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2022

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Ultrafast Molecular Dynamics Investigated by Femtosecond Soft X-ray Transient
Absorption Spectroscopy at the Carbon K-Edge

by

Tian Xue

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Stephen R. Leone, Chair

Professor Daniel M. Neumark

Professor David Attwood

Fall 2022

Ultrafast Molecular Dynamics Investigated by Femtosecond Soft X-ray Transient
Absorption Spectroscopy at the Carbon K-Edge

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By

Tian Xue

Abstract

Ultrafast Molecular Dynamics Investigated by Femtosecond Soft X-ray Transient Absorption Spectroscopy at the Carbon K-Edge

By

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Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Stephen R. Leone, Chair

Ultrafast soft X-ray transient absorption spectroscopy has exhibited remarkable sensitivity to electronic and molecular structures with element specificity and short temporal resolution. At the carbon K-edge, X-ray probe pulses enabled the capability to investigate molecular dynamics of photoinduced organic chemicals. In the study of the photodynamics of pentamethylcyclopentadiene (C_5Me_5H), two timescales of $C_5Me_5\bullet$ radical formation following UV excitation are directly observed, which are attributed to a fast channel likely coming from C_5Me_5H with an active C-H vibration stretching mode and a slow channel taking time for the vibrational energy to redistribute into this vibrational mode for the dissociation. The transition state $1B_2$ and the photoproduct $C_5Me_5\bullet$ are spectroscopically characterized by carbon 1s core-to-valence transitions.

Additionally, the ultrafast state crossing in the photorelaxation of benzaldehyde upon 267 nm excitation was investigated. Two well-separated core level absorption features at 281.8 and 282.8 eV are tentatively assigned to the population transfer to $S_1(n\pi^*)$ followed by the intersystem crossing to the triplet state in about 12 ps. The evolution of the core-to-valence resonances at the carbon K-edge identifies the excited singlet and triplet states involved in the photorelaxation of benzaldehyde.

Finally, the electronic structure of $C_2F_4I\bullet$ radical, the photodissociation fragment of $C_2F_4I_2$, is characterized by a carbon 1s X-ray feature at lower energy, 286.4 eV, resulting from a transition to the singly occupied molecular orbital (SOMO). After the loss of an iodine atom, the shift in the carbon 1s orbital is greater than the shift in the antibonding orbital upon going from the closed-shell molecule to the radical.

To my family

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Acknowledgments

Reflecting on the time I have spent in Berkeley, first and foremost I would like to thank my advisor Professor Stephen Leone for giving me the opportunity to join his group and learn about this exciting field. Steve has been a supportive mentor and guided me to think about research creatively and critically. His dedication to scientific research continues to inspire me. I also appreciate Professors Daniel Neumark, David Attwood, Ronald Cohen, and Eric Neuscamman for taking their time to be on my qualifying exam and/or thesis committee.

The work presented in this dissertation would not have been possible without the help of many other people, especially the colleagues in the Leone Group. I am grateful to my lab mentors Aditi Bhattacharjee, and Kirsten Schnorr who patiently taught me all the principles and fundamentals in the lab. Zheyue Yang, Michael Epshtein, Valeriu Scutelnic, and Eric Haugen have been amazing lab mates and I cherish the time we struggled through the failure of instruments and experiments. I appreciate the insightful science discussions and caring personal conversations with Andrew Attar, Chris Kaplan, Kristina Chang, Bethany Lamoureux (de Roulet), Andrew Ross, Nicolette Puskar, and John Beetar, and everyone else in the Leone group.

Diptarka Hait is not only a supportive collaborator in research but also a warm and understanding friend. I have had the pleasure of working with him and his contribution to the work is critical.

Lastly, I want to thank my family who has been supporting me unconditionally along the journey. There were times over the years I was feeling stressful or hopeless and they gave me the courage to take a pause and then keep going.

Chapter 1: Introduction

The Born-Oppenheimer approximation is one of the best-known assumptions in molecular dynamics.¹ It is the assumption that the wavefunctions of atomic nuclei and the electrons in a molecular system can be treated separately. Due to the fact that mass of atomic nuclei is much larger than that of the electrons, as the coordinates of the nuclei are changed, the electrons can approximately instantaneously go through rearrangements to minimize the energy. This approximation is used to establish potential energy surfaces along the chemical reaction coordinates.² In molecular dynamics, potential energy surfaces are greatly used to find the optimized molecular geometry and the rate of a chemical reaction process. However, it is common for polyatomic molecules to have two or more potential energy surfaces intersect and the nonadiabatic couplings between these states exist.³ As a result, the Born-Oppenheimer approximation breaks down, and the coupling between the electronic and nuclear motion allows rapid crossing between excited states in photochemistry to take place. Photoinduced chemical reactions are occurring on the ultrafast timescale. For example, Figure 1.2 shows four typical chemical processes that occur on different timescales spanning from nanoseconds (10^{-9} s) to femtoseconds (10^{-15} s), including photodissociation, vibrational relaxation, proton transfer, and internal conversion as well as intersystem crossing.¹ From the experimental perspective, capturing and investigating these chemical processes on a molecular scale requires ultrafast temporal resolution on the order of femtoseconds.^{6,7} It has become a primary goal for modern chemical dynamics research to characterize the evolution of both molecular and electronic structures with atomic scale sensitivity.^{4,5} In this thesis, ultrafast soft X-ray transient absorption spectroscopy is used to investigate photoinduced molecular dynamics. This is a pump-probe technique with 100 fs resolution using a UV beam as the pump pulse and a soft X-ray as the probe pulse to characterize the excited states and transient species by core-to-valence transitions.

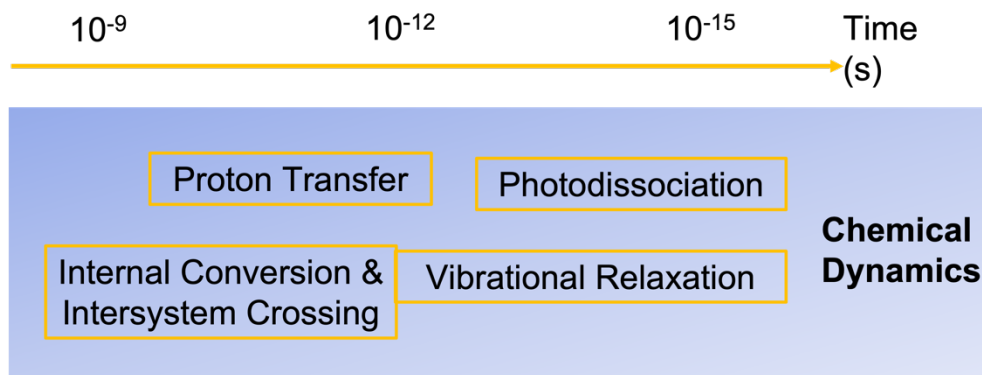


Figure 1.1: Representation of chemical dynamic processes that occur on different timescales spanning from nanoseconds (10^{-9} s) to femtoseconds (10^{-15} s).

1.1: Pump-probe Experiments

This thesis will cover three different projects of photoinduced molecular dynamics in the gas phase. A femtosecond laser is used to investigate the ultrafast chemical processes like photodissociation or state crossing via a conical intersection. Pump-probe spectroscopy uses light separated into two pulses, a pump pulse for photoexcitation and a probe pulse to characterize the excited species at a given time. Pump-probe experimental techniques have been developed to record the real-time evolution of chemical reactions in order to follow nuclear dynamics on the potential energy surfaces of electronically excited molecules and to spectroscopically characterize the corresponding transient species. The breakthrough led to a Nobel Prize in chemistry that was awarded to Ahmed H. Zewail in 1999 “For his studies of the transition states of chemical reactions using femtosecond spectroscopy”.⁷

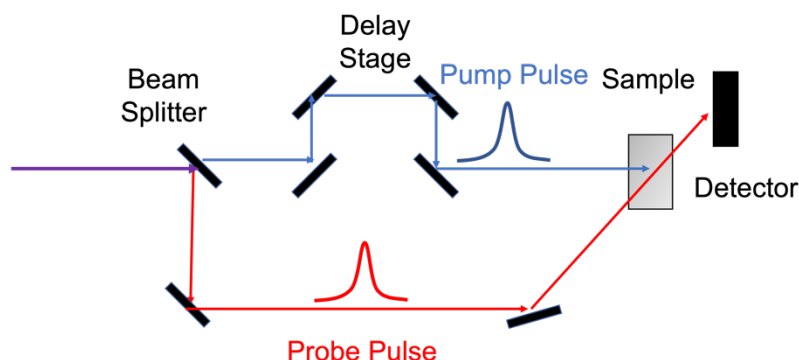


Figure 1.2: Schematic presentation of a pump-probe experiment. The laser source is split into the pump and probe pulses normally at different wavelengths. Then, the pump pulse goes through a delay stage to induce a photoexcitation on the chemical sample. The probe pulse goes through another pathway to characterize the excited state and the transmitted photons are recorded by the detector.

In our setup, we are using a third harmonic generated UV pulse at 267 nm as the pump pulse and high harmonic generated X-rays as the probe pulse. The absorption spectra are taken as the characterization information of the excited state and transient species. With only the probe pulse, the chemical system remains in its electronic ground state, and the probe would only characterize the ground state by measuring the static absorption. Once the pump pulse is sent to the chemical species to initiate the ultrafast processes, the probe pulse can be used to measure the transient molecular dynamics of the system at a time delay with respect to the pump pulse. By physically altering the path length of one of the pulses with the distance being converted to time by dividing by the speed of light, the time delays between the pump and probe pulses can be changed.¹⁸ The probe pulse acts as a camera, taking pictures of the system at any given time, and by changing the delays with respect to the pump, this turns the pictures into a molecular movie allowing the dynamical evolution to be viewed in real time.^{16,17}

1.2: X-ray Spectroscopy

The accessible information gained from pump-probe experiments depends on the probing pulse wavelength. Since the birth of femtochemistry, many probing techniques have been developed, mostly using ultraviolet (UV), visible, and infrared (IR) laser pulses, to investigate chemical reactions in both gas and condensed phases.⁷⁻¹⁴ UV and visible light are used to probe the evolution of the valence electronic structure, and the IR pulses are primarily used to study the vibrational dynamics. However, the molecular dynamic information obtained from optical probes in the visible or UV region is limited by the inherent spatial delocalization of the valence orbitals involved. Ultrafast extreme-ultraviolet (EUV) and soft X-ray give the capability to excite or ionize from the core orbitals that are highly localized to specific atomic sites, alleviating this limitation.

The transition energies from the core levels to the vacant molecular orbitals are much more separated than those from the valence orbitals. Each element has distinct core shell energy levels. Taking organic chemicals, for example, the common atoms involved, carbon, nitrogen, and oxygen, have their K-edge 1s core level at 284, 410, and 543 eV respectively.¹⁵ Therefore, the behavior of different elements can be easily distinguished. Meanwhile, X-ray spectroscopy has sensitivity to different molecular geometries, oxidation states, and spin states as well as the chemical environments.¹⁵ It has been successfully applied in the investigation of a ring-opening reaction,³² photodissociation,^{33, 34} and ultrafast state crossings via conical intersections.³⁵ The transition energies from the core orbitals to the unoccupied molecular valence orbitals contain information about both the core shell and the valence shells. The energetic differences among core orbitals can be extracted by comparing the transition energies to the same vacant valence orbital. In a similar manner, the energetic differences among the valence orbitals can be extracted by

comparing the transition energies from the same core orbital.

1.3: X-ray sources

X-rays are commonly used in projectional radiography like dental imaging and bone-fracture imaging, computed tomography, and other medical fields. X-rays can be generated by an X-ray tube, a vacuum tube that uses a high voltage to accelerate the electrons released by a hot cathode to a high velocity. The electrons with high velocity collide with a metal target, the anode, resulting in the creation of X-rays.¹⁹ This X-ray generation process can provide an abundance of photons. However, the X-rays are not coherent and cannot provide the time resolution needed for ultrafast pump-probe spectroscopy. In order to use X-ray pulses as probe pulses in the pump-probe experiment, a stable, high photon flux and short pulse duration source of X-ray is critical.

For scientific X-ray sources, the gold standard for many years was synchrotron radiation.²⁰⁻²⁴ The undulator or wiggler forces the electrons into a sinusoidal path, which generates light from the acceleration of each oscillation and the generated X-ray photons' energy can be changed by using different magnet spacings. Synchrotron X-ray sources are achieved by firstly accelerating electron packets in storage rings of order one kilometer circumference to high velocities. Then the electrons are directed into an undulator or wiggler (the array of magnets) which supplies strong magnetic fields perpendicular to the electron beams, forcing the electrons into a sinusoidal path, which generates photons from the acceleration of each oscillation. The energy of the generated photons can be changed by using different magnet spacings. The X-rays from synchrotrons can be very bright, with a high flux in the range of 10^{20} photons/ (s*mm²*mrad²*0.1% bandwidth).²² However, the pulse duration of synchrotron radiation can only be achieved in the 10s of picoseconds based on the electron pulse durations. The picosecond timescale is useful for applications like ultrafast electron diffraction, but it is relatively long for the molecular dynamics of interest in this thesis, on the femtosecond timescale.

Free electron lasers are another X-ray radiation source with better brightness. It also starts with the acceleration of electrons in a sinusoidal path. But the electron bunches interact with the X-ray light to force the electrons into microbunches evenly spaced leading to constructive interference and coherence in the emitted X-rays. This technology amplifies the generation of X-ray photon flux up to 10^{35} photons/ (s*mm²*mrad²*0.1% bandwidth) and narrows down the pulse duration to 2 fs.²⁵⁻²⁸ Both synchrotron radiation and free electron lasers are incredibly useful scientific X-ray sources. While due to the nature of the generation, they require one to several kilometer lengths to accelerate the electrons.

Another type of X-ray source is called high harmonic generation (HHG). It can be done on a tabletop apparatus in a laboratory room. The details about the generation process and instrumental specifications will be discussed in the next chapter. HHG is capable of generating energies up to 100s of eV.^{29, 31} Although HHG does not produce nearly as many photons as synchrotron radiation, only producing 10^8 photons/s in the soft X-ray, it is a sufficient flux for running X-ray transient absorption spectroscopy at the carbon K-edge (284 eV). Also, HHG has a much better temporal resolution with pulses down to 43 attosecond,³⁰ which gives us the capability to investigate molecular dynamics and electron motion.

The following chapters will discuss first the experimental method to conduct time-resolved soft X-ray transient absorption experiments at the carbon K-edge (Chapter 2) and then the use of the technique to reveal fundamental factors in organic chemical molecular dynamics, such as the radical formation in pentamethylcyclopentadiene (Chapter 3), photorelaxation of benzaldehyde (Chapter 4) and the photodissociation of 1,2-diiodotetrafluoroethane (Chapter 5).

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Chapter 2: Experimental

To investigate the photoinduced molecular dynamics of organic chemical systems, an apparatus is needed to perform the femtosecond soft X-ray transient absorption spectroscopy at the carbon K-edge. The apparatus comprises a UV pump pulse to excite the molecular system, an X-ray probe pulse to trace and characterize the excited states with femtosecond resolution, a sample interaction region for pump-probe experiments, and a detector to record the spectral features. This chapter addresses the working principles behind such an apparatus and key improvements that have been achieved in its performance.

2.1: High Harmonic Generation

High harmonic generation can be described by a semi-classical three-step model,^{1,2} shown in Figure 2.1. The first step is tunnel ionization in a medium that normally is a noble gas, such as neon, argon, and helium. In our case, we used helium. The reason behind this choice of target gas is the high ionization potential, which accesses the highest possible harmonics. A high-intensity incident infrared beam carries an electric field that is strong enough to lower the binding potential of the electrons and it increases the probability of tunneling ionization. The second step is called propagation where the electron is accelerated away from the nucleus in the first half cycle of the electric field of the incident laser beam and back in the second half. As the electron accelerates, it gains kinetic energy. In the last step, the fast-moving electron has a small probability^{3,4} to collide with the nucleus in space and recombination occurs. The recombination of the two emits a photon with the energy that equals the summation of the ionization potential of the atom and the kinetic energy carried by the electron.

$$E_{\text{photon}} = IP + KE_{\text{electron}}$$

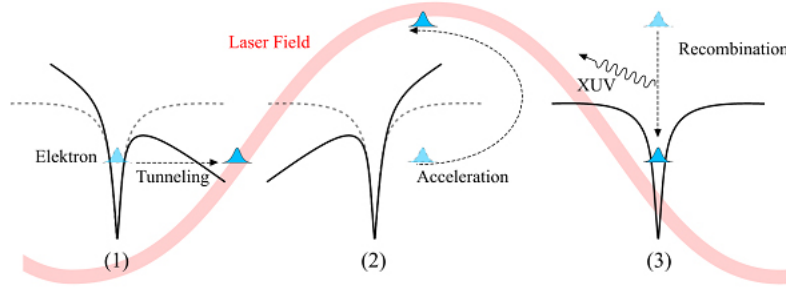


Figure 2.1: Three step picture of harmonic generation: (1) The Coulombic potential of a gas atom is lowered by the laser field allowing for an electron to tunnel out of the barrier to the vacuum level. (2) Once free, the electron is accelerated away from the atom and back again by the E-field of the laser. (3) The electron recombines with the ionized atom emitting radiation. Adapted from Ref 16.

The kinetic energy of the electron can be calculated as the integral of the energy the electron gains in the electric field; it is worth noting the maximum photon energy is:

$$E_{\text{photon (max)}} = IP + 3.17U_p$$

Where U_p is pondermotive energy, which is the cycle averaged kinetic energy of a free electron in an oscillating electric field. The cycle averaged kinetic energy can be expressed as

$$U_p = \frac{e^2 E_0^2}{4m\omega^2}$$

Where e is the charge of the electron, E_0 is the electric field amplitude, m is the mass of the electron, and ω is the frequency of the incident laser pulse. Based on this equation, it is clear the maximum photon energy, or cutoff energy of HHG is proportional to E_0^2 and is inversely proportional to ω^2 of the driving laser. In other words, the relationship between the cutoff energy of HHG and the driving laser is:

$$U_p \propto E_0^2 \lambda^2$$

Where λ is the wavelength of the driving laser pulse. With this, the infrared light can be converted into extreme ultraviolet and X-rays.

On the other hand, helium atoms has the largest binding energy for the outmost electron across the period table, which makes it a great candidate to further increase the cutoff energy for HHG.

2.2: Layout of Experimental Apparatus

The experimental apparatus is composed of four major sections, 1) pump UV beam, 2) probe soft X-ray beam, 3) chemical sample chamber for interaction and 4) grating chamber to spread the soft X-ray wavelengths onto the camera. The diagrammatic description is shown in Figure 2.2.

