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Photochemical Reaction Dynamics Studied by Femtosecond Soft X-ray Transient Absorption Spectroscopy

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Photochemical Reaction Dynamics Studied by Femtosecond Soft X-ray Transient Absorption Spectroscopy

By

Andrew Richard Attar

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 T. Attwood

Fall 2016
Photochemical Reaction Dynamics Studied by Femtosecond Soft X-ray Transient Absorption Spectroscopy

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Abstract

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University of California, Berkeley

Professor Stephen R. Leone, Chair

The ability to discern and understand the time evolution of both molecular and electronic structure during a chemical reaction in real-time, and with atomic-scale sensitivity, is a primary goal of modern chemical dynamics research. In this dissertation, femtosecond extreme ultraviolet/soft x-ray transient absorption spectroscopy is developed on a table-top apparatus and applied to investigate the evolution of both vibrational and electronic degrees of freedom in molecules following photoexcitation or ionization. Several molecular systems are considered in detail. In the first study, the strong-field ionization of a heteronuclear diatomic molecule, IBr, and the ensuing vibrational wavepacket dynamics in the electronic ground state of the neutral molecule are characterized with atomic-site sensitivity. The element-specificity of the core-level transient absorption technique is further extended to investigate the multichannel ultraviolet photodissociation reaction of bromiodomethane, CH₂IBr. The core-to-valence absorption spectrum of the bromomethyl radical, CH₂Br, which is formed via the major C-I photodissociation coordinate at 266 nm, is characterized for the first time. The measured C-I dissociation time (~50 fs) differs significantly from the C-Br dissociation time (~110 fs), which indicates that more than one excited-state surface is involved. In the third study, the evolution of the transient valence electronic structures in the transition state regions of both the methyl and allyl iodide photodissociation reactions are directly observed and characterized. As the C-I bond is breaking, new 4d(I) core-to-valence resonances localized on the I atom are observed and assigned to repulsive valence-excited transition-state regions. The transition-state resonances directly probe the evolving valence electronic structure during these fundamental bond-breaking reactions. Finally, a full-scale apparatus upgrade was undertaken to extend the femtosecond light source into the soft x-ray energy domain up to and beyond 300 eV. With this new setup, the first femtosecond soft x-ray transient absorption experiments at the carbon K-edge (~284 eV) are performed. In particular, the ultrafast electrocyclic ring-opening reaction of 1,3-cyclohexadiene is investigated and the evolution of the valence electronic structure during the ~180 fs ring-opening process is directly captured. The core-to-valence spectroscopic signatures of the elusive transient intermediate excited states, which lead to ring-opening, are characterized, in combination with time-dependent density functional theory calculations, to reveal overlap and mixing of the frontier valence orbital energy levels.
To my parents
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Chapter 1

Introduction

The energies of vibrational levels within electronic states of polyatomic molecules define the timescale of nuclear motion on a molecular scale. Typical vibrational spacings of organic molecules range from ~4000-100 cm\(^{-1}\), corresponding to periods of ~8-300 femtoseconds (1 fs = \(10^{-15}\) seconds). Due to the far greater mass of atomic nuclei compared to the electrons, vibrational motion in molecules is generally thought to be accompanied by instantaneous rearrangement of the electrons to minimize the energy. This adiabatic assumption is the basis of the Born-Oppenheimer approximation (BOA), which is used to establish distinct potential energy surfaces along chemical reaction coordinates. In a dynamic process, the gradients of the potential energy surface along the vibrational coordinates determine the minimum-energy reaction path. In Fig. 1.1, a simple photodissociation reaction in this adiabatic potential energy surface picture is schematically represented. However, the breakdown of the BOA, which leads to significant and rapid mixing of vibrational and electronic degrees of freedom, is common in excited states of polyatomic molecules. This nonadiabatic coupling is a key step in a myriad of photochemical and photobiological processes. Examples of particularly important reactions that rely on nonadiabatic coupling of electronic states include the key step in the photobiological synthesis of Vitamin D\(_3\) in the skin and the photoisomerization reaction in the photoreceptive pigment, rhodopsin, which is responsible for the first step in vision. Whether the BOA forms an accurate depiction of the dynamic process or not, all chemical reactions are “vibronic” in the sense that the motion of the nuclei and the evolution of the valence electronic structure are intimately intertwined. As a result of the ubiquity of vibronic dynamics in photoinduced processes of polyatomic molecules, the ability to discern the evolution of both molecular and electronic structure, with atomic-scale sensitivity, is a primary goal of modern chemical dynamics research.

From an experimental perspective, capturing and investigating, in real-time, the fundamental vibronic processes that underlie chemical reactions on a molecular scale (bond breaking, bond making, isomerization, charge migration, etc.), requires ultrafast time resolution on the order of femtoseconds. One of the most general techniques used to investigate chemical reaction dynamics is known as the pump-probe method wherein a sufficiently short laser pulse -- typically on the order of 10-100 fs -- is used to “pump” (initiate) a chemical reaction and, at a well-defined time delay, a second laser pulse is used to “probe” the system as the reaction occurs. Fig. 1.2 shows a schematic depiction of the pump-probe concept. By scanning the relative time delay, \(\Delta t\), between the pump and probe pulses, a “movie” of the photoinduced process can be extracted through time-resolved spectroscopic “snapshots” taken by the probe pulse. In the late 1980’s and early 1990’s, the first uses of the pump-probe method launched the field known as “femtochemistry.”

The accessible information gained from the molecular-scale “movie” of a reaction depends on the probing process. Since the birth of femtochemistry, many probing schemes have been developed, primarily using UV, visible, and IR laser pulses, to investigate countless chemical reactions in both gas and condensed phases. These time-resolved probes combine the
established analytical capabilities of static spectroscopic methods including fluorescence, absorption, photoelectron, photoion, and Raman spectroscopy, as well as multidimensional coherent spectroscopies, with the ultrafast time-resolution made possible by the pump-probe technique. Each probing method provides important information about the dynamic processes, with IR and Raman spectroscopy primarily used for investigating vibrational dynamics and optical probes using visible or UV pulses capable of probing the evolution of valence electronic structure. In some cases, it is even possible to discern both the vibrational dynamics and the electronic population dynamics simultaneously. However, using optical probes in the visible or ultraviolet regions, the ability to probe vibronic dynamics with atomic-scale precision has been limited by the inherent spatial delocalization of the valence electronic orbitals involved. To alleviate this limitation, ultrafast extreme-ultraviolet (XUV) and x-ray spectroscopies, which involve excitation or ionization from core-orbitals that are highly localized to specific atomic sites, are being developed.

Over the last 15-20 years, the advancement of methods for generating ultrashort X-ray pulses using large-facility free electron lasers (FELs), X-ray slicing at synchrotrons, and compact, table-top high harmonic generation (HHG) sources, has initiated a revolution in femtochemistry and has even initiated the rising field of attosecond science (1 as $= 10^{-18}$ seconds). These developing tools aim to exploit the powerful advantages of x-ray spectroscopy and scattering techniques, which have been well established in static measurements over many decades, now in the ultrafast time domain. While x-ray scattering offers a remarkably detailed view of the molecular structure (i.e. the relative positions of the nuclei), x-ray spectroscopies probe the electronic structure of molecules with element-specificity, revealing detailed information regarding the oxidation states, spin-states, and chemical environments of specific atomic sites. By extending these capabilities into the time domain, femtosecond time-resolved x-ray scattering methods, for example, have enabled a direct view into the motions of the nuclei and chemical bonds of molecules during a chemical reaction. Alternatively, recent ultrafast x-ray spectroscopic experiments have allowed a detailed view into the complementary evolution of valence electronic structure during photochemical and photophysical processes.
Although femtosecond time-resolved x-ray spectroscopies using large-facility sources have been applied in recent years at different energies spanning the soft x-ray to hard x-ray regimes, ultrafast pump-probe experiments using table-top HHG sources have so far been limited to extreme ultraviolet (XUV) probe energies ranging from ~20-120 eV. In recent years, new developments in HHG sources have led to the efficient production of x-ray pulses extending into the soft x-ray regime and reaching up to ~1 keV. A primary appeal of developing such table-top sources for ultrafast x-ray spectroscopic measurements is the accessibility of the laboratory-scale tools required to build such experiments. With the development of efficient, cost-effective, laboratory-scale, ultrafast x-ray light sources, the proliferation of ultrafast x-ray science is likely to be significantly accelerated. In the following sections, a detailed discussion is first given to describe the recent development of HHG sources to produce x-ray pulses spanning the soft x-ray energy domain, followed by a description of the general use of both XUV and x-ray HHG sources for ultrafast transient absorption spectroscopy, which is the general technique used throughout this dissertation.

1.1 Extension of HHG Sources to the X-ray Regime

The production of ultrashort XUV and x-ray pulses for time-resolved x-ray spectroscopy on a laboratory benchtop is accomplished using the highly nonlinear frequency upconversion of optical/near-IR laser sources via the technique known as high harmonic generation (HHG). The mechanism of HHG can be understood from the semi-classical “three step model” described by Paul Corkum in 1993. Briefly, the three-step model involves the instantaneous interaction between the valence electrons of an atomic or molecular system with the time-varying electric field of an intense optical or near-IR laser pulse. In step one, the electric field of the laser pulse becomes strong enough to overcome the Coulombic binding potential of the outermost valence electrons of the system, leading to field ionization. In step two, the emitted electron is driven by the electric field away from the parent ion and, once the electric field changes sign, back towards the ion core, gaining significant kinetic energy via the ponderomotive force. In the third and final step of the process, at the zero-crossing of the electric field, the electron is able to recombine with the parent ion with some finite probability and, if recombination occurs, the energy is conserved by emission of either another photoelectron (nonsequential double ionization) or emission of a photon (HHG).
In HHG, the photon energy emitted is equal to the kinetic energy gained by the electron while propagating in the continuum plus the ionization potential of the valence electron in the field-free system:

$$\hbar \omega_{HHG} = I_P + E_K$$  \hspace{1cm} (1.1)

where $\hbar \omega_{HHG}$ is the emitted photon energy, $I_P$ is the ionization potential of the system, and $E_K$ is the kinetic energy gained by the electron in the electric field. The ionization potential is fixed for the particular atom or molecular system being used for HHG, but a range of kinetic energies is possible, depending on the amount of time the electron spends in the continuum or, in other words, the phase of the electric field when electron emission (step 1) occurs. This leads to the possibility of broadband spectral emission. Due to the half-cycle periodicity of the high harmonic process, interference between emission events at different half cycles leads to the production of odd harmonics of the fundamental laser frequency. The maximum possible kinetic energy gained by an electron in the field at the moment of recombination is given by:

$$E_K = 3.17 U_P = 3.17 \frac{e^2E_0^2}{4m\omega^2} = \frac{e^2}{2ce_0m\omega^2} I$$  \hspace{1cm} (1.2)

where $U_P$ is known as the ponderomotive energy, which is the mean kinetic energy of a free electron in an electromagnetic field, $e$ is the electron charge, $E_0$ is the electric field amplitude, $m$ is the effective mass of the electron, $\omega$ is the laser carrier frequency, $c$ is the speed of light in vacuum, and $e_0$ is the vacuum permittivity. For the most commonly used ultrafast laser sources, which utilize a solid-state Ti:Sapphire lasing medium and have efficient emission centered near 800 nm, HHG is most efficient in producing pulses in the vacuum-ultraviolet (VUV) and XUV energy domains (~10-100 eV).\(^{47,49}\) In Fig. 1.3, a typical HHG emission spectrum generated using 800 nm driving wavelength in Ne is plotted, which was collected

![Fig. 1.3 HHG emission spectrum generated using 800 nm driving wavelength in Ne](image-url)
using the experimental apparatus described in this dissertation. Now, with a simplified theoretical framework in place for understanding the generation of broadband VUV and XUV pulses using HHG on a table-top apparatus, the extension of these sources towards the soft x-ray (100's of eV) and even hard x-ray domain (>1 keV) will now be discussed.

Upon inspection of equations 1.1 and 1.2, the first obvious method for achieving high cutoff energies is to utilize a gaseous HHG medium with a high ionization potential. However, typical ionization potentials of gases only range between ~10-25 eV. The noble gases, for example, which are the most commonly used media for HHG, have ionization potentials that range between 12.13 eV (Xe) and 24.58 eV (He). It is immediately clear that varying the Ip by changing the HHG medium cannot extend the cutoff energy by the ~100's of eV necessary to push into the x-ray domain from the XUV region. It should be noted that increasing the ionization potential of the HHG medium leads to a dramatic increase in the field intensities needed to tunnel ionize (step 1 in HHG). The emitted electrons therefore experience, on average, higher electric field intensities once propagating in the continuum, which, according to equation 1.2, leads to an increase in the kinetic energy gained by the electron before recombination occurs. The effective increase in the HHG emission energies is observed to be larger than the strict increase in the ionization potential energy of the medium, but not enough to efficiently extend into the soft x-ray domain. The general intensity-scaling of the HHG emission energies will be discussed further below.

With the control of the ionization potential limited to a narrow energy range, the following term in equations 1.1, the kinetic energy gained by the electron in the laser field, is considered next. First, before going any further with this discussion, it is important to note that the energy-dependent efficiency of HHG is controlled by both the microscopic, single-atom response, which has been the focus of the discussion so far, and also macroscopic effects involving the propagation of both the laser field and the generated XUV/x-ray field in the dispersive gaseous medium and laser-generated plasma. From the macroscopic perspective, the coherent build-up of HHG intensity over the laser pulse envelope is dependent on the constructive interference of many single-atom emitters, which is known as phase matching.

The requirement for phase matching in HHG is that the wave vector (phase) mismatch, $\Delta k$, between the driving laser field and the generated XUV or soft x-ray field in the HHG medium approaches zero over a macroscopic range within the focal volume:

$$\Delta k = mk(\omega_f) - k(\omega_f) = 0 \quad (1.3)$$

where $k(\omega_f)$ is the wave vector of the fundamental driving laser field and $mk(\omega_f)$ is the wave vector of the $m^{th}$ harmonic.\textsuperscript{47} Several effects contribute to the frequency-dependent phase mismatch, including dispersion in the neutral gas ($\Delta k\text{disp}$), dispersion in the laser-generated plasma ($\Delta k\text{plasma}$), and the geometric dispersion from focusing and propagation of the laser itself ($\Delta k\text{geom}$). The total phase mismatch is given by:

$$\Delta k = \Delta k\text{disp} + \Delta k\text{plasma} + \Delta k\text{geom} \quad (1.4)$$

where, at XUV and soft x-ray harmonic energies:

$$\Delta k\text{disp} \propto n(\omega_f) - n(m\omega_f) > 0 \quad (1.5)$$
\[ \Delta k_{\text{plasma}} < 0 \quad (1.6) \]
\[ \Delta k_{\text{geom}} < 0 \quad (1.7) \]

where \( n(\omega_f) \) is the refractive index of the fundamental laser in the neutral HHG gas medium and \( n(m\omega_f) \) is the refractive index of the \( m^{th} \) harmonic frequency. The magnitudes of \( \Delta k_{\text{disp}} \) and \( \Delta k_{\text{plasma}} \) depend on the neutral gas density and plasma density, respectively, and both depend on harmonic order. The magnitude of \( \Delta k_{\text{geom}} \) depends on the harmonic order and focusing conditions. By tuning all of these parameters for a given driving laser frequency and XUV/soft x-ray energy range, the phase mismatch can be minimized to zero within the focal volume.

With all of this in mind, from equation 1.2, the two experimental parameters that can be controlled to extend the HHG cutoff energy for a given gaseous medium, are the laser intensity and frequency. In the single-atom response limit, the cutoff energy is proportional to the square of the electric field strength (i.e. linear with the intensity: \( E_0^2 \propto I \)) and inversely proportional to the square of the laser frequency. Therefore, by simply varying the optical/near-IR laser parameters used for HHG (i.e. pulse energy, focusing, or pulse duration), the field intensity can be increased and thus increase the theoretical high-harmonic cutoff energy in the single-atom limit. However, when macroscopic effects are considered, it becomes clear that arbitrarily increasing the field intensity is limited by the loss of phase matching at high plasma densities.\(^{47}\) For a femtosecond, near-IR laser pulse centered near 800 nm, the limits imposed by the increasing field intensities preclude the efficient generation of soft x-ray energies.

![Fig. 1.4 Schematic representation of the high-resolution dual-grating XUV/soft x-ray spectrometer. The metal filter is used to prevent gas leakage or stray laser light from the sample chamber into the spectrometer chamber.](image)
Therefore, the next experimental control parameter considered is the driving laser wavelength. In the single-atom limit, the HHG cutoff energy increases quadratically with increasing wavelength (i.e. $E_k \propto \frac{1}{\omega^2} = \lambda^2$). However, with increasing wavelength, in the single-atom picture, the recombination efficiency (step 3 of HHG) decreases significantly (on the order of $\lambda^{-5.5}$). The strong wavelength dependence of the recombination efficiency imposes a general limitation on arbitrarily increasing the wavelength of the driving laser to increase the cutoff energy. That said, with modest increases in the wavelength to 1200-1800 nm compared to 800 nm, and by tuning the macroscopic parameters, especially the neutral gas density to increase the number of single-atom emitters, this limitation can be overcome to efficiently produce HHG pulses with photon energies spanning into the soft x-ray domain. More details regarding the increase in driving laser wavelength and other experimental details are provided in the section 1.2.

Along with the increase in the driving laser wavelength and the increase in the neutral gas density required to generate soft x-ray pulses extending beyond 300 eV, a custom high-resolution, dual-grating x-ray spectrometer has also been constructed in order to optimally resolve energies ranging from ~35 eV to ~1 keV. The spectrometer design is depicted in Fig. 1.4. The principle elements of the spectrometer are the two concave gratings with variable line-spaced groove density, which are used to spectrally disperse the XUV and x-ray energies. One of the two gratings (Hitachi, 001-0660), has grooves with a so-called blaze angle.
optimized for the XUV range while the other (Hitachi 001-0659) has grooves with a blaze angle optimized for the XUV range. More details regarding the blaze angle can be found in the reference. The variable line spacing of the grating grooves ensures that a large range of wavelengths either in the XUV or x-ray range are dispersed onto a flat plane at the focus of the grating. In the spectrometer used here, the traditional exit slit is replaced by a CCD camera with 1340 (20 μm x 20 μm) pixels along the axis of spectral dispersion. This, in combination with the flat-field focus provided by the variable line spacing of the grating, allows for an optimal resolution to be achieved over a broad range of XUV and x-ray energies simultaneously. Although the chip size itself permits simultaneous detection over a relatively broad range of energies, in order to detect the whole spectral range from 35 eV to 1 keV, the CCD has to be moved along the flat spectral plane. To achieve this, a home-built mechanical translation apparatus in combination with a custom flexible membrane bellow is used to hold and position the CCD camera (see Fig. 1.4). The design of the translation apparatus has been adapted from a similar spectrometer that has been previously described.

With the new apparatus developed, including the longer wavelength driver and the new dual-grating XUV/x-ray spectrometer, HHG pulses with energies spanning into the soft x-ray domain can be efficiently produced and detected. To demonstrate this, in Fig. 1.5, the HHG emission collected from the experimental apparatus used in this dissertation is plotted as a function of photon energy for different HHG driving laser wavelengths in Ar, Ne, and He. A careful balance of the neutral gas pressure in the HHG cell and the laser focusing parameters allows for efficient generation of soft x-ray pulses up to ~310 eV. Note that higher energies can be produced but currently with less acceptable efficiencies for use in time-resolved x-ray experiments.

