $\rho=7.5 \times 10^9/\text{cm}^{-1}$  for the ground state versus  $1.5 \times 10^5/\text{cm}^{-1}$  for the  $A$  state, would favor internal conversion directly to the ground state.

In principle, one would expect a signal due to ionization from a lower electronic state to grow in over time. A close inspection of the longer delay times in Fig. 2 does indeed reveal a signal level at low electron energies that is larger at late delay times than at early times and might be due to ionization from a lower electronic state. However, the effect is extremely small, if at all present. This can be understood if it is taken into account that due to the large energy gap internal conversion from the  $B$  state will result in vibrationally highly excited states with poor Franck-Condon factors for transitions into low-lying ionic states. As the excess energy available for the ion is only 1.3 eV, we are not able to see the ionic states to which the most intense transitions would be expected. This effect will be even more pronounced if the  $B$  state converts directly to the ground state. Also a broad distribution of vibrational energies can be expected at later times, which should lead to a broad distribution of photoelectron energies with small intensities at any given energy, making the detection difficult.

Inspection of the  $[2+2]$  MPI spectra<sup>5</sup> shows that a few other vibrational bands can be excited in a two-photon pump process. Thus we tuned the pump wavelength to 494.5 nm in order to examine the  $B\ 7_0^1$  band, which can be regarded as a CCC-bending vibration. The time-resolved photoelectron spectrum looks similar, although the signal is considerably smaller. The decay of the signal can again be well fitted by a single exponential with a time constant  $\tau=16 \pm 2$  ps, meaning that the nonradiative decay of the  $7_0^1$  band is slightly faster than the decay of the  $0_0^0$  band. When the laser was tuned, the magnitude of the pump-probe signal followed the published MPI spectra.<sup>5</sup> At wavelengths in between the two bands, i.e., around 497 nm, no pump-probe signal was observed.

In conclusion, we demonstrated that medium-sized hydrocarbon radicals can be studied by time-resolved photoelectron spectroscopy with short laser pulses, as shown for the allyl radical. The lifetime of low-lying vibrational levels of the electronically excited  $B$  state, which decays by internal conversion was determined to be around 20 ps. Further experiments aimed at studying the  $C\ ^2B_1$  state and obtaining state-selective decay rates for higher vibrational levels in the  $B$  state are currently underway.

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