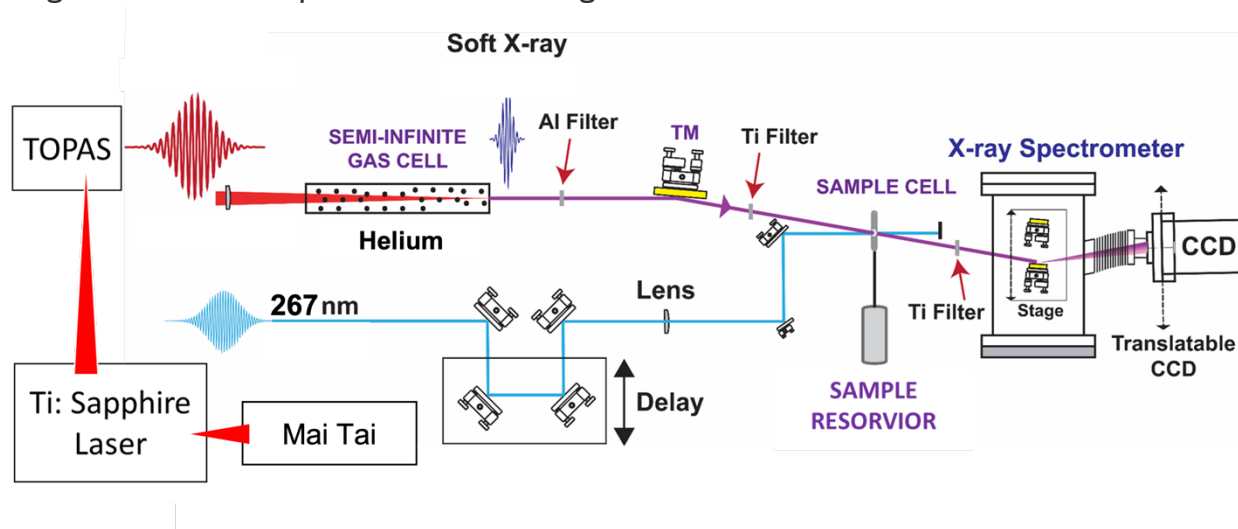


Figure 2.2: A schematic diagram of the experimental apparatus of soft X-ray transient absorption spectroscopy at the carbon K-edge.

Both the pump and probe beam generation need to start with a high power 800 nm laser source. The Mai Tai oscillator from Spectra Physics produces 800 nm with 60 nm bandwidth and 42 MHz repetition rate. The 800 nm pulse is lengthened and sent into a two-stage regenerative Ti: Sapphire amplifier and an additional one pass amplifier (Spitfire) to increase the power to 12 W, 1 kHz repetition rate, and compressed into 35 fs pulse duration. The output from Spitfire is split into two arms with a ratio of 10:90 to generate the pump and probe beam, respectively.

1) The 10% arm is used for the third harmonic generation of the UV pump beam at 267 nm. After testing both types I and type II (with waveplate to match polarization) β -barium borate (BBO) crystals with different thicknesses, 0.3 mm thick type I BBO crystal is chosen and produces a UV pulse with 100 μ J energy and 1.8 nm bandwidth. It is thus sufficient to study both linear and nonlinear absorption behaviors for molecular systems that have an absorption band at 267 nm and cross-sections equal to or larger than 10^{-19} cm²/molecule.

2) The 90% 800 nm output arm from the amplifier is sent into a high energy tunable optical parametric amplifier (HE-TOPAS) for the probe beam, which is the soft X-ray generation. The TOPAS has the capability to convert 800 nm IR into signal pulses ranging from 1300 nm to 1600 nm in the mid-IR. The tunability gives us flexibility in changing the phase-matching condition for HHG. In other words, we can change the HHG cutoff energy as well as the maximum photon flux position with respect to the soft X-ray photon energy. In order to generate soft X-ray pulses

covering the carbon K edge, 284 eV, mid-IR with a wavelength longer than 1300 nm is chosen. The 2.5 mJ mid-IR pulses are focused by a 30 cm lens into a differentially pumped semi-infinite gas cell filled with 1500 Torr or higher pressure of helium gas.¹⁴ The soft X-ray output is transmitted through a 100 nm thick aluminum filter to block the residual high-intensity mid-IR left from HHG. Then, a toroidal mirror focuses the HHG into the chemical sample chamber and overlaps it with the UV beam for the pump-probe experiment.

3) The chemical sample chamber serves as the interaction region for the chemical, as well as the pump and probe laser beams. A chemical sample reservoir is attached externally for supplying the chemical. Inside the chamber, there is a 3D motorized translational stage holding the sample cell. By changing the position of the stage along with the laser beam direction, it can shift the sample cell to the focal point of the soft X-ray and benefit from its maximal intensity at this region. Also changing the position in the plane perpendicular to the laser propagation direction can help us make sure that most of the chemical molecules can interact with both laser beams. The 267 nm UV pulses are focused by a 45 cm lens outside of the sample chamber to cross the broadband soft X-ray pulses at a 1° angle. This non-collinear design helps us to block the UV beam from the X-ray grating effectively. At the interaction region, the UV beam waist is 120 μm with 10^{11} W/cm^2 maximal intensity. The UV focus remains larger than the X-ray focus for all settings, ensuring a homogeneously pumped interaction volume.

4) The grating chamber is assembled with a camera to disperse the transmitted HHG photons and detect the photon counts. There are two gratings mounted on a one-dimensional translational stage in the grating chamber, Hitachi 0010-0660 (1200 grooves/mm) and Hitachi 0010-0659 (2400 grooves/mm). The Hitachi 0010-0660 grating has a blaze wavelength at 3 nm (413.3 eV) and the other grating has a blaze wavelength at 9 nm (137.8 eV).⁸⁻¹⁰ Based on this difference, we label them X-ray grating and EUV grating. Even though the X-ray grating has half of the grooves per mm compared to EUV grating, due to its blaze wavelength being much closer to carbon K-edge (284 eV), the diffraction efficiency is much better. Transmitted X-ray photons are dispersed by the grating onto a PIXIS charged-couple device (CCD) camera chip with 1340x40 pixels where each pixel occupies 20 microns.

2.3: Data Acquisition and Analysis

2.3.1: Data Acquisition

Soft X-ray absorption spectral data are acquired by central control of an integrated LabVIEW program, written by Valeriu Scutelnic. The program controls the pump beam shutter, UV pump beam delay stage, and camera acquisition. The CCD camera is cooled to -30 °C to reduce dark counts. Before producing photoexcited chemical species, the static soft X-ray absorption spectrum is collected. In this case, only the soft X-ray probe beam is sent to the chemical. With enough sample vapor in

the gas cell, the camera exposure time is set to one second for one image. The soft X-ray spectrum on the camera without the sample is set as the background spectrum. For each image, the collected spectrum is analyzed by the Beer-Lambert Law using the following equation

$$A = -\text{Log}_{10}\left(\frac{I_{in}}{I_{out}}\right)$$

Where A is the absorbance of the target chemical, I_{in} is the intensity of soft X-ray at each pixel with chemical sample supply, and I_{out} is the intensity of soft X-ray at each pixel without chemical sample. In order to increase the signal-to-noise ratio, normally 64 images with chemical in and out are collected and averaged. For a sample with low absorptivity, 192 images can be necessary.

For soft X-ray transient absorption spectra recorded at a certain time delay, the UV pulse needs to be sent prior to the probe pulse to initiate photoexcitation. After setting up the delay time, the transient absorption spectrum of excited chemical species can be recorded as the difference between the spectra with the UV shutter open and closed. The transient absorption is calculated in a similar way as the static spectrum as following

$$\Delta A = -\text{Log}_{10}\left(\frac{I_{with\ UV}}{I_{without\ UV}}\right)$$

At each time delay, normally these images are repeated 32 times and coadded to improve statistical results. All interested time delays need to be measured separately to generate a 2D colormap of transient soft X-ray absorption with respect to time evolution.

2.3.2: Pixel to Photon Energy Calibration

Once the soft X-ray photons are dispersed on the CCD camera, the relationship between the camera pixel and photon energy needs to be determined. The relationship can be described by the following equation

$$\text{Pixel Number} = A_0 - B \tan\left(\frac{\pi}{2} - \sin^{-1}\left(\sin\alpha - \frac{1.4878}{E}\right)\right)$$

Where A_0 is an offset term, B is a scaling factor from pixel to distance and α is the actual angle at which X-ray photons hit the grating. A_0 , B , and α are parameters to be fit using reference chemical species and literature values. This equation is derived from the grating dispersion equation.⁴

There are two reference chemicals we are using, argon and allyl iodide. Argon has $L_{2,3}$ edges corresponding to $2p \rightarrow$ Rydberg state transitions at 240 – 260 eV.⁶ Using the transitions of $2p_{3/2} \rightarrow 4s$ (at 244.4 eV), $2p_{3/2} \rightarrow 3d$ (at 246.9 eV), $2p_{3/2} \rightarrow 4d$ (at 247.7 eV) and $2p_{1/2} \rightarrow 4s$ (249.1 eV), a proper pixel-to-energy relation can be established, as shown in Figure 2.3 after each column of pixel has been integrated.

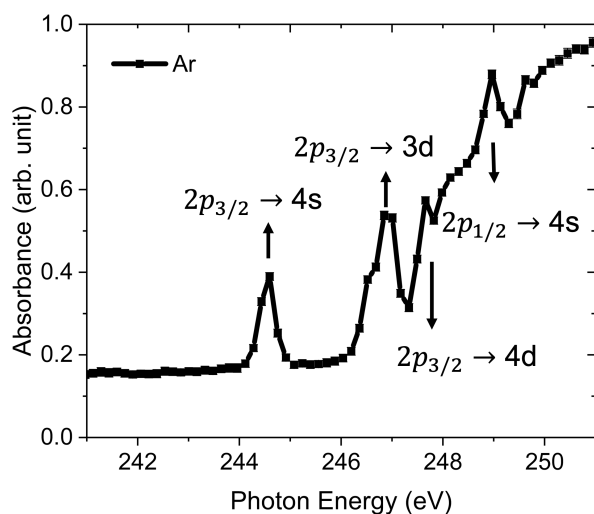


Figure 2.3: A calibrated argon absorption spectrum at $L_{2,3}$ edges using literature values⁵ to establish the relationship between camera pixel number and photon energy.

Since the core absorption of argon at the $L_{2,3}$ edges is still more than 30 eV away from the carbon K edge (284 eV), it would be better to have a carbon-containing chemical species added to the calibration curve. Allyl iodide serves as the other reference molecule. It has been observed both by our group and other past studies that allyl iodide can dissociate within 200 fs into allyl free radical and an iodine atom. Also, the X-ray absorption spectrum of allyl free radical has been reported at 282 and 282.4 eV.⁷ Then the complete calibration curve covering the carbon K-edge is achieved by using both argon and allyl free radical as reference species. A calibrated absorption spectrum of allyl radical is shown in Figure 2.4.

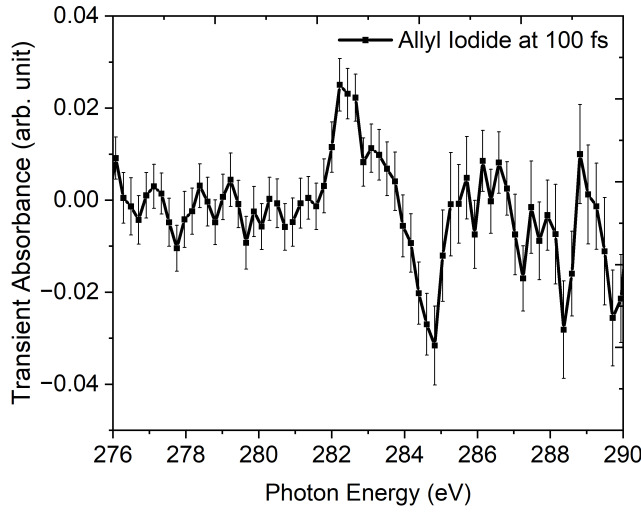


Figure 2.4: A calibrated transient absorption at the carbon K-edge of allyl radical at 100 fs time delay between X-ray and UV pulses to complete the relationship between camera pixel number and photon energy.

2.3.3: Determination of Spectral Resolution

Transitions with known Lorentzian width can also be used to determine the spectral resolution of the instrument. Peak broadening in general comes from two types, homogeneous broadening, and inhomogeneous broadening. The homogeneous broadening can be classified into natural broadening which is the result of the finite radiative lifetime and pressure broadening which is the result of the finite lifetime in the quantum state owing to collisions. Together the homogeneous broadening can be characterized by a Lorentzian linewidth. The inhomogeneous broadening characterized by a Gaussian width is due to the Doppler effect of the measured species, the dispersion capability of the grating, and the pixel resolution of the CCD camera.¹¹ The convolution of these two types of broadening effects can be described by a Voigt function as following equation¹²

$$I(E) = I_0 + A \frac{2\ln 2}{\pi^{3/2}} \frac{w_L}{w_G^2} \int_{-\infty}^{+\infty} \frac{e^{-t^2}}{(\sqrt{4\ln(2)} \frac{E - E_c}{w_G})^2 + (\frac{w_L}{w_G} \sqrt{\ln 2})^2} dt$$

where $I(E)$ is the intensity at certain energy, E the energy, E_c is the peak center, I_0 and A are fitting parameters, w_L is the Lorentzian linewidth and w_G is the extrapolated spectral resolution.

In argon, the $2p_{3/2} \rightarrow 4s$ transition is well separated from other transitions in its $L_{2,3}$ edges and its Lorentzian linewidth has been reported as 114 meV. Thus, it has been chosen to determine the spectral resolution. When the spectral resolution is not good enough, this fitting is also an indicator that the optical alignment needs to be corrected. In Figure 2.5, the best spectral resolution of the current apparatus is determined to be 266 ± 12 meV.

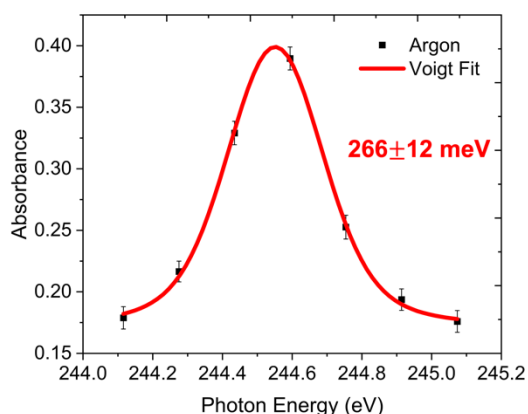


Figure 2.5: The $2p_{3/2} \rightarrow 4s$ transition observed in argon and fitted with a Voigt function using a Lorentzian linewidth of 114 meV. The spectrum is measured with the X-ray grating. With optimizing the optical alignment of soft X-ray, the best spectral resolution is 266 meV.

2.3.4: Determination of Temporal Resolution

Since soft X-ray transient absorption spectroscopy is a pump-probe time-resolved spectroscopy, it is important to know the temporal resolution. To determine the temporal resolution, the Stark shift in the Rydberg state of argon has been monitored with the soft X-ray transition in the presence of a moderately intense UV field with a peak intensity of 10^{12} W/cm^2 . As the shifted peak's intensity scales linearly with respect to the strength of the electric field it experiences from the UV pulse, the peak's intensity directly maps out the cross-correlation between the UV pump and soft X-ray probe. Thus, analyzing the change in intensity of the shifted peak with respect to time tells the information of the temporal resolution.¹¹

The $2p_{3/2} \rightarrow 4s$ Rydberg transitions experience an apparent upward shift of 0.2 eV. By fitting the trace of this shift, the temporal resolution with this pump-probe setup can be analyzed. Based on the time-bandwidth product derived from the uncertainty principle,¹⁴ the broadband soft X-ray pulse has a much shorter pulse duration compared to the pulse width that would be expected from the 2 nm bandwidth UV beam. Then the temporal resolution is greatly dependent on the UV pulse duration. By changing the compression inside the amplifier and the delay stage in the third harmonic generator, the UV pulse duration as well as the temporal resolution can be optimized to $82 \pm 13 \text{ fs}$ as shown in Figure 2.6.

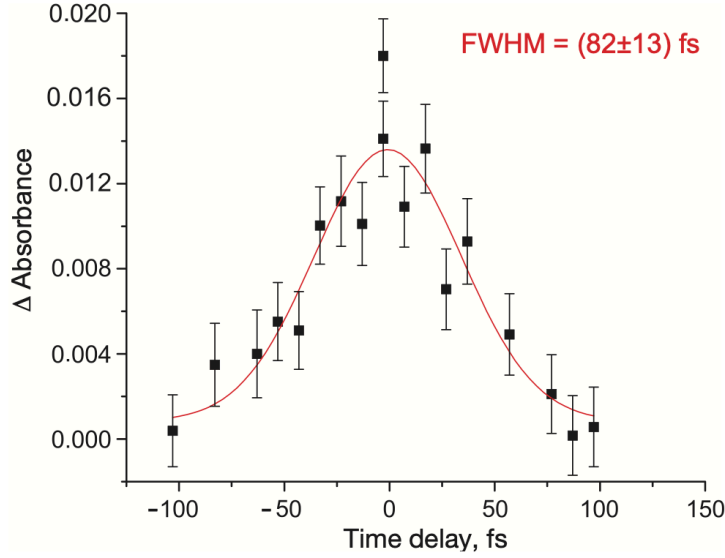


Figure 2.6: Optimized temporal resolution determined to be 82 ± 13 fs using the shift in the $2p_{3/2} \rightarrow 4s$ transition in argon. The UV beam has a pulse energy of 30 μJ and is focused with a 45 cm lens.

2.4: Optimization of Instrumental Capability

2.4.1: HHG Extension

In order to have sufficient photon flux at the carbon K edge (284 eV) and possibly to extend the cutoff energy of HHG to nitrogen K-edge (410 eV), a set of experimental parameters have been modified to improve soft X-ray generation.

Firstly, since the cutoff energy of HHG is proportional to λ^2 of the driving IR beam, the longer the wavelength, the higher the cutoff energy of HHG could be. Figure 2.7 clearly demonstrates the difference between using 1430 and 1500 nm as the driving IR sources. The cutoff energy of HHG has been extended by more than 25 eV. It is worth noting that the TOPAS produces the highest power at 1300 nm signal beam, and with increasing wavelength the power drops slightly. But in this region, the impact of lowering the electric field strength is almost negligible compared to the effect of increasing the wavelength. Also, every time the driving IR wavelength is changed, the phase matching condition needs to be re-established by changing the medium gas pressure, incident beam size, as well as the compression of 800 nm beam from the amplifier.