1.2 Ultrafast XUV/X-ray Absorption Spectroscopy on a Table Top

With the availability of XUV and soft x-ray pulses on a table-top apparatus using HHG, the source is implemented into a pump-probe transient absorption scheme to study ultrafast photochemical reaction dynamics. The general schematic representation of the XUV/soft x-ray transient absorption experiment used in this dissertation is presented in Fig. 1.6, which is an upgrade of an existing XUV transient absorption setup that has been previously described. First, the output of a commercial femtosecond Ti:Sapphire laser system (1 kHz rep rate, 800 nm central wavelength) is split into two beam paths, with the majority of the beam used for HHG of broadband XUV/soft x-ray pulses in the “probe arm,” and the other portion of the beam used to initiate the photochemical reaction of interest by either ionization or photoexcitation of the gaseous reactant molecules. In the former case, the fundamental 800 nm beam is used directly to ionize the gaseous sample via strong-field ionization, which will be discussed further in Chapter 2. In the experiments described in this dissertation where excitation of the sample is performed by single-photon absorption, the fundamental 800 nm beam is first used to pump a home-built third-harmonic generator to generate 266 nm pulses. The 266 nm pulses produced are attenuated by an iris and focused by a lens into a gas cell, which is continuously flowing with the sample gas of interest.

For XUV absorption experiments, the 800 nm in the probe arm is further split by a 95:5 beamsplitter and the minor part (5%) of the beam is frequency doubled to generate ~25 μJ of 400 nm. The broadband XUV pulses are produced via HHG in a semi-infinite gas cell filled with ~50-120 Torr of argon or neon gas. The HHG process is driven by both 800 nm + 400 nm
Pulses, which are spatially and temporally recombined at the exit of the semi-infinite gas cell, producing both even and odd harmonics of the fundamental 800 nm driving laser, up to and beyond the 47th harmonic (~73 eV). The resulting XUV pulses provide continuous spectral coverage over the 40-73 eV range due to the overlapping wings of the strong individual harmonics. A typical XUV spectrum generated in this way is shown in Fig 1.3. The residual 800 nm and 400 nm beams are blocked by two 0.6 μm Al filters. XUV energies up to ~73 eV are transmitted through the filters, but there is a sharp cut off of XUV radiation due to the Al absorption at ~73 eV.

In the soft x-ray experiments, the 800 nm beam in the probe arm is first used to pump a high-energy optical parametric amplifier (HE-TOPAS, Light Conversion). The TOPAS produces tunable mid-IR pulses with wavelengths between 1.2-2.6 μm. In the experiments described here, the TOPAS is tuned to generate a signal wavelength of 1.32 μm, which is separated from the idler beam using a dichroic wavelength separator. The transmitted idler beam is dumped into a beam block. The reflected 1.32 μm signal beam is used to drive HHG in a semi-infinite gas cell filled with ~600-700 Torr of helium. The HHG process is sensitively dependent on the HHG gas medium, the wavelength of the driving laser field, and, depending on those chosen parameters, the precise phase matching conditions achieved in the gas cell.

Firstly, two factors are taken into account when choosing the gas medium – the ionization potential and the recombination efficiency in step 3 of HHG. For the noble gases, which are typically used as HHG gas media, the ionization potential increases as the size of the atom decreases. As the ionization energy is increased, the field intensity required to tunnel ionize (step 1 in HHG) increases dramatically, which leads to the emitted electrons experiencing, on average, higher electric field intensities once propagating in the continuum. According to equation 1.2, this results in an increase in the kinetic energy gained by the electron before recombination occurs and therefore effectively increases the HHG cutoff energy. The effective

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**Fig. 1.6** Schematic representation of the IR/UV pump, XUV/soft-x-ray probe transient absorption experimental setup used in this dissertation. The broadband XUV/soft x-ray probe pulses are produced by high-harmonic generation in a semi-infinite gas cell filled with Ar, Ne, or He gas. The diverging XUV/soft x-ray beam is focused by a toroidal mirror (TM) into the sample target. The XUV/soft x-ray spectrometer consists of a plane grating, which spectrally disperses the XUV/soft x-ray beam onto a PIXIS:XO 400B X-ray camera.
increase in the HHG photon energies is observed to be larger than the trivial increase in the ionization potential energy term in equation 1.1. However, the average single-atom recombination efficiency (step 3 in HHG) decreases significantly for decreasing atomic radius of the HHG gaseous medium. Therefore, the choice of gas is a trade-off between the HHG photon energies produced and the XUV/x-ray flux. Secondly, due to the significant reduction in the HHG single-atom recombination efficiency as the wavelength of the driving wavelength is increased (\( \lambda^{-5.5} \)), the choice of wavelength is also a trade-off between HHG cutoff energy and flux. For the purposes of the work described in this dissertation, the optimal balance between HHG flux and cutoff energy is met by using a driving wavelength of 1320 nm (signal beam) in helium. The relatively poor mode quality of the idler beam produced by the TOPAS in its current configuration precluded significant testing at wavelengths beyond 1600 nm. Finally, the phase matching conditions for a given choice of driving wavelength and HHG medium are tuned by adjusting the pressure, focal position, and incoming beam diameter (using an iris placed before the lens that focuses the beam into the semi-infinite gas cell). Typical soft x-ray pulses used in this dissertation have a bandwidth ranging from \(~160-310\) eV (Fig. 1.5). The residual IR beam after HHG is blocked by a 100 nm thick Al filter.

After the HHG chamber, the XUV/soft x-ray beam is focused by a Toroidal mirror at 5° grazing incidence into the flowing gas cell, where it overlaps with either the 800 nm or 266 nm pump beam at a 1° crossing angle. The 800 nm or 266 nm pump pulses are used to ionize or photoexcite the sample of interest, respectively, and are subsequently blocked between the sample chamber and the spectrometer. After the XUV/soft x-ray probe beam is transmitted through the gas sample, it is spectrally dispersed onto a CCD camera using a grating. The XUV/soft x-ray signal is measured as a function of the photon energy.

For static absorption measurements, the pump beam is blocked completely before the sample chamber and the XUV/soft x-ray spectrum recorded with the sample gas flowing, referenced to another spectrum taken in the absence of the sample gas in order to obtain the absorption spectrum \( OD = -\log \left( \frac{l_{\text{gas}}}{l_{\text{no gas}}} \right) \). All spectral regions are collected at once due to the broadband XUV/soft x-ray continuums generated by HHG (40-73 eV for the XUV probe and 160-310 eV for the soft x-ray probe). For transient absorption measurements, the XUV/soft x-ray differential absorption signal, \( \Delta OD \), is obtained by measuring the XUV/soft x-ray signal in the presence of the pump pulse \( (I_{\text{on}}) \) at a given pump-probe time delay relative to the XUV/soft x-ray signal in the absence of the pump pulse \( (I_{\text{off}}) \): \( \Delta OD = -\log \left( \frac{I_{\text{on}}}{I_{\text{off}}} \right) \). This is identical to subtracting the static absorbance spectrum taken with the pump beam blocked \( (OD_{\text{off}}) \) from the absorbance spectrum taken in the presence of the pump beam \( (OD_{\text{on}}) \) to obtain the change in absorbance \( (\Delta OD) \). Note that an electronic linear delay stage in the pump arm controls the relative delay between the arrival of pump and probe pulses with \(~1\) fs accuracy. At a specific time delay, the “\( I_{\text{on}} \)” spectrum is recorded and referenced to an “\( I_{\text{off}} \)” spectrum by utilizing an electronic shutter to block the pump beam before the delay stage moves to the next time delay. The stage moves through the progression of time delays in order (not randomly) and after the final time delay, the stage moves back to the first position and begins another scan through the progression of time points. Several \( \Delta OD \) spectra at each time delay are averaged by moving the stage through the progression of time delays multiple times and collecting both “\( I_{\text{on}} \)” and “\( I_{\text{off}} \)” spectra at each iteration. This procedure allows to correct for any long-term fluctuations in the XUV/soft x-ray flux. For a time scan, the differential
absorption spectrum is recorded in 10-20 fs steps, averaging several scans. For every time step, the “I_on” spectrum is again referenced to a “I_off” spectrum by utilizing the electronic shutter and ΔOD is calculated.

In the XUV/soft x-ray transient absorption experiments described here, the time-resolution in these experiments is established by controlling the precise relative timing of the IR or UV pump pulses with the arrival of XUV or x-ray probe pulses. The instrument response function characterizing the experiments is determined by an in-situ cross-correlation between the pump and probe pulses. In the case of 800 nm strong-field ionization experiments, including the investigation described in Chapter 2 of this dissertation, the strong-field ionization of noble gas atoms can be used to determine time-zero and the instrument response function, as previously described. However, in the case of 266 nm photoexcitation experiments, this method is not possible. The description of an in-situ cross correlation between UV and XUV/soft x-ray pulses, which was developed to solve this problem, is presented in the following section.

1.3 Cross-correlation between UV and XUV/Soft x-ray Pulses

By synchronizing XUV/x-ray pulses with infrared/optical lasers, ultrafast photochemical processes can be monitored in real-time by x-ray spectroscopic methods. The time-resolution in these experiments is established by controlling the precise relative timing of the IR, visible, or UV pump pulses with the arrival of XUV or x-ray probe pulses. To extract accurate time constants characterizing ultrafast dynamical processes, a cross-correlation between the pump and probe pulses is needed to deconvolute the instrument response function characterizing the experiment. Nonlinear optical methods for determining the precise temporal overlap and cross- or auto-correlation of two pulses in the visible, near-UV, and near-IR regions are well established. Typical sum-frequency generation cross-correlations, however, are impractical when applied to the XUV and x-ray domains, due to small cross sections and extremely low fluences.

Therefore, in recent years, a few approaches have been put forward to establish spatiotemporal overlap of UV, Visible, or IR lasers with XUV or x-ray pulses. Such methods include the use of laser-induced sidebands in photoelectron spectra, the exploitation of an x-ray induced change in the optical reflectivity of various materials, and the use of electromagnetically induced transparency (EIT) in the X-ray absorption spectrum in the presence of a near-IR field. The latter example exploits a laser control scheme wherein the near-IR field introduces near-resonant coupling to neighboring Rydberg states of an X-ray photoexcited atom. Dramatic modifications to x-ray and XUV absorption spectra of atoms through coupling of nearby core-excited Rydberg states by near-IR laser fields have been studied in detail. The spectral modifications of ultrashort x-ray or XUV pulses can even occur over individual subcycles of the near-IR field. Since the response is instantaneous relative to even a single optical cycle, the x-ray or XUV spectral alterations can directly map the shape of the external field, and hence provide a cross correlation of the two pulses. These types of coupling schemes are therefore ideally-suited for direct extraction of the XUV or X-ray cross correlation with ultrashort laser pulses.

Typical laser coupling schemes involve external near-IR fields, but when the laser excitation pulses of shorter wavelengths are used, particularly in the near-UV, the laser photon energies almost always exceed the binding energies of core-excited Rydberg states populated
by x-rays or XUV radiation, allowing bound-continuum state coupling effects to become dominant.\textsuperscript{74} The coupling of highly polarizable, core-excited Rydberg states to the continuum leads to ponderomotive energy shifting and broadening of the core-to-Rydberg resonances. The ponderomotive energy, $U_p$, is classically the mean kinetic energy of a free electron in an oscillating electric field, as given in equation 1.2, which is proportional to the electric field intensity ($U_p \propto I = E_0^2$). The ponderomotive shifting of weakly-bound Rydberg states has been studied extensively and observed by both direct and indirect spectroscopic methods.\textsuperscript{73,75,76}

The common scheme involves a resonant excitation pulse to populate the Rydberg state of interest and a perturbing laser field with a fundamental photon energy that exceeds the binding energy of the Rydberg state, but whose energy is much smaller than any transition energy out of the ground state. In such a scenario, the net shift of the transition energy between the ground state and the Rydberg state is expected to match the full ponderomotive energy, as defined in equation 1.1.\textsuperscript{77}

In the following, it is demonstrated via XUV and soft x-ray transient absorption spectroscopy that in the presence of a moderately intense near-UV (266 nm) field, coupling of bound, core-excited Rydberg states with continuum states in two representative noble gas atoms, Xe and Ar, results in ponderomotive shifting and broadening of the XUV/x-ray absorption resonances near ~65 eV and ~244 eV, respectively. In this case, the XUV/x-ray pulse is acting as the pump pulse, exciting either Xe to the $4d_{5/2}^{-1}6p$ core-excited Rydberg state or Ar to the $2p_{3/2}^{-1}4s$ core-excited Rydberg state, and the 266 nm pulse couples these states to the $4d_{5/2}^{-1}$ and $2p_{3/2}^{-1}$ continua, respectively. As an example, the schematic energy level diagram for the case of Xe (excluding spin-orbit splitting of the levels for simplicity) is shown in Fig. 1.7. The interaction leads to a ponderomotive energy upshift of the resonances. The resonance

![Fig. 1.7](image.png)

**Fig. 1.7** The schematic energy level diagram of Xe atomic orbitals is depicted as an example to aid in the description of the general in-situ cross-correlation technique between UV and XUV/soft x-ray pulses. The XUV pulse in this example promotes Xe to a $4d^{-1}6p$ core-excited Rydberg state and the 266 nm pulse couples this state to the $4d^{-1}$ continuum, leading to ponderomotive energy shifting and broadening of the XUV absorption line shape in the presence of the 266 nm field.
shifting/broadening is measured as a function of the time delay between the XUV/x-ray pulse and the 266 nm pulse to establish a novel and completely in-situ method for cross-correlation between XUV/soft x-ray and UV pulses. Here, the pulse duration of the resonant XUV/x-ray excitation is shorter than the perturbing 266 nm field. Therefore, due to the linear dependence of the ponderomotive energy shift on the square of the instantaneous 266 nm field strength, this effect can be used to directly map out the temporal overlap of the 266 nm and XUV/x-ray pulses.

1.3.1 Demonstration of Cross-correlation in Xe and Ar

Fig. 1.8 shows the static XUV absorption spectrum of Xe near the $N_{4,5}$ edge. The assignments of the resonances are given in the figures. As a first example of the cross-correlation technique in application, Fig. 1.9 shows a snapshot of the ponderomotive energy upshift of the Xe $4d_{5/2}^1 6p$ core-excited Rydberg state at spatiotemporal overlap between an XUV pulse and a UV pulse with a peak intensity of $\sim 1.0-1.5 \times 10^{12}$ W/cm$^2$. Since the $4d_{5/2}^1 6p$ core-excited Rydberg state of Xe is weakly-bound ($< 2.5$ eV binding energy) compared to both the 266 nm photon energy of 4.65 eV and the deeply bound ground state, both spectral effects, namely the energy upshift of the transition energy and the broadening of the lineshape, can be understood in the context of bound-continuum state coupling by the moderately intense 266 nm field. The energy upshift is attributed to a ponderomotive shifting mechanism, as described above. Simultaneously, single photon ionization of the core-excited Rydberg states by the 266 nm photons (see Fig. 1.7) introduces an additional decay pathway of these states, which results in an energy broadening of the resonances, compared to the absorption spectrum in the absence of the UV field. The additional lifetime broadening depends on the ionization cross section out of the Rydberg state of interest, $\sigma(E)$ at 266 nm, and the intensity (I) of the 266 nm field such that the final linewidth, $\Gamma$, is proportional to both of these parameters: $\Gamma \propto I \sigma(E)$.\(^{76}\)

The energy upshift of the core-excited Rydberg states and the broadening of the lineshapes in the presence of the 266 nm field are both linear functions of the intensity. Due to
the linearity, the shift in the XUV absorption energy as a function of the pump-probe time delay directly maps the intensity cross correlation of the 266 nm and XUV pulses. In the transient absorption timescans, the intensity cross correlation is traced by monitoring the change in the absorption amplitude on the high-energy side of the $4d_{5/2}^{-1}6p$ resonance in xenon at ~65.2 eV. A representative example of such a time trace is plotted in Fig. 1.10. The full-width at half maximum of the representative cross-correlation trace plotted is measured to be 80 ± 3 fs.

In order to demonstrate the generality of this technique for different XUV and x-ray spectral regions, another cross-correlation experiment is performed, this time using the soft x-
ray pulse spanning ~160-310 eV. For this measurement, the core-excited Rydberg states near the L_{2,3} edge of Ar (~245 eV) are used. Fig. 1.11 shows the static x-ray absorption spectrum of Ar near the L_{2,3} edge. In this cross-correlation measurement, the 2p_{3/2}^{-1}4s core-excited Rydberg state at 244.4 eV is excited by the soft x-ray pulse and the ponderomotive shifting of this resonance is measured in the presence of the 266 nm UV pulse. Again, since the 2p_{3/2}^{-1}4s state binding energy (~4.3 eV) is less than the 266 nm photon energy of 4.65 eV, bound-continuum state coupling is possible. Fig. 1.12 shows a snapshot of the ponderomotive energy upshift of the Ar 2p_{3/2}^{-1}4s resonance at spatiotemporal overlap between the x-ray pulse and a UV pulse.

**Fig. 1.11** Static soft x-ray absorption spectrum of Ar near the L_{2,3} edge.

**Fig. 1.12** Snapshot of the ponderomotive energy upshift of the Ar 2p_{3/2}^{-1}4s resonance at spatiotemporal overlap between the x-ray pulse and a UV pulse with a peak intensity of ~1.0-1.5 x 10^{12} W/cm^2.
with a peak intensity of ~1.0-1.5 x 10^{12} \text{ W/cm}^2. \text{ A clear energy upshift and broadening of the resonance is observed in the presence of the UV field, analogous to the effects observed in the Xe resonance near 65 eV. In Fig. 1.13, the change in the soft x-ray absorption of the Ar } 2p_{3/2}^{-1}4s \text{ resonance is plotted as a function of the delay time between the UV and soft x-ray pulses. The instrument response function extracted for this representative UV/soft x-ray cross-correlation measurement is } 120 \pm 15 \text{ fs.}

\textbf{Fig. 1.13} Time trace showing the change in the soft x-ray absorption of the Ar } 2p_{3/2}^{-1}4s \text{ resonance as a function of the delay time between the UV and soft x-ray pulses}

\text{In summary, an in-situ cross-correlation experiment between near-UV and XUV/x-ray pulses, which takes advantage of ponderomotive energy shifting of weakly bound core-excited Rydberg states of noble gas atoms, is developed and described. The generality of the technique for use with various XUV and x-ray spectral regions is demonstrated by exploiting core-excited Rydberg states of vastly different energies in Xe (~65 eV) and Ar (~244 eV). The spectral palette offered by the noble gas atoms and their various core edges allows this technique to be applied over a large range of XUV and x-ray energies.}

\textbf{1.4 Bibliography}

(2) Huber, K. P.; Herzberg, G. In \textit{Molecular Spectra and Molecular Structure}; 1979.


Stöhr, J. NEXAFS spectroscopy; Springer, 1996.


(60) Ott, C. Attosecond multidimensional interferometry of single and two correlated electrons in atoms, 2012.


(70) Ott, C. Science 2013, 340, 716.


Chapter 2

Investigation of vibrational wave packets and element-specific strong-field ionization dynamics of iodine monobromide

2.1 Introduction

When the electric field of a laser pulse becomes comparable to the Coulombic potential of the valence electrons of an atom or a molecule, suppression of the ionization continuum threshold can occur, leading to tunnel ionization\(^1\) or above-threshold ionization.\(^2\) This strong-field ionization (SFI) effect can populate multiple ionic excited states\(^3,4\) and can lead to hole-orbital alignment in the remaining photoion.\(^5,6\) SFI is the critical first step in high-harmonic generation of coherent attosecond extreme-ultraviolet (XUV) and x-ray pulses.\(^7\) Molecules, in contrast to atoms, have additional nuclear degrees of freedom, enabling additional phenomena resulting from SFI, including Coulomb explosion,\(^8\) dissociative ionization,\(^3,9\) and ground-state wavepacket formation.\(^10-12\) Moreover, the spatial distribution of the electron density representing the molecular orbital from which ionization occurs can determine the electron hole localization within the molecule.\(^13\) In such cases, the coherent population of multiple ionic electronic states leads to charge migration on few or sub-femtosecond timescales,\(^8\) opening exciting avenues for studies of fundamental valence electron dynamics.

