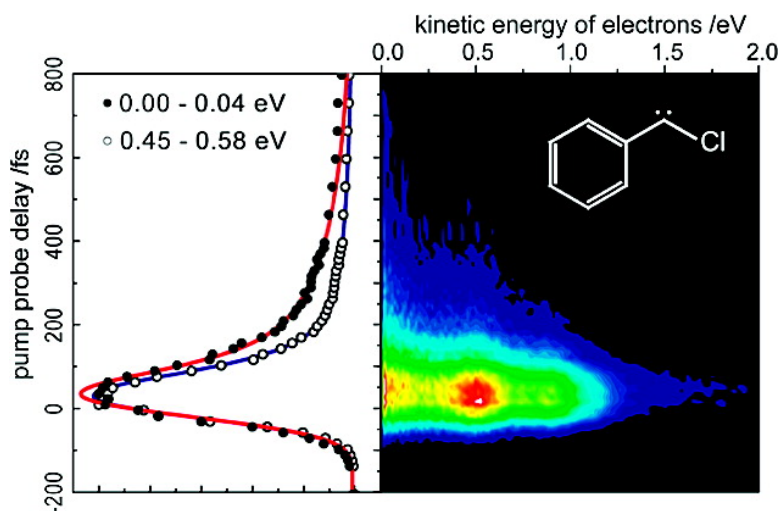


Femtosecond Dynamics of Isolated Phenylcarbenes

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Femtosecond Dynamics of Isolated Phenylcarbenes

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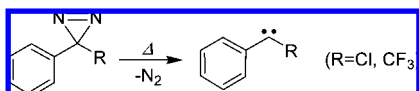
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The ultrafast dynamics of two phenylcarbenes ($R = \text{Cl}, \text{CF}_3$) was investigated by femtosecond time-resolved pump probe spectroscopy¹ in the gas phase. Carbenes are ideal model systems for examining nonadiabatic coupling due to their large number of low-lying electronically excited states.² Spectroscopic experiments on phenylcarbenes have mainly been performed in rare gas matrices.³ Experiments on isolated triatomic halocarbenes showed evidence of predissociation.⁴ Time-resolved femtosecond spectroscopy documents the formation of phenylcarbenes by photolysis of diazirines,⁵ but no information is available on the primary photophysical processes of the phenylcarbenes themselves. This limits the understanding of the carbene photochemistry since species rarely react from the initially excited electronic state.⁶

The experiments were performed in a standard molecular beam apparatus. A cold beam of phenylcarbenes was prepared by supersonic jet flash pyrolysis of the corresponding diazirines, as shown in Scheme 1. Evidence proving clean carbene generation is provided as Supporting Information.

Scheme 1. Supersonic Jet Flash Pyrolysis of Diazirines



Both carbenes show a strong absorption at 265 nm. They were excited at this wavelength and ionized in a multiphoton process with 795 nm light.⁷ Figure 1 depicts the time dependence of the ion signal for chlorophenylcarbene (CPC) in the top trace and trifluoromethylphenylcarbene (TFPC) in the bottom. Both intermediates show a two step deactivation process after excitation. The model used in the best fit (solid line) was a transient “I” decaying to transient “II”, then to transient “III” relaxation convoluted by a Gaussian (fwhm = 105 fs for CPC, 95 fs for TFPC) instrument response function.⁸ For comparison the best fit to a one step deactivation model (transient “I” to “II”) is depicted as a dashed line. As shown, it does not represent the decay properly. The model with two time constants indicates a fast decay of the primary populated transient “I” to transient “II” for both carbenes ($\tau_1 = 40\text{--}60$ fs) followed by a slower decay of transient “II” ($\tau_2 = 350$ fs for CPC and 500 fs for TFPC). A secure assignment of the two relaxation steps to precise deactivation processes is uncertain using the ion signal alone, but the observation excludes a single step deactivation.