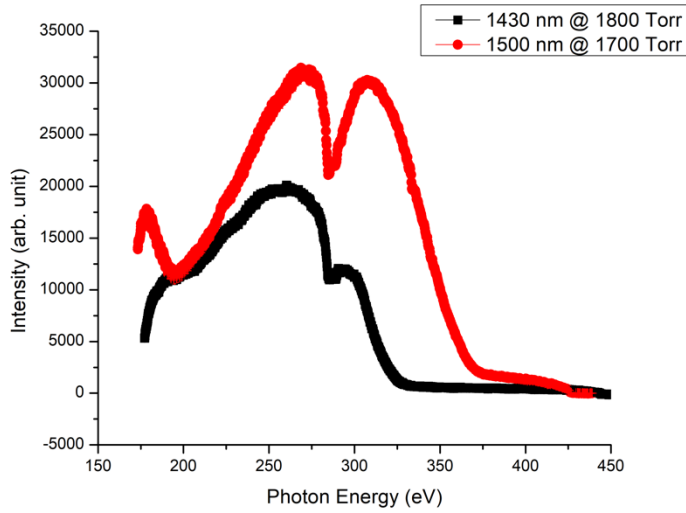


Figure 2.7: HHG readout on the X-ray camera with 1430 and 1500 nm driving IR wavelength. The helium gas pressure has been adjusted to reestablish phase matching condition at the carbon K-edge.

2.4.2: Improvement of Spectral Resolution

The resolving power of a grating is a measure of its ability to spatially separate two wavelengths. It is determined by applying the Rayleigh criteria to the diffraction maxima; two wavelengths are resolvable when the maxima of one wavelength coincides with the minima of the second wavelength. The chromatic resolving power R is defined by the following function

$$R = \frac{\lambda}{\Delta\lambda} = nN$$

where $\Delta\lambda$ is the resolvable wavelength difference, n is the diffraction order and N is the number of grooves illuminated. Based on this equation it is clear that the EUV grating with 2400 grooves/mm has higher resolution compared to the X-ray grating with 1200 grooves/mm. However, the instrumental spectral resolution is not solely dependent on the grating resolving power but also on the optical quality of all components and the system alignment. It has been found that the spectral resolution can be improved from 370 meV to 266 meV by optimizing the optical alignment up to the X-ray grating, as well as the distance to the camera.

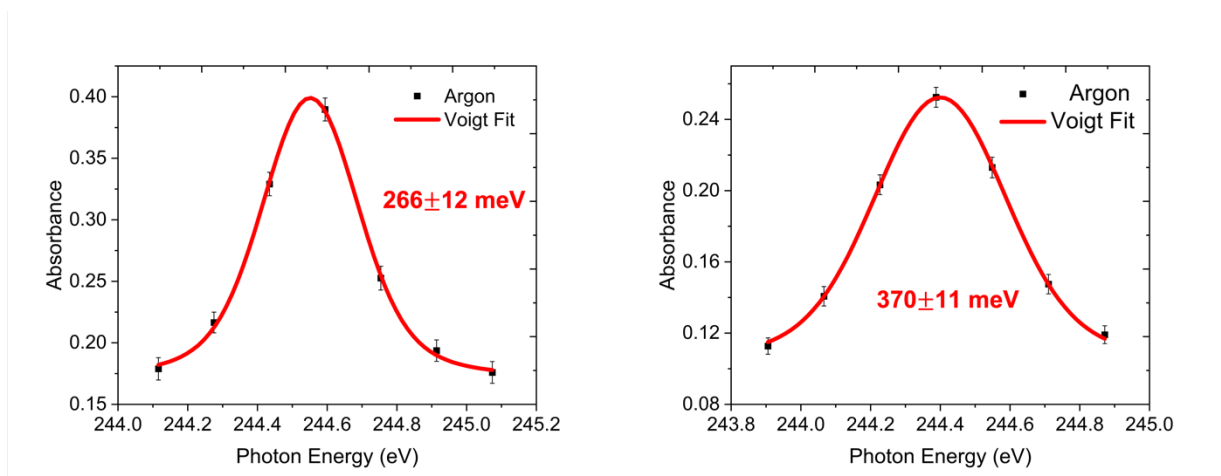


Figure 2.8: The comparison between a) optimized optical alignment and b) normal optical alignment of $2p_{3/2} \rightarrow 4s$ transition observed in argon and fitted with a Voigt function using a Lorentzian linewidth of 114 meV. Both spectra are measured with the X-ray grating. By optimizing the optical alignment of the soft X-ray, the resolution improved from 370 to 266 meV.

The other two possible solutions to improve spectral resolution are first extending the laser table length and placing the CCD further away from the grating and second purchasing an X-ray grating with blaze wavelength at carbon K-edge and more grooves per mm. The current X-ray grating has its blaze wavelength at the nitrogen K-edge; if in the future the soft X-ray can be extended to nitrogen K-edge, the spectral resolution can be characterized by a nitrogen-containing molecule and there should be a better resolution.

2.4.3: Sample Supply Modification

In order to study heavy molecular systems with a low vapor pressure at room temperature, the sample supply line and sample cell have been modified. Firstly, the sample reservoir has been changed to a larger diameter to increase sample absorption and increase volume to surface area. Secondly, the sample line connecting from the external sample reservoir all the way to the inside line attached to the sample cell has been wrapped with heating tape. A positive heating gradient needs to be achieved from the reservoir to the interaction region at the sample cell. Three thermostats have been set up on the sample reservoir, sample line, and copper heating jacket on the sample cell. For example, to supply enough vapor for soft X-ray absorption but also to avoid clogging of pentamethylcyclopentadiene vapor along the flow path, the reservoir has to reach 60 °C, the line has to reach 70 °C and the heating jacket needs to reach 80 °C.

Meanwhile, the sample cell design has been changed with a larger hole and a longer pathlength. The hole size has been increased from 200 to 300 microns to let chemical vapor diffuse away from the sample cell. Meanwhile, the path length has

been increased from 2 mm to 4 mm to increase absorption pathlength. A sidewise gas cell design drawing is illustrated in figure 2.9.

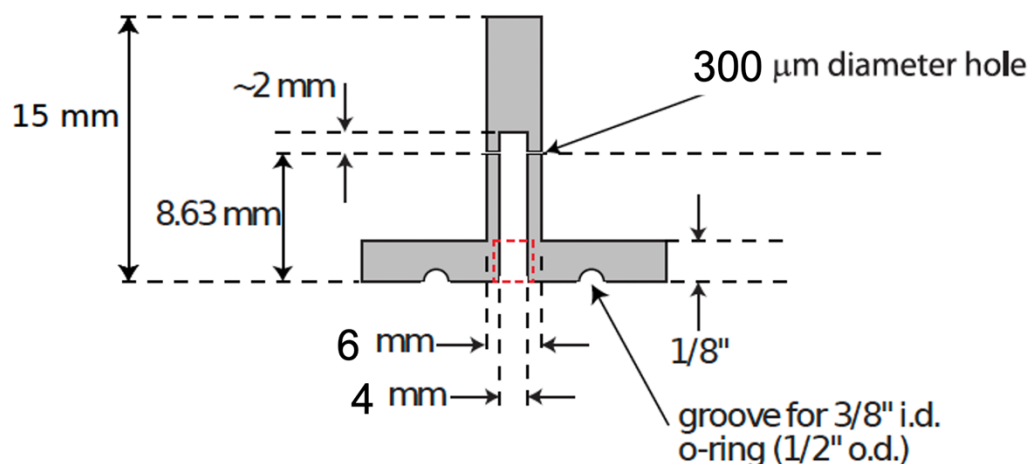


Figure 2.9: Gas cell design drawing, side view.

With the above modifications, both the static (without UV excitation) absorption of the soft X-ray spectrum has been increased significantly as shown in Figure 2.10.

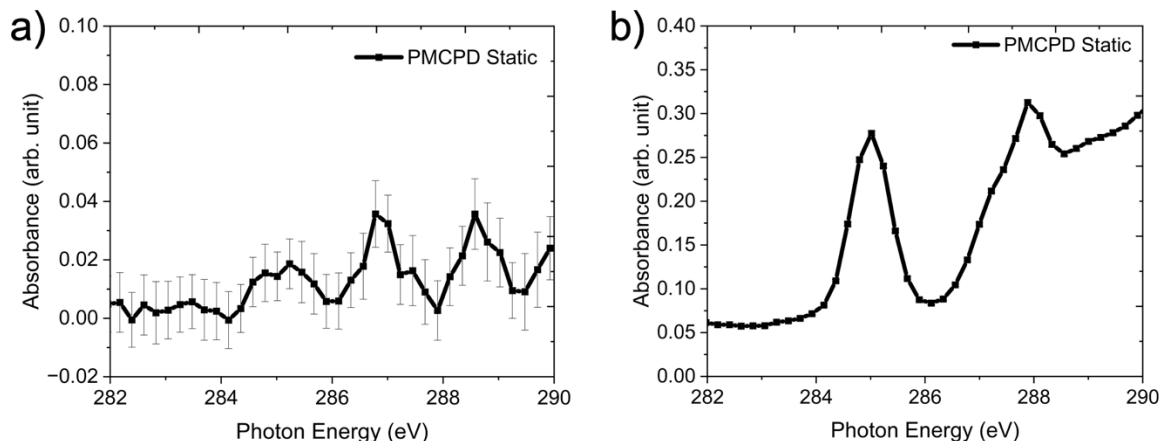


Figure 2.10: Static soft x-ray absorption spectra a) without sample supply modification and b) with sample supply modification of pentamethylcyclopentadiene (PMCPD) averaged with 192 images.

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Chapter 3: Radical Formation from Pentamethylcyclopentadiene

Conjugated cyclic dienes undergo rich dynamics following ultraviolet (UV) excitation, which is responsible for considerably important photochemistry. We report site-specific soft X-ray transient absorption spectroscopic measurements to elucidate the fundamental photodynamics of pentamethylcyclopentadiene (PMCPD, C_5Me_5H). Core-level X-ray spectroscopy at the carbon K-edge (284 eV) is applied to identify the electronic ground state, the initial excited state, and a previously unobserved radical photoproduct of PMCPD (loss of the H atom from the saturated carbon site on the ring). The excited state dynamics initiated at 267 nm (1^1B_2 , $\pi\pi^*$) is investigated using broadband soft X-ray pulses produced by the process of high harmonic generation. In combination with density functional theory calculations of the X-ray absorption spectra for the excited 1^1B_2 state at the Frank-Condon (FC) geometry from the ground state, the 1^1B_2 optimized geometry, the transition state geometry to form the radical, and the radical itself (PMCPD $\cdot$, $C_5Me_5\cdot$), the photodissociation mechanism of PMCPD is elucidated. The X-ray core level transient absorption spectra provide a direct observation of PMCPD $\cdot$ radical formation, attributed to two formation times following UV excitation: a fast channel likely comes from PMCPD with an active C-H vibration stretching mode and a slow channel takes time for the vibrational energy to redistribute into this vibrational mode for the dissociation. The evolution of the core-to-valence resonances at the carbon K-edge, together with theory, suggests that the 1^1B_2 state is the likely excited electronic state involved in the formation of the PMCPD $\cdot$ radical photoproduct.

3.1: Introduction

Light is very useful in chemical reactions, not only because it can provide photon energy that can be absorbed by chemicals, but also because the molecular photoexcited states can undergo reactions that are otherwise symmetry-forbidden in their electronic ground state. The photochemistry of unsaturated molecular systems can be found to be widely involved in many biochemical processes. Sometimes they are for the benefit of living organisms, such as vitamin D synthesis, which happens through a photoinduced electrocyclic ring opening reaction.^{1,2} Another is the vision chromophore, retinal, which goes through ultrafast photoisomerization that ultimately results in visual perception.³ In other cases, a photochemical reaction can be harmful, such as cycloaddition can cause DNA damage and lead to skin cancer.⁴ Thus, a detailed understanding of the unsaturated molecular systems' electronic properties, photochemical behavior, and excited state structure is imperative, making them ideal targets for ultrafast time-resolved spectroscopic studies and theoretical calculations.

The photoinduced molecular dynamics of pentamethylcyclopentadiene (PMCPD) has been investigated by resonance-enhanced multiphoton ionization mass spectrometry and ultrafast photoelectron spectroscopy (PES).⁵⁻⁷ Based on their spectral observation, the photorelaxation mechanism of PMCPD was proposed to be the following: the initially populated 1^1B_2 state via 267 nm photoexcitation decays to a dark 2^1A_1 state through a conical intersection, followed by further internal conversion to revert to the ground 1^1A_1 state with excess vibrational energy within 300 fs. It is well-known that under UV excitation, cyclohexadiene (CHD) undergoes a ring opening reaction on the femtosecond timescale.⁸ It is interesting that with one less carbon participating in the ring, the photorelaxation mechanism is quite different. In this work, we would like to determine if the relaxation back to the electronic ground state is the only relaxation pathway of PMCPD under 267 nm UV excitation and what are the photophysical mechanisms for the relaxation of the initially excited state.

Near edge soft X-ray transient absorption fine structure (NEXAFS) spectroscopy has proven to be a powerful tool to elucidate photoinduced molecular dynamics. It is sensitive to molecular geometry, electronic structure, oxidation state, and chemical environment. Here, time-resolved NEXAFS at the carbon K-edge (280 eV to 300 eV) is used to investigate the photodynamics of a benchmark cis-diene molecule, PMCPD. With the help of electronic structure calculations, it is observed that PMCPD dissociates into a hydrogen atom and PMCPD• radical via two timescales; one appears right after UV excitation, and the other continues up to 1 ps timescale. The fast channel likely comes from PMCPD with an active C-H vibration stretching mode and a slow channel takes time for the vibrational energy to redistribute into this vibrational mode for the dissociation. From the theory, and corroborated with the experimental dynamical results, the radical formation process likely involves the initially excited 1^1B_2 state. The radical mechanism is different from that assigned by photoelectron studies,⁵⁻⁷ which describe an internal conversion to the ground state. In contrast to valence photoionization spectra, core level spectra have a greater specificity to distinguish the radical from the hot ground state.

3.2: Literature Understanding of PMCPD Photodynamics

Cyclopentadiene (CPD) is a prototype for the electronic spectroscopy of a conjugated electron system. The excited state electronic structure of CPD has been investigated thoroughly both experimentally and theoretically. Due to the closed ring form of CPD, the two double bonds are locked in the cis conformation. The locations and assignments of various singlet, intervalence π to π^* and Rydberg transitions have been a major subject of optical UV spectroscopic studies.⁹⁻¹² Spin forbidden singlet to triplet transitions have also been investigated by electron impact¹³ and electron energy loss spectroscopy (EELS). The interpretation of the electronic spectra of CPD remains a challenge for both experiment and theory due to the difficulties caused by the appearance of several strongly allowed Rydberg series that overlap the broad

and diffuse bands that are usually assumed to arise from π to π^* valence type excitations. Several different theoretical works have been made to understand the assignment of the observed transitions including multiconfigurational second-order perturbation theory,¹⁴ multireference perturbation theory with complete active space self-consistent field,¹⁵ the equation of motion coupled cluster method,^{16,17} and symmetry-adapted cluster-configuration interaction method.¹⁸

Cyclopentadiene (CPD) itself is also an important model compound for photochemical reactions of cyclic diene systems. In the presence of various photochemical sensitizers, CPD can receive energy transferred from a sensitizer's excited triplet state and form cycloaddition photoproducts via a reactive CPD triplet intermediate. The photochemical products from high power pulsed laser illumination were found to be bicyclopentene (Bp) and tricyclopentane (Tp) with low quantum yield, in the 1970s.¹⁹ In 2005, Trushin's group performed the first ultrafast photoelectron spectroscopy (PES) study on CPD with 240 nm pump and 810 nm probe beams.²⁰ They noticed two competing photorelaxation pathways, which are hydrogen migration leading to a hot ground state and electrocyclic ring closure to form Bp and Tp.

There are four π character molecular orbitals (MOs) involved in PMCPD. Two bonding orbitals labeled as π_1, π_2 , and two antibonding orbitals labeled as π_1^*, π_2^* . The first optical absorption band of PMCPD corresponds to the transition from $\pi_1 \rightarrow \pi_1^*$ (these four molecular orbitals have been shown in Figure 3.1 a) through d)). UV absorption spectroscopy has shown that methyl-substituted CPDs exhibit the first absorption band maximum for $S_1 \leftarrow S_0$ at lower energy compared to CPD.

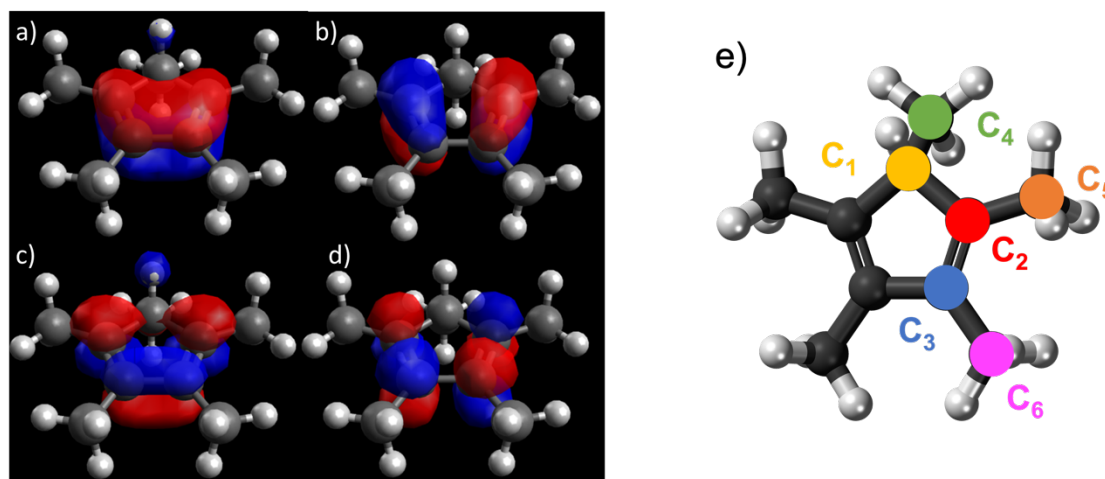


Figure 3.1: The conjugated π molecular orbitals of PMCPD. They are labeled a) π_1 b) π_2 c) π_1^* and d) π_2^* (in increasing order of energy). The π_1 and π_2 levels are bonding while π_1^* and π_2^* are antibonding. And e) is the ball and stick model of PMCPD molecule with color-labeled and numbered C atoms. Calculations by D. Hait.

Weber's group applied resonance-enhanced multiphoton ionization mass spectrometry and structure-sensitive PES to investigate the photodynamics of methylated CPDs such as tetramethylcyclopentadiene (TMCPD) and PMCPD.^{5,6} A 400 nm beam is used as the ionizing probe beam. The ionization energy of TMCPD (PMCPD) is 7.28 (7.29) eV. After UV excitation at the Franck-Condon (FC) region, one 400 nm photon is sufficient to ionize the molecule from the 1^1B_2 state. The time-resolved PES method provides two series of features. The first sets of features come from the photoelectron ejected from the 1^1B_2 state. The second set of features at a later time delay and higher energy is assigned to another excited state, an optically dark state 2^1A_1 . The photoelectron energy difference is explained for the case when some electronic energy has been transferred to vibrational energy, and it requires two probe photons to eject photoelectrons. Since there was no differential photoelectron signal after 300 fs, the photoproduct was assigned as hot ground state PMCPD. Time-resolved mass spectra detected parental and fragmental ions with cleavage of methyl groups.⁶ The observed decay of the parent ion signal and the rise of the fragment signals were assigned to the lifetimes of the 1^1B_2 and 2^1A_1 states.