The formation of ground-state wavepackets in the presence of a strong non-resonant laser field has been studied in detail recently in simple diatomic molecules including H\(_2\), D\(_2\), I\(_2\), and Br\(_2\).\(^10-12,14\) One mechanism invoked in these studies to describe this phenomenon is the so-called Lochfraß mechanism, which can involve either preferential ionization as a function of the bond-length (R) of the unperturbed ground-state and ionic potential energy curves or enhanced ionization at a critical internuclear separation resulting from the distortion of the potentials in the field. Impulsive stimulated Raman scattering is another mechanism that can result in the formation of ground-state wavepackets in molecules in the presence of a strong non-resonant laser field;\(^15\) this is an effect that is expected to be present to some degree in the studies presented here.

In the case of Lochfraß, the formation of the wavepacket is understood based on an R-dependent tunneling ionization rate, where preferential ionization occurs at internuclear separations other than the equilibrium bond length (R\(_{eq}\)). A requirement for wavepacket formation within this asymmetric ionization scheme is an initial thermal population of vibrationally excited states, such that ionization depletes two or more vibrational levels of the electronic ground state coherently. The R-dependence leaves the remaining ground-state vibrational amplitude on either the inner or outer turning point preferentially. In the case of Br\(_2\) and I\(_2\), the ground ionic state has a shorter R\(_{eq}\) than the neutral ground state and therefore the ionization energy decreases as the internuclear separation decreases. Therefore, since the tunneling rate increases with decreasing ionization energy for a given molecule, the
The ionization rate of the unperturbed potentials is expected to be maximized nearer to the inner turning point.

The strong-field ionization dynamics of Br₂ and resulting wavepacket formation was previously explored using femtosecond time-resolved extreme-ultraviolet (XUV) transient absorption spectroscopy. In that investigation, the remarkable sensitivity of the core-to-valence absorption energy of Br₂ as a function of internuclear separation was exploited to characterize the wavepacket localization in real-time. At the investigated field intensity (~1.6 x 10¹⁴ W/cm²), it was determined that the R-dependent ionization of the unperturbed potentials dominates and the ground-state vibrational amplitude is selectively depleted at short bond-lengths.

In the case of I₂, on the other hand, at the field intensities used in the experiment of Ref ¹¹ (~4.6 x 10¹³ W/cm²), preferential ionization occurs at the outer turning point. In the I₂ experiment, the distortion of the field-free potentials leads to enhanced ionization at bond lengths longer than Rₑ, which is caused by the so-called R-critical enhanced ionization mechanism (REI). The intuitive picture describing this REI mechanism is schematically represented in Fig. 2.1. The double-well potential representing an arbitrary diatomic molecule is shown in the presence of a strong external electric field (e.g. for a particular half-cycle of an intense laser pulse). When the bond is short (Fig. 2.1A), the outermost electrons in the highest-occupied molecular orbital (HOMO) of the diatomic, represented by a blue cloud, are delocalized over the two atomic centers, in accordance with the spatial distribution of the HOMO electron density. However, when the bond is stretched to some “critical” bond length (Rₑ), as in Fig. 2.1B, an inner potential barrier forms, and the HOMO electron density localizes at the two atomic centers. In the strong electric field, the potential energy of the electron near the up-field atom center is raised, while the potential energy of the down-field atom center is lowered. Enhanced tunneling ionization can then occur through the inner barrier, which is much more favorable than tunneling through the outer barrier (between the down-field atom and the continuum), owing to the smaller width and height of the inner barrier. This mechanism leads to a much higher rate of ionization at stretched bond lengths near Rₑ.
For \( I_2 \), at the investigated field intensity (\( \sim 4.6 \times 10^{13} \text{ W/cm}^2 \)), the REI mechanism is found to dominate over the field-free R-dependent ionization mechanism.\(^{11}\) Note that, in both the \( \text{Br}_2 \) and \( I_2 \) experiments, impulsive stimulated Raman scattering is thought to play a non-negligible role. In order to distinguish the mechanism of wavepacket formation, the phase of the vibration is extracted in each case. A phase of 0 or \( \pi \) indicates that R-dependent ionization occurs preferentially at either the inner or outer turning point, which points to Lochfraß or REI as the dominant mechanism. Impulsive stimulated Raman scattering, however, would result in a vibrational phase of \( \pi/2 \).\(^{11}\)

In heteronuclear diatomic molecules, such as \( \text{IBr} \), which is the subject of the present investigation, the situation becomes even more complex (and therefore interesting). First, depending on the symmetry of the molecular orbital involved in ionization, significant Stark shifts of both the neutral and ion energy levels can occur due to the interaction between the
external electric field and the permanent dipole moment of the molecule. The strong dependence of the energy levels as a function of the relative orientations of the permanent dipole moment and the external electric field can lead to significant asymmetry in the electron emission probability from the perspective of the molecular frame. Further, in the mechanism of REI in the case of a heteronuclear diatomic molecule, the symmetry in the HOMO electron density in the molecule is broken, which also leads to preferential ionization that can occur from one particular atomic center. This point will be revisited later in sections 2.6 and 2.7 of this chapter.

In the present experiment, femtosecond time-resolved XUV transient absorption spectroscopy is used to investigate the strong-field ionization dynamics of IBr and the resulting ground-state vibrational wavepacket in the neutral molecule. Here, we exploit the unique element-specificity of core-level XUV absorption spectroscopy, probing transitions localized on the I and Br atoms separately, yet simultaneously, to explore these dynamics from the perspective of the individual atomic sites. The concept of the experiment is schematically represented in Fig. 2.2. The interaction with an intense 800 nm laser pulse leads to ionization of the IBr molecule and production of a vibrational wavepacket in the neutral ground state. A broadband (45—72 eV) XUV pulse produced via high-harmonic generation probes the ensuing dynamics in both the ion and neutral molecules through time-evolving changes in the I(4d) and Br(3d) core-to-valence absorption spectra.

In neutral IBr, the resonances that dominate the spectra at these XUV energies involve promotion of 4d(I) and 3d(Br) core orbital electrons into the $\sigma^*$ (IBr) lowest-unoccupied molecular orbital (LUMO). In Fig. 2.2, the core-excited states are labeled such that the element from which the core electron is promoted is given in parentheses, followed by the specific orbital in which the core hole is generated in the final state. The “-1” in the superscript indicates hole formation in that core orbital and the subscript refers to the nominal total angular momentum quantum number, J, which characterizes the core-hole spin-orbit state. Finally, after the comma, the valence or Rydberg orbital to which the core-electron is promoted is specified. The core-hole spin orbit splitting is ignored in Fig. 2.2 for schematic simplification. Due to the repulsive nature of the $(I)4d_{3/2}^{-1},\sigma^*$ and $(Br)3d_{3/2}^{-1},\sigma^*$ core-excited states, which will be discussed further below, the core-to-valence transition energies are strongly dependent on the internuclear separation. This enables us to directly map the vibrational wavepacket motion in the ground-state potential energy surface and to extract the relative phase of the vibration.

The ionization energy required to remove an electron from the HOMO of IBr to reach the lower ground-state ($X^2\Pi_{3/2}$) of the IBr$^+$ ion is 9.79 eV. The ionization energy required to remove an electron from the HOMO-1 to reach the $A^2\Pi_{3/2}$ state of IBr$^+$, on the other hand, is 11.99 eV. Since the tunneling rate decreases rapidly (exponentially) with increasing ionization energy for a given molecule, strong-field ionization to the ground-state manifold of IBr$^+$ is expected to dominate at the field intensities used in the present investigation. As discussed later in this chapter, evidence for the formation of IBr$^+$ in the $A$-state manifold is not found. When the IBr$^+$ ion is formed with a hole in the $\pi^*$ HOMO, new transitions are opened from the 4d(I) and 3d(Br) core orbitals to the vacancy in the $\pi^*$ orbital. By monitoring the local 4d(I) and 3d(Br) core transitions separately, but simultaneously, the rise times of the ion transitions from the perspective of each element are found to differ significantly. Specifically, the $(Br)3d_{5/2}^{-1},\pi^*$ resonance in the Br window is delayed by ~40-50 fs with respect to the $(I)4d_{5/2}^{-1},\pi^*$ resonance in the I window.
A tentative interpretation of the element-specific dynamics is presented in terms of a $R$-dependent ionization of the molecule and an asymmetric ionization probability from the HOMO. Specifically, it is determined that strong-field ionization at extended bond lengths of IBr dominates via the REI mechanism, forming IBr$^+$ ions preferentially at the outer turning point. As will be discussed in detail below, the HOMO electron density of IBr is primarily localized on the I atom. In the REI picture, at extended internuclear separations, the HOMO is localized further on the I atom and trapped by the inner potential barrier. Therefore, in the initially formed stretched IBr$^+$ ions, the inner barrier traps the hole density on the I atom immediately following ionization. When the ion begins to contract toward its equilibrium internuclear separation (half-period of IBr$^+$ is ~55 fs), the inner barrier is reduced and the hole density is able to delocalize over both the Br and I atomic sites.

2.2 Experimental Methods

The experimental apparatus used in this study has been described in detail, and a simplified schematic of the experimental layout is shown in Fig. 2.3. Briefly, the employed laser system (Spectra-Physics, Spitfire-Pro) delivers ~2.8 mJ pulses at 1 kHz repetition rate, 40 fs pulse duration, with a wavelength centered at 800 nm. Using an 80:20 beamsplitter, the output from the laser system is split into two arms, with the majority (80%) of the beam used for HHG of broadband XUV pulses in the “probe arm,” and the other 20% of the beam is used for SFI in the “pump arm.” The probe arm is further split by a 95:5 beamsplitter and the minor part (5%) of the beam is frequency doubled to generate 25 $\mu$J of 400 nm. The broadband XUV pulses are produced via HHG in a semi-infinite gas cell filled with 110 Torr of Neon gas. The diverging XUV beam is focused by a toroidal mirror (TM#1) into the sample target. The XUV spectrometer consists of another toroidal focusing mirror (TM#2) and a plane grating with uniform line spacing of 600 lines/mm, which spectrally disperses the XUV beam onto a PIXIS:XO 100B X-ray camera.

Fig. 2.3 Schematic representation of the IR-pump, XUV-probe transient absorption experimental setup. The broadband XUV probe pulses are produced by high-harmonic generation in a semi-infinite gas cell filled with 110 Torr of Neon. The diverging XUV beam is focused by a toroidal mirror (TM#1) into the sample target. The XUV spectrometer consists of another toroidal focusing mirror (TM#2) and a plane grating with uniform line spacing of 600 lines/mm, which spectrally disperses the XUV beam onto a PIXIS:XO 100B X-ray camera.
odd harmonics of the fundamental 800 nm driving laser, up to and beyond the 47th harmonic (~73 eV). The resulting XUV pulses provide continuous spectral coverage over the 40-73 eV range due to the overlapping wings of the strong individual harmonics. The residual 800 nm and 400 nm beams are blocked by two 0.6 μm Al filters. XUV energies up to ~73 eV are transmitted through the filters, but there is a sharp cut off of XUV radiation due to the Al absorption at ~73 eV.

The resulting XUV beam is focused to a beam diameter of 40 μm into a heated sample gas cell, which is filled with ~10 Torr (1.3 kPa) of IBr gas. The XUV beam is overlapped at a 1° crossing angle with the 800 nm pump beam, which has pulse energies of either 150 μJ or 450 μJ for “low” and “high” intensity experiments, respectively. The 800 nm pump pulses are focused to a beam diameter of 80 μm in the sample cell, reaching field intensities of approximately 1.5 x 10^{14} W/cm^2 and 4.5 x 10^{14} W/cm^2 for low and high intensity scans, respectively, and inducing SFI of the IBr molecules. The IBr reservoir, the sample line, and the sample gas cell are all heated to ~80 °C in order to reach an appropriate and constant gas pressure and to avoid formation of condensation in the sample cell. This also slightly increases the Boltzmann population of the vibrationally excited states of IBr. Constant pressure in the cell is confirmed by monitoring the overall flux of the XUV in regions of non-resonant absorption by the gaseous sample.

After the XUV probe pulses are transmitted through the gas sample, the beam is spectrally dispersed onto a CCD camera, where the XUV signal is measured as a function of the photon energy. For static absorption measurements, the pump beam is blocked completely before the sample chamber and the XUV spectrum recorded with the sample gas flowing, referenced to another spectrum taken in the absence of the sample gas in order to obtain the absorption spectrum \( OD = -\log \left( \frac{I_{\text{gas}}}{I_{\text{no gas}}} \right) \). All spectral regions are collected at once due to the broadband XUV continuum (40-73 eV).

For transient absorption measurements, the XUV differential absorption signal, ΔOD, is obtained by measuring the XUV signal in the presence of the pump pulse \( I_{\text{on}} \) at a given pump-probe time delay relative to the XUV signal in the absence of the pump pulse \( I_{\text{off}} \): \[ \Delta OD = -\log \left( \frac{I_{\text{on}}}{I_{\text{off}}} \right). \] This is identical to subtracting the static absorbance spectrum taken with the pump beam blocked (OD_{off}) from the absorbance spectrum taken in the presence of the pump beam (OD_{on}) to obtain the change in absorbance (ΔOD). Note that an electronic linear delay stage in the pump arm controls the relative delay between the arrival of pump and probe pulses with ~1 fs accuracy. At a specific time delay, the “\( I_{\text{on}} \)” spectrum is recorded and referenced to an “\( I_{\text{off}} \)” spectrum by utilizing an electronic shutter to block the pump beam before the delay stage moves to the next time delay. Several ΔOD spectra at each time delay are averaged by moving the stage through the progression of time delays multiple times and collecting both “\( I_{\text{on}} \)” and “\( I_{\text{off}} \)” spectra at each iteration. This procedure allows to correct for any long-term fluctuations in the XUV flux. For a time scan, the differential absorption spectrum is recorded in 20 fs steps, averaging 32 scans. For every time step, the “\( I_{\text{on}} \)” spectrum is again referenced to a “\( I_{\text{off}} \)” spectrum by utilizing the electronic shutter and ΔOD is calculated. Each time step is recorded with an integration time of 0.2 s, corresponding to 200 laser pulses. A full time scan is completed in ~1 hour.
2.3 Calculations

Ground-state vibrational wavepacket motion in IBr is probed via time-evolving energy shifts of the core-to-valence absorption spectrum. Restricted excitation window time-dependent density functional theory (REW-TD-DFT) calculations implemented in NWChem\textsuperscript{22,23} are performed on neutral IBr to determine how the \((I)4d_{\frac{7}{2}}^{-1},\sigma^*\) core-excited energy changes as a function of internuclear separation. The \((Br)3d_{\frac{5}{2}}^{-1},\sigma^*\) core-excited energy is expected to exhibit a qualitatively similar R-dependence, but these states are not considered here. The calculations do not take into account the 1.7 eV spin-orbit splitting between the \((I)4d_{\frac{5}{2}}^{-1},\sigma^*\) and \((I)4d_{\frac{3}{2}}^{-1},\sigma^*\) states, but rather give a spin-orbit averaged energy. The important question is how the relative transition energy depends on the internuclear separation. The calculated transition energies are plotted as a function of internuclear separation in Fig. 2.4 along with the corresponding oscillator strengths. The calculations show that the core-

![Figure 2.4](image)

**Fig. 2.4** R-dependence of the XUV transition energy to the \((I)4d_{\frac{7}{2}}^{-1},\sigma^*\) core-excited state of IBr as calculated by the REW-TD-DFT calculations. Inset shows the corresponding oscillator strength calculated as a function of internuclear separation.

excited state is highly repulsive near the equilibrium bond length \((R_{eq} = 2.47 \text{ Å})\), which will lead to a decreasing XUV transition energy as the internuclear separation of IBr is increased. With this information, the observed energy shifts in the XUV absorption resonances of neutral IBr can be mapped directly to relative internuclear separation.

2.4 Static XUV absorption spectrum of IBr and assignments

In Fig. 2.5, the static, ground state XUV absorption spectrum of IBr is plotted between 46 and 72 eV. The spectrum covers both the Iodine N\textsubscript{4/5} edge and the Br M\textsubscript{4/5} edge, corresponding to transitions originating from the 4d core orbital of I and 3d core orbital of Br, respectively. The I N\textsubscript{4/5} pre-edge resonant transitions occur between \(\sim 46-58\) eV, while the Br M\textsubscript{4/5} pre-edge resonances occur between \(\sim 64-72\) eV. The large spectral separation (\(\sim 10-20\) eV)
of the two regions allows for well-separated, yet simultaneous probing of the local atomic centers. The resonant transitions are labeled A-F, and they overlap with an underlying, non-resonant contribution due to valence and core-level ionization. The assignments of the resonances are shown in Table 2.1 with assignment labels given in accordance with a one-electron core-to-valence transition, as described in the introduction to this chapter. A spin-orbit doublet is observed for each core-to-valence resonant transition, with a spin-orbit energy.

**Fig. 2.5** The static XUV absorption spectrum of IBr. The transitions marked A, B and C, D correspond to excitation of I(4d) core electrons to \( \sigma^*(I-Br) \) and 6p,4f(I) unoccupied valence and Rydberg orbitals, respectively. A spin-orbit doublet is observed for each final state electron configuration, characterized by the spin-orbit splitting of the I(4d) or Br(3d) core-hole states. The transitions marked E, F correspond to excitation of Br(3d) core electrons to the \( \sigma^*(I-Br) \) orbital. There is an underlying non-resonant absorption throughout the spectrum due to valence and core-level ionization. The broad, underlying absorption edge at energies above 56 eV corresponds to a delayed onset of 4d(I) core-level ionization, referred to as a “giant resonance.”

<table>
<thead>
<tr>
<th>Peak</th>
<th>Photon Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>49.1</td>
<td>( (I)4d_{5/2}^{-1}, \sigma^* )</td>
</tr>
<tr>
<td>B</td>
<td>50.8</td>
<td>( (I)4d_{3/2}^{-1}, \sigma^* )</td>
</tr>
<tr>
<td>C</td>
<td>55.7</td>
<td>( (I)4d_{5/2}^{-1}, 6p, 4f )</td>
</tr>
<tr>
<td>D</td>
<td>57.4</td>
<td>( (I)4d_{3/2}^{-1}, 6p, 4f )</td>
</tr>
<tr>
<td>E</td>
<td>68.2</td>
<td>( (Br)3d_{5/2}^{-1}, \sigma^* )</td>
</tr>
<tr>
<td>F</td>
<td>69.1</td>
<td>( (Br)3d_{3/2}^{-1}, \sigma^* )</td>
</tr>
</tbody>
</table>

**Table 2.1** Static XUV absorption pre-edge transitions of IBr
splitting of ~1.7 eV characterizing the core-excited states with an I 4d core hole and a splitting of ~1.0 eV for the final states with a Br 3d core hole. The broad, underlying absorption edge at energies above 56 eV corresponds to the onset of 4d(I) core-level ionization, referred to as a “giant resonance.” Note that the slight discontinuities in absorption at, for example, 47.0 eV, 48.5 eV, 53.4 eV, 55.0 eV, 58.2 eV, 59.8 eV, 61.3 eV, 62.9 eV, etc. are caused by the sharp contrast in the flux at the peaks and valleys of the high harmonic photon flux. Discontinuities in absorption occur near the regions of low flux in the harmonic valleys.

2.5 Spectral observation of strong-field ionization and assignments

Fig. 2.6A and 2.6B show, in the iodine and bromine windows, respectively, a snapshot of the differential absorption spectrum in the “long time delay” limit (averaging time delays between 250-750 fs) following 800 nm strong-field ionization with a field intensity of ~1.5 x 10^{14} W/cm². Due to the broadband nature of the XUV probe pulses, the core-to-valence transitions in both the iodine and bromine windows are observed simultaneously. Strong-field ionization populates not only the ground state, but also excited electronic states of the generated ions. At this field intensity, ionization of the highest-occupied molecular orbital (HOMO) is expected to dominate, leading to formation of the IBr⁺ cation in both the ground state (X ²Π_{3/2}) and spin-orbit excited state (X ²Π_{1/2}). The spin-orbit energy splitting between these two states is ΔE_{SO} = 0.58 eV.