Ab initio calculations are available for CPC, which is known to have a singlet ground state.⁹ The corresponding energy diagram has been reproduced by time dependent density functional theory¹⁰ (TD-B3P86/6-311++G**) and is shown in Figure 2. The latter

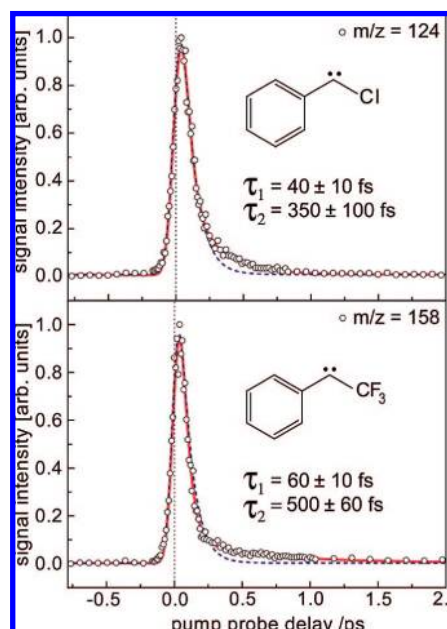


Figure 1. Ion signal intensity of CPC ($R = \text{Cl}$, top) and TFPC ($R = \text{CF}_3$, bottom) as a function of the time delay (pump 265 nm, probe 795 nm).

calculation provides a zeroth-order picture of the 265 nm excitation of CPC that is consistent with that of ref 9. Excitation takes place into the fourth excited singlet state ($3^1A'$). This transition holds by far the largest oscillator strength in the calculations and is predominantly described by a transfer of an electron from a π orbital of the aromatic ring (MO 30) into the LUMO (MO 33) of the molecule, which contains a contribution of the p-orbital at the carbene center. Several electron configurations contribute to the levels $2^1A'$ to $4^1A''$. They involve the promotion of an aromatic electron. Note that there is a relatively large energy gap between the A^1A'' and the $2^1A'$ state of 2.4 eV, whereas the states from $2^1A'$ to $4^1A''$ are close in energy and presumably strongly coupled. The A^1A'' state has a dominant electronic configuration corresponding to the promotion of an electron at the carbene center (MO 32 to MO 33).

Additional information on the excited-state dynamics can be obtained from time-resolved photoelectron spectra (TRPES),⁶ recorded by velocity map imaging and processed by the pBASEX algorithm.¹¹ The TRPES for CPC is depicted in Figure 3 as a contour map. It presents the photoelectron intensity as a function of kinetic energy (horizontal axis) and time delay (vertical axis). Most of the signal originates from a broad band of electrons with a kinetic energy between 0.3 eV and ~ 0.9 eV. It shows the same time dependence as the mass selected delay curve in Figure 1. For a proper description of the time dependence of electrons with a kinetic energy below 0.04 eV (see Supporting Information for a

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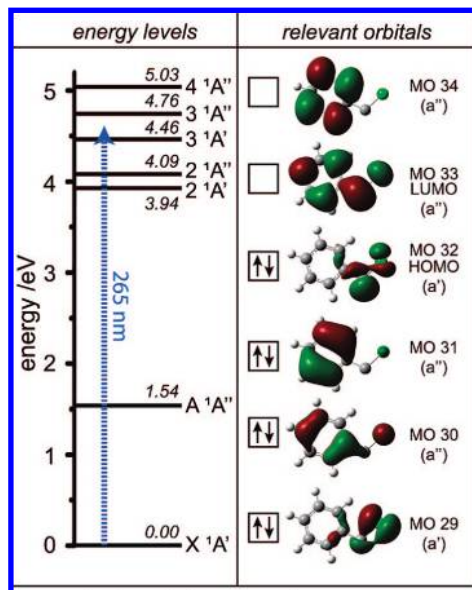


Figure 2. Vertical excited states of CPC (TD-B3P86/6-311++G**). Irradiation of the carbene around 265 nm excites the molecule into the fourth excited singlet state.

comparison with high kinetic energy electrons), an additional time constant $\tau_3 \approx 1$ ps is required. The individual contribution of each of the three components to the overall decay is presented on the left-hand side of Figure 3.