Stolow's group used ultrafast PES with a tunable pump pulse ranging from 240 to 278 nm and a probe pulse at 322 nm to study the dynamics of CPD and methyl-substituted CPDs.⁷ The timescales of the observed dynamics have furthermore been suggested to be dependent on specific nuclear motions as exemplified in the slow-down of the dynamics from CPD to the methyl-substituted CPDs. The photorelaxation mechanism of this molecular beam jet-cooled PMCPD experiment was proposed to be the following: the initially populated 1^1B_2 state decays to a dark 2^1A_1 state through a conical intersection, here considered to be the S_1 state based on the order of the global minimum energy of each state, followed by internal conversion to revert to the ground state with excess vibrational energy.

Subsequently, Martínez's group used ab initio multiple spawning with multi-state reference perturbation theory treatment of the electronic state and simulated the non-adiabatic excited state dynamics of CPD and TMCPD following excitation to the bright $1^1B_2, S_1$ state, which is defined by the order of energy at the optimized geometry of the ground electronic state.²¹ In this work, we also use this definition of the 1^1B_2 state as the S_1 state. They calculated both bands of the potential energy surface on TMCPD and assigned them to originate from ionization out of the same adiabatic state, 1^1B_2 . The disappearance of the low-energy one-photon band is a consequence of a fast increase in ionization potential from 1^1B_2 to 2^1D_0 , the ground state of the cation, where the wavepacket leaves the FC region and slides down the potential energy surface. Those results indicate that there is not necessarily another excited state involved besides the 1^1B_2 state in the photodynamics of methyl-substituted CPDs.

In 2014, Unterreiner's group also collaborated with Stolow's group and used ab initio multiple spawning simulations to understand the dynamics of

hexamethylcyclopentadiene.²² They found an unprecedentedly large spectral delay of 310 ± 20 fs in PES experiments, explained by a stepladder modeled relaxation via only the 1^1B_2 state with decreasing energy along the potential energy surface. In additional simulations that replace the methyl groups with hydrogen atoms having a mass of 15, they showed an induction time of 108 ± 10 fs, which could be directly assigned to progress along a torsional mode leading to the intersection seam with the molecular ground state. It is worth noting that in these PES studies, they used a molecular beam source and a skimmer to create an intense beam of jet-cooled molecules for study. But in our case, we heat the sample of PMCPD to 333.15 K to get enough vapor.

Here, we first present the X-ray absorption spectrum at the carbon K-edge of the electronic ground state PMCPD. Then, differential X-ray absorption spectra at time delays from 0 fs to 210 fs in 30 fs steps are reported to investigate the photodynamics following excitation by 267 nm light. A 1 ps time delay is chosen to study the final photoproduct of PMCPD, revealing the radical PMCPD•, which is unique in the X-ray spectrum. X-ray absorption spectra are understood by calculations with orbital optimized density functional theory (OO-DFT). The calculations indicate the formation of the radical, as the computed X-ray absorption features for this species agree well with the experiment. Finally, a schematic potential energy surface of the photophysics of PMCPD at 267 nm is presented to understand the observed mechanism related to PMCPD radical formation.

3.2: Results

3.2.1: Soft X-ray absorption spectra of electronic ground state PMCPD

The near-edge X-ray absorption fine structure spectrum at the carbon K edge of PMCPD (Figure 3.2, solid black line connecting the datapoints, with error bars corresponding to 95% confidence interval over 192 scans summed together) shows two strong peaks at 284.8 and 287.7 eV with a low energy shoulder at 287.0 eV. They are labeled as peaks A-C in order of increasing energy. Distinct spectral features cannot be observed for energies greater than 289 eV due to ionization from the 1s electrons. The carbon 1s core electron binding energy of CPD has been estimated by DFT to be 289.5 eV.²⁵

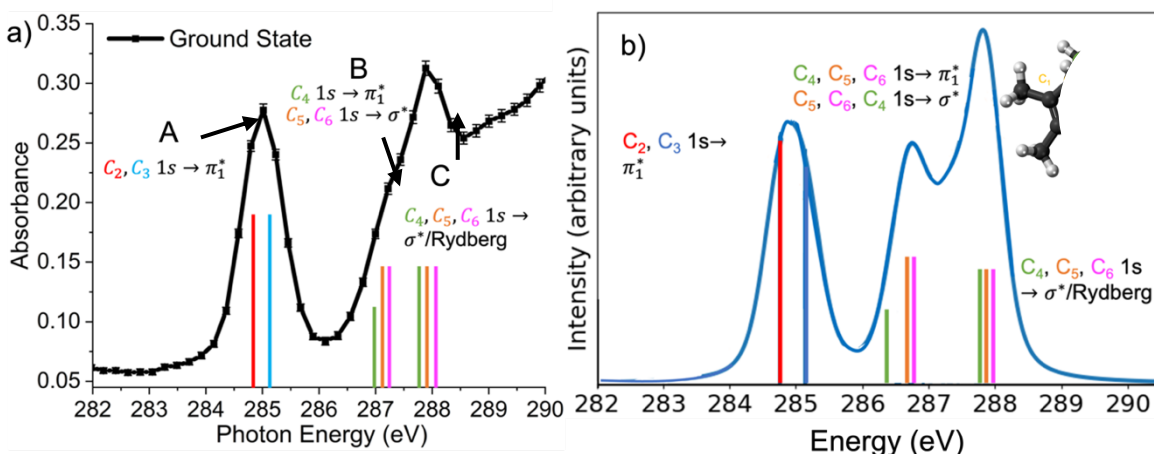


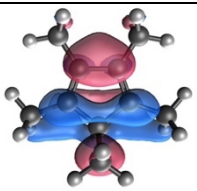
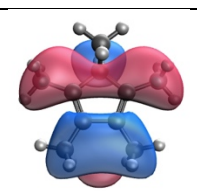
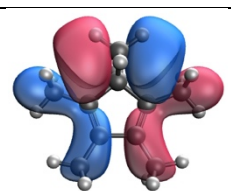
Figure 3.2: a) Static near-edge X-ray absorption spectrum of PMCPD in the ground state (the solid black line connecting the data points, error bars correspond to 95% confidence interval over the sum of 192 scans). b) Calculated X-ray absorption spectrum of PMCPD in the ground state showing specific carbon atoms (color-coded) participating in the prominent core–valence transitions (see text for assignment). A Gaussian broadening of 0.3 eV is applied to the stick spectrum to obtain the blue predicted spectrum. Only the lowest energy core-excited states for each atom are included, and therefore the rising photoionization edge is not computed. Calculations by D. Hait.

Due to the sensitivity of soft X-ray absorption spectroscopy to different molecular geometries and chemical environments, as well as considering the symmetry of the molecule, the ten carbon atoms in PMCPD can be classified into six different types of carbons (C₁–C₆) (see the colored ball and stick structure of PMCPD in Figure 3.1 e)). OO-DFT calculations with the restricted open-shell Kohn-Sham (ROKS) formalism simulate the core absorption spectrum of ground state PMCPD at the carbon K-edge, shown in comparison to the experimental results on the right of Figure 3.2 a). The detailed transition assignments for the spectral features are presented in Table 3.1 along with the electron density for the associated molecular orbitals presented in Table 3.2.

Table 3.1: Assignments of X-ray absorption spectral features observed at the C K-edge of ground electronic state PMCPD. Calculations by D. Hait.

Peak Label	Peak Energy (eV)		Transition Assignment
	Experimental	Theoretical	
A	284.8	284.8	$C_2\ 1s \rightarrow \pi_1^*$
		285.2	$C_3\ 1s \rightarrow \pi_1^*$
B	287.0	286.5	$C_4\ 1s \rightarrow \pi_1^*$
		286.7	$C_5\ 1s \rightarrow \sigma^* (C-H)$
		286.8	$C_6\ 1s \rightarrow \sigma^* (C-H)$
C	287.7	287.8	$C_{4,5}\ 1s \rightarrow \sigma^* (C-H)$ with Rydberg character
		287.9	$C_6\ 1s \rightarrow \sigma^* (C-H)$ with Rydberg character

Table 3.2: Calculated electron density of unoccupied molecular orbitals in the ground state of PMCPD. Calculations by D. Hait.

Molecular orbital	Electron density
LUMO π_1^*	
$\sigma^* (C-H)$	
$\sigma^* (C-H)$ With Rydberg character	

Based on the calculated energies, feature A can be assigned to be composed of two transitions from C_2 and C_3 core (1s) orbitals to the LUMO, π_1^* . The electron

density of the LUMO has been plotted (Table 3.2), showing it is mostly centered on the C_2 and C_3 atoms; the good overlap between the wavefunctions of the C_2 and C_3 core electrons and the LUMO orbital provide for the observed large transition probability in the X-ray absorption. In the experimental spectrum, these two transitions show up as one peak, as the energy difference between the core orbitals of C_2 and C_3 is only 0.38 eV, which is close to the experimental spectral resolution limit of 0.36 eV (see Figure 3.3). This is also similar to the calculated difference, 0.31 eV, obtained for CPD²⁵. The shoulder feature B centered at 287 eV corresponds to two sets of transitions: C_4 1s to the delocalized π_1^* and $C_{5,6}$ 1s to their σ^* (C-H) orbitals. The calculated electron density of π_1^* indicates that the delocalization of the LUMO can extend to the C_4 methyl group but not to C_5 and C_6 in the other methyl groups. The experimental feature labeled C is centered at 287.7 eV and is assigned to transitions from C_{4-6} 1s to their σ^* (C-H) with some Rydberg orbital character. This assignment is similar to Hitchcock's²⁶ for the inner shell excitation energy of CPD. Compared to CPD, methyl substitutions in PMCPD lower the energies of the Rydberg orbitals and induce more mixing between the σ^* (C-H) and Rydberg orbitals.

As mentioned in the experimental chapter, the spectral resolution can be determined by applying a Voigt function on argon soft X-ray absorption spectrum peak at 244.4 eV corresponding to $2p_{3/2} \rightarrow 4s$ transition. With known Lorentzian width of 114 meV, the spectral resolution is determined to be 359 ± 13 meV. The resolution explains why the transitions in ground state PMCPD that correspond to C_2 and C_3 transitions to the LUMO (with the calculated difference of 380 meV) are hard to distinguish in our spectrum.

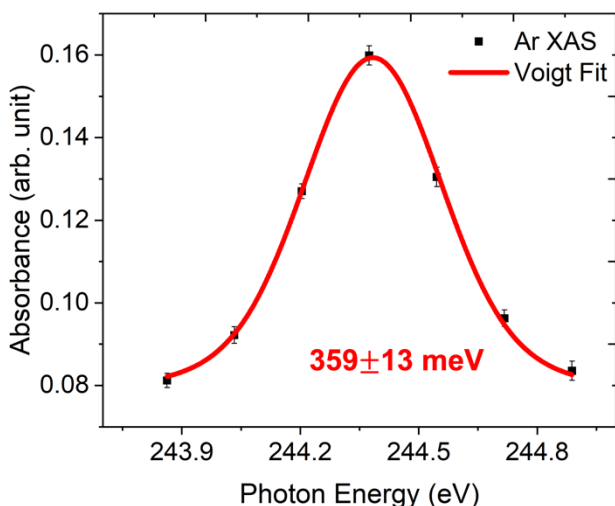


Figure 3.3: The experimental soft X-ray absorption spectrum (XAS) of ground electronic state argon corresponding to the $2p_{3/2} \rightarrow 4s$ transition and fitted with a Voigt function using a Lorentzian linewidth of 114 meV. The spectral resolution is determined to be 359 ± 13 meV.

3.2.2: Transient Absorption Spectra of PMCPD

The transient X-ray absorption spectra at the carbon K-edge show absorption changes that are the differences in absorption with and without the 267 nm excitation pulse at each time delay. A two-dimensional color map of the transient X-ray absorption spectrum of PMCPD upon UV excitation for time delays from 0 to 210 fs in 30 fs steps and 1 ps is shown in Figure 3.4 with smoothing to connect individual time delays; here yellow-red and blue-black contours denote positive and negative ΔA features, respectively. There are five observable positive (increased) features, labeled as D-G, in the near-edge over the 210 fs set of times. Features A-C are in depletion (decreased absorption). Up to 210 fs, depletion of the S_0 state is observed at 284.8 eV (depletion A) and stays negative. Depletions of the ground state transitions at 287, and 287.7 eV (depletions B, C) are observed up to 120 fs and then diminish because of their overlap with the high energetic end of a positive ΔA feature at 285.9 eV (peak G). Four new positive absorption features appearing at 280.5, 282.2, 283.9, and 285.9 eV (peaks D, E, F, and G) gradually grow in until around 200 fs. At 1 ps, peak D disappears, and the ratio of peak E to F increases at 1 ps. Importantly, peak E persists until 1 ps, and it is indicative of the presence of an open-shell species due to its low energy of 282.2 eV.

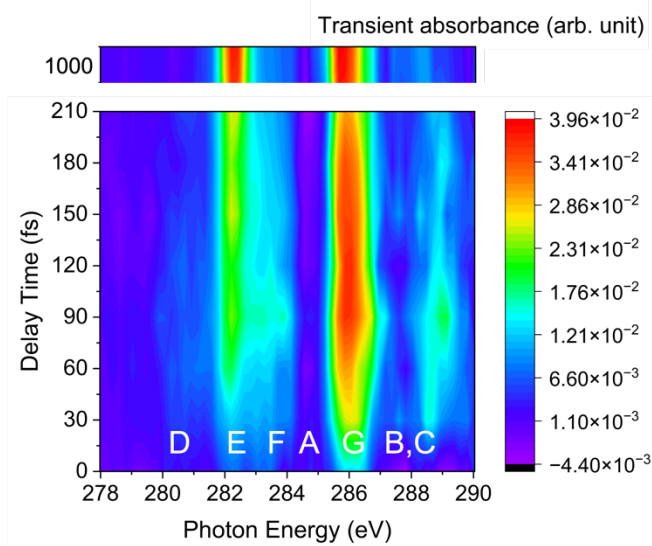


Figure 3.4: Two-dimensional contour map of the experimentally measured 267 nm induced excited-state X-ray dynamics in PMCPD. The color key on the right provides the scale for the measured differential soft X-ray absorption (ΔA). Each transient X-ray absorption spectrum was collected at 30 fs steps from 0 to 210 fs and combined with a smoothing effect, and one separate spectrum is acquired at 1 ps. The major peaks observed and discussed in the text are annotated.

Taking a closer look at the time-resolved soft X-ray transient absorption spectra, lineouts at three chosen time delays (30 fs, 60 fs and 1 ps) are presented in

Figure 3.5. Figure 3.5 presents the comparison between the experimental transient absorption spectra, add-back experimental absorption spectra and calculated X-ray absorption spectra of 1^1B_2 state at FC region and local minimum geometry. Row 1) figures are presenting the experimental transient absorption at the carbon K-edge. Row 2) figures are pure excited state absorption spectra generated by adding back the ground state bleach. The added ground state percentage of 5% is determined by eliminating the ground state bleach effect. The computed spectra shown in a3) and b3) are calculated at 1^1B_2 Franck Condon region and 1^1B_2 optimized geometries, respectively. The computed radical spectrum is shown in c3).

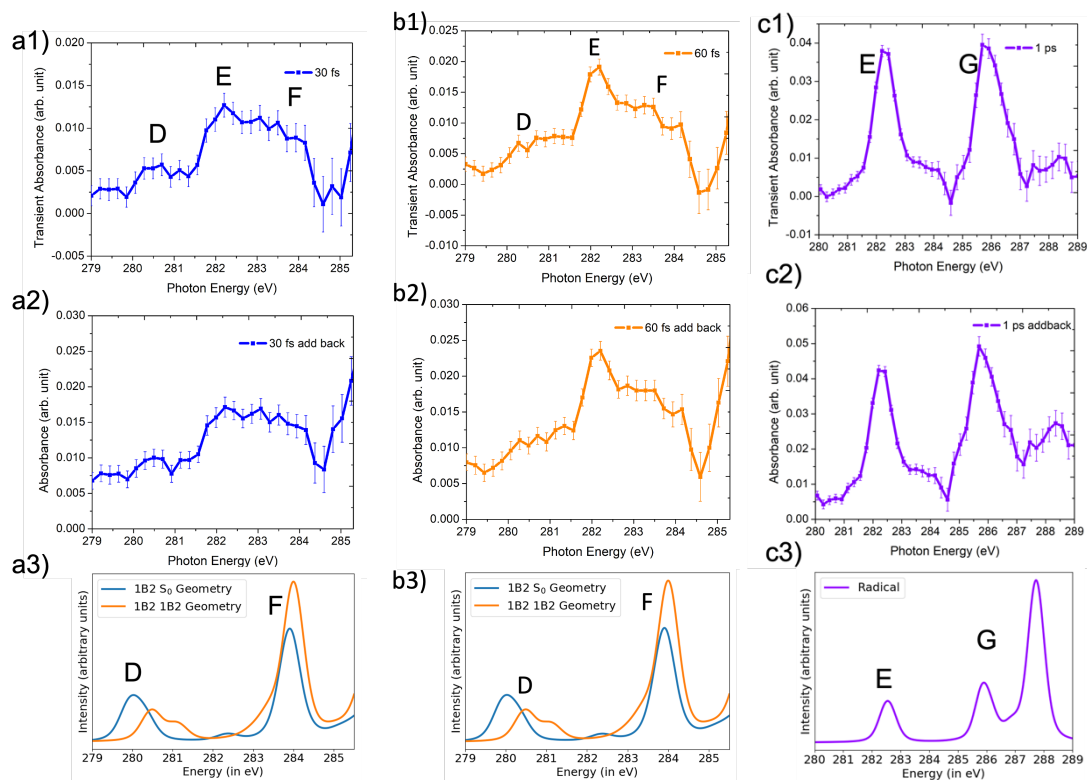


Figure 3.5: Comparison between experimental differential X-ray absorption spectra, pure excited state absorption spectra, and theoretical spectra at different time delays, calculated by D. Hait. Column a) are corresponding to a 30 fs delay, column b) are corresponding to a 60 fs delay, and column c) are corresponding to a 1 ps delay. Row 1) figures are presenting the experimental transient absorption at the carbon K-edge. Row 2) figures are pure excited state absorption spectra generated by adding back the ground state bleach. The added ground state percentage of 5% is determined by eliminating the ground state bleach effect (see text). The computed spectra shown in a3) and b3) are calculated at 1^1B_2 Franck Condon region and 1^1B_2 optimized geometries, respectively. In c3) the computed radical spectrum is shown, where the exclusivity of peak E provides the primary evidence for the radical assignment.