Fig. 2.6 Transient absorption spectrum following strong-field ionization of IBr at 1.5 x 10^{14} W/cm². The left panel shows the iodine window and the right panel displays the bromine window. In the iodine window, the product absorption peaks at 46.1 and 47 eV correspond to I and I⁺ atomic transitions, respectively. The product absorption resonance at 47.9 eV corresponds to the ²Π_{3/2}→(I)4d_{5/2}⁻¹,π⁺ resonance of IBr⁺. The negative-amplitude peaks at 49.1 eV and 50.8 eV represent the depletion of the IBr neutral molecule. In the Br window, the product absorption peaks at 64.5 eV and 65.1 eV correspond to Br and Br⁺ atomic transitions, respectively. The product absorption resonances at 66.7 and 67.1 eV correspond to ²Π_{3/2}→(Br)3d_{5/2}⁻¹,π⁺ and ²Π_{3/2}→(Br)3d_{3/2}⁻¹,π⁺ transitions of IBr⁺, respectively. Depletion of the IBr neutral is seen in the Br window as negative-amplitude peaks at 68.3 eV and 69.3 eV.
In the iodine window (Fig. 2.6A), three distinguishable product absorption features appear at energies below the depletions of the 4d→σ* transitions of the neutral parent molecule. As an indication of dissociation of the parent molecule, either by dissociative ionization or by population of dissociative neutral excited states, the two sharp features at 46.1 eV and 47 eV correspond to 4d→5p core-to-valence transitions of atomic iodine in both the spin-orbit ground state (2P3/2) and excited state (2P1/2). The resonance at 46.1 eV corresponds to the 2P3/2→2D5/2 transition of ground-state I atom and the resonance at 47 eV corresponds to the 2P1/2→2D3/2 transition of spin-orbit excited iodine, referred to as I*. The most prominent positive absorption feature centered at 47.9 eV in Fig. 2.6A is assigned as a (I)4d→π* transition of the IBr+ ion, specifically as 2Π3/2→(I)4d5/2,σ*. Another resonance of atomic I, namely the 2P3/2→2D3/2 transition at ~47.8 eV, is obscured by the IBr+ ion signal at 47.9 eV. Furthermore, there is at least one more product absorption feature overlapping the (I)4d5/2,σ* depletion of neutral IBr at ~49.1 eV. This is evident by comparing the relative intensities of the (I)4d5/2,σ* and (I)4d5/2,σ* depletions in the differential absorption spectrum of Fig. 2.6A with the relative intensities of these resonances in the static absorption measurement in Fig. 2.5. The overlapping product absorption at ~49.1 eV is attributed to the X 2Π1/2→(I)4d3/2,σ* resonance of the spin-orbit excited IBr+ ion, the initial state of which lies 0.58 eV above the ground state (X 2Π3/2). Taking into account the energy difference of 1.7 eV that needs to be added to access the 4d3/2 core-hole state compared to the 4d5/2 core-hole state of the same final-state electron configuration, the X 2Π1/2→(I)4d3/2,σ* resonance is estimated to appear 1.12 eV above the X 2Π3/2→(I)4d5/2,σ* resonance (at 47.9 eV). This analysis leads to the assignment of the overlapping product absorption feature with the parent depletion at ~49.1 eV to the X 2Π1/2→(I)4d3/2,σ* resonance of the spin-orbit excited IBr+ ion.

Turning to the bromine window in Fig. 2.6B, product absorption resonances involving the Br 3d core levels are identified, which are analogous to those observed in the iodine window. First, the product absorption features at 64.5 eV and 65.1 eV are the 2P3/2→2D5/2 and 2P1/2→2D3/2 resonances of atomic Br in the ground state and spin-orbit excited state, respectively. The 2P3/2→2D3/2 transition of Br at 65.5 eV is too weak to be distinguished in the spectrum. These atomic Br resonances are correlated with the atomic I resonances observed in the iodine window, which are formed due to either dissociative ionization or dissociation of neutral excited states, which can be populated during the interaction with the near-IR field. If the neutral atomic I and Br species are formed by dissociative ionization, then the formation of Br+ and I+, respectively, is expected. However, the I+ and Br+ XUV absorption resonances occur at ~74.5 eV and ~66.6 eV, respectively, which overlap strongly with the IBr+ signals in the I and Br windows. Therefore, the appearance of I+ and Br+ cannot be explicitly confirmed. The strong product resonance at 66.7 eV is the X 2Π3/2→(Br)3d5/2,σ* transition of IBr+ and the shoulder at 67.1 eV is assigned to the X 2Π1/2→(Br)3d5/2,σ* transition of the spin-orbit excited IBr+ ion. The analysis of the splitting between the X 2Π3/2→(Br)3d5/2,σ* and the X 2Π1/2→(Br)3d5/2,σ* states is similar to that made for the analogous transitions in the iodine window. Finally, on the high-energy side of the neutral IBr (Br)3d3/2,σ* depletion, an overlapping product absorption near ~70 eV is observed, which is assigned to a (Br)3d5/2,σ* resonance of the IBr+ ion.
2.6 Neutral Dynamics

In fig. 2.7, lineouts of the differential absorption amplitude at 49.5 eV and 51.2 eV, on the high-energy side of the $(I)4d_{5/2}^{-1},\sigma^*$ and $(I)4d_{3/2}^{-1},\sigma^*$ resonances, are plotted as a function of pump-probe time delay. A clear oscillation is evident in the transient absorption lineouts after interaction with the 800 nm laser pulse occurs at time-zero. A cosinusoidal fit to the transient absorption lineout at 49.5 eV is plotted as a solid red line. From the cosinusoidal fit, a period of $T_p = 124 \pm 2$ fs is extracted, which corresponds to a vibrational frequency of $269 \pm 5$ cm$^{-1}$. The measured frequency matches the reported $\nu_0\nu_1$ vibrational spacing in the ground electronic state of IBr, which is 268.64 cm$^{-1}$. The observed oscillatory pattern is therefore assigned to vibrational wavepacket motion in the neutral ground state of IBr.

![Fig. 2.7](image)

The vibrational phase, $\varphi_R$, of the wavepacket in terms of the internuclear separation, $R$, is defined through $R(t) = R_{eq} + \Delta R \cos\left(t \left(\frac{2\pi}{T_p}\right) - \varphi_R\right)$, where $\Delta R$ is the relative change in $R$ and $T_p$ is the period of the oscillation. Since the absorption amplitude on the high-energy side of the $(I)4d_{5/2}^{-1},\sigma^*$ and $(I)4d_{3/2}^{-1},\sigma^*$ resonances in IBr is maximized when the wavepacket is near the inner turning point of the ground-state potential energy curve (small $R$), the cosinusoidal oscillation observed in Fig. 2.7 is phase-shifted by $\sim\pi$ relative to $R(t)$. Taking this into account, the phase of the wavepacket in terms of the oscillating effective internuclear separation is measured to be $\varphi_R = 0.74\pi \pm 0.06\pi$ from the cosinusoidal fit. A phase of $\varphi_R = 0$
or \( \pi \) indicates that \( R \)-dependent ionization occurs preferentially at either the inner or outer turning point, respectively. The phase of \( \varphi_R = 0.74\pi \pm 0.06\pi \) measured here indicates that the ionization occurs preferentially at longer bond lengths, leaving the remaining probability density in the neutral IBr molecules initially localized near the inner turning point. The IBr\(^+\) molecules are initially formed with extended bond lengths relative to their equilibrium internuclear separation.

In the case of I\(_2\), Br\(_2\), and IBr, in the absence of distortion of the potential energy curves by an external field, the ionization energy increases at internuclear separations longer than \( R_{eq} \), and therefore the ionization rate is expected to decrease as a function of \( R \). In the Lochfraβ picture, this would lead to preferential ionization at the inner turning point of the neutral ground state and wavepacket formation near the outer turning point, which corresponds to a vibrational phase of \( \varphi_R = 0 \). The phase of the vibrational wavepacket in Br\(_2\), following SFI at a field intensity of \(~1.6 \times 10^{14}\ W/cm^2\), was measured to be \( \varphi_R = 0.21\pi \pm 0.05\pi \), indicating that \( R \)-dependent ionization in the field-free picture dominates. In I\(_2\), at a field intensity of \(~4.6 \times 10^{13}\ W/cm^2\), the phase was measured to be \( \varphi_R = 0.81\pi \), suggesting that the \( R \)-critical enhanced ionization mechanism dominates, which involves increased ionization probability with increasing \( R \) and peaking at a particular critical internuclear separation greater than \( R_{eq} \). In both studies on I\(_2\) and Br\(_2\), the Lochfraβ mechanism was determined to dominate, however, the fact that the phase was somewhat less than \( \pi \) in the case of I\(_2\) and somewhat greater than 0 in the case of Br\(_2\) suggests that impulsive stimulated Raman scattering may also play a role in both molecules.

In the present study, the measured phase of \( \varphi_R = 0.74\pi \pm 0.06\pi \) also suggests that, at a field intensity of \(~1.5 \times 10^{14}\ W/cm^2\), ionization of IBr occurs preferentially from the outer turning point, suggesting that Lochfraβ is a primary mechanism in the observed wavepacket formation and that the ionization rate increases at values of \( R \) greater than \( R_{eq} \). The measured phase therefore also indicates that distortion of the potential energy surfaces of IBr plays a role during the ionization and leads to \( R \)-critical enhanced ionization, as is the case in I\(_2\) (at \(~4.6 \times 10^{13}\ W/cm^2\)). However, the fact that the measured phase is between \( \pi/2 \) and \( \pi \), indicates that wavepacket formation via impulsive stimulated Raman scattering, which would result in a phase of \( \pi/2 \), is competing with the Lochfraβ mechanism.

At the field intensity used for the present investigation of the IBr vibrational wavepacket, the signal-to-noise in the Br window is too low to observe the oscillations through the \((Br)3d_{\pi\pi}^{-1},\sigma^*\) transitions. The wavepacket is observed in the Br window at higher field intensities, due to the larger signal-to-noise, but the data did not offer any additional insight into the wavepacket formation. Therefore, those data are left out of the present discussion.

### 2.7 Ion Dynamics

Due to the asymmetry of heteronuclear diatomic molecules, strong-field ionization can lead to asymmetric electron emission, depending on the spatial distribution of the molecular orbital involved in ionization and/or the direction of the permanent dipole moment. The unique element-specificity of core-level, XUV absorption spectroscopy is exploited to search for atomic-site specific differences in the ionization dynamics through the local I and Br core-level transitions. In Fig. 2.8A and 2.8B, time traces following the appearance of the IBr\(^+\) resonances, \( X^2\Pi_{3/2} \rightarrow (I)4d_{5/2}\pi^* \) in the iodine window and \( X^2\Pi_{3/2} \rightarrow (Br)3d_{5/2}\pi^* \) in the bromine...
window, are plotted, respectively. The time traces are fit to broadened step functions (convolution of a step function with a Gaussian function). A clear delay is observed in the rise of the \( X^2\Pi_{3/2} \rightarrow (I)4d_{5/2}^{-1}, \pi^* \) resonance of IBr\(^+\) in the iodine window relative to the \( X^2\Pi_{3/2} \rightarrow (Br)3d_{5/2}^{-1}, \pi^* \) resonance of IBr\(^+\) in the bromine window. The delay time of 50 ± 20 fs is measured as the difference between the locations of the corresponding steps, which are marked by vertical dashed lines. Due to the low signal-to-noise of the time traces in the Br window in Fig. 2.8A and 2.8B, at a field intensity of ~1.5 x 10\(^{14}\) W/cm\(^2\), the experiment is repeated at a field intensity of ~4.5 x 10\(^{14}\) W/cm\(^2\). The time traces following the appearance of the IBr\(^+\) resonances in both the iodine and bromine windows, at the higher intensity, are plotted in Fig. 2.9A and 2.9B, respectively. Again, the time traces are fit to broadened step functions and a delay time of 40 ± 5 fs is measured as the difference between the locations of the corresponding steps. The higher signal-to-noise in the Br window at a field intensity of ~4.5 x 10\(^{14}\) W/cm\(^2\) both
confirms the observation of the delay in IBr⁺ signal of the Br window and allows for a more accurate measure of the delay time.

In order to develop a model to understand the observed delay between the \((Br)3d_{5/2}^{-1,\pi^*}\) and \((I)4d_{5/2}^{-1,\pi^*}\) resonances, we make two assertions about the initial ionization process, which are followed by their corresponding justifications. The first is that electron emission leading to ground-state IBr⁺ formation is primarily localized from the I atom. To justify this assertion, first of all, it has recently been shown that SFI is sensitive to the spatial distribution in the electron density of the molecular orbital involved in the ionization, which in the present case is the \(1\pi^*\) HOMO of IBr.\(^4,13\) The valence shell of the interhalogen molecules, X\(Y\), can in general be written as \((1\sigma_Y)^2(1\sigma^*X)^2(2\sigma_Y)^2(1\pi_Y)^4(1\pi^*X)^4\), where \(X\) is the halogen of higher atomic weight, on the basis of atomic orbital energies.\(^27\) In the present case, \(X = I\), indicating that the \(1\pi^*\) HOMO is localized primarily on the I atom, while the \(1\pi\) HOMO-1 is

![Fig. 2.9](image-url)

**Fig. 2.9** Pump-probe time traces collected at a field intensity of \(4.5 \times 10^{14}\) W/cm\(^2\) for the appearance of the (A) \(^3\Pi_{3/2} \rightarrow (I)4d_{5/2}^{-1,\pi^*}\) resonance of IBr⁺ in the iodine window and (B) \(^3\Pi_{3/2} \rightarrow (Br)3d_{5/2}^{-1,\pi^*}\) resonance of IBr⁺ in the bromine window. The delay in the \(^3\Pi_{3/2} \rightarrow (Br)3d_{5/2}^{-1,\pi^*}\) resonance relative to the \(^3\Pi_{3/2} \rightarrow (I)4d_{5/2}^{-1,\pi^*}\) resonance is clearly shown by the vertical dashed lines. The measured delay is \(40 \pm 5\) fs.
localized primarily on the Br atom. Photoelectron spectra support this picture; the reasoning is as follows. The spin-orbit splitting of the X$^2\Pi_{3/2}$ and X$^2\Pi_{1/2}$ states of IBr$^+$, which are populated by removal of a HOMO electron, has been measured to be 0.58 eV, which is only 11-12% smaller than the spin-orbit splitting between the X$^2\Pi_1$ states of I$_2^+$ ($\Delta_{SO} = 0.65$ eV) and the X$^2\Pi_1$ states of HI$^+$ ($\Delta_{SO} = 0.66$ eV).\(^{27}\) While, on the other hand, the spin-orbit splitting between the A$^2\Pi_1$ states of IBr$^+$, which are populated by removal of an electron from the HOMO-1, has been measured to be 0.39 eV,\(^{27}\) which is comparable to the spin-orbit splitting of the X$^2\Pi_1$ states Br$_2^+$ ($\Delta_{SO} = 0.35$ eV) and X$^2\Pi_1$ states of HBr$^+$ ($\Delta_{SO} = 0.33$ eV).\(^{27,28}\) The interpretation is that the HOMO of IBr is localized mostly on the I atom and the HOMO-1 is localized mostly on the Br atom, which leaves the hole density localized on either the I or Br centers when ionization occurs to the X$^2\Pi_1$ states or A$^2\Pi_1$ states, respectively.

The second assertion is that IBr undergoes enhanced ionization at extended bond lengths, which has been determined by the vibrational wavepacket phase in the remaining neutral molecules, described in the previous section. The intuitive picture behind this mechanism is schematically represented in Fig. 2.1 and described in section 2.1 of this chapter. The result of the R-dependent enhanced ionization of IBr is that the IBr$^+$ ions are initially formed at large internuclear separations such that the inner barrier observed in Fig. 2.1B is present in the nascent IBr$^+$ ions.

With this in mind, two possible explanations are given for the observed delay in the X$^2\Pi_{3/2} \rightarrow (Br)3d_{5/2}^{-1},\pi^*$ resonance in the bromine window relative to the X$^2\Pi_{3/2} \rightarrow (I)4d_{5/2}^{-1},\pi^*$ resonance in the iodine window. The first hypothesis involves a delay due to vibrational dynamics of the IBr$^+$ ion and the second involves a field-induced delay within the envelope of the 800 nm field. In both scenarios, enhanced ionization occurs at extended bond lengths of IBr and the hole density is initially highly localized on the I atom. The rise of atomic-site-specific transitions from the 4d(I) core orbitals to the valence hole, namely the X$^2\Pi_{3/2} \rightarrow (I)4d_{5/2}^{-1},\pi^*$ transitions, rise directly with the formation of IBr$^+$ ions. However, due to the inner barrier formed in the stretched IBr$^+$ ion, the hole density is temporarily “trapped” within the potential well of the I center. Highly localized transitions from the 3d(Br) core orbitals to the valence hole, namely the X$^2\Pi_{3/2} \rightarrow (Br)3d_{j}^{-1},\pi^*$ transitions, are initially not observed. In the first hypothesis, the delay in the rise of the (Br)$3d_{5/2}^{-1},\pi^*$ resonance is attributed to the time required for the IBr$^+$ bond to contract, which would reduce the inner barrier and allow for the hole density to delocalize over both atoms. Since a vibrational coherence in the IBr$^+$ ion is not observed under the present experimental conditions, the possibility of a coherent oscillation in the hole density between atomic centers is not expected. The measured time delay of $40 \pm 5$ fs in the rise of (Br)$3d_{5/2}^{-1},\pi^*$ resonance compared to the (I)$4d_{5/2}^{-1},\pi^*$ is less than half of the ground-state vibrational period of IBr$^+$ ($T_p = 109$ fs).

In a second hypothesis, the intriguing element-specific delay is attributed to a field-induced effect wherein the hole density remains localized on the I atom following formation of IBr$^+$ and throughout the duration of the 800 nm pulse. In this picture, the remaining electron density of the IBr$^+$ ion is polarized by the strong external field with a strong favorability for localization on the Br atom, which has a significantly deeper well in comparison to the I atom. In this case, the highly-local transitions from the 3d(Br) core-level to the valence hole are blocked by the charge localization while the field is present. Due to the similarity between the 800 nm pulse duration (~80 fs) and the vibrational period of the IBr$^+$ ion, the observed time delay is reasonably explained by both mechanisms. In future experiments with much better
temporal resolution (e.g., using few-femtosecond 800 nm pulses for strong-field ionization of IBr and isolated attosecond XUV probe pulses), the role of vibrational dynamics, if any, in the element-specific delay observed in the IBr\(^+\) resonances, will be addressed.

2.8 Concluding remarks

In summary, femtosecond XUV transient absorption spectroscopy spanning the I M\(_{4,5}\) and Br N\(_{4,5}\) edges is used to investigate the atomic-site-specific ionization dynamics of IBr and SFI-induced wavepacket formation in the remaining neutral molecules. Due to the strong-sensitivity of the XUV core-to-valence transition energies to the internuclear separation, the time-evolving XUV absorption spectrum can be directly mapped to the ground-state vibrational motion. In this way, SFI of IBr is found to occur preferentially at large internuclear separations, leaving the wavepacket probability density localized near the inner turning point of the remaining IBr neutral molecules. This observation indicates that the R-critical enhanced ionization mechanism dominates, as is the case in I\(_2\),\(^{11}\) compared with the field-free R-dependent ionization mechanism, which dominates in the case of Br\(_2\).\(^{12}\) By probing the core-to-valence transitions localized at the I and Br atoms separately, but simultaneously, a distinct delay is observed in the rise of the IBr\(^+\) ion from the perspective of the Br 3d core-to-valence transitions compared to the I 4d core-to-valence transitions.

