# Time-resolved photoelectron spectroscopy and ab initio multiple spawning studies of hexamethylcyclopentadiene

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**Abstract:** Time-resolved photoelectron spectroscopy and ab initio multiple spawning were applied to the ultrafast non-adiabatic dynamics of hexamethylcyclopentadiene. The high level of agreement between experiment and theory associates wavepacket motion with a distinct degree of freedom.

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## 1. Introduction

The ultrafast excited state dynamics of small polyenes have been investigated in many studies either by experimental methods or via dynamical simulations. Only few, however, have used a combination of both approaches [1,2]. In this contribution, we propose a combination of time-resolved photoelectron spectroscopy (TRPES) and ab initio multiple spawning (AIMS) simulations for a profound understanding of excited state dynamics in polyenes. We aim at understanding the connection between phenomena observed in TRPES and AIMS simulations. In time-resolved photoelectron spectra we study the molecular dynamics of small polyenes by exciting the molecules with a pump pulse and following the dynamics through ionization with a probe pulse. The signature appearing immediately after time zero is often slightly delayed throughout the spectrum. In dynamical simulations, depopulation of the initially excited electronic state is often observed to be preceded by an induction time [3]. In hexamethylcyclopentadiene ($CPDMe_6$), both effects are expected to be easily observed because of an expected decrease of the relaxation time as compared to unsubstituted cyclopentadiene [4] due to the increased inertia. Thus, it is an ideal benchmark molecule for the investigation of their connection.

## 2. Methods

Time-resolved photoelectron spectra in the gas phase were recorded in a magnetic bottle spectrometer described in detail elsewhere [5]. Pump pulses at 267 nm (2.6 µJ / pulse) and probe pulses at 320 nm (2 µJ / pulse) were set to magic angle and focussed into the interaction region. $CPDMe_6$ was supersonically expanded into vacuum by a pulsed Even-Lavie valve using 3 bar helium as a backing gas. The cross-correlation of the pulses was measured to be 130±10 fs.

The details of the employed theoretical methods are described in Ref. [2]. Briefly, electronic structure calculations and geometry optimizations were performed with MS-MR-CASPT2/6-31G** using the MOLPRO2006.1 program package [6] and employing a complete active space consisting of four π orbitals and four electrons. For dynamical simulations, an in-house code was used combining AIMS dynamics with MS-MR-CASPT2/6-31G** in MOLPRO. Initial conditions were sampled from a Wigner distribution in the electronic ground state. 38 trajectory basis functions were propagated for ≈300 fs. The methyl substituents were approximated as hydrogens with a mass of 15 amu. Time-resolved photoelectron spectra were simulated employing Dyson orbitals. The resulting stick-spectra were convoluted with Gaussians in energy and time to account for the limited energy and time resolution of the experiment. Systematic errors were compensated by shifting the spectra by a correction factor. In the case of 2-photon ionization, relative cross-sections were scaled to the experimental data.

## 3. Results and Discussion

Fig. 1 a) shows the experimental time-resolved photoelectron spectra of $CPDMe_6$. They can be partitioned in regions with contributions from ionization with one ([1,1'], left of yellow line) or two photons ([1,2'], right of yellow line). Observable features of both regions refer to the same underlying dynamics. The photoelectron bands appearing earliest in the high energy part of both regions are delayed and broadened in time throughout the photoelectron spectrum. The coefficients of a fit quantifying the delay are inserted as black circles.

   In Fig. 1 b) the population density time-evolution from the AIMS simulation is shown. Population decay is preceded by an induction period of 108 fs. The latter can be associated with wavepacket evolution in a single molecular degree of freedom, which experiences a considerable change between the Franck-Condon region and the conical intersection to the ground state. A simulated time-resolved photoelectron spectrum based on the AIMS results is depicted in Fig. 1 c). It also exhibits a considerable delay and broadening of the photoelectron signature from high to low photoelectron kinetic energies. The quantitative disagreement on the time scales of the dynamics between experimental and simulated is attributed to the approximation of the methyl groups as heavy hydrogens.
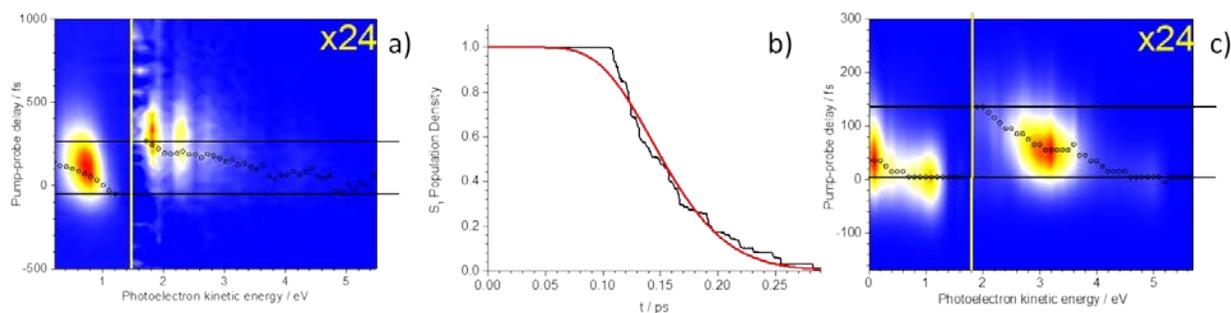


Fig. 1: a) Experimental time-resolved photoelectron spectra. Red refers to high, violet to low photoelectron intensities. The yellow line marks the cutoff between [1,1'] and [1,2'] ionization regions. Parameters of a fit quantifying the spectrally dependent delay of the photoelectron signature are inserted as black circles. b) Simulated population density evolution (black) and fit by a simple stepladder model (red). c) Like a), but with simulated time-resolved photoelectron spectra. Note the high qualitative agreement of spectra a) and c) and the disagreement in time scales.

   To connect the spectral delays in experimental and simulated TRPES data to the wavepacket evolution, a simple stepladder-type model is employed [7]. It describes the wavepacket evolution as time-dependent distribution of population density onto a series of discrete steps between the Franck-Condon region and the conical intersection. A fit of this model to the population density evolution is shown as a red curve in Fig. 1 b). Induction period and depopulation can together be quantified by a single model parameter, the characteristic time $t_{ch}= 140$ fs at the point of inflection of the S-shaped decay in the fit. By providing each step of the model with a spectral signature, the model is also able to describe the delay of the photoelectron bands in the time-resolved photoelectron spectra. In the case of the simulated spectra, it can be fitted using the same value of $t_{ch}$ as in the fit of the population density evolution. In the case of the experimental spectra, the fit yields $t_{ch}= 540$ fs. Thus, by employing this simple stepladder model, the induction time as well as the spectrally dependent delay of the photoelectron signature can be directly associated with wavepacket evolution in a distinct molecular degree of freedom. This finding seems of more general validity for excited state dynamics of small polyenes. The results emphasize the potential of the combined approach of TRPES and AIMS for a profound understanding of excited state dynamics.

## 4. References

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