3.3: Discussion

3.3.1: Radical formation as the dissociative photoproduct

A broad and strong X-ray absorption peak feature E appears in the experimental transient X-ray absorption spectra at all of the measured time delays. This feature is persistent and grows in as time increases from 30 fs to 1 ps. Also, it is centered at 282.2 eV, which is 2.6 eV lower in energy than the first carbon K-edge absorption for the electronic ground state of PMCPD at 284.8 eV (peak A). This observation indicates a photorelaxation pathway of PMCPD that is different from the ultrafast relaxation back to the hot electronic ground state that was reported by previous photoelectron spectroscopy studies. Feature E is furthermore energetically well-resolved from features in the static spectrum of ground state PMCPD, and therefore it is ideal for elucidating the dynamics of photoexcited PMCPD. The low energy of this feature indicates that it corresponds to an open-shell species. Specifically, feature E is in the same energetic regime as C K-edge excitations to the singly occupied molecular orbital (SOMO) of radicals.^{27,28} Comparing to OO-DFT calculations, we find that absorption feature E agrees well with the PMCPD radical formed by the loss of H from C₁. There appear to be two timescales leading to the dissociation of PMCPD into its radical and the H atom, one relatively faster and one somewhat slower. Before conclusively assigning the observed feature E to the radical channel, however, we first consider other possible pathways, such as ionization and absorption from excited states.

The core to valence transition corresponding to feature E could come from either a different electronic state of PMCPD, an ion, or a new chemical species, for example, a photofragment, or an isomer. Even though there is no direct experimentally measured absorption cross section at 267 nm of PMCPD, a pump power dependence study has been performed to rule out of the possibility of forming PMCPD cations through nonlinear optical processes. We vary the average UV pump power from $8 \times 10^{10} \text{ W/cm}^2$ to $3.2 \times 10^{11} \text{ W/cm}^2$ by $8 \times 10^{10} \text{ W/cm}^2$ steps and measured the X-ray transient absorption spectra at each UV power. Since the pre-edge absorption features labeled D and E have no overlap with the ground state bleach, they would be the best candidates to check the linearity of the UV absorption process. To verify that the UV excitation in PMCPD is indeed due to one photon, the X-ray spectra have been recorded at different UV powers. 192 scans are run at 8, 16, 24, and $32 \times 10^{10} \text{ W/cm}^2$ of average UV excitation power. The averaged spectrum is presented in Figure 3.6; it shows lower pump power results in a weaker signal, while the overall shape of the spectrum does not change significantly, in particular, the ratio of the bands peaking at 280.5 and 282.4 eV is nearly the same. Features D and E are determined to be related to linear absorption processes. The dependence of both peaks on the UV power, in comparison, is demonstrated in Figure 3.7, where the log of peak intensity is plotted versus the log of UV excitation power. Peak D results in a slope of 0.93 ± 0.14 , whereas peak E has a slope of 1.06 ± 0.08 .

In summary, we did a power dependent study by varying the UV pump pulse power to check for non-linear absorption processes (as shown in Figure 3.6). The vertical ionization potential of PMCPD is reported to be 7.35 eV, obtained by means of He I photoelectron spectroscopy. In our experiment, from the linearity of the plot between log absorbance vs log of UV power (4.66 eV) (Figure 3.7) it is clear that under the experimental conditions there is only a one-photon absorption process. It would require two photons to generate the PMCPD cation. Therefore, an initial argument can be made that cations are not likely to be responsible for peak E in the spectrum. Moreover, the ion would be formed immediately by the laser pulse, while peak E grows in over time. Thus, the ion is excluded.

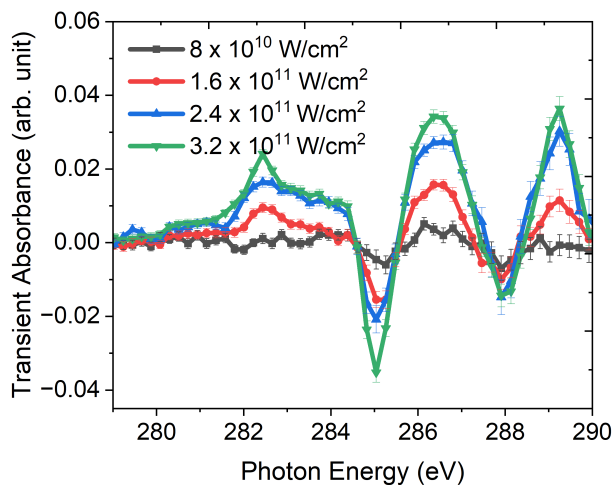


Figure 3.6: Pump power dependence of X-ray absorption spectra. Differential absorption spectra were acquired at 200 fs delay. The error bar represents one standard deviation of 192 measurements.

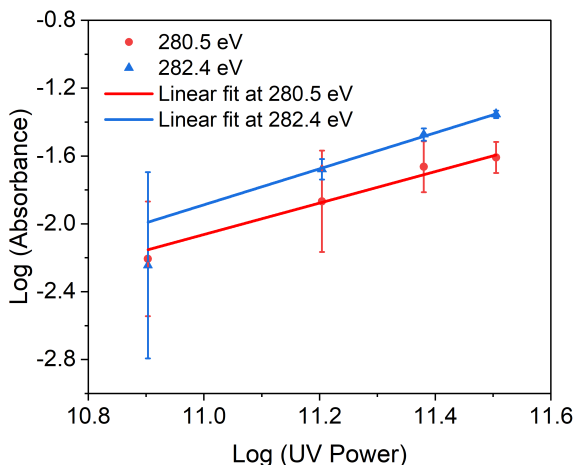


Figure 3.7: Log of absorbance intensity with respect to the log of UV power of features D and E fitted with linear fits. The slope of feature D is 0.93 ± 0.14 and the slope of

feature E is 1.06 ± 0.08 . The resulting slopes, which are close to 1, indicate this is a one photon absorption process when the UV power is less than 3.2×10^{11} W/cm².

There are four remaining candidates that can preserve the bonding network of PMCPD and can plausibly persist until 1 ps: the lowest energy triplet (T_1), the lowest energy excited singlet (S_1), highly vibrationally excited S_0 , and PMCPD with loss of a hydrogen atom either from the ring or from the methyl groups. If the feature either comes from a newly formed chemical species or an excited state of PMCPD, we can classify them into closed-shell or open-shell hydrocarbons. The ground states of closed-shell hydrocarbons typically have their first X-ray absorption of the carbon K-edge at 284 eV or higher energy. The much lower energy of peak E suggests it must arise from an open-shell species or from an excited state. Open-shell species can absorb in this regime and would live for a picosecond timescale.

We used OO-DFT to calculate the lowest excitation energy for all of the possible open shell and excited state cases (Table 3.3, calculations by D. Hait). The T_1 state is unlikely to form within 1 ps, even though its first core to valence transition appears at 282.6 eV, as PMCPD lacks atoms heavier than carbon and this state has the same symmetry as S_1 , which makes intersystem crossing between them El-Sayed forbidden. For comparison, El-Sayed-allowed intersystem crossing in an acetylacetone chromophore is determined to take ~ 1.5 ps, highlighting the unlikelihood of the PMCPD T_1 state being involved in the observed dynamics. A long-lived S_1 state could be considered, but we have experimentally observed and theoretically predicted the X-ray absorption spectrum of the $1B_2$ state, and there is only a weak absorption feature at 280.5 eV but not at 282.2 eV. The absorption feature D corresponds to the transition from carbon 1s to π^* transitions involving the sp^2 carbon atoms for this state.

The calculations were done at equilibrium geometry rather than the FC region since the nuclei will have sufficient time to relax in the 1 ps long time delay window. The calculated energies are shown in Table 3.3. Three different types of radicals can form with H loss from the methyl group, which are lost from C_{4-6} . And the lowest C K-edge transition energies for these radicals are listed in the order of the numbering scheme.

Table 3.3: Calculated lowest carbon K-edge transition energy for possible open-shell species photogenerated from PMCPD. Calculations by D. Hait.

Species Type	Chemical Species	Lowest C K-edge Transition Energy (eV)
Radical	Radical with H loss from the ring	282.4
	Radical with H loss from methyl	282.2, 282.7, 283.2
Long-lived excited state	T_1	282.6
	S_1	280.5

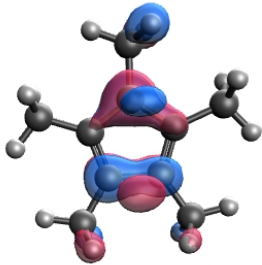
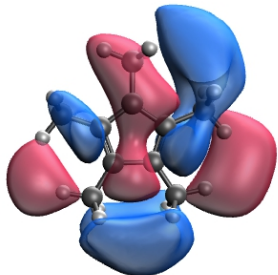
The PMCPD radical can form with the loss of an H atom either from the methyl groups or from the H atom attached to C₁ in the ring. We calculated the binding energy of each radical, which is 3.71 eV for the radical with a single electron on C₁ and 4.75 eV for a radical with a single electron on C₄. This 1 eV difference comes from the resonance stabilization in the former case. After losing the H atom from C₁, the non-bonding electron in its partially filled 2p orbital can interact with the adjacent methyl group coming from C₄, which has three filled σ (C-H) orbitals to give an extended molecular orbital that increases the stability of the system. As a result, of the various PMCPD radicals formed by a loss of H, the most stable form is by losing H from C₁. The energy difference between the stabilized radical and ground state PMCPD is computed to be 3.7 eV, and the 267 nm photon (4.66 eV) used in this experiment carries sufficient energy to form the photoproduct.

To compare the experimental X-ray absorption of the radical photoproduct with the calculated radical X-ray absorption spectrum, the S₀ state absorption spectrum of the parent PMCPD was added back to the transient absorption spectrum at 1 ps under the assumption of a 20% excitation, thus simulating a “pure” long-time-delay X-ray absorption spectrum of the radical. The calculated carbon K-edge X-ray absorption spectrum of the PMCPD radical (Fig 3.4 c3)) shows strong features at 282.2 and 286 eV, which match very well with the addback experimental spectrum. The band E centered at 282.4 eV is composed of two transitions from C₁ and C₃ 1s orbitals to the singly occupied molecular orbital (SOMO), which is π_2 with 2p character. The detailed transition assignment is presented in Table 3.4 along with the electron density maps of each orbital presented in Table 3.5. Due to the delocalization of the SOMO across the ring (shown in Table 3.5), the C₁ and C₃ carbon atom core orbitals have good overlap with the SOMO. The feature G at 285.6 eV corresponds to the transitions from C₂ and C₃ 1s orbitals to a higher open valence orbital with Rydberg character. It is valuable to examine next whether there exists a low barrier path to C-H bond breaking in the excited state, which could lead to radical formation.

Table 3.4: Experimental and theoretical transition energies and assignment of X-ray spectra of PMCPD at 1 ps time delay after 267 nm excitation. Calculations by D. Hait.

Peak Number	Peak Energy (eV)		Transition Assignment
	Experimental	Theoretical	
E	282.2	282.4	C ₁ 1s → SOMO ($\pi/2p$)
		282.6	C ₃ 1s → SOMO ($\pi/2p$)
G	285.6	285.8	C ₂ 1s → Rydberg
		286.2	C ₃ 1s → Rydberg

Table 3.5: Calculated electron density map of involved half-filled or open valence molecular orbitals, calculated by D. Hait.

Molecular orbital	Electron density
SOMO π with 2p character	
Rydberg	

3.3.2: Pathway to radical formation

The occurrence of feature E beginning at 30 fs indicates there is a rapid timescale pathway for CH bond breaking. We computationally find a local minimum on the S_1 surface with the ring remaining planar, and this minimum is 0.7 eV below the FC region on the S_1 surface (equivalent to being 3.9 eV above the electronic ground state minimum in energy). This local minimum is likely to be representative of nearly planar structures that result from the relaxation from the FC region at very short times. This S_1 state local minimum is computed to have a very long C-H bond (1.15 Å vs 1.10 Å in the ground state) with a quite low stretching vibrational frequency of 2400 cm^{-1} (compared to a typical C-H stretch of $\sim 3000 \text{ cm}^{-1}$). A low barrier pathway to C-H bond fission would thus permit radical formation before the ring deplanarizes and the conical intersection to the ground state becomes accessible. Calculations by D. Hait reveal such a path, taking into consideration the zero-point energy (ZPE), with a barrier to the transition state of only 0.17 eV. Indeed, a comparison of the ZPE and the barrier height seems to indicate that only the ground state of the CH stretching mode is bound, with even the $v=1$ vibrationally excited state (0.45 eV) having enough energy to lead to H atom loss. The significant increase in the CH bond length from the FC region indicates that this mode is FC active, and thus a significant proportion of the molecules can undergo very rapid H loss as soon as the planar local minimum geometry is accessed.

Since the π^* orbital has a symmetry that can smoothly mix with the σ_{CH}^* level, in order for there to be C-H bond cleavage, it does not require nonadiabaticity, which means there is no need to have a nonadiabatic state crossing between the S_1 state with a σ_{CH}^* occupied state along the dissociation coordinate up to the transition state. The mixing between the π^* and σ_{CH}^* orbitals leads to the continuous transformation from excited singlet to the PMCPD radical and H atom. The orbital transformations associated with this process are presented in Fig 3.8.

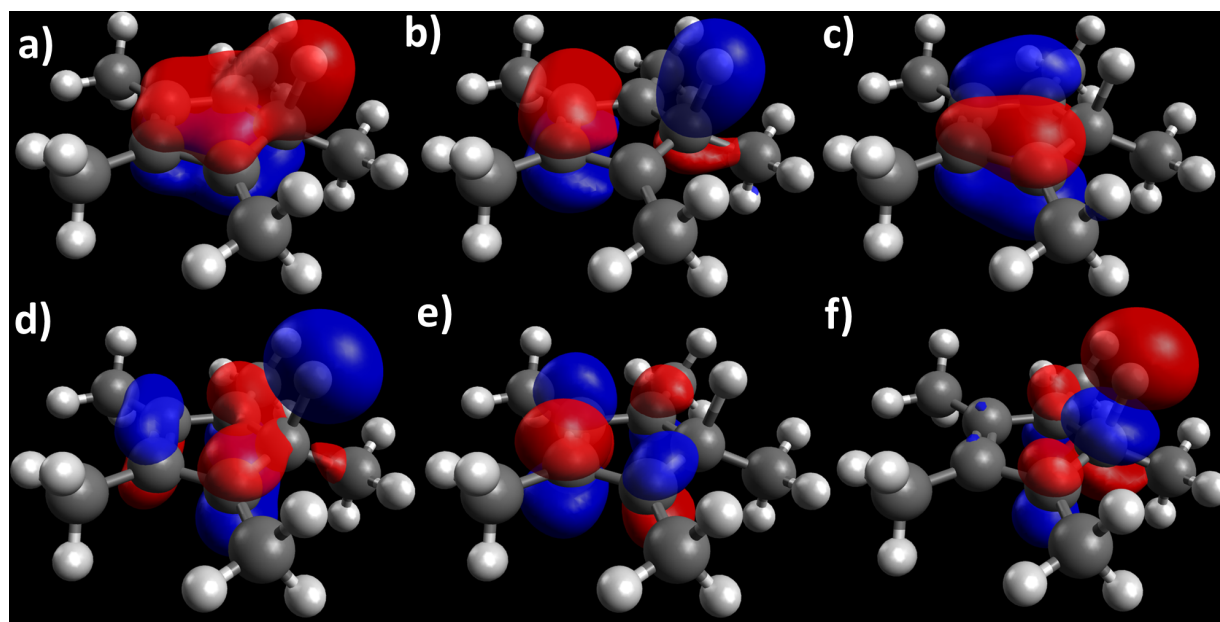


Figure 3.8. Orbitals showing the mixing of the π system and $\sigma_{CH}/\sigma_{CH}^*$ at the transition state for H loss. a) and b) represent symmetric and antisymmetric combinations of π_1 and σ_{CH} , c) π_2 , d) and e) symmetric and antisymmetric combinations of π_1^* and σ_{CH}^* . a) and b) are doubly occupied and become doubly occupied π orbitals in the PMCPD radical. c) and d) are singly occupied, with c becoming the π symmetry SOMO of PMCPD while d) becomes the 1s of the dissociating H atom. e) and f) are unoccupied and become unoccupied π^* levels of the PMCPD radical. Calculations by D. Hait.

Theoretically, rapid PMCPD radical formation can thus occur as soon as the π system relaxes to the neighborhood of the S_1 local minimum, as the CH bond is activated and the barrier to dissociation is quite small relative to the ZPE. The computed frequency for this CH stretching mode indicates that the time for the H atom to reach the classical turning point for this stretching mode is 3.5 fs, indicative of how rapid the process could be. Experimentally, we are not able to resolve such short timescales with the apparatus used for these investigations. However, the theoretical calculations support this mechanism, which explains the formation of some of the radicals at early times. Even though neither the harmonic approximation for the ZPE, nor the Born-Oppenheimer approximation for the dissociating mechanism can be quantitative, it is reasonable to conclude qualitatively that the

barrier for H loss is sufficiently small that nuclear quantum effects of the departing H atom are significant and accelerate the dissociation.

The feature E is nearly unchanged from 90 to 210 fs, indicating rapid exhaustion of all molecules that have FC activated CH stretches. However, further growth occurs between 210 fs and 1 ps, indicating a second, slower timescale for radical formation.

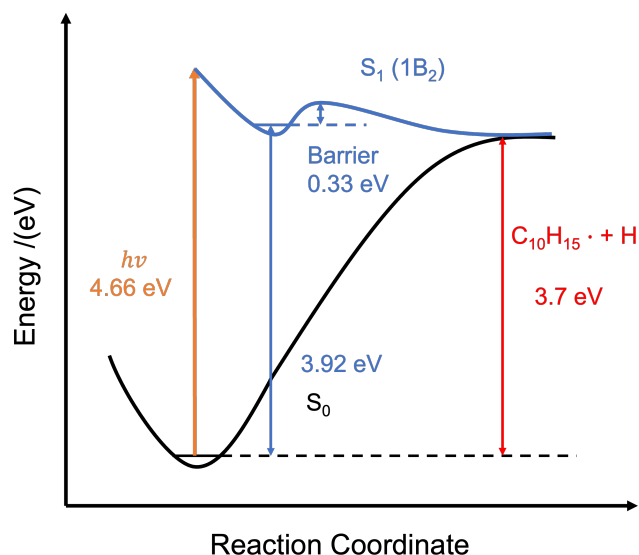


Figure 3.9: Calculated potential energy surface of PMCPD with respect to photo-induced dissociation reaction coordinate (C-H bond length). The black solid curve corresponds to the electronic ground state S_0 , and the blue solid curve corresponds to the first excited singlet S_1 , 1^1B_2 . The orange arrow indicates the UV photon energy, the blue arrows indicate energy differences related to the S_1 surface, and the red arrow indicates the energy difference with respect to the photoproduct. Calculations by D. Hait.