A tentative interpretation of this observation is presented in terms of the R-dependent ionization of the molecule and an asymmetric ionization probability from the HOMO. First, due to the preferential ionization at extended bond lengths of IBr, the nascent IBr\(^+\) ions are formed at the outer turning point. In the REI picture, at extended internuclear separations, ionization from the HOMO orbital, which is localized on the I atom, leaves a hole density that is initially trapped by the inner potential barrier. When the ion begins to contract toward its equilibrium internuclear separation (half-period of IBr\(^+\) is ~55 fs), the inner barrier is reduced and the hole density is able to delocalize over the Br center.

2.9 Bibliography

Chapter 3

Element-specific femtosecond photodissociation dynamics of CH₂IBr and core-to-valence extreme ultraviolet spectroscopy of the CH₂Br radical

The content and figures in this chapter are reprinted or adapted with permission from A.R. Attar, L. Piticco, and S.R. Leone, “Core-to-valence spectroscopic detection of the CH₂Br radical and element-specific femtosecond photodissociation dynamics of CH₂IBr,” Journal of Chemical Physics, 2014, 141, 164308, Copyright 2014 The American Institute of Physics

3.1 Introduction

The UV photodissociation of halogenated methanes is an important source of both reactive halogen atoms and halomethyl radicals that have an impact on atmospheric chemistry.¹-⁵ Reactive halogens have an adverse impact via ozone depletion,⁴,⁵ and the possible role of halomethyl radical intermediates in the chemistry of the troposphere has been identified.¹-³ In a landmark paper by Welz et al,¹ the reaction of the CH₂I halomethyl radical with molecular oxygen is shown to produce the simplest and first experimentally-observable Criegee intermediate. Halomethyl radicals display important bonding characteristics, attributed to the π-bonding interaction between the lone pair electrons on the halogen atom with the unpaired radical electron, resulting in anomalously short C-X (X=F,Cl,Br,I) bonds compared to closed-shell analogs.⁶-⁸ The partial C-X π-bond causes an extra stability of these radicals. The electronic structure has the π*(C-X) orbital as the singly-occupied molecular orbital (SOMO) with electron delocalization onto the halogen. The magnitude of the carbon-halogen interaction in halomethyl radicals depends on the π-donor ability of the halogen atom, which is known to increase going down the periodic table from fluorine to iodine.⁶

The reactivity of various halomethyl radicals in the atmosphere can vary dramatically, and these differences can have significant implications in the atmospheric photochemistry of multiply-substituted halomethanes (e.g. CH₂IBr, CH₂ICl, etc.). In particular, the wavelength of UV radiation absorbed by these species governs the branching ratio of C-X dissociation and therefore determines which reactive halogen and halomethyl radical is released.⁹-¹¹ In CH₂IBr considered here, UV excitation at 248 nm leads to a dominant C-I dissociation pathway, while 210 nm excitation produces almost exclusively cleavage of the stronger C-Br bond.¹⁰ Depending on the wavelength of light absorbed, either CH₂Br radicals or CH₂I radicals can be released from the photodissociation of the parent molecule.

In the present study, we investigate the multichannel photodissociation dynamics of the bichromophoric system, CH₂IBr, with 266 nm excitation, by probing the local electronic
structure of the major halomethyl radical photoproduct, CH₂Br, and the formation times of the Br and I atoms. This is accomplished through femtosecond time-resolved core-level transient absorption spectroscopy.

Core-level spectroscopies involving X-ray, or XUV, radiation are powerful techniques to probe the oxidation states, spin-states, chemical environment, and electronic structure of molecules.¹²⁻²⁰ Due to the highly localized nature of core orbitals on specific atoms in a molecule, core-to-valence transitions probed by X-ray and XUV absorption are element-specific. By tuning the energy of the X-ray or XUV radiation near the binding energy of a core orbital localized on an individual element, one can selectively interrogate specific atomic sites. The local chemical environment, oxidation state, and local electronic structure involving these atomic sites are encoded in the near-edge and pre-edge structures of the core-to-valence transitions.¹⁷,¹⁹ Furthermore, since the unoccupied valence electronic structure is directly probed, core-to-valence absorption spectroscopy is exceptionally well-suited to detect open-shell radical species. In particular, the core transitions into the SOMO can act as a unique fingerprint of the radical.²¹ Although there are still very limited published examples of core-to-valence absorption spectra of elusive radical reaction intermediates, the method has been exploited in a few static absorption experiments, in combination with the element-specificity of the technique, to identify and characterize the radical intermediates and even to uncover the spatial localization of the SOMO on certain atomic sites.²¹⁻²⁴

The powerful advantages of X-ray and XUV absorption spectroscopy, when extended into the time-domain, make it an ideal candidate to study multichannel reaction dynamics. In the present study, the element-specificity of the technique is exploited to monitor photodissociation along both the C-I and C-Br reaction coordinates of CH₂IBr through the 4d(I) N₄/₅ and 3d(Br) M₄/₅ core-to-valence transitions in the 45-58 eV and 64-73 eV ranges, respectively. The large spectral separation of the core-orbital binding energies allows for the atomic-site specific dynamics to be probed individually, yet simultaneously, as well as a function of time. Furthermore, the unique sensitivity to chemical environment and electronic structure of the core-to-valence transitions is leveraged to identify the major radical photoproduct and to probe the local electronic structure involving the halogen atom.

The UV absorption spectrum of CH₂IBr is characterized by two broad resonances peaking at 270 nm and 215 nm, referred to as the A band and B band, respectively.¹⁰ The A band is assigned to n(I)→σ*(C-I) transitions, which represent the promotion of a nonbonding electron localized on the iodine atom to an antibonding orbital of the C-I bond. The higher energy B band is assigned as n(Br)→σ*(C-Br). As noted, previous studies provide the intuitive picture of the bichromophoric photoexcitation where the n(I)→σ*(C-I) transition leads primarily to C-I bond fission and excitation of the n(Br)→σ*(C-Br) leads primarily to C-Br bond fission. Preferential dissociation of the stronger C-Br bond when exciting the B band occurs by a direct ultrafast dissociation mechanism, circumventing intramolecular vibrational redistribution (IVR), which might have played a role in the bond breaking. Due to the overlap of these bands between 215 nm and 270 nm, photoexcitation in this region can induce both n(I)→σ*(C-I) and n(Br)→σ*(C-Br) transitions, leading to dissociation along both the C-I and C-Br coordinates.¹⁰ At 248 nm, there is appreciable C-Br dissociation, with a lower limit of 1.2:1 for C-I:C-Br bond fission at this wavelength.¹⁰

In the experiments described here, the multichannel 266 nm photodissociation dynamics of CH₂IBr are investigated in real-time by the novel method of femtosecond
time-resolved UV-pump, XUV-probe transient absorption spectroscopy. The extremely broad bandwidth of the XUV probe produced by high harmonic generation allows, for the first time, simultaneous observation of C-I and C-Br dissociation channels in real-time. With this capability, C-I dissociation following 266 nm excitation is observed to be the dominant pathway and also leads to a faster dissociation than the C-Br bond at this wavelength. The difference in dissociation times is rationalized in terms of the acceleration of the fragments in the Frank-Condon regions of the different excited state potentials and also the larger percentage of energy deposited as internal excitation during C-Br dissociation compared to C-I dissociation. The major radical product formed in the 266 nm photodissociation of CH₂IBr is CH₂Br, which is detected through XUV core-to-valence absorption spectroscopy for the first time, obtaining the 3d(Br)→SOMO transitions.

The remainder of this chapter is organized as follows: The experimental methods applied in the studies presented here are described in Sec. 3.2. The static XUV absorption spectrum of CH₂IBr, the differential XUV absorption spectra following 266 nm photodissociation, and transient absorption time scans are presented in Secs. 3.3A, 3.3B, and 3.3C, respectively. The experimental results are discussed in more detail in Sec. 3.4 and the paper concludes with a summary of significant results and outlook in Sec. 3.5.

3.2 Experimental Methods

The experimental apparatus is presented in Fig. 3.1 and has been described in detail.\(^\text{25, 26}\) Previously, experiments on this apparatus were initiated by strong field ionization and dissociative ionization with 800 nm light. Here, the apparatus has been modified to permit single-photon dissociation in the ultraviolet for the first time. The pump arm of the pump-probe set up has been altered to include a third-harmonic generator, producing 266 nm pulses, 80 fs, 20 µJ at 1 kHz. The 266 nm pump is focused to a beam diameter of 120 µm in a heated sample gas cell filled with 5-10 Torr (0.67-1.3 kPa) of CH₂IBr gas. The CH₂IBr reservoir, the sample line, and the sample gas cell are all heated

![Fig. 3.1 Experimental setup of the UV-pump, XUV-probe transient absorption apparatus. The XUV probe is produced by high harmonic generation utilizing a semi-infinite gas cell. The high harmonics are refocused by a toroidal mirror into the sample chamber. The XUV spectrometer consists of another toroidal focusing mirror and a uniform line spaced reflection grating (600 lines/mm), which disperses the harmonics onto an x-ray CCD camera (PIXIS:XO 100B).](image-url)
to ~80 °C in order to reach an appropriate and constant gas pressure and to avoid formation of condensation in the sample cell. Constant pressure in the cell is confirmed by monitoring the overall flux of the XUV in regions of non-resonant absorption by the gaseous sample.

In the probe arm, broadband XUV probe pulses are produced via high harmonic generation (HHG) in a semi-infinite gas cell filled with 110 Torr of neon gas. The HHG process is driven by 800 nm (1.6 mJ) + 400 nm (25 μJ), 40 fs, linearly-polarized light, which produces both even and odd harmonics of the fundamental 800 nm driving laser. The residual 800 nm and 400 nm beams are blocked by two 0.6 μm Al filters. XUV energies up to ~73 eV are transmitted through the filters, but there is a sharp cut off in the Al transmission of XUV radiation at ~72.5 eV. The resulting XUV beam is focused to a beam diameter of 40 μm in the gas cell, where it overlaps the 266 nm pump beam at a 1° crossing angle. The transmitted XUV photons are spectrally dispersed onto a CCD camera where the transmitted intensity is recorded as a function of photon energy. The spectrum is then referenced to another spectrum taken in the absence of the sample gas in order to obtain the optical density (OD) of the sample as function of photon energy. The XUV transient absorption signal is obtained by measuring the OD in the presence of the pump pulse relative to the static absorption in the absence of the pump pulse to yield the change in optical density (ΔOD). Each transient absorption timescan is recorded in 10- or 20-fs steps, averaging 32 scans with an integration time of 0.2 s at each time delay. For every time step, the spectrum is referenced to a “pump off” spectrum by utilizing an electronic shutter to block the pump beam in between each “pump on” spectrum, which helps to correct for any long-term fluctuations in the XUV flux.

Measuring the cross-correlation of the 266 nm pump and the XUV probe to extract the instrument response function (IRF) was achieved using the ponderomotive shift in the XUV absorption transition energies of Xe Rydberg states in the presence of the moderately intense, non-resonant field of the 266 nm pump (see chapter 1).27 Since the bound electron energy levels shift in accordance with the instantaneous field strength,28 the shifting of the XUV absorption energies maps the cross-correlation of the pump and probe directly. The full-width at half-maximum (FWHM) of the resulting cross-correlation trace is used as a fixed IRF in the fitting routine of the pump-probe time traces.

3.3 Results

3.3.1 Static XUV absorption spectrum of CH₂IBr

In Fig. 3.2, the static XUV absorption spectrum of CH₂IBr is plotted. The absorption spectrum is obtained from the spectrally-dispersed XUV transmission through 5-10 Torr of CH₂IBr gas, referenced to the XUV transmission in the absence of the sample gas. The spectrum contains I N_{4/5} and Br M_{4/5} edge and pre-edge features (i.e. transitions originating from the 4d and 3d core orbitals of I and Br atoms, respectively). The resonant pre-edge transitions are labelled with letters A-F and overlap with an underlying, non-resonant contribution due to valence and core-level ionization. The assignments of the pre-edge transitions are given in Table 1. The broad, underlying absorption edge at energies above 56 eV corresponds to a delayed onset of 4d(I) core-level ionization, referred to as a “giant resonance.”29 Note that the slight discontinuities in absorption at 59.9 eV, 63.1 eV, 64.7 eV, 66.2 eV, etc. are caused by the sharp contrast in the flux at the peaks and valleys of the
high harmonic photon flux. Discontinuities in absorption occur near the regions of low flux in the harmonic valleys.

The I Na\textsubscript{4/5} pre-edge resonant transitions occur between 48-58 eV, while the Br M\textsubscript{4/5} pre-edge resonances occur between 68-72.5 eV. After subtracting the contributions by non-resonant valence ionization and the 4d(I) “giant resonance,” these specific energy regions are plotted in Figs. 3.3a and 3.3b, respectively. Again, each distinct transition is labelled

| Table 3.1 Static XUV absorption pre-edge transitions of CH\textsubscript{2}IBr |
|-----------------|-----------------|-----------------|
| Peak | Photon Energy (eV) | Assignment |
| A | 50.6 | 4d(I) → σ\textsuperscript{*}(C-I), (4d\textsubscript{5/2})\textsuperscript{-1} |
| B | 52.3 | 4d(I) → σ\textsuperscript{*}(C-I), (4d\textsubscript{3/2})\textsuperscript{-1} |
| C | 54.8 | 4d(I) → 6p,7p, (4d\textsubscript{5/2})\textsuperscript{-1} |
| D | 56.5 | 4d(I) → 6p,7p, (4d\textsubscript{5/2})\textsuperscript{-1} |
| E | 70.5 | 3d(Br) → σ\textsuperscript{*}(C-Br), (3d\textsubscript{5/2})\textsuperscript{-1} |
| F | 71.5 | 3d(Br) → σ\textsuperscript{*}(C-Br), (3d\textsubscript{3/2})\textsuperscript{-1} |
with letters A-F (same as Fig. 3.2) and the assignments are given in Table 1. The solid black circles represent the experimental absorption data points. The dashed black lines are Gaussian functions fit to each peak in the experimental data and the solid red line is the sum of the Gaussian fitting functions for each plot. Free fit parameters include the peak position, width, and amplitudes of the Gaussian function. The peak energies of each transition are taken as the central peak positions of the Gaussian functions. In Fig. 3.3a, there are slight discontinuities in the absorption at 51.8 eV and 53.2 eV caused by valleys in the harmonic flux near those energies as previously noted.

Fig. 3.3 The static XUV absorption spectrum of CH$_2$IBr in the iodine window (3a) and bromine window (3b) after subtracting the contributions by non-resonant valence and core-level ionization. The solid black circles represent the experimental absorption data points. The dashed black lines are Gaussian functions fit to each peak in the experimental data and the solid red line is the sum of the Gaussian fitting functions for each plot. The peaks are marked with letters A-F and assigned in Table 1.

The large spectral separation (~20 eV) of transitions originating from the I or Br core orbitals in the same molecule highlights the element and atomic-site specificity inherent to core-level spectroscopy. A spin-orbit doublet is observed for each core-to-valence transition in the figures and Table 1. The doublets have distinct energy separations due to the spin-orbit splitting that characterizes the core-holes in the 4d(I) and 3d(Br) orbitals. The extracted I 4d$_{5/2,3/2}$ and Br 3d$_{5/2,3/2}$ spin-orbit splittings are 1.7 eV and 1.0 eV, respectively, which is in agreement with previous literature values.\textsuperscript{29-32}
It is valuable to compare the energetics of this static spectrum to the reported XUV absorption spectra of methyl iodide\textsuperscript{29} and methyl bromide.\textsuperscript{30} In fact, the 4d(I)→σ*(C-I) and 3d(Br)→σ*(C-Br) resonances of CH\textsubscript{2}IBr are observed at the same energies, respectively, within the spectral resolution, as the analogous transitions of CH\textsubscript{3}I and CH\textsubscript{3}Br. This observation is reasonable due to the atomic-site specificity of the core-valence transitions and the nearly identical C-I and C-Br bond lengths in the monosubstituted species compared to those of CH\textsubscript{2}IBr.

### 3.3.2 XUV spectral observation of one-photon photodissociation of CH\textsubscript{2}IBr at 266 nm

Figs. 3.4 and 3.5 show the transient absorption spectrum following 266 nm photodissociation of CH\textsubscript{2}IBr, after the dynamics have finished taking place. Due to the extremely broadband nature of the XUV probe pulses, with energies spanning several tens of eV, core-to-valence transitions in the transient absorption spectrum are observed near both the 4d(I) N\textsubscript{4/5} and 3d(Br) M\textsubscript{4/5} edges simultaneously. In the range 44-58 eV, shown in Fig. 3.4, we observe resonances corresponding to promotion of 4d(I) core electrons into unoccupied valence orbitals. In the same spectrum, but zoomed into the energy range 63-72.5 eV in Fig. 3.5, we observe resonances corresponding to promotion of 3d(Br) core orbital electrons into unoccupied valence orbitals. We probe, separately, but

![Fig. 3.4 Transient absorption spectrum following 266 nm photodissociation of CH\textsubscript{2}IBr, in the iodine window. The unfilled circles represent the experimental absorption data points. The dashed red lines are Gaussian functions fit to each peak in the experimental data and the solid black line is the sum of the Gaussian fitting functions for each plot. The peaks at 46.2 eV, 46.9 eV, and 47.9 eV correspond to atomic iodine transitions from the I(4d) core level, whereas the negative amplitude peaks at 50.6 eV, 52.3 eV, 54.8 eV, and 56.5 eV represent the depletion of the parent molecule following 266 nm photodissociation. There are several sharp positive features overlapping the 4d(I)→6p,7p, (4d\textsubscript{3/2,5/2}) depletion of the parent molecule, which correspond to 4d(I)→6p,7p transitions of atomic iodine, including the fitted peaks at 55.6 eV, 57.2 eV, 57.4 eV, and 57.8 eV.](image)
simultaneously, time-resolved changes in the local chemical environments of both the iodine and bromine atomic centers. In the differential absorption spectra, the energy ranges will be referred to as: 44-58 eV, the “iodine window” and 63-72.5 eV, the “bromine window.” In both spectra, the open circles represent the experimental data. The individual peaks are fit to Gaussian functions, shown as dotted lines, and the sum of these Gaussian functions is represented by the solid black line.

Focusing first on the transient spectrum in the iodine window shown in Fig. 3.4, the product absorption features at 46.2 eV, 46.9 eV, and 47.9 eV correspond to the well-known 4d→5p core-to-valence transitions of atomic iodine in both the spin-orbit ground state (2P3/2) and excited state (2P1/2). The three transitions, in ascending order of energy, are assigned to the 2P3/2→2D5/2, 2P1/2→2D3/2, and 2P3/2→2D3/2 transitions of atomic iodine, respectively. The first and third of these resonances indicate C-I bond cleavage to form ground state I atoms while the middle peak represents the formation of spin-orbit excited I atoms, referred to as I* atoms. Photodissociation specifically along the C-I coordinate forming both I and I* photoproducts is observed through the appearance of these sharp atomic resonances in the iodine window. Note that an underlying resonance at ~47.9 eV, which is assigned to the CH2IBr⁺ ion formed from multiphoton ionization, is distorting the relative amplitude of the 2P3/2→2D3/2 resonance of atomic iodine. The four negative-amplitude peaks at 50.6 eV, 52.3 eV, 54.8 eV, and 56.5 eV represent the depletion of the parent molecule following 266 nm photodissociation. There are several sharp positive

Fig 3.5 Transient absorption spectrum following 266 nm photodissociation of CH2Br, in the bromine window. Broad negative amplitude background from the depletion of the parent molecule 4d(I) core-ionization at energies below 66 eV has been subtracted. The unfilled circles represent the experimental absorption data points. The dashed red lines are Gaussian functions fit to each peak in the experimental data and the solid black line is the sum of the Gaussian fitting functions for each plot. The peaks at 64.6, 65.1, and 65.6 eV correspond to atomic bromine transitions from the Br(3d) core level. The weak resonance observed at 66.6 eV is attributed to CH2IBr⁺ ion formed by multiphoton ionization. The two broad product absorption features at 68.5 eV and 69.5 eV are attributed to 3d(Br)→SOMO transitions of the CH2Br radical intermediate and the negative amplitude peaks at 70.5 eV and 71.5 eV represent the depletion of the parent molecule following 266 nm photodissociation.
features overlapping the $4d(I)\rightarrow 6p,7p, (4d_{3/2}^{-1})$ depletions of the parent molecule, which correspond to $4d(I)\rightarrow 6p,7p (4d_{5/2,3/2}^{-1})$ transitions of atomic iodine, including the fitted peaks at 55.6 eV, 57.2, 57.4, and 57.8 eV. There is a slight discontinuity in the product absorption on the low energy side of the $^2P_{3/2}\rightarrow ^2D_{5/2}$ atomic iodine resonance at 45.7 eV, which is caused by the extremely low flux in the valley of the harmonics in this energy region. Finally, there is a weak resonance at 49.4 eV, which is likely due to the CH$_2$I radical formed in the minor C-Br dissociation channel, but could also be attributed to CH$_2$IBr$^+$.