Since the close-lying coupled excited states between 3.9 and 5.0 eV are not expected to result in separated bands in the TRPES, they presumably yield the observed broad feature at ~ 0.5 eV in a $[1 + 3']$ ionization process.⁷ The TRPES is consistent with the assumption that CPC deactivates in a three step process. With regard to the IE_{vert} of the carbene and the low electronic energy of the A-state, multiphoton ionization out of the A $1A''$ state will produce electrons with low kinetic energy. Thus ionization out of the A $1A''$ state will produce electrons with low kinetic energy. The 1 ps decay, which is observed for the low energy electrons only, can be explained by the decay of this level. The signal will be weak due to missing resonances. This is consistent with the observation in Figure 1 that the ion signal apparently decays to zero after a long period of time. Since autoionization from the higher electronic states can also produce low kinetic electrons, all three time constants are visible in this energy range. The other two time constants, 40 and 350 fs, have to be assigned to the dynamics involving higher lying states. The assignment of the first fast decay constant of CPC (40 fs) is not straightforward. It could correspond to a relaxation within the dense manifold of excited states between 3.9 and 5.0 eV. But since the states are very close in energy, the pump pulse will produce a wave packet superposing electronic as well as vibrational states. A movement of the wave packet, incorporating geometric deformations, out of the Franck–Condon region, also delivers an explanation for the fast 40 fs decrease of the ion signal intensity. A subsequent relaxation by internal conversion into the A $1A''$ state is likely. We assign the time constant of 350 fs to this process. Hereby the excess electronic energy is converted to internal energy. From the experiments it is not clear whether the A $1A''$ deactivates to the dark ground state or a photochemical reaction takes place.

An excited-state isomerization to 1-chlorocyclohepta-1,2,4,6-tetraene is unlikely to occur, and experiments on isolated small halocarbenes found C-Hal predissociation to be an important

reaction channel.⁴ We do not observe any fragment signal to grow in at long delays and expect internal conversion to be fast. Therefore we suggest that τ_3 corresponds to the relaxation time of the A $1A''$ state to the ground state, forming vibrationally hot species.

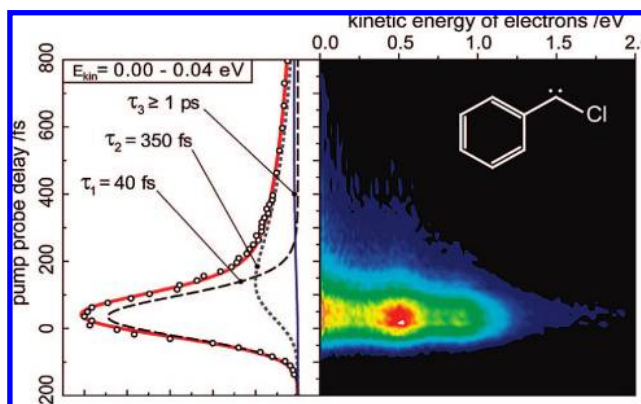


Figure 3. TRPES of CPC excited with 265 and ionized with 800 nm by multiphoton ionization, showing only the unpolarized part of the photoelectron distribution. Slow photoelectrons (left) show an offset at long delay times indicating the presence of a third time constant with small amplitude (see Supporting Information for an enlarged version).

In contrast to CPC, TFPC is known to have a triplet ground state.³ Nevertheless the results of Figure 1 suggest that its initial dynamics follows a similar scenario as the one found for CPC.

In conclusion we observe a first very rapid decay of the initially prepared transient. A three step deactivation process takes place. The A $1A''$ state presumably deactivates within ~ 1 ps to the hot ground state, which holds enough internal energy for further reactions. TDDFT calculations show that promotions of ring electrons are involved in the initially prepared transition. Lower excited states correspond to promotions of electrons from the carbene center to the ring.

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Supporting Information Available: Experimental setup, mass spectra, TRPES, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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