This most likely occurs through the transfer of energy from other vibrational modes to the C-H stretch in molecules where this mode is not initially activated. The two timescales associated with the process are difficult to obtain from the available experimental data but appear to be < 90 fs for the rapid channel and ~ 1 ps for the slower one. We also note that some of the apparent increase in the radical signal from 210 fs to 1 ps can also arise from the peak being significantly broadened at early times due to the activation of the C=C stretching modes (via the relaxation from the FC region), which significantly affects the energy of the π symmetry SOMO level. Vibrational energy redistribution out of these modes to other modes that have less of an influence on the SOMO energy (such as methyl groups) can thus lead to a narrowing of the peak and a consequent increase in peak intensity, even without any new radical being formed.

The H loss mechanism presented here is distinct from the ultrafast internal conversion pathway that previous work indicated to be the key nonradiative decay channel for PMCPD. It is thus important to contextualize our results. Previous experimental time-resolved PES investigations saw no signal from one pump photon plus one probe photon ionization at long times and concluded that relaxation back to the ground state was the mechanism. However, the PMCPD radical, if formed, would also not show any photoelectron signal, as it has an ionization energy very close to PMCPD and most of the pump energy has been dissipated by C-H bond breaking. Previous computational nonadiabatic dynamics studies following the PES experiments modeled methyl groups of methylated CPDs as H atoms of mass 15 amu to approximate the inertial effects, but this approach has some shortcomings, as made evident by the experimental and theoretical values of the induction time (for reaching the conical intersection seam via out of plane motion) differing by almost a factor of three for hexamethylcyclopentadiene (HMCPD) (310 fs vs 108 fs, respectively).²⁴ This indicates that those computational models potentially made the conical intersection appear to be more accessible.

Indeed, the previous works report that the S_1/S_0 conical intersection is ~ 2 eV lower in energy than the FC region with the CPD model, but calculations of D. Hait find that it is only 1.3 eV below, using the actual PMCPD molecule and more robust electronic structure methods. It is therefore quite possible that the previous computational studies overestimated the overall rate at which relaxation to the conical intersection occurs, while missing the role of H loss due to the lack of nuclear quantum effects and use of the cyclopentadiene model system. We also note that the differences in experimental induction time between HMCPD and other highly methylated CPDs with an attached ring H atom are somewhat surprising, as the out of plane motion to access the conical intersection should involve distortion of mostly the same atoms and therefore should not have a greater inertial barrier. It is possible that HMCPD is a clear example for relaxation back to the ground state via a conical intersection, while the other CPD species have dynamics affected by H loss too. We also note that photodissociation from substituted CPDs is experimentally known, with hexachloro- and hexabromo- CPDs undergoing halogen loss to form resonance stabilized radicals upon excitation by 315 nm light.

Overall, while nonradiative relaxation back to the ground state is possible for methylated CPDs, the required out-of-plane motion for the π network is less likely (relative to CPD) because of the heavier substituents, permitting H loss as a competing mechanism. While we have shown the existence of the H loss channels in this study, determination of the relative proportions of each channel will require more extensive studies with better experimental time-resolution, as well as theoretical methods that account for nonadiabatic dynamics, nuclear quantum effects, and strong electron correlation.

3.4: Conclusion

Time-resolved soft X-ray transient absorption spectroscopy using a broadband carbon K-edge high-harmonic probe elucidates an additional relaxation channel in the 267 nm photoexcitation of PMCPD. Combining with OO-DFT calculations, strong evidence is given that the identity of the photoproduct is PMCPD radical with the loss of an H atom from C₁ in the ring. While the exact timescales are difficult to extract from the experimental data, a rapid formation timescale (< 90 fs) for PMCPD radical is clearly detected, while there is some evidence for a slower (~1 ps) pathway for further radical generation. The faster timescale is likely to arise from PMCPD molecules that have the C-H stretch vibrational mode active in the ultraviolet excitation, while the slower channel potentially occurs through the transfer of energy from other vibrational modes to the C-H stretch in PMCPD when the mode is not initially activated.

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Chapter 4: Photorelaxation of Benzaldehyde

Upon UV excitation, benzaldehyde has complicated photorelaxation pathways due to the close-lying singlet and triplet excited states. We study the photorelaxation of benzaldehyde via time-resolved soft X-ray transient absorption spectroscopy. The absorption spectrum of ground state benzaldehyde from carbon core 1s levels has been measured, and the excited state dynamics initiated by 267 nm excitation to the S_2 ($\pi\pi^*$) state is investigated using broadband soft X-ray pulses produced by high harmonic generation at carbon K-edge. At 200 fs time delay, two well-separated core level absorption features at 281.8 and 282.8 eV are assigned to the population transfer to S_1 ($n\pi^*$). The lifetime of the S_1 singlet state is about 12 ps followed by the intersystem crossing to a $\pi\pi^*$ triplet state through a conical intersection. The evolution of the core-to-valence resonances at the carbon K-edge identifies the excited singlet and triplet states involved in the photorelaxation of benzaldehyde following 267 nm photoexcitation.

4.1: Introduction

The photoinduced reactions of benzaldehyde (C_6H_5CHO), an aromatic carbonyl molecule, have been interests of experimental and theoretical work for decades.¹⁻⁷ The close-lying $n\pi^*$ and $\pi\pi^*$ excited states in both singlet and triplet manifolds make benzaldehyde an ideal molecular candidate for the study of physical processes of intersystem crossing (ISC) and internal conversion, as well as photochemical processes of valence isomerization, bond breakage, and atom transfer. Unlike aromatic hydrocarbons, it is commonly known that aromatic carbonyls have a much smaller fluorescence quantum yield. This behavior implies there is a relatively fast ISC process for aromatic carbonyls from the singlet state to the triplet state, which is promoted by strong spin-orbit coupling.⁸

Previous experimental results show that the two lowest excited singlet states, S_1 and S_2 , are assigned to $n\pi^*$ and $\pi\pi^*$ transitions, respectively. The origin of S_1 was found to lie 26919 cm^{-1} above the ground state by a tunable dye laser used in sensitized phosphorescence excitation spectroscopy and 26920 cm^{-1} (3.34 eV) by sensitized surface photoelectron ejection spectra.^{1,9} S_2 has its origin at 35200 and 35191 cm^{-1} (4.36 eV) relative to the ground state, also as seen in the phosphorescence excitation spectrum and ionization excitation spectrum, respectively.^{10,2} The two lowest triplet states T_1 ($n\pi^*$) and T_2 ($\pi\pi^*$) are found lying below the S_1 state and close to each other in the surface sensitized experiments, whereas only the $n\pi^*$ triplet state has been successfully located in the gas phase.^{14,15}

According to photolysis and multiphoton ionization (MPI) experiments,¹⁶⁻²⁰ benzaldehyde dissociates into benzene and carbon monoxide. The photorelaxation mechanism is summarized as the following. Upon excitation to the S_2 state,

benzaldehyde relaxes to the S_1 state minimum via an ultrafast internal conversion. Following the femtosecond conversion to S_1 ,⁷ it goes through intersystem crossing to the triplet state and then forms the photoproducts. The lifetime of the S_2 ($\pi\pi^*$) state was measured by time-resolved photoelectron spectroscopy (TRPES) by Stolow's group.⁷ It was noticed that the lifetime of the S_2 state decreases with an increase of vibrational energy upon changing the excitation wavelength from 284 nm to 277 nm; the lifetime is shortened from 440 fs to 300 fs. Ultrafast electron diffraction (UED) experiments observed a bifurcation leading to a rapid intersystem crossing to the "quinoidlike" $\pi\pi^*$ triplet state as well as the formation of photoproducts benzene and carbon monoxide through an intermediate state. Multiconfiguration second-order perturbation theory through the multistate extension (MS-CASPT2) found a conical intersection between the hypersurfaces of S_1 and T_2 , providing a possible explanation for the singlet-triplet intersystem crossing.³ Later, a $S_1/T_2/T_1$ three-state interaction region was discovered by complete active space self-consistent field (CASSCF) calculations with state-averaged (SA) treatment and configuration interaction with second-order perturbation theory (CIPT2).⁶ Since the S_1/T_2 and T_2/T_1 intersections are indistinguishable from one another in structure and the two triplet states, T_1 and T_2 , have a similar energy, the $S_1 \rightarrow T_1$ intersystem crossing can occur efficiently, in analogy to other systems. With the available excess energy, benzaldehyde can overcome the barriers to $C_1 - C_7$ and $C_7 - H$ bond cleavage in the $\pi\pi^*$ triplet state and form the corresponding ground state products (the ball-stick structure of benzaldehyde and the numbering scheme are shown in Figure 4.1 b). Given the rather small transition state energy difference of 4 kcal/mol, both dissociation channels are expected to be accessible with a preference for $C_1 - C_7$ cleavage that produces phenyl and formyl radicals. Subotnik's group used time-dependent density functional theory (TD-DFT) and localized diabaticization to investigate the conical intersection in benzaldehyde and their results suggest the intersystem crossing is rapid not only because of a strong spin-orbit coupling but also because of a fortuitous small energy barrier.²² A schematic photorelaxation process of benzaldehyde is shown in Figure 4.1. In Fig 4.1, the ground state and the participating excited singlet and triplet states are color-coded, and the arrows represent the nonradiative processes including internal conversion and intersystem crossing.

Near-edge X-ray transient absorption spectroscopy (XAS) has been proven to be a powerful technique for elucidating photoinduced molecular dynamics with femtosecond temporal resolution. XAS is atom-specific and sensitive to the electronic state, enabling it to report on both electronic and nuclear dynamics following photoexcitation. We utilize XAS with soft X-rays at the carbon K-edge (280-300 eV) to investigate the dynamics of C_6H_5CHO , following excitation with 267 nm UV photons. In this chapter, preliminary results are presented for benzaldehyde, with a few suggestions for the assignment of the observations. Based on the preliminary experimental results, we have the capability to distinguish the excited singlet states

and possibly the excited triplet states of benzaldehyde from the time evolution of carbon core absorption spectra. The dynamics agree well with previous experimental interpretations and the theoretical prediction that the lifetime of the S_2 state is around 200 fs,⁷ as well as the intersystem crossing between the S_1 and T_2 states occurs at around 12 ps.²² For future work, accurate experimental time zero needs to be determined, more time points need to be taken, and theoretical calculations need to be done to support the tentative assignments of excited states and the core transitions associated with them.

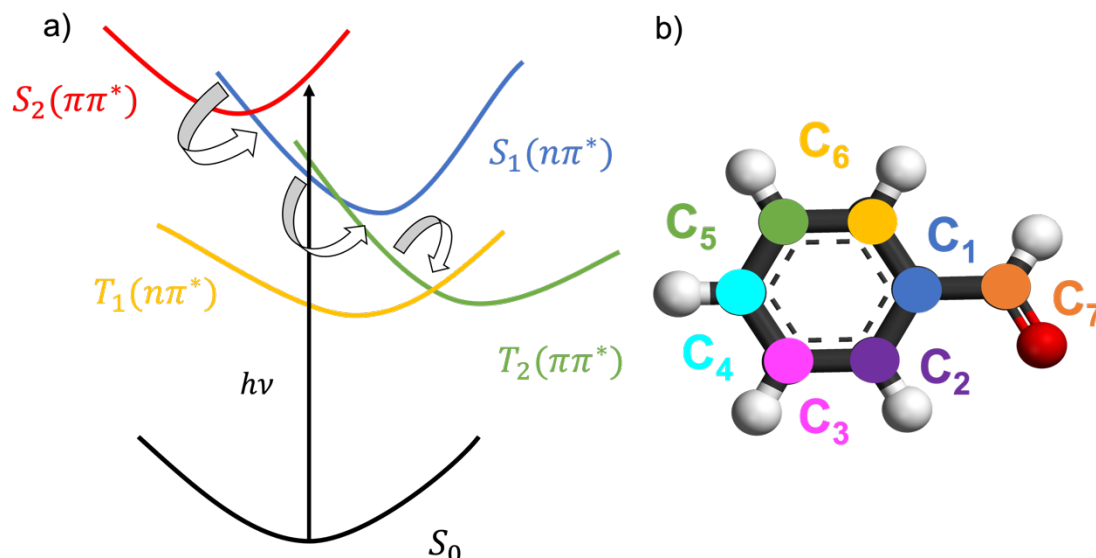


Figure 4.1: a). Schematic graphs of the photorelaxation process of benzaldehyde upon 267 nm excitation. The first two excited singlet and triplet states are involved (color-coded for different state and electron configurations). From left to the right, the three arrows represent the rapid change between states, which are internal conversion between S_1 / S_2 , intersystem crossing from S_1 to T_2 , and internal conversion from T_2 to T_1 . b) schematic ball-stick structure with the labeling of carbon atoms.

4.2: Results

4.2.1: Static X-ray absorption Spectrum of Benzaldehyde at Carbon K-edge

The near-edge X-ray absorption spectrum at the carbon K-edge of ground state benzaldehyde is presented in Figure 4.2 (the solid black line connecting the datapoints, with error bars corresponding to 95% confidence interval over 192 scans summed together). This spectrum is also called static X-ray absorption spectrum. The ground state X-ray absorption spectrum shows four strong peaks at 285.0, 285.9, 287.7, and 290.2 eV. They are labeled as peaks A – D in order of increasing energy. Distinct spectral features cannot be observed for energies greater than 290.5 eV due to the ionization from the carbon 1s electrons. The seven carbon atoms in

benzaldehyde can be classified into three types of carbons based on the bond connectivity, C_1 represents the carbon connecting the ring and the carbonyl group, C_7 represents the carbon atom participating in the carbonyl group and C_{2-5} represents the five carbons in the benzene ring. The carbon 1s shell ionization potential for these three types of carbon atoms was determined by X-ray photoelectron spectroscopy, and they are well separated, as 290.5 for C_{2-5} , 291.5 eV for C_1 , and 293.3 eV for C_7 .¹¹

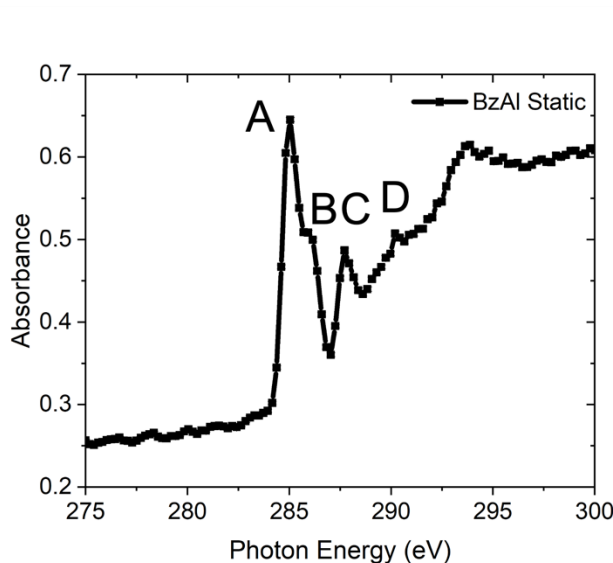


Figure 4.2: Static near-edge X-ray absorption spectrum of electronic ground state benzaldehyde at the carbon K-edge (the solid black line connects the datapoints; error bars correspond to 95% confidence interval over the sum of 192 scans).

Our X-ray absorption spectrum at the carbon K-edge of ground state benzaldehyde matches well with the inner shell spectrum measured by Hitchcock.¹² Our experimental peak energies are presented in Table 4.1 in comparison to the transition energies from this reference and the tentative transition assignments are shown alongside. It is worth noting that the spectral resolution of electron energy loss spectroscopy for the inner shell spectrum was 0.6 eV and that for our X-ray absorption spectroscopy it is 0.3 eV (as shown in the experimental chapter). From the experience of our previous studies, the 1s core level energy difference for the carbon atoms in the planar benzene ring, C_{2-5} , can be as small as 0.1- 0.2 eV, which is indistinguishable in our case. However, if the molecular excited state has a ring-distorted geometry that makes one or more carbon atoms in the ring move away from the plane, it can shift the core 1s level significantly. Peaks A and B arise from the transition for C_{2-5} and C_1 to the first π_1^* from the conjugated ring. The 0.9 eV energy difference is similar to the 1 eV difference from the core ionization energy of these two core levels. Feature C comes from the transition of C_7 to the π^* orbital of the carbon – oxygen double bond as well as a transition from C_{2-5} to the $\pi_2^*(C=C)$ which is

the second π^* of the benzene ring. The last feature D comes from the transition of C_7 1s to the π_2^* (C=C), and C_1 core 1s to the third π_3^* (C=C) from the benzene ring.

Table 4.1: Tentative assignments of X-ray absorption spectral features observed at the carbon K-edge of ground state benzaldehyde in comparison to the inner shell excitation energies from Ref. 12.

Peak	Experimental Energy (eV)	Reference Energy (eV)	Tentative Assignment
A	285.0	285.07	$C_{2-5} 1s \rightarrow \pi_1^*(C=C)$
B	285.9	286.0	$C_1 1s \rightarrow \pi_1^*(C=C)$
C	287.7	287.7	$C_7 1s \rightarrow \pi^*(C=O)$
D	290.2	290.3	$C_{2-5} 1s \rightarrow \pi_2^*(C=C)$
			$C_7 1s \rightarrow \pi_2^*(C=C)$
			$C_1 1s \rightarrow \pi_3^*(C=C)$

4.2.2: Time-resolved Soft X-ray Transient Absorption Spectra of Benzaldehyde

The transient X-ray absorption spectra at the carbon K-edge show absorption changes that are the differences in absorption with and without the 267 nm excitation pulse at each time delay. A two-dimensional color map of the transient X-ray absorption spectrum of benzaldehyde upon UV excitation for time delays at 100, 200, 500 fs, and 1, 3, 12, and 15 ps is shown in Figure 4.3 with smoothing to connect individual time delays; here yellow-red and blue-black contours denote positive and negative ΔA features, respectively. There are five observable positive (increased) features, labeled as peaks E-I, in the near-edge over the set of delay times. Features in the static spectra of Fig. 4.2 would be in depletion (decreased absorption) in Fig. 4.3. Up to 15 ps, the depletion of the ground state benzaldehyde would be observed as depletions of A (285 eV) and B (285.9 eV) and stay negative. The depletion of feature C at 287.7 eV is obscured due to its overlap with the high energetic end of a positive feature at 287.4 eV (peak I).