Fig. 3.6 Integrated XUV absorbance of peaks centered at (a) 46.2 eV corresponding to atomic iodine, (b) 64.6 eV corresponding to atomic bromine, and (c) 66.6 eV corresponding to CH$_2$IBr$^+$ as a function of 266 nm pump power (intensity in the interaction region varies linearly with measured 266 nm power). The integrated XUV absorbances of atomic iodine and bromine resonances have a linear dependence on the 266 nm pump intensity, with slopes of 0.9±0.17 and 1.0±0.12, respectively, indicating these atoms are each formed by single-photon excitation of the parent molecule. The integrated XUV absorbance of the resonance at 66.6 eV, on the other hand, has a non-linear dependence on pump intensity with a slope of 3.8±0.31 in the log-log plot. The peak at 66.6 eV therefore is assigned to CH$_2$IBr$^+$, which is formed by 3-4 photon ionization of the parent molecule.
formed by a minor contribution from multiphoton ionization of the parent molecule. The 4d(I) core-to-valence absorption spectrum of the CH$_2$I radical likely has a resonance in this energy region, but this has not yet been confirmed.

Turning to the bromine window, in Fig. 3.5, the two negative-amplitude resonances marked at 70.5 eV and 71.5 eV represent the depletion of the 3d(Br)→$\sigma^*$(C-Br) transitions of the parent molecule following 266 nm photodissociation. The sharp product absorption features at 64.6, 65.1, and 65.6 eV are the well-known $^2$P$_{3/2}$→$^4$D$_{5/2}$, $^2$P$_{1/2}$→$^4$D$_{3/2}$, and $^2$P$_{3/2}$→$^4$D$_{3/2}$ transitions, respectively, of the Br atom in the ground state ($^2$P$_{3/2}$) and spin-orbit excited state ($^2$P$_{1/2}$). These atomic Br resonances indicate photodissociation along the C-Br coordinate following photoexcitation at 266 nm. The integrated absorption intensities of these atomic Br resonances are weaker than the analogous I atom resonances. As will be discussed further in Section IV C, dissociation along the C-I coordinate is indeed determined to be the major channel following 266 nm photoexcitation of CH$_2$Br. The weak resonance observed at 66.6 eV is attributed to CH$_2$IBr$^+$ ion formed by multiphoton ionization.

The two broad product absorption features at 68.5 eV and 69.5 eV are attributed to 3d(Br)→SOMO transitions of the CH$_2$Br radical intermediate, and the justification for the assignment is discussed further below. There is another product absorption feature that overlaps the 3d(Br)→$\sigma^*$(C-Br), 3$d_{3/2}^{-1}$ depletion of the parent molecule at ~71.5 eV. This is evident by comparing the ratio of the intensities of the 3d(Br)→$\sigma^*$(C-Br), 3$d_{3/2}^{-1}$ and 3d(Br)→$\sigma^*$(C-Br), 3$d_{5/2}^{-1}$ resonances of the parent molecule static absorption at 70.5 eV and 71.5 eV, seen in Fig. 3.3b, with the ratio of the depletion intensities of these resonances in Fig. 3.5. In the static absorption, the 3$d_{5/2}^{-1}$ : 3$d_{3/2}^{-1}$ ratio of integrated intensities is 1.32 ± 0.066. The analogous ratio of the depletions, seen in Fig. 3.5, is 4.06 ± 1.31. The overlapping product absorption at ~71.5 eV is attributed to a 3d(Br)→$\sigma^*$(C-Br) transition of the radical. The three resonances at 68.5 eV, 69.5 eV, and ~71.5 eV represent, to our knowledge, the first observation of core-to-valence absorption by a halomethyl radical. The detailed assignments of the radical peaks are discussed further in Section IV A.

### 3.3.3 Timescales for the 266 nm photodissociation of CH$_2$IBr along the C-I and C-Br reaction coordinates

In the time domain, the multidimensional dissociation channels are tracked simultaneously with atomic-site specificity by monitoring the rises of each of the Br and I atomic absorption signals. In the iodine window, time traces following the $^2$P$_{3/2}$→$^2$D$_{5/2}$ and $^2$P$_{1/2}$→$^2$D$_{3/2}$ resonances representing dissociation along the C-I coordinate to form both I and I* photoproducts are plotted in Fig. 3.7a and 3.7b, respectively. The time traces are fit to a single exponential growth function convoluted with the Gaussian IRF. The Gaussian IRF, with a FWHM of 91±12 fs, is determined separately in a 266 nm + XUV cross
correlation, as described in Sec. II. The 91±12 fs FWHM of the Gaussian is fixed in the fitting of the time traces. The dissociation times are taken as the rise time of the exponential growth function. The measured I and I\(^*\) rise times are 48 ± 12 fs and 44 ± 4 fs, respectively. These dissociation times are essentially identical within the time resolution of the experiment, and 45 fs will be used later in the discussion. Dissociation along the C-Br coordinate to form ground-state Br atoms is traced by the \(^2\)P\(_{3/2}\)→\(^2\)D\(_{5/2}\) resonance at 64.6 eV in the Br window in Fig. 3.7c. The measured Br rise time is 114 ± 17 fs. In the kinetics

**Fig. 3.7** Pump-probe time traces for the appearance of (a) the I atoms at 46.2 eV (b) the I\(^*\) atoms at 46.9 eV and (c) the Br atoms at 64.6 eV.
scans, the signal-to-noise of the $^2P_{1/2} \rightarrow ^2D_{3/2}$ resonance of the Br* atomic species is too small to accurately fit the rise time of this spin-orbit excited atom. The atomic-site specificity of the XUV transient absorption technique allows for a simultaneous observation of multiple dissociation channels in real-time, elucidating distinct dissociation kinetics leading to each product. The distinctly different timescales of C-I and C-Br dissociation channels in this experiment suggest that the bond breaking pathways correlate with separate electronic excited states accessible by the 266 nm photon.

3.4 Discussion

3.4.1 XUV core-to-valence absorption by the CH$_2$Br radical intermediate

As noted, the differential absorption spectrum in the Br window after 266 nm photodissociation of CH$_2$IBr has taken place is shown in Fig. 3.5. There are two broad product absorption peaks at 68.5 eV and 69.5 eV, which are 2 eV below the 3d(Br)$\rightarrow$\*C(Br) depletions of the parent molecule, and another broad product absorption feature overlapping the parent molecule depletion at $\sim$71.5 eV. The peaks at 68.5 eV and 69.5 eV are split by 1 eV, indicating that they represent the spin-orbit doublet of a 3d(Br) core-excited electronic configuration. As for the absorption at 71.5 eV, the second peak in the 3d(Br) spin-orbit doublet is expected to be at $\sim$72.5 eV, but this is not observed due to the Al filter cut off in the XUV spectral profile above $\sim$72 eV.

To justify the assignment of these broad product absorption features, we first consider the possible photodissociation products containing a Br atom. As will be discussed in detail in Sec. IV C, the major photodissociation channel in this study leads to cleavage of the C-I bond to produce I/I* and a CH$_2$Br radical following one-photon absorption at 266 nm. To a relatively minor degree, there is overlapping absorption by the B band of CH$_2$IBr at 266 nm, leading to dissociation of the C-Br bond to form Br and Br* atoms. An alternative pathway including molecular dissociation to IBr is known to be negligible at wavelengths longer than 210 nm.\(^{10}\) Dissociation to form HI + CHBr and HBr + CHI have been ruled out by other studies at all UV wavelengths investigated.\(^{10}\) Therefore, the possible photodissociation products containing Br in this study are Br, Br*, and CH$_2$Br. Atomic Br and Br* do not have resonances at 68.5 eV, 69.5 eV, or 71.5 eV.\(^{31}\) These features in the product absorption spectrum are thus at first assigned to the CH$_2$Br radical, and the rationalization of their assignments to specific 3d(Br) core-to-valence transitions is further made by considering the energetics of the peaks in the context of the radical’s frontier electronic structure.

Electronic structure calculations in conjunction with experimental data on the geometry of halomethyl radicals indicate there is $\pi$-donation by the halogen onto the radical carbon atom, forming a partial C-X $\pi$-bond.\(^{6, 7, 36, 37}\) The frontier electronic structure, specifically of the CH$_2$Br halomethyl radical, is depicted in a molecular orbital picture in Fig. 3.8. The lowest unoccupied molecular orbital (LUMO) is the antibonding $\sigma$*(C-Br) orbital. The SOMO takes on the character of a $\pi$* orbital formed by the 2p$_y$ of C and 4p$_y$ of Br, with a majority of the contribution by the C atom.\(^{38}\) The highest fully-occupied molecular orbital (HFOMO) is a lone-pair orbital formed by the 4p$_x$ of Br. The HFOMO-1 is a $\pi$-bonding
orbital formed by 2p_y of C and 4p_y of Br, with most of the contribution from the Br atom. The HFOMO-2 is the σ-bonding orbital between C and Br.

Fig. 3.8 Molecular orbital picture for the ground state of the CH_2Br radical. The LUMO is the antibonding σ*(C-Br) orbital. The SOMO takes on the character of a π* orbital formed by the 2p_y of C and 4p_y of Br. The highest fully-occupied molecular orbital (HFOMO) is a lone-pair orbital formed by the 4p_z of Br. The HFOMO-1 is a π-bonding orbital formed by 2p_y of C and 4p_y of Br. The HFOMO-2 is the σ-bonding orbital between C and Br.

In order to assign the overlapping absorption feature at 71.5 eV and rationalize its position in energy, the geometry of the radical is taken into consideration. Due to the partial C-Br π bond formed as indicated by the electronic structure depicted in Fig. 3.8, the C-Br bond in the CH_2Br radical is shorter compared to closed-shell analogs, such as CH_3Br and CH_2IBr.\(^7,8,39\) The shortened C-Br bond relative to the CH_2IBr parent molecule leads to a
destabilization of the antibonding $\sigma^*(C{-}Br)$ orbital of the radical (energetically higher orbital) compared to the $\sigma^*(C{-}Br)$ orbital of the parent molecule. NEXAFS studies on the R-dependence of $\sigma^*$ resonances in a variety of different molecules have shown that, as a particular bond is contracted, the characteristic core-to-$\sigma^*$ resonance shifts to higher energies.\textsuperscript{19} From this argument, one expects that transitions from the 3d(Br) core orbital into the $\sigma^*(C{-}Br)$ LUMO orbital of the CH$_2$Br radical would shift to higher energies relative to the analogous transitions in the parent molecule. NEXAFS studies on the R-dependence of $\sigma^*$ resonances in a variety of different molecules have shown that, as a particular bond is contracted, the characteristic core-to-$\sigma^*$ resonance shifts to higher energies.

In the present experiments, core-to-valence transitions observed in XUV absorption can directly probe the local electronic structure of the reporter atom due to the proximity of the available valence orbitals and the core electrons. The observation of 3d(Br)$\rightarrow\sigma^*$ transitions (i.e. a significant transition dipole moment) in this region of Br core-level absorption at 68.5 eV and 69.5 eV suggests there is appreciable contribution to the radical SOMO by the Br atom. Due to the atomic-site specificity of core-orbitals, core-to-valence transitions involving unoccupied orbitals that do not have density on the reporter atom being probed are not observed.\textsuperscript{24,40} In the CH$_2$Br radical, the SOMO is a $\pi^*$ orbital with character on both Br and C atoms due to $\pi$-donation by Br onto the carbon. The destabilization of the $\pi^*$ orbital is related to the strength of the $\pi$-donation by the Br atom. Any shifting in the $\pi^*$ orbital energy would be accompanied by a predictable shift in the 3d(Br)$\rightarrow\pi^*$ resonances. Future studies can replace the hydrogen atoms with electron donating or withdrawing substituents to study the effect of these groups on the energetics of the 3d(Br)$\rightarrow\pi^*$ resonances. This method has potential to illuminate the correlation between the SOMO energy and the reactivity of these halomethyl radicals in combustion-relevant reactions.

### 3.4.2 Element-specific photodissociation dynamics

The extremely broad bandwidth and atomic-site specificity of the XUV probe allows for simultaneous observation of C-I and C-Br dissociation channels in real-time. The time-traces of the ground-state I atom and Br atom signals reveal that, at 266 nm photoexcitation, dissociation along the C-I coordinate proceeds in approximately 45 fs while dissociation along the C-Br coordinate occurs in approximately 114 fs. Firstly, the distinctly different timescales of C-I and C-Br dissociation channels in this experiment indicate that the bond breaking pathways correlate with separate electronic excited states accessible by the 266 nm photon. C-I dissociation occurs via excitation of n(I)$\rightarrow\sigma^*(C{-}I)$ transitions in the A band of CH$_2$IBr while C-Br dissociation occurs via overlapping excitation of n(Br)$\rightarrow\sigma^*(C{-}Br)$ transitions in the red wing of the B band. In order to
rationalize the difference in dissociation times along the different reaction coordinates, two effects are discussed.

The first is the acceleration of the recoiling fragments on different excited states with different repulsive slopes in the corresponding Frank-Condon regions. A 266 nm photon, for example, excites very near the peak of the A band \((n(I)\rightarrow\sigma^*(C-I)\) transitions), but accesses only the red wing of the B band \((n(\text{Br})\rightarrow\sigma^*(C-\text{Br})\) transitions), closer to the asymptotic region of the repulsive potentials. In a groundbreaking study by Zewail et al. on the photodissociation of ICN,\textsuperscript{41} the authors have shown that excitation onto the repulsive state using higher photon energies to access steeper parts of the potential results in a reduced dissociation time. In the case of \(\text{CH}_2\text{IBr}\) with 266 nm excitation, it is possible that the potential surface leading to C-I dissociation is steeper in the Frank-Condon region than the potential surface leading to C-Br dissociation in the red wing of the B band. However, without accurate potential energy curves for each excited state leading to the different I and Br atomic species, it is uncertain whether or not the potential at the maximum of the A band absorption is actually steeper than the potential in the red wing of the B band absorption. The direct observation here of slower C-Br dissociation compared to C-I dissociation following 266 nm excitation of \(\text{CH}_2\text{IBr}\) suggests that this is the case.

Another effect that can potentially lead to an observed difference in C-I and C-Br dissociation times is the vibrational/rotational energy deposited into the molecular fragments in each channel. For example, photofragment translational energy studies reveal that during dissociation of the C-I bond to form either I or I* at 248 nm excitation, approximately 65% and 64% of the available energy is deposited as internal energy into the \(\text{CH}_2\text{Br}\) radical, respectively.\textsuperscript{10} On the other hand, dissociation of the C-Br bond at this wavelength results in approximately 74% of the available energy being deposited as internal energy of the \(\text{CH}_2\text{I}\) radical. Under the “semi-rigid radical” interpretation of both \(\text{CH}_2\text{Br}\) and \(\text{CH}_2\text{I},\textsuperscript{42} the difference in the percentage of available energy that is deposited as internal energy is caused by the different mass combinations in each radical. In this sense, the \(\text{CH}_2\text{I}\) is the “softer” of the two radicals, which allows for a larger percentage of the available energy to be converted into internal energy of the fragment. The distribution of energy between translational energy and internal energy of the fragments can affect photodissociation times, with the slower being the pathways leading to greater internal excitation of the fragments.\textsuperscript{43}

The difference in the dissociation times measured here for C-I and C-Br bond-breaking at 266 nm photoexcitation can likely be attributed to a combination of the two effects in the previous paragraphs. Accurate potential energy curves of each excited state involved in the photodissociation of C-I and C-Br bonds would help to determine the possible contribution of different instantaneous slopes of the potentials leading to each dissociation channel.

\subsection*{3.4.3 Multichannel dissociation branching ratio}

The observation of both atomic Br and I resonances in the transient absorption spectra reveal the multichannel photodissociation process in \(\text{CH}_2\text{IBr}\) following 266 nm excitation. One photon at 266 nm (107 kcal/mol) or at 248 nm (115 kcal/mol), used in previous studies, has insufficient energy to break both the C-I and C-Br bonds; this would require approximately 118 kcal/mole.\textsuperscript{35} Photoexcitation at 266 nm can therefore only lead to
dissociation of either the C-I bond or the C-Br bond, but not both. Power dependence studies, shown in Fig. 3.6, taking the integrated absorbance intensities of I and Br resonances at several powers and fixed sample gas pressure, confirm that one-photon excitation leads to formation of both I and Br atomic species. The dissociation of either C-I or C-Br bonds results from overlapping excitation of either the A-band or the B-band and the branching ratio is wavelength dependent. At 248 nm used in previous studies, the authors found that the lower limit ratio of C-I:C:Br bond fission is 1.2:1.

In order to estimate the ratio of C-I:C-Br bond fission following 266 nm photoexcitation in the present experiments, the relative integrated absorbance intensities of the I atom and Br atom resonances in the ∆OD spectra are compared. The density of each atomic species is proportional to the integrated absorbance of each corresponding resonance, however, a one-to-one comparison can only be made if the relative XUV absorption cross sections of these atomic species are known. To estimate this, we performed a separate experiment on the 266 nm photodissociation of IBr. In the case of IBr dissociation, the only possible products are I/I* and Br/Br* via the following pathways:

\[
\begin{align*}
\text{IBr} \rightarrow & \quad \text{I} + \text{Br} \quad \text{(1a)} \\
& \quad \text{I}^* + \text{Br} \quad \text{(1b)} \\
& \quad \text{I} + \text{Br}^* \quad \text{(1c)} \\
& \quad \text{I}^* + \text{Br}^* \quad \text{(1d)}
\end{align*}
\]

Previous state-selective ion time-of-flight experiments extracted the branching ratios of these four pathways and the total I/I* and Br/Br* branching ratios have been determined.\(^{44}\) In our experiments, 266 nm photodissociation of IBr is probed by XUV transient absorption and the individual I, I*, Br, and Br* XUV absorption peaks are integrated at a fixed time delay at which the dissociation process is complete. Assuming there are no overlapping or interfering peaks at the energies of the I, I*, Br, and Br* resonances, the relative integrated intensities can be compared with the published spin-orbit branching ratios. In this way, we can estimate the relative I:Br (\(^2\)P\(_{3/2} \rightarrow \)\(^2\)D\(_{5/2}\)) and I*:Br* (\(^2\)P\(_{1/2} \rightarrow \)\(^2\)D\(_{3/2}\)) integrated XUV absorption cross section ratios. The I:Br (\(^2\)P\(_{3/2} \rightarrow \)\(^2\)D\(_{5/2}\)) ratio is 0.6±0.2 and the I*:Br* (\(^2\)P\(_{1/2} \rightarrow \)\(^2\)D\(_{3/2}\)) ratio is found to be 0.8±0.3.