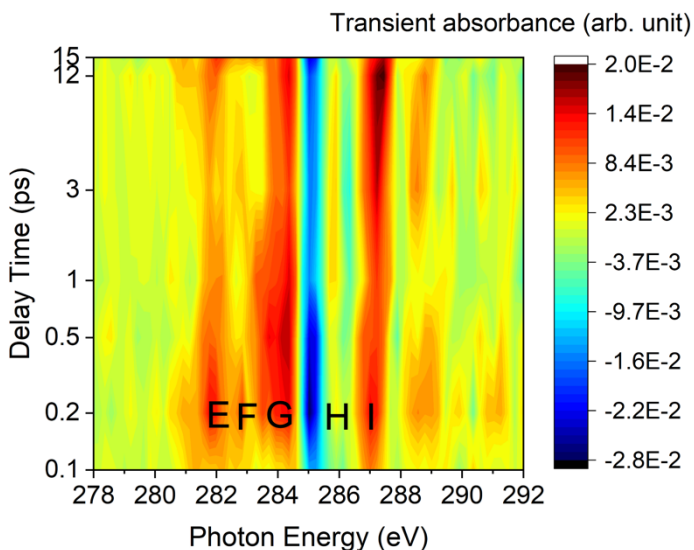


Figure 4.3: Two-dimensional colormap of the experimentally measured 267 nm induced excited-state X-ray dynamics in benzaldehyde. The color key on the right provides the scale for the measured differential soft X-ray absorption (ΔA). Each of the transient X-ray absorption spectra was collected at the following time delays: 100, 200, 500 fs, and 1, 3, 12, and 15 ps, respectively. They are plotted with respect to a logarithmic scale on the y-axis and combined with a smoothing effect. The major peaks observed and discussed in the text are annotated.

In order to gain a better understanding of the photoinduced molecular dynamics of benzaldehyde upon 267 nm excitation, time-resolved soft X-ray transient absorption spectra of benzaldehyde lineouts at four chosen time delays, 100 fs, 200 fs, 3 ps, and 12 ps, are presented in Figure 4.4. It shows the comparison between several experimental transient absorption spectra and add-back experimental absorption spectra at each time delay along with the next time delay to study the dynamical changes. Row a) figures are the raw experimental transient absorption at the carbon K-edge. Row b) figures are pure excited state absorption spectra generated by adding back the ground state bleach. The added ground state percentage of 15% is determined by the excitation probability based on the 2×10^{11} W/cm² UV photon flux and the absorption cross section of benzaldehyde at 267 nm, which is 1.86×10^{-18} cm²/molecule.²¹ The transition energies for each absorption feature are reported in Table 4.2, along with the tentative assignment of their identities.

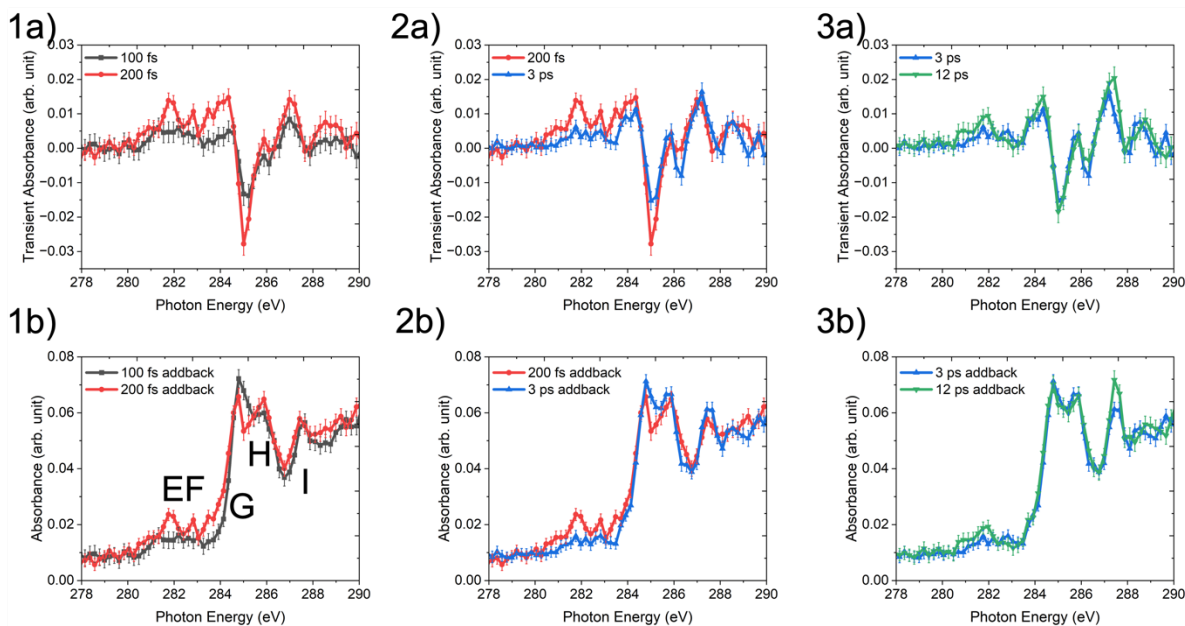


Figure 4.4: Comparison between experimental differential X-ray absorption spectra and pure excited state absorption spectra at different time delays. Column 1) figures correspond to 100 and 200 fs delay, column 2) correspond to 200 fs and 3 ps delay, and column 3) correspond to 3 ps and 12 ps delay. Row a) figures present the raw experimental transient absorption at the carbon K-edge. Row b) figures are pure excited state absorption spectra generated by adding back the ground state bleach. The added ground state percentage of 15% is determined by the UV excitation probability (see text).

Table 4.2: Tentative assignments of X-ray transient absorption spectral features observed at the carbon K-edge of excited states benzaldehyde

Peak	Experimental Energy (eV)	Tentative Assignment
E	281.8	$C_{2-5} 1s \rightarrow \pi(C=C)$
F	282.8	$C_1 1s \rightarrow \pi(C=C)$
G	284.8	$C_{2-5} 1s \rightarrow \pi_1^*(C=C)$
H	285.9	$C_1 1s \rightarrow \pi_1^*(C=C)$
		$C_7 1s \rightarrow \pi^*(C=O)$
I	287.4	$C_1 1s \rightarrow \pi_2^*(C=C)$

4.3: Discussion

At 100 fs time delay, there is a broad absorption feature in the region of 280.5 – 283.3 eV. It is likely this broad feature comprises multiple transitions from different C 1s orbitals to the half-occupied π orbital (vacancy comes from UV excitation). Peaks G and H at 284.8 and 285.9 eV are assigned to the transitions from core 1s orbitals of

C₂₋₅ and C₁ to the singly occupied $\pi_1^*(\text{C}=\text{C})$. Here the separation between these two transitions is 1.1 eV, which is slightly larger than the separation (0.9 eV) in the ground state. 267 nm photon absorption induces a $\pi^* \leftarrow \pi$ transition and the transition is mainly localized in the aromatic ring. This transition has a large influence on the structure of the ring but not the carbonyl group. To be more specific, the two unpaired electrons in the S₂ state are delocalized into the aromatic ring, which results in a uniform increase of the ring C-C bond length from 1.40 Å in the ground state to 1.44 Å in the $\pi\pi^*$ excited state.¹³ This geometrical change of benzaldehyde explains the further separation of peaks G and H. The peak I is assigned to the transitions C₇ → $\pi^*(\text{C}=\text{O})$ and C₂₋₅ → $\pi_2^*(\text{C}=\text{C})$.

At 200 fs time delay, the pure excitation add back absorption spectrum at 200 fs has distinct changes of peaks E, F, and G compared to 100 fs. These spectral changes can be an indication that benzaldehyde has relaxed into a different electronic state, S₁ ($n\pi^*$), through internal conversion. Firstly, the peaks E and F are well separated by 1 eV from each other, and the intensity of both peaks is higher than those at 100 fs delay. The increase in absorption intensity could possibly be due to a better overlap between the core 1s and the final orbital wavefunctions. The 1 eV separation can come from a geometry change along the S₁ to T₂ state potential surfaces. When benzaldehyde is approaching the T₂/ S₁ conical intersection, the aromatic ring changes into a quinoid shape with C₂-C₃ and C₅-C₆ bonds becoming shortened and the rest of the four C-C bonds slightly elongated⁶ (carbon atom labeling can be seen in Figure 4.1). Compared to the geometry of the ground state, the carbonyl bond in S₁ is elongated by 0.1 Å, as calculated by Ref 6, and Ref 22. This geometrical change makes the C₇ further away from the withdrawing oxygen atom. This explains why the feature I corresponding to the transition from C₇ → $\pi^*(\text{C}=\text{O})$ appears at 287.4 eV which is 0.3 eV lower than the transition in the ground state. The appearance of the S₁ state at 200 fs also matches with the time-resolved photoelectron spectroscopy observations that under 267 nm excitation, the lifetime of the S₂ state is around 250 fs.⁷

From 200 fs to 3 ps, the pure excited state absorption spectra at the carbon K-edge does not have a significant change. The peaks E and F merge into one broad feature and the peak G is also broadened. These three features are all associated with the transitions from the C₂₋₅ and C₁ 1s levels. The broadening change can come from vibrational redistribution in the S₁ ($n\pi^*$) state.

Peak I corresponds to the transitions C₇ 1s → $\pi^*(\text{C}=\text{O})$ and C₂₋₅ 1s → $\pi_2^*(\text{C}=\text{C})$. At 12 ps time delay, the peak I at 287.4 eV increases in its intensity. The absorption intensity was previously lower than that of peak H from 100 fs to 3 ps, but at 12 ps it is clearly higher than the intensity of peak H. This change can be an indication that

benzaldehyde photorelaxation goes into a new electronic state, T_2 ($n\pi^*$) through the intersystem crossing. Theoretical calculations have predicted the C_1 - C_7 bond length would be shortened by 0.07 Å from the S_1 to T_2 excited state. The change might induce more mixing between the second π^* orbital of the aromatic ring with the carbonyl group. As a result, the transition $C_{2-5} \rightarrow \pi_2^*(C=C)$ could have a strong absorption intensity. The appearance of T_2 ($n\pi^*$) also agrees with TD-DFT calculation's prediction that the intersystem crossing rate is $8 \times 10^{10} \text{ s}^{-1}$.²²

4.5: Conclusion and Future Work

We have preliminarily investigated the photorelaxation of benzaldehyde by femtosecond soft X-ray transient absorption spectroscopy at carbon K-edge. Without 267 nm excitation, the X-ray absorption spectrum of the ground state benzaldehyde has been measured and features match well with inner shell spectrum obtained by electron energy loss spectroscopy.¹² A set of time delays were chosen to study the photoinduced dynamics of benzaldehyde. We observed spectral features corresponding to the occurrence of S_2 ($\pi\pi^*$), S_1 ($n\pi^*$), and T_2 ($\pi\pi^*$) excited states. The internal conversion to S_1 from the S_2 state occurs at approximately 250 fs and it takes about 12 ps to undergo intersystem crossing between S_1 and T_2 . The lifetimes observed in our study are in the range of previous theoretical predictions.²²

In the future, more short time delay transient absorption spectra need to be collected and accurate time zero needs to be determined to obtain the lifetimes for each of the excited states. Also, the assignment of the spectral features needs to be supported by theoretical calculation of X-ray absorption spectra for each excited state.

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Chapter 5: Photodissociation of 1,2-Diiodotetrafluoroethane

The ultrafast photodissociation of 1,2-diiodotetrafluoroethane excited at 267 nm is investigated at the carbon K-edge by femtosecond soft X-ray transient absorption spectroscopy. The electronic structure of $\text{C}_2\text{F}_4\text{I}$ is characterized by a carbon 1s X-ray feature at lower energy, 286.4 eV, resulting from a transition to the singly occupied molecular orbital (SOMO) of the radical. Upon the photodissociation of $\text{C}_2\text{F}_4\text{I}_2$ to yield $\text{C}_2\text{F}_4\text{I}$ radical, the loss of the electron-withdrawing iodine atom donates the electron density back to carbon and shields the carbon 1s level of the carbon involved in the broken C-I bond. This carbon 1s orbital is blue-shifted 1.6 eV in the X-ray spectra. Meanwhile, the $\sigma^*(\text{C-F})$ orbital is also blue-shifted by 0.7 eV resulting in a 0.9 eV red shift of the carbon 1s to $\sigma^*(\text{C-F})$ orbital transition. However, the $\sigma^*(\text{C-C})$ is redshifted 0.6 eV, resulting in a 2.2 eV red shift of the carbon 1s to $\sigma^*(\text{C-C})$ for the carbon atom in 1,2-diiodotetrafluoroethane which is not involved in the C-I bond breakage, the carbon core 1s level is not impacted by the loss of the iodine atom. The results suggest that the shift in the carbon 1s orbital is greater than the shift in the antibonding orbital upon going from the closed-shell molecule to the radical.

5.1: Introduction

The photodissociation of 1,2-diiodotetrafluoroethane ($\text{C}_2\text{F}_4\text{I}_2$) has been extensively studied.¹⁻¹⁰ The UV excitation of $\text{C}_2\text{F}_4\text{I}_2$ results in the rapid dissociation of an iodine atom. The elimination of two iodine atoms from $\text{C}_2\text{F}_4\text{I}_2$ by one-photon absorption is a nonconcerted two-step sequential process involving the $\text{C}_2\text{F}_4\text{I}$ radical intermediate in the ground state.

Using picosecond excitation of the dissociative A band at 308 nm in combination with kinetic energy resolved time-of-flight (KETOF) mass spectrometry, Lee's group found the first iodine splits off within 200 fs. But it takes 25 ps for the second iodine atom to be eliminated by overcoming an estimated 0.6 eV barrier.⁵ Zewail's group studied the elimination of halogen atoms from $\text{C}_2\text{F}_4\text{I}_2$ using femtosecond pulses centered at 277 nm to dissociate the parent molecule. A resonance-enhanced multiphoton ionization (REMPI) measurement centered at 304 nm detecting the I atomic fragment was used in combination with KETOF.³ The recoil anisotropy was determined using polarized femtosecond pulses. These measurements conclusively excluded the possibility of breaking the two C-I bonds concertedly after excitation to the dissociative A band. The structural dynamics of transient intermediates in the elimination reaction of 1,2-diiodotetrafluoroethane under 307 and 267 nm excitation was studied by Zewail's group using ultrafast time-resolved electron diffraction (UED).^{1,6} With 307 nm excitation, the reaction time of the second C-I bond breakage is determined to be 17 ± 2 ps. Upon 267 nm excitation, the

lifetime of the intermediate C_2F_4I is determined to be 20 ± 5 ps. It was concluded that the structure of the short-lived radical is more favorable to the classical structure than to the bridge radical structure. The photodissociation of $C_2F_4I_2$ in solution was also reported.⁴ Upon 266 nm excitation, the molecular iodine can form within a few picoseconds via the dissociation of the haloethyl radical and geminate recombination of iodine atoms. Later, the dissociation of $C_2F_4I_2$ following two-photon excitation at 396 nm was reported using velocity map imaging of molecular iodine. It was found there is an electron transfer between the two iodine atoms in the parent molecule, which leads to Coulombic attraction and the creation of an ion-pair state in the molecular iodine fragment.²

Recently, a UED study with FOMO-CASCI excited state dynamics simulation reported that under 265 nm excitation, $C_2F_4I_2$ is promoted to a state characterized by a transition from the iodine $5p \perp$ orbital to a mixed $5p \parallel \sigma$ hole and $CF_2\bullet$ antibonding orbital which results in the cleavage of one of the carbon-iodine bonds. And it was found the radical reaches a stable classical structure in less than 200 fs.⁹

Ultrafast transient absorption spectroscopy provides a robust way to study the short-lived reaction intermediates. Selective bond-breaking, made possible by photodissociation at a specific wavelength, produces desirable transient species in a consistent fashion. Furthermore, transient absorption spectroscopy, as opposed to electron or ion spectroscopy, is capable of detecting not only charged species, but also neutral ones, thus allowing studies of the altered electronic structure resulting from neutral dissociation or ionization. Recent progress toward core-level spectroscopy centered on the carbon K edge demonstrates the power of using X-ray spectroscopic techniques to study the dynamics and the electronic structures of transient species.

Near-edge X-ray transient absorption spectroscopy (XAS) has been proven to be a powerful technique for elucidating photoinduced molecular dynamics with femtosecond temporal resolution. XAS is atom-specific and sensitive to the electronic state, enabling it to report on both electronic and nuclear dynamics following photoexcitation. We utilize XAS with soft X-rays at the carbon K-edge (280-300 eV) to investigate the dynamics of 1,2-diiodotetrafluoroethane, following excitation with 267 nm UV photons. In this chapter, preliminary results are presented for 1,2-diiodotetrafluoroethane, with a few suggestions for the assignment of the observations. The C_2F_4I radical is characterized by a lower energy absorption feature at 286.4 eV. The preliminary experimental results suggest that upon the breakage of the C-I bond, the loss of the electron-withdrawing iodine atom donates the electron density back to carbon and shields the carbon 1s level of the carbon involved in the broken C-I bond. This carbon 1s orbital is blue-shifted 1.6 eV. Meanwhile, the $\sigma^*(C-F)$ orbital is also blue-shifted for 0.7 eV resulting in a 0.9 eV red shift of the carbon 1s to $\sigma^*(C-F)$ orbital transition. However, the $\sigma^*(C-C)$ is redshifted 0.6 eV, resulting in 2.2 eV red shift of the carbon 1s to $\sigma^*(C-C)$. For the carbon atom in 1,2-

diiodotetrafuloroethane that is not involved in the C-I bond breakage, the carbon core 1s level is not impacted by the loss the iodine atom. The results suggest that the shift in the carbon 1s orbital is greater than the shift in the antibonding orbital upon going from the closed-shell molecule to the radical.

5.2: Results

5.2.1: Static X-ray absorption Spectrum of 1,2-iodotetrafuloroethane at Carbon K-edge

Figure 5.2 shows the static X-ray absorption spectrum of the ground state $C_2F_4I_2$ at the carbon K (1s) edge. The experimental absorption energies and tentative assignment are shown in Table 5.1. There are three major absorption peaks showing at the carbon K edge, labeled in the order of energy as A, B and C at 290.0, 293.1 and 297.4 eV, respectively. Peak A is assigned as the transition from C (1s) to the lowest unoccupied molecular orbital (LUMO), $\sigma^*(C - I)$, peak B is the transition to $\sigma^*(C - F)$ and peak C comes from the transition to $\sigma^*(C - C)$ orbitals. It is worth noting that the peak width of the B and C features are much wider than that of feature A. There are two possible reasons behind it. Firstly, here we are assuming all of the $C_2F_4I_2$ molecules are anti conformers and the two carbon atoms are identical due to symmetry, but there are two stable conformers at 1,2-diiodotetrafuloroethane at its ground state, anti and gauche. The structure models of anti and gauche conformers are shown in Figure 5.1. The gauche conformers will introduce the transition from the core to the valence level at different energies, which is likely within our spectral resolution. It has been estimated that there is about a 9:1 ratio between the anti- and gauche- conformers. In our experimental setup, we are using 298 K as the experimental temperature which will result in a higher percentage of gauche conformers.⁹ Secondly, the previous theoretical work has found there is strong character mixing between the Rydberg and σ antibonding orbitals, and the character mixing can lead to the result that peaks B and C compose multiple transitions rather than the one transition we are assigning here.

To our knowledge, there was no carbon 1s excitation or absorption energies of $C_2F_4I_2$ reported before. A similar molecule, C_2F_6 , has reported transition energies to at 295.4 eV and 300.5 eV, and the proposed assignment of these two transitions are from carbon 1s to $\sigma^*(C - F)$ and $\sigma^*(C - C)$ orbitals, respectively.¹¹ 1,2-Diiodotetrafuloroethane has less fluorination compared to C_2F_6 thus the carbon 1s inner shell is less impacted by the withdrawing effect since iodine atoms have weaker electronegativity than fluorine atoms. This explains the transition from 1s to $\sigma^*(C - F)$ in $C_2F_4I_2$ is 2.3 eV lower than the same transition in C_2F_6 . For the same reason, the transition to $\sigma^*(C - C)$ is 3.1 eV in $C_2F_4I_2$, which is lower than this transition in C_2F_6 . These transition energy differences indicate that the substitution

from fluorine to iodine atoms in the halogen-substituted ethanes not only shifts the carbon 1s inner shell to higher energy but also shift the $\sigma^*(C - C)$ to slightly higher energy, 0.8 eV. For peak A at 290.2 eV, the 3 eV energy difference compared to peak B comes from the fact that the C-I bond is much weaker than the C-F bond.

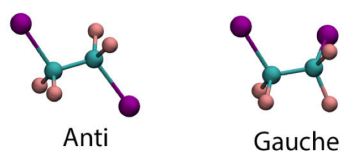


Figure 5.1: Structural models of 1,2-diiodotetrafluoroethane for both the anti and gauche conformers.

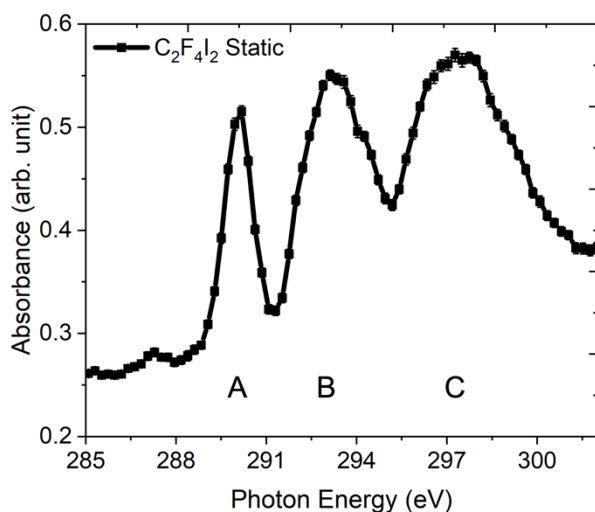


Figure 5.2: Experimental static near-edge X-ray absorption spectrum of electronic ground state 1,2-iodotetrafluoroethane ($C_2F_4I_2$) at the carbon K-edge (the solid black line connects the datapoints; error bars correspond to 95% confidence interval over the sum of 64 scans).

Table 5.1: Tentative assignments of X-ray absorption spectral features observed at the carbon K-edge of ground state 1,2-iodotetrafluoroethane.

Peak	Experimental Energy (eV)	Tentative Assignment
A	290.0	$C(1s) \rightarrow \sigma^*(C - I)$
B	293.1	$C(1s) \rightarrow \sigma^*(C - F)$
C	297.4	$C(1s) \rightarrow \sigma^*(C - C)$

5.2.2: Transient X-ray Absorption Spectra of 1,2-diiodotetrafluoroethane

The transient X-ray absorption spectra at the carbon K-edge show absorption changes that are the differences in absorption with and without the 267 nm excitation pulse at each time delay. A two-dimensional color map of the transient X-ray absorption spectrum of 1,2-diiodotetrafluoroethane upon UV excitation for time delays from -50 fs to 300 fs in 50 fs steps is shown in Figure 5.3 with a smoothing effect to connect individual time delays; here yellow-red and blue-black contours denote positive and negative ΔA features, respectively. Time-resolved soft X-ray absorption spectra of $C_2F_4I_2$ lineouts at three representative time delays, 50, 150, and 250 fs are presented in Figure 5.3 to understand the details of the photodissociation of $C_2F_4I_2$ upon 267 nm excitation. Figure 5.3 a) is the raw experimental transient absorption at the carbon K-edge and b) shows pure excited state absorption spectra generated by adding back the ground state bleach. The added ground state percentage of 15% is estimated by the excitation probability and based on the $2.6 \times 10^{11} \text{ W/cm}^2$ UV photon flux and the absorption cross section of a similar molecule, C_2F_5I , at 267 nm, which is $6.5 \times 10^{-19} \text{ cm}^2/\text{molecule}$. The transition energies for each absorption feature are reported in Table 5.2, along with the tentative assignment of their identities. There are six major observable absorption features in the add-back spectra, labeled as peak D-I, in the near-edge over the set of delay times. It is worth noting that not all six absorption features are observable in the transient absorption spectra because some of them are overlapping with the transitions in the ground state.

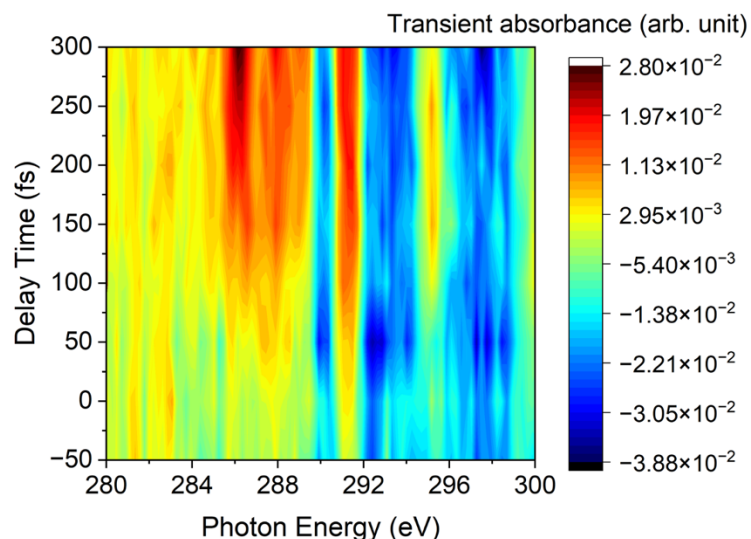


Figure 5.3: Two-dimensional colormap of the experimentally measured 267 nm induced excited-state X-ray dynamics in 1,2-diiodotetrafluoroethane. The color key on the right provides the scale for the measured differential soft X-ray absorption (ΔA). Each of the transient X-ray absorption spectra was collected at time delays from -50 to 300 fs with 50 fs steps. They are combined with smoothing.

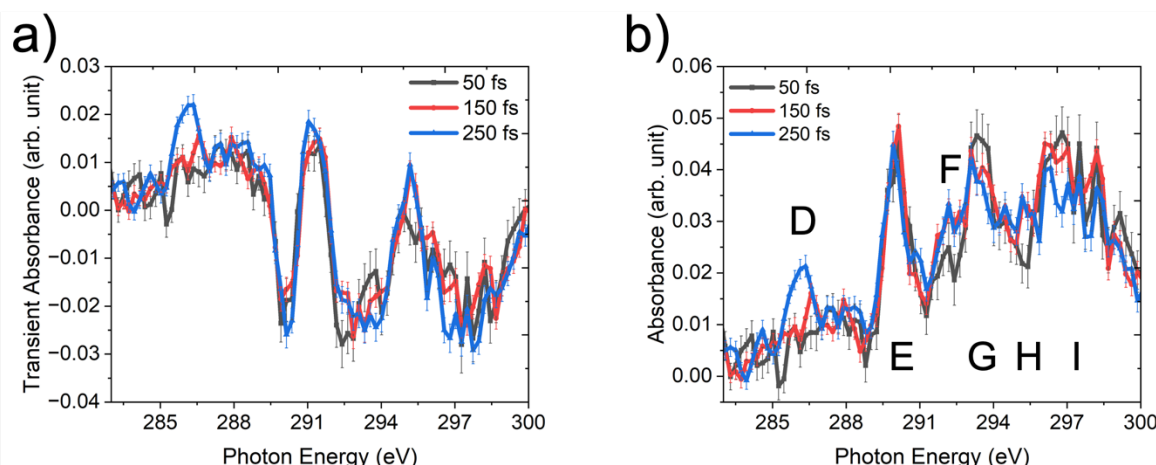


Figure 5.4: a) Experimental differential X-ray absorption spectra at 50, 150, and 250 fs and b) pure excited state absorption spectra at 50, 150, and 250 fs time delays. The pure excited state absorption spectra are generated by adding back the ground state bleach. The added ground state percentage of 15% is determined by the UV excitation probability (see text).

Table 5.2: Tentative assignments of X-ray transient absorption spectral features observed at the carbon K-edge of excited states of 1,2-diiodotetrafluoroethane as well as the C_2F_4I radical.

Peak	Experimental Energy (eV)	Tentative Assignment
D	286.4	$C_\alpha 1s \rightarrow C_\alpha 2p$ (SOMO)
E	290.1	$C_\beta 1s \rightarrow \sigma^*(C - I)$
F	292.2	$C_\alpha 1s \rightarrow \sigma^*(C - F)$
G	293.1	$C_\beta 1s \rightarrow \sigma^*(C - F)$
H	295.2	$C_\alpha 1s \rightarrow \sigma^*(C - C)$
I	296.8	$C_\beta 1s \rightarrow \sigma^*(C - C)$

Table 5.2: Tentative assignments of X-ray transient absorption spectral features observed at the carbon K-edge of excited states of 1,2-diiodotetrafluoroethane as well as the C_2F_4I radical.

5.3: Discussion

At short time delays, 50 – 150 fs, the add-back pure excited state X-ray absorption spectra exhibit five major peaks, E-I, which are associated with the $C_2F_4I_2$ with elongated C-I bond. A photon with 267 nm wavelength can excite the transition of an electron from the highest occupied molecular orbital (HOMO) to the lowest

unoccupied molecular orbital (LUMO), which is from the nonbonding orbital of the iodine atom to the σ^* of the C-I bond. This is the driving force to have iodine dissociation in 1,2-diiodotetrafluoroethane at 267 nm. The broad but small shoulder at 287 eV is likely due to the elongation of C-I bond which shifts the transition of carbon 1s to σ^* (C-I) to lower energy at the carbon K-edge. Once one of the C-I bonds is elongated, the two carbon atoms in the molecule are no longer identical in $\text{C}_2\text{F}_4\text{I}_2$. As the result, we can label them as C_α , which is the atom involved in the dissociative C-I bond, and the other carbon atom as C_β . Peak E at 290.1 eV is assigned to the transition $C_\beta 1s \rightarrow \sigma^*(C - I)$, it appears almost at the same energy compared to this transition in ground state $\text{C}_2\text{F}_4\text{I}_2$. It is indicating that the energy difference between $C_\beta 1s$ and $\sigma^*(C - I)$ almost does not change before and after UV excitation and dissociation. The peak F and G are assigned to the transitions from C_α and C_β to $\sigma^*(C - F)$, at 292.2 and 293.1 eV respectively. The 0.9 eV transition energy difference can come from the difference of the carbon 1s level as well as the σ^* of the C-F bond due to the C-I bond distance change, where the C-F groups are also sitting in different chemical environments. For the same reason, the peak H and I are assigned to the transition from C_α and C_β to $\sigma^*(C - C)$. However, since the final orbital for these two transitions is the same, the splitting between these two transitions is only coming from the core 1s level splitting which is 1.6 eV. Then, comparing the transition energies between $C_\alpha 1s \rightarrow \sigma^*(C - C)$ at short time delay to $\text{C } 1s \rightarrow \sigma^*(C - C)$ in the ground state of $\text{C}_2\text{F}_4\text{I}_2$, since the $C_\alpha 1s$ orbital level blue-shifts to 1.6 eV higher energy, but the transition energies red-shifts 2.2 eV, the remaining 0.6 eV difference is coming from the red-shift of the $\sigma^*(C - C)$ orbital. This red-shift of $\sigma^*(C - C)$ orbital also explains the red-shift of the transition $C_\beta 1s \rightarrow \sigma^*(C - C)$ at short time delay compared to this transition in the ground state of 1,2-diiodotetrafluoroethane. As a summary, the effect of C-I bond dissociation of $\text{C}_2\text{F}_4\text{I}_2$ on the molecular orbitals is presented in Figure 5.5 as a schematic molecular orbitals' energy shift.

At 250 fs time delay, there is a new peak at 286.4 eV rising up. It is assigned to the transition from carbon 1s to carbon 2p (SOMO of the radical). This is the indication of C-I bond cleavage. Since it has been known that the iodine dissociation in $\text{C}_2\text{F}_4\text{I}_2$ is sequential and nonconcerted, the other iodine atom is still connected to C-I and the peak from the C_β to $\sigma^*(C - I)$ still exists. Therefore, the absorption peaks E, G, and I associated with the transitions from $C_\beta 1s$ still exist. Also, the peaks F and H corresponding to the transitions from $C_\alpha 1s$ to the antibonding orbitals of C-F and C-C bonds exist and their transition energies do not change much compared to these transitions at 50- 150 fs time delay between UV and the X-ray probe pulses.

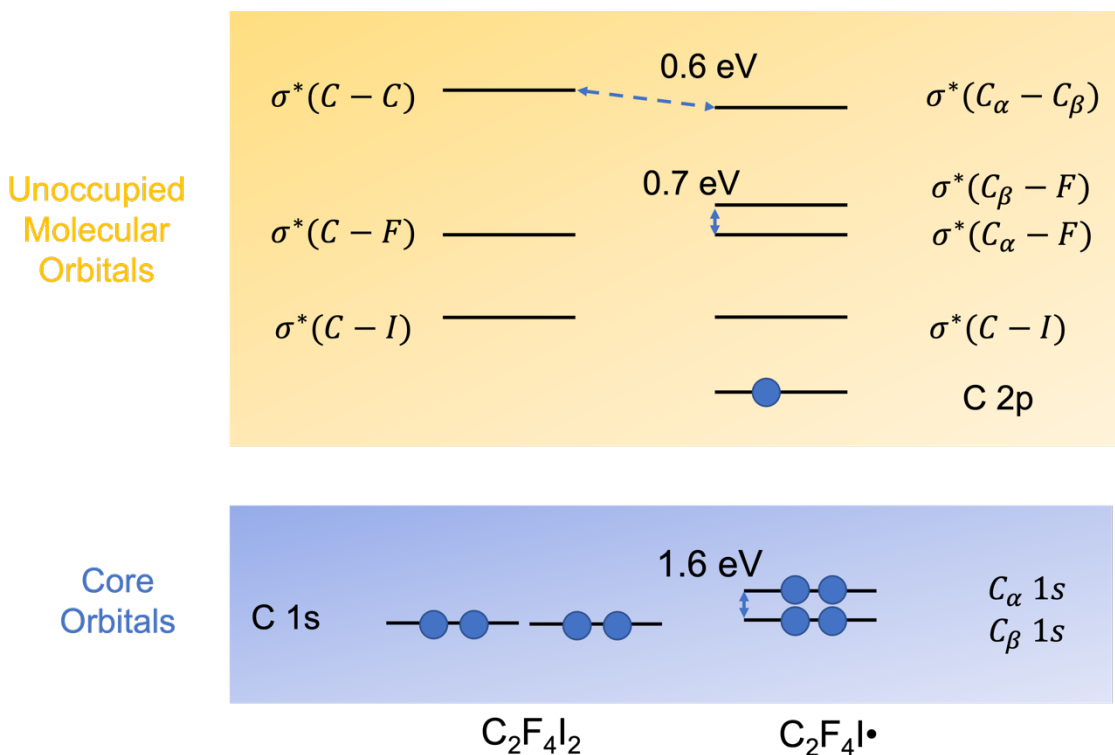


Figure 5.5: Schematic diagram of the molecular orbitals involved in the parent molecule $\text{C}_2\text{F}_4\text{I}_2$ and the photoproduct radical $\text{C}_2\text{F}_4\text{I}^\bullet$

The results are now compared to the results of the photodissociation of CH_2ClI our group has reported.¹² The C_α can be seen as equivalent to the carbon atom in CH_2ClI , and $\text{C}_\beta\text{F}_2\text{I}$ can be seen as the substitution of the H atom. Both of these two studies observe the blue-shift of carbon 1s orbital, ΔE_c , which is involved in the broken C-I bond. Meanwhile, both studies observe the red-shift of the σ antibonding orbital of the carbon atom to halogen atom bond, ΔE_σ^* . Interestingly, the redshift in the C 1s to the antibonding orbitals of carbon and halogen bonds signifies the shift in the carbon 1s core energy, ΔE_c due to the disappearance of the electron withdrawing effect from the iodine is larger than the shift in the antibonding orbital of carbon-halogen bond, resulting in 0.9 eV in the case of 1,2-diiodotetrafluoroethane, which is almost the same as that in chloriodomethane, 0.8 eV.¹²

It is worth noting that we have not done a power dependent study to rule out the possibility of two photon absorption. The ionization potential of ground state $\text{C}_2\text{F}_4\text{I}_2$ is 10.1 eV¹³ which means it will take three 266 nm photons to ionize the ground state parent molecule. A power dependent study would still be needed to check the linearity of the UV absorption process.

5.4: Conclusion

The ultrafast photodissociation of 1,2-diiodotetrafluoroethane upon excitation at 267 nm has been investigated by femtosecond soft X-ray transient absorption spectroscopy at the carbon K-edge. The photoproduct, $\text{C}_2\text{F}_4\text{I}$ radical, is characterized by a feature at 286.4 eV corresponding to the transition from the carbon 1s to the SOMO. Removal of an iodine atom changes the oxidation state of the carbon atom involved in the broken C-I bond, well reflected in the absorption spectra of the $\text{C}_2\text{F}_4\text{I}$ radical at the carbon K-edge. This carbon 1s orbital is blue-shifted 1.6 eV. Meanwhile, the $\sigma^*(\text{C-F})$ orbital is also blue-shifted by 0.7 eV resulting in a 0.9 eV red shift of the carbon 1s to $\sigma^*(\text{C-F})$ orbital transition. However, the $\sigma^*(\text{C-C})$ is redshifted 0.6 eV, resulting in a 2.2 eV red shift of the carbon 1s to $\sigma^*(\text{C-C})$. For the carbon atom in 1,2-diiodotetrafluoroethane that is not involved in the C-I bond breakage, the carbon core 1s level is not impacted by the loss the iodine atom.

5.5: Bibliography

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