With this information, the integrated intensities of the individual atomic resonances following photodissociation of CH\(_2\)IBr are used to determine the ratio of C-I:C-Br bond fission at 266 nm photoexcitation, which is 4.8±1.2. The ratio of 4.8±1.2 for C-I:C-Br bond fission indicates that at this wavelength, 78-86% of photoexcited CH\(_2\)IBr molecules undergo C-I dissociation.

### 3.5 Concluding remarks

The multidimensional photodissociation of a bichromophoric molecule, CH\(_2\)IBr, following 266 nm excitation has been investigated with atomic-site specificity using femtosecond time-resolved XUV transient absorption spectroscopy. Dissociation of either the C-I or C-Br bonds has been observed through the XUV spectral observation of atomic I and Br resonances. The major C-I dissociation channel is accompanied by formation of the CH\(_2\)Br radical. This has led to the first observation of core-to-valence absorption by a short-lived halomethyl radical. Product absorption features observed at 68.5 eV, 69.5 eV,
and ~71.5 eV are assigned to $3d(\text{Br}) \rightarrow \pi^*$, $3d_{5/2}^{-1}$, $3d(\text{Br}) \rightarrow \pi^*$, $3d_{3/2}^{-1}$, and $3d(\text{Br}) \rightarrow \sigma^*$, $3d_{5/2}^{-1}$ transitions of CH$_2$Br, respectively. There is approximately a 3 eV difference in energy between $3d(\text{Br}) \rightarrow $SOMO states and $3d(\text{Br}) \rightarrow $LUMO states. The observation of the $3d(\text{Br}) \rightarrow $SOMO resonances of the CH$_2$Br radical indicates there is appreciable contribution to the radical SOMO by the Br atom. This provides direct support for the existence of a partial C-Br π-bond formed through π-donation by the halogen in this particular halomethyl radical. Future studies can replace the hydrogen atoms with electron donating or withdrawing substituents to study the effect of these groups on the energetics of the SOMO. This method has potential to illuminate the correlation between the SOMO energy and the reactivity of these halomethyl radicals in combustion-relevant reactions.

The broad bandwidth and atomic-site specificity of the XUV probe allows for simultaneous observation of C-I and C-Br dissociation channels in real-time. From the integrated intensities and relative cross sections of these atomic features, assuming there are no interfering peaks, we have estimated that 78–86% of photoexcited parent molecules dissociate along the C-I coordinate. The minor C-Br dissociation channel is attributed to excitation of overlapping n(Br)→σ*(C-Br) transitions in the red wing of the B band. Kinetic studies have been carried out in order to track, simultaneously, the rise of I and Br atomic species. The measured rise times of I, I*, and Br atomic species are 48 ± 12 fs, 44 ± 4 fs, and 114 ± 17 fs. The slower C-Br dissociation has been rationalized in terms of the difference between the repulsive slopes of the excited states accessed by the 266 nm photon and the relative internal energy deposited into the CH$_2$I radical during C-Br dissociation compared to the CH$_2$Br radical from C-I dissociation. The results are in agreement with previous studies that have shown the “steepness” of the repulsive excited state accessed in the Frank-Condon region and the distribution of energy between translational energy and internal energy of the fragments can largely affect the dissociation times.  

The results are in agreement with previous studies that have shown the “steepness” of the repulsive excited state accessed in the Frank-Condon region and the distribution of energy between translational energy and internal energy of the fragments can largely affect the dissociation times. It is likely that both effects lead to the total difference in the measured dissociation times in this work.

### 3.6 Bibliography


Chapter 4

Direct Observation of the transition state region in the photodissociation reactions of methyl iodide and allyl iodide


4.1 Introduction

Through the fingerprint of core-to-valence transitions, XUV/x-ray absorption spectroscopy is an exceptionally powerful method for probing the electronic structure of molecules. While steady state XUV and X-ray absorption measurements provide remarkable sensitivity to the oxidation states, spin-states, chemical environment, and electronic structure of long-lived reactants and products, a key to understanding chemical reaction dynamics is in the characterization of the transition state region, between the thermodynamic minima of reactants and products. With the development of methods for generating ultrashort x-ray pulses using high-harmonic generation (HHG), X-ray slicing, and Free Electron Lasers (FELs), the uniquely powerful capabilities of core-to-valence spectroscopies are now being applied in the ultrafast time-domain to study short-lived states and species, and even to gain unprecedented access to the electronic structure of transition states of chemical reactions. While other spectroscopic methods have enabled the detection and temporal tracing of transition states in the recent past, the frontier of femtosecond x-ray techniques is now aiming to exploit its particular advantages to reveal detailed, atom-specific chemical information regarding the bonding and valence electronic structure in the transition state region. In the work presented in this chapter, we apply femtosecond XUV transient absorption spectroscopy based on a HHG source to directly observe the evolving valence electronic structure in the transition state regions of two fundamental photoinduced bond-breaking reactions, namely the UV photodissociation of methyl iodide and allyl iodide.

The photodissociation of halogenated hydrocarbons constitutes a class of benchmark reactions in chemistry and has been the subject of an unprecedented number of studies. Electronic excitation of alkyl iodides is known to consist of multiple bands, the lowest energy of which is a continuum in the 220-300 nm range, referred to as the A-band. Accessed via a $n$(5p, I)$\rightarrow$$\sigma^*$(C-I) excitation, the A-band absorption spans five
electronic states which arise from spin-orbit interactions and has been studied extensively.\textsuperscript{24} In the electric dipole approximation, transitions to only three of these states are allowed: a strong parallel transition to the $^3Q_0$ state and two weak perpendicular transitions to the $^3Q_1$ and $^1Q_1$ states. In the asymptotic limit, the former correlates with the spin-orbit excited $^2P_{1/2}$ state of atomic I while the latter two correlate with the $^2P_{3/2}$ state, hereafter denoted as I* and I, respectively. A-band decomposition reveals that 266 nm absorption in both methyl and allyl iodide is characterized essentially entirely by the $^3Q_0$ state, correlating to the spin-orbit excited $^2P_{1/2}$ state of atomic I, or I*.\textsuperscript{24} There is a conical intersection near the Franck-Condon window for absorption, allowing crossing onto the $^1Q_1$ surface, which is correlated to the ground state I atom ($^2P_{3/2}$).\textsuperscript{32} An important feature of halogenated hydrocarbon photodissociation reactions involving multiple excited state surfaces is the branching ratio of the product fragments, which in this case are the I and I* products.\textsuperscript{33,34} The branching ratios for the 266 nm photodissociation of methyl and allyl iodide, defined as $I^*/(I+I^*)$, have been previously measured to be 0.83 ± 0.08 and 0.90 ± 0.10, respectively. Femtosecond clocking measurements that probe the rise of the final atomic products have determined methyl iodide dissociation times for the I and I* channels of 84±12 fs and 94±6 fs, respectively. Due to the larger mass of the allyl fragment, the dissociation timescales of allyl iodide are expected to be slightly longer. In fact, recent femtosecond clocking measurements on linear chain alkyl iodide molecules have shown the dissociation time increases linearly with the mass of the alkyl fragment.\textsuperscript{35} Although the photodissociation of allyl iodide has not been measured, the photodissociation time of n-propyl iodide, which has an alkyl fragment of nearly identical mass to that of allyl iodide, has been measured to be ~160 fs. In the experiments presented here, we utilize 4d(I) core-to-valence transitions in both methyl and allyl iodide to follow the dissociation process through the $^3Q_0$ and $^1Q_1$ transition state regions and to the final I and I* atomic products.

4.2 Experimental methods

The UV-pump, XUV-probe transient absorption experimental apparatus is presented in Fig. 4.1. The gas-phase methyl iodide and allyl iodide molecules are photoexcited into the A band by one-photon absorption at 266 nm (5-10 µJ, sub-70 fs pulses). The pump pulse energies are chosen to eliminate saturation and/or multiphoton excitation effects. A linear dependence of the absorption signal on the 266 nm pulse energies used in these experiments was confirmed. The total instrument response function (time-resolution) is measured to be 70 ± 5 fs using the in-situ XUV-UV cross-correlation experiment described in Chapter 1. The sample gas cell is continuously flowing with a pressure of ~5-10 Torr (0.67-1.3 kPa) of either methyl or allyl iodide. In the probe arm, broadband (35-60 eV) XUV pulses are produced via high harmonic generation (HHG) in a semi-infinite gas cell filled with 50 Torr of Argon gas. The HHG process is driven by two-color 800 nm (1.6 mJ) + 400 nm (25 µJ), 35 fs pulses, which produces both odd and even harmonics of the fundamental 800 nm driving laser, providing continuous spectral coverage by the probe. The residual 800 nm and 400 nm beams are blocked by two 0.6 µm thick Al filters. The resulting XUV beam is focused to a beam diameter of 40 µm in the gas cell, where it overlaps the 266 nm pump beam at a 1º crossing angle. For static absorption measurements, the pump beam is blocked completely before the sample chamber and the XUV spectrum recorded with the sample gas flowing is referenced to
another spectrum taken in the absence of the sample gas in order to obtain the absorption spectrum \( OD = -\log \left( \frac{I_{\text{gas}}}{I_{\text{no gas}}} \right) \). All spectral regions are collected at once due to the broadband XUV continuum (35-60 eV).

For transient absorption experiments, the XUV differential absorption signal, \( \Delta OD \), is obtained by measuring the XUV signal in the presence of the pump pulse (\( I_{\text{on}} \)) at a given pump-probe time delay relative to the XUV signal in the absence of the pump pulse (\( I_{\text{off}} \)): \( \Delta OD = -\log \left( \frac{I_{\text{on}}}{I_{\text{off}}} \right) \). This is identical to subtracting the static absorbance spectrum taken with the pump beam blocked (\( OD_{\text{off}} \)) from the absorbance spectrum taken in the presence of the pump beam (\( OD_{\text{on}} \)) to obtain the change in absorbance (\( \Delta OD \)). Note that an electronic linear delay stage in the pump arm controls the relative delay between the arrival of pump and probe pulses with ~1 fs accuracy. At a specific time delay, the “\( I_{\text{on}} \)” spectrum is recorded and referenced to an “\( I_{\text{off}} \)” spectrum by utilizing an electronic shutter to block the pump beam before the delay stage moves to the next time delay. Several \( \Delta OD \) spectra at each time delay are averaged by moving the stage through the progression of time delays multiple times and collecting both “\( I_{\text{on}} \)” and “\( I_{\text{off}} \)” spectra at each iteration. This procedure allows to correct for any long-term fluctuations in the XUV flux. For a time scan, the differential absorption spectrum is recorded in 20 fs steps, averaging 32 scans. For every time step, the “\( I_{\text{on}} \)” spectrum is again referenced to a “\( I_{\text{off}} \)” spectrum by utilizing the electronic shutter and \( \Delta OD \) is calculated. Each time step is recorded with an integration time of 0.2 s, corresponding to 200 laser pulses. A full time scan is completed in ~1 hour.

4.3 Results and discussion – methyl iodide
The probing scheme is qualitatively presented in Figure 4.2a from the perspective of the potential energy curves along the C-I reaction coordinate of methyl iodide and in Figure 4.2b-e from the molecular orbital perspective, showing the relevant orbitals. Transient core-to-valence resonances of the dissociating molecule are observed for the first time, which represent the evolution of the valence electronic structure from the transition state region to the products. The observations can be understood in terms of a simple one-
electron transition picture, wherein the 4d core electrons are promoted to fill the “optical hole” in the n(1) valence orbital following 266 nm excitation.

The ground-state electronic configuration of methyl iodide in C$_{3v}$ symmetry is \((4d)^{10}(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2 (2e)^4(4a_1)^0\). The relevant orbitals in bold include the 4d(I) core orbitals, the 2e nonbonding orbitals on the iodine atom, which represent the highest occupied molecular orbital (HOMO), and the 4a$_1$ orbital, which is the \(\sigma^*(C-I)\) lowest unoccupied molecular orbital (LUMO). In Figure 4.3, the static, ground state XUV absorption spectrum of methyl iodide is shown, and the result is an excellent match to the spectrum previously obtained using a synchrotron source.$^{36}$ The resonant pre-edge transitions are labelled A-F and overlap with an underlying, non-resonant absorption due to...

![Fig. 4.3](image_url) The static “pump off” XUV absorption spectrum of methyl iodide is plotted near the I N$_{4d5/2}$ edge. Peaks and assignments match the high-resolution photoabsorption spectrum measured with a synchrotron source.$^{36}$ Pre-edge, core-to-valence resonances labeled A and B correspond to promotion of a 4d(I) core electron into the \(\sigma^*(C-I)\) orbital of the molecule. Resonances marked C-F correspond to transitions from the 4d(I) core orbital into the labeled Rydberg orbitals, which converge on the spin-orbit split (I 4d$_{5/2}$)$^{1-1}$ and (I 4d$_{3/2}$)$^{1-1}$ ionization limits.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Photon Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50.6</td>
<td>4d(I) (\rightarrow \sigma^*(C-I), (4d_{5/2})^{1-1})</td>
</tr>
<tr>
<td>B</td>
<td>52.3</td>
<td>4d(I) (\rightarrow \sigma^*(C-I), (4d_{3/2})^{1-1})</td>
</tr>
<tr>
<td>C</td>
<td>54.3</td>
<td>4d(I) (\rightarrow 6pe (4d_{5/2})^{1-1})</td>
</tr>
<tr>
<td>D</td>
<td>54.8</td>
<td>4d(I) (\rightarrow 6pa_{1} (4d_{5/2})^{1-1})</td>
</tr>
<tr>
<td>E</td>
<td>56.0</td>
<td>4d(I) (\rightarrow 6pe (4d_{3/2})^{1-1})</td>
</tr>
<tr>
<td>F</td>
<td>56.5</td>
<td>4d(I) (\rightarrow 6pa_{1} (4d_{3/2})^{1-1})</td>
</tr>
</tbody>
</table>
to valence and core-level ionization. The assignments of the resonances are shown in Table 1.\textsuperscript{36} A spin-orbit doublet is observed for each final state electron configuration, characterized by the \(\sim 1.7 \text{ eV}\) spin-orbit splitting of the \((4d_{5/2})^{-1}\) and \((4d_{3/2})^{-1}\) states with an \(I(4d)\) core-hole.\textsuperscript{36–38} The most prominent doublet, with resonances at 50.6 eV and 52.3 eV corresponds to promotion of a 4d(I) core electron to the \(\sigma^*\) (C-I) molecular orbital, resulting in a core-excited final state with an electron configuration of \(\cdots(4d)^9(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2(2e)^4(4a_1)^1\) as depicted in Figure 4.2b.

The 266 nm excitation in the A band of methyl iodide leads to direct dissociation of the C-I bond, forming a methyl radical and an \(I^2P_{3/2}\) or \(I^*2P_{1/2}\) atom. Figure 4.4 shows a representative dataset (out of >50 datasets) of the differential absorption in the “long delay time” limit, capturing the transient absorption spectrum of the asymptotic products after photodissociation of methyl iodide. The transient absorption spectrum in Figure 4.4 is a time-averaged spectrum taken by summing the results of 28 time delays ranging from 300 fs to 1.5 ps. The sharp product absorption features at 46.2 eV, 46.9 eV, and 47.9 eV correspond to the well-known \(4d\rightarrow5p\) core-to-valence transitions of atomic I and \(I^*\) (Figure 4.2a). In order of ascending energy, these transitions are known to be \(2P_{3/2}\rightarrow2D_{5/2}\), \(2P_{1/2}\rightarrow2D_{3/2}\), and \(2P_{3/2}\rightarrow2D_{3/2}\) transitions of atomic iodine, respectively.\textsuperscript{39,40}

In order to capture the dissociating molecule in the transition state region, transient spectra at short time delays between 0 fs and 100 fs are compared to the final spectrum obtained from long delay times of the same time scan. Figure 4.5a shows a representative example (out of six datasets) of the XUV absorption spectra near the \(I/I^*\) product resonances measured during a time scan, comparing a transient spectrum captured at a time

![Image](image.png)

**Fig. 4.4** XUV Transient absorption spectrum following completed 266 nm photodissociation of methyl iodide. Open circles are the experimental absorption data points and the dashed red lines are Voigt functions fit to each peak. The solid black line is the sum of all the individual peak functions. Atomic \(4d\rightarrow5p\) product resonances of \(I/I^*\) appear between 46 eV and 48 eV.\textsuperscript{39} Inset: magnified plot between 49–58 eV. The negative amplitude peaks represent the depletion of the parent molecule static absorption. There are weak \(4d(I)\rightarrow6p,7p(I)\) product transitions of atomic iodine overlapping the molecular \(4d(I)\rightarrow6p(I)\) depletions of the parent molecule in the energy region between 55 eV and 57 eV.\textsuperscript{40}
delay of 50 fs with the final product spectrum from long time delays of the same time scan. In the spectrum at 50 fs, there are clear transient features, labelled A and B, that disappear in the final spectrum at long time delays. Transient feature A appears at ~45.6 eV as a

Fig. 4.5 (a) XUV transient absorption snapshots from a representative pump-probe timescan. The transient absorption spectra at a short delay time of 50 fs (during the photodissociation reaction) and in the long delay time limit (after dissociation is fully completed) are plotted in blue circles and black squares, respectively. Transient resonances not belonging to the asymptotic products are observed during the dissociation process at ~45.6 eV and ~47.3 eV and are labeled Transient A and Transient B, respectively. (b)-(c) The differential absorption amplitudes at transient A (45.6 eV) and transient B (47.3 eV) are plotted as a function of pump probe time delay in (b) and (c), respectively. The open circles are the experimental absorption data points and the blue lines are Gaussian fits. Gaussian fits are used as approximations to the convolution of the transient decays with the Gaussian instrument response function. The overlapping contribution from the asymptotic product absorption has been subtracted (see text).
shoulder on the low-energy side of the I atom \(^2P_{3/2} \rightarrow ^2D_{3/2}\) resonance. Transient feature B appears as a shoulder at \(~47.3\) eV, on the high-energy side of the I* \(^2P_{1/2} \rightarrow ^2D_{3/2}\) resonance, and it is the more prominent of the transients. A third weaker transient feature near 48.4 eV appears at a time delay of \(~50\) fs in some datasets, but not in others (including the representative dataset plotted in Figure 4.5a). Six datasets have been taken and every dataset reveals transient features A and B, but only two datasets reveal the third transient at \(~48.4\) eV. This third transient is apparently at the edge of the detection limit and is therefore not included in the present analysis of methyl iodide, but it will be addressed in the following section on allyl iodide, where it is more prominent.

In Figure 4.5b-c, the temporal behaviors of the transient features A and B at short time delays are shown as lineouts of the differential absorption amplitude at 45.6 eV and 47.3 eV as a function of time. Since transients A and B are slightly overlapping the final product absorption, the transient absorption signals at these energies do not decay completely to zero, but rather decay to an asymptote corresponding to the small absorption amplitude in the final product spectrum (see Figs. 4.6 and 4.7). In order to decouple the effect of a rising product absorption that underlies the pure transient population, a scaled reference spectrum representing the final product absorption at long time delays has been subtracted at each time delay. The scaling is performed by normalizing the pure I* atomic absorption rise at the resonance center to the asymptotic amplitude at the transient resonance energy as seen in Fig. 4.6. The scaled atomic iodine product rise is then subtracted from the transient lineout at 47.3 eV. In this way, the background contribution from the rise of the pure I* atomic resonance to the absorption amplitude at transient B is subtracted. The same procedure is performed for transient feature A at \(~45.6\) eV, subtracting the background from the low energy wing of the I atom \(^2P_{3/2} \rightarrow ^2D_{5/2}\) resonance (Fig. 4.7). The final background-subtracted lineouts of a representative dataset (out of six) are plotted in Figure 4.5b and 4.5c. The transient features A and B rise within the temporal resolution of the experiment, peaking at \(~40\) fs, at which point they decay back to zero amplitude by \(~90-100\) fs.

The results can be interpreted based on the well-known photodissociation mechanism in the A band of methyl iodide. Immediately following the 266 nm \(n(1) \rightarrow \sigma^*(C-I)\) valence excitation to the \(^3Q_0\) state, \(4d \rightarrow n(I)\) XUV transitions from the 4d core orbital of I to the \(n(I)\) non-bonding orbital become available in the \(^3Q_0\) transition state region (Figure 4.2a and 4.2d). On a \(~20\) fs timescale, \(^32\) a part of the wavepacket crosses onto the \(^1Q_1\) surface via the conical intersection near the Frank-Condon window and XUV \(4d \rightarrow n(I)\) transitions also become available from the \(^1Q_1\) transition state region. The XUV \(4d \rightarrow n(I)\) transitions are expected to be similar in energy to the XUV \(4d \rightarrow 5p\) atomic iodine transitions due to the 5p\(\pi\) character of the \(n(I)\) nonbonding orbital, but may be shifted due to the interaction with the methyl fragment. As seen in Figure 4.5a, the transient features are close in energy to the pure atomic \(4d \rightarrow 5p\) resonances. The core-excited final states resulting from XUV \(4d(I) \rightarrow n(I)\) transitions have an electron configuration of \(\ldots (4d)^0 (1a_1)^2 (2a_1)^2 (1e)^4 (3a_1)^2 (2e)^4 (4a_i)\) \(^1\) (Figure 4.2d), which is identical to the core-excited final states accessed via XUV \(4d(I) \rightarrow \sigma^*(C-I)\) transitions from the ground state (Figure 4.2b). There are two final states available, separated in energy by the characteristic spin-orbit splitting of the 4d core-hole, labelled in Figure 4.2a as \((4d_{3/2})^1 \sigma^*\) and \((4d_{3/2})^1 \sigma^*\).
To rationalize the relative energetic positions of the transient features compared with the atomic resonances to which they converge, we consider a simplified one-electron transition picture. From this picture, we can postulate that the XUV 4d\(\rightarrow\)n(I) transitions should appear at energies corresponding to the difference between the 4d(I)\(\rightarrow\)\(\sigma^*\)(C-I) transitions and the n(I)\(\rightarrow\)\(\sigma^*\)(C-I) transitions, or in other words, the difference in energy between the valence excited states, \(3^3Q_0\) and \(1^1Q_1\), and the core-excited states, \((4d_{5/2})^1\sigma^*\) and \((4d_{3/2})^1\sigma^*\). Although the potential energy surfaces of the core-excited states are not known along the dissociating C-I reaction coordinate, the energies are known at the ground-state equilibrium C-I bond length and in the asymptotic regions from the static XUV absorption spectra of CH\(_3\)I and atomic I/I*, respectively. Taking this as a starting point, the \(n(I)\rightarrow\sigma^*\)(C-I) transition to the \(3^3Q_0\) state is 4.7 eV above the ground state, while the \((4d_{5/2})^1\sigma^*\) and \((4d_{3/2})^1\sigma^*\) core-excited states are found from the static absorption measurement to be 50.6 eV and 52.3 eV above the ground state, respectively (Peaks A and B in Figure 4.3). Therefore, we can expect transition energies of 45.9 eV and 47.6 eV for the \(3^3Q_0\rightarrow(4d_{5/2})^1\sigma^*\) and \(3^3Q_0\rightarrow(4d_{3/2})^1\sigma^*\) resonances, respectively, at the equilibrium bond length. In the asymptotic region, the \(3^3Q_0\) state correlates with the \(2^2P_{1/2}\) state of atomic iodine and the upper core-excited states become \(2^2D_{5/2}\) and \(2^2D_{3/2}\). The energy differences between the \(2^2P_{1/2}\) state and the two atomic core-excited states are 46.9 eV and 45.2 eV, respectively. Although the \(2^2P_{1/2}\rightarrow2^2D_{5/2}\) transition in the asymptotic region is forbidden by the dipole selection rule, the energy difference between these two states puts a lower limit on the \(3^3Q_0\rightarrow(4d_{5/2})^1\sigma^*\) resonance in the transition state region. From the energetic considerations above, one can predict two possible resonances from the \(3^3Q_0\) transition state region; the \(3^3Q_0\rightarrow(4d_{5/2})^1\sigma^*\) transition between 45.9 eV and 45.2 eV and the \(3^3Q_0\rightarrow(4d_{3/2})^1\sigma^*\) transition between 47.6 eV and 46.9 eV. These predicted resonance energies agree well with the observed energies of the observed transients A and B at \(\sim 45.6\) eV and \(\sim 47.3\) eV.

The same procedure can be performed for the \(1^1Q_1\) transition state region, subtracting the energy of 5.2 eV\(^2\) for the \(1^1Q_1\) state at the equilibrium bond length from the 50.6 eV and 52.3 eV energies of the \((4d_{5/2})^1\sigma^*\) and \((4d_{3/2})^1\sigma^*\) states and comparing to the final product resonance energies of 46.2 eV (47.9 eV) for the \(2^2P_{3/2}\rightarrow2^2D_{5/2}\) \((2^2P_{3/2}\rightarrow2^2D_{3/2}\) transition in the asymptotic region. In this way, the \(1^1Q_1\rightarrow(4d_{5/2})^1\sigma^*\) resonance is predicted to appear in the range of 45.4 eV-46.2 eV and the \(1^1Q_1\rightarrow(4d_{3/2})^1\sigma^*\) resonance should appear between 47.1 eV and 47.9 eV. Again, these predicted resonance energies match well with the observed energies of transients A and B at \(\sim 45.6\) eV and \(\sim 47.3\) eV. Apparently, both transients A and B could arise from absorption in either or both of the \(3^3Q_0\) and \(1^1Q_1\) transition state regions. In the present study, transients A and B appear with similar intensities in both parallel and perpendicular pump-probe polarization configurations. Based on energetics, transient A is assigned to transitions into the \((4d_{5/2})^1\sigma^*\) core-excited state and transient B assigned to transitions into the \((4d_{3/2})^1\sigma^*\) core-excited state, but the assignment of contributions to \(3^3Q_0\) and \(1^1Q_1\) is not yet determined. Although further calculations and experiments are needed to determine the relative contribution of each transition to the observed transient spectrum, the simple and intuitive one-electron transition picture already provides predictive power for the experimental observations without detailed calculations of the accessible states. In another recent publication on the 266 nm photodissociation dynamics of methyl iodide using XUV transient absorption spectroscopy by Drescher et al,\(^{16}\) the authors successfully reproduced the qualitative observations described in this dissertation. In particular, Drescher et al
observe spectral shifting of the 4d→n(I) transitions at early time delays (sub-100 fs) through sub-eV changes in the center of gravity of the atomic I resonances, which eventually converge on the spectrum of the pure atomic resonances. The direction of the energetic shift for both I and I* resonances, as well as the approximate timescales of these shifts, agree with the results presented in this dissertation.

Previous femtosecond clocking experiments, which probe the rise of products in the asymptotic region, determined the A-band photodissociation times of methyl iodide to be 84±12 fs and 94±6 fs for I and I*, respectively. The dynamics of the transient features A and B observed in the present studies reflect the motion of the photoexcited methyl iodide molecule through the transition state region before reaching the asymptotic region. Both transient features observed here rise to a maximum at ~40 fs and decaying completely on a timescale shorter than ~90 fs, providing the lifetimes of the transition states and
connecting well to the picture of the dissociation timescales measured in the clocking experiments. Given the sub-100 fs timescale of the entire bond-breaking process, the transients still shift too fast to capture a continuous energetic shift via the spectrum, which would allow one to map more detail about the core-excited potential energy surfaces. Instead, the intensity is spread over a broader range with shifted centers of gravity relative to the pure atomic resonances, which reflects the average energy difference between valence- and core-excited states in the transition state region compared to the asymptotic region. Nevertheless, transients A and B represent a direct observation of the evolving valence electronic structure in the localized vicinity of the I atom of methyl iodide during dissociation, exemplifying the unique capabilities of time-resolved x-ray spectroscopy to reveal detailed chemical information on transition states with atomic-site specificity.

4.4 Results and discussion – allyl iodide

4.4.1 Static XUV absorption spectrum

Figure 4.8 shows the static XUV absorption spectrum of allyl iodide in the region of the I N\textsubscript{4s/5} edge. The underlying non-resonant valence and core-level ionization is subtracted.\textsuperscript{36} Four distinct peaks are observed in the spectrum, similar to those shown earlier in case of methyl iodide and CH\textsubscript{2}IBr. Again, they represent two distinct core-to-valence transitions involving the 4d core electron of I atom, one to the antibonding orbital (\(\sigma^*\)) of the C-I bond and the other to the high-lying 6p Rydberg state of I. Each transition is further composed of a doublet due to the \(d_{5/2,3/2}\) spin-orbit splitting (1.7 eV) of the core holes. Gaussian functions with a variable width are used to fit each peak in order to identify the center frequency of the transitions. The observed peak positions are 50.7 eV, 52.4 eV,

![Fig. 4.8 Static XUV absorption spectrum of allyl iodide. Hollow black circles are the experimentally measured datapoints and error bars indicate the standard deviation evaluated over all datasets. Each peak is fitted to a Gaussian function shown as solid gray lines. The overall fit to all the peaks obtained by summing the individual Gaussian functions is shown by the solid red line.](image)

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54.6 eV, and 56.2 eV, similar to the core-to-valence transitions observed in CH$_3$I and CH$_3$IBr.$^{12,36}$ The spin-orbit splitting is therefore found to be 1.7 eV and 1.6 eV for the two core-to-valence excited states, $(4d)^1\sigma^*$ and $(4d)^16p$, respectively. It must be mentioned that the smaller sub-structures in the ~54 eV and ~56 eV peaks of CH$_3$I representing the 4d→6p(e) and 4d→6p($a_1$) transitions could not be resolved in the case of allyl iodide. Also, as a single Gaussian function does not capture the shape of the 4d→6p resonances exactly because of the unresolved sub-structure, slight differences (0.1 eV in the present case) may occur in the measured spin-orbit splitting from the known value of 1.7 eV.

### 4.4.2 Transient absorption at long time delays and dissociation kinetics

Figure 4.9 shows a transient XUV absorption spectrum of allyl iodide measured between 400 fs and 1200 fs (in steps of 50 fs) after irradiation with a 266 nm pulse and averaged over all the time-points. As evident from the timescales characterizing C-I bond dissociation, the result is representative of spectra obtained in the final product region of the reaction coordinate, specifically, where the growth of the reaction products plateaus out. The power of the pump pulse was kept sufficiently low (< 5 μJ) in order to remain in the regime of single-photon excitation and avoid spurious ion peaks arising from multiphoton ionization of the molecule, based on our prior knowledge of the photochemistry of halogenated hydrocarbons and the spectroscopic positions of the ionic species therein (confirmed by power dependence studies of the corresponding peaks).$^{12}$ The negative ΔOD features in the region between 49 eV and 57 eV in Figure 4.9 arise from depleted population in the ground state of the parent molecule induced by the UV pump pulse.

![Fig. 4.9 Transient XUV absorption spectrum of allyl iodide at low pump power (< 5 μJ) measured in the long delay limit (between 400 fs and 1200 fs). Positive peaks represent the product I atom absorption (see text for assignment) while negative peaks represent the ground state depletion of the parent molecule. Each peak is fitted to a Gaussian function shown in solid gray line. The overall fit to all the peaks is shown by the solid red line. Error bars correspond to one standard deviation over all datasets.](image)
and therefore resemble an inverted version of the static XUV absorption spectrum shown in Figure 4.8. This part of the spectrum does not contain any new features due to the UV excitation and is therefore not discussed any further. Two new sharp features with positive ΔOD are apparent at 46.1 eV and 46.8 eV that correspond to the known 4d electronic transitions of I atom products of the C-I bond dissociation induced by the pump pulse. Specifically, they represent the $^2P_{3/2} \rightarrow ^2D_{5/2}$ and $^2P_{1/2} \rightarrow ^2D_{3/2}$ transitions of atomic iodine, respectively. A third peak could be identified at 47.6 eV at slightly higher pump energies (~ 8 to 10 μJ). This corresponds to the weaker $^2P_{3/2} \rightarrow ^2D_{3/2}$ transition of atomic I in the ground state and is in agreement with the transient XUV absorption spectra of CH$_2$IBr and CH$_3$I presented earlier. However, it must be noted that in the case of the transient XUV absorption spectra measured following photodissociation of CH$_2$IBr, the relative amplitude of the $^2P_{3/2} \rightarrow ^2D_{3/2}$ atomic I transition is misleadingly increased by an underlying resonance of CH$_2$IBr$^+$. The CH$_2$IBr$^+$ ions are formed in that particular experiment by a minor multiphoton ionization process that competes with single-photon absorption. While the first and third peaks correspond to I atoms produced in the ground state, the central peak corresponds to I*. The lower peak amplitude of the $^2P_{3/2} \rightarrow ^2D_{3/2}$ transition (47.6 eV) of ground state I in allyl iodide compared to CH$_3$I at comparable pump excitation powers is already indicative of the higher I*/(I+I*) branching ratio in allyl iodide (0.9 for allyl iodide versus 0.76 for CH$_3$I).  

The time-resolved transient absorption spectra are analyzed to map out the dissociation kinetics by monitoring the change in the XUV absorption maxima of the reactant and product species as a function of time (Figure 4.10). The time behaviors are

![Fig. 4.10 Kinetics traces for rise of I*(red circles), I (blue triangles), and ground state depletion of the parent molecule (black squares) obtained by plotting the change in the absorption maxima/ minima of each peak as a function of pump-probe delay. Solid lines represent fits to the time traces involving an exponential rise convolved with a Gaussian instrument response function (~70 fs). The exponential rise-times of the I* and I channels are obtained as 74 ± 4 fs and 104 ± 12 fs, respectively. The decay of the parent molecule is characterized by a time constant of 99 ± 19 fs (error bars correspond to one standard deviation).]
fitted to exponential functions convolved with a Gaussian component representing the instrument response function (~70 fs). The exponential rise-times of the I* and I channels are obtained as 74 ± 4 fs and 104 ± 12 fs, respectively, whereas the decay of the parent molecule is characterized by a time constant of 99 ± 19 fs (errors correspond to one standard deviation of measurements made over three time-scans). It is interesting to note that the rise time of the I atom product channel is slower compared to that of I* despite the more steep slope of the repulsive 1Q1 surface compared to the 3Q0. This is suggestive of a delayed onset of ground state I atoms, possibly if they are produced from a curve crossing of the 3Q0 and 1Q1 surfaces instead of a direct excitation on 1Q1.

4.4.3 Transient absorption at short time delays

Figure 4.11 shows a comparison of the transient absorption spectra acquired at high pump power (~8 μJ) at two separate pump-probe time delays, one at 70 fs (red squares) and another measured and averaged between 280 fs to 530 fs (black circles). These timescales represent spectroscopic windows into the TS region and the product region, respectively. Averaging is performed in the long time-delay limit where the product absorption reaches a plateau in order to improve the signal-to-noise ratio. On the other hand, a single time-point (70 fs) is chosen to represent the TS region where the new features attain maximum intensity, although the features are found to gradually rise and decay in the 0 fs to 180 fs timescale, as discussed later (Section 4.4.5). In the 70 fs time trace, enhanced absorptions can be clearly identified at ~45.3 eV, ~47.4 eV and ~48.4 eV, labelled as transients A, B, and C in the figure, which are absent at long time delays. Transient A appears 0.8 eV to the red side of the 2P3/2→2D5/2 (I) transition while transients B and C appear 0.6 eV and 0.9 eV to the blue side of 2P1/2→2D3/2 (I*) and 2P3/2→2D3/2 (I).

![Fig. 4.11 Comparison of transient absorption spectra of allyl iodide measured using ~8 μJ pump power at two separate pump-probe time delays of 70 fs (red squares) and between 280 to530 fs (black circles). Transient peaks are identified at 45.3 eV (A), 47.4 eV (B), and 48.4 eV (C) in the 70 fs time trace which disappear at long time delays.](image)
transitions, respectively. Interestingly, the spectroscopic positions of the transient features are similar to those identified in the photodissociation of CH$_3$I (although feature C was not always observed in CH$_3$I). This suggests that these peaks arise from similar transitions on the evolving valence-excited state surface of the molecule to the core-excited states and that the potential energy curves along the C-I reaction coordinate for the nσ* state are not affected by the type of alkyl substituent as the state is largely localized on the C-I bond. An important difference between the transient features observed in case of CH$_3$I and those seen in case of allyl iodide is that peak C is much more prominent in allyl iodide and exhibits experiment-to-experiment reproducibility. In order to confirm that the transients A, B, and C are not a result of any multiphoton absorption due to the 8 μJ pump power used in the measurements, transient absorption spectra are also recorded at lower pump power (5 μJ). All three features are detected in the low pump power scan as well although the high pump power scan reveals them with better signal-to-noise ratio due to the higher fraction of excited molecules in the pump volume, at the cost of slight saturation of the 2P$_{1/2}$→2D$_{3/2}$ (I*) peak in the XUV spectra at long time delays. As shown in Figure 4.11, there is a fair degree of overlap between the absorption peaks of transient B (~47.4 eV) and the atomic I* absorption at 46.8 eV, whereas the contributions of the atomic resonances to the transient features A and C are expected to be less as the transient peaks are energetically more separated from the atomic resonances.

### 4.4.4 Assignment of the transients

In the case of CH$_3$I, the spectroscopic positions of the observed transients (A and B) are validated using a one-electron transition picture. The energies of the 4d→n(I) transitions from the valence-excited TS region are conjectured to lie between the core electron absorption energy on the repulsive nσ* state at the ground state equilibrium bond length (i.e. the Franck-Condon region) and the atomic I/I* 4d→5p resonance energies in the asymptote (at 46.2 eV and 46.9 eV). The former was calculated as the difference between the 4d(I)→σ*(C-I) static XUV transition energies from the molecular ground state [(4d$_{5/2}$)$^{1}$σ$^{*}$ at 50.6 eV and (4d$_{5/2}$)$^{1}$σ$^{*}$ at 52.3 eV] and the n(I)→σ*(C-I) vertical excitation energy to the $^{3}$Q$_{0}$ and $^{1}$Q$_{1}$ surfaces (4.7 eV and 5.2 eV, respectively). This led to the prediction that the transients from the $^{3}$Q$_{0}$ surface would lie in the energy range 45.2 eV to 45.9 eV $[^{3}$Q$_{0}$$→$(4d$_{5/2}$)$^{1}$σ$^{*}$] and 46.9 eV to 47.6 eV $[^{3}$Q$_{0}$$→$(4d$_{3/2}$)$^{1}$σ$^{*}$] whereas those from the $^{1}$Q$_{1}$ surface would lie in the energy range 45.4 eV to 46.2 eV $[^{1}$Q$_{1}$$→$(4d$_{5/2}$)$^{1}$σ$^{*}$] and 47.1 eV to 47.9 eV $[^{1}$Q$_{1}$$→$(4d$_{3/2}$)$^{1}$σ$^{*}$]. Indeed, the experimentally observed values of 45.6 eV and 47.3 eV for transients A and B were found to be in close agreement with the predictions and they were accordingly assigned to the (4d$_{5/2}$)$^{1}$σ$^{*}$ and (4d$_{3/2}$)$^{1}$σ$^{*}$ core-excited states, respectively. Note the equivalence of the electronic configurations for the final states of the 4d→n(I) XUV transitions from the TS region and the (4d)$^{1}$σ$^{*}$ states accessed via XUV absorption in the ground state. However, any direct assignment to the $^{3}$Q$_{0}$/ $^{1}$Q$_{1}$ surface was not possible in the absence of relevant reports on XUV absorption in the transition state region of related molecules. A third weak transient (C), identified at 48.4 eV, was not found to be reproducible from scan-to-scan because it was at the limit of the detection and was therefore not discussed further. However, it is quite clear from the above argument that such a transient essentially lies outside the energy range predicted for
4d→n(I) transitions (45.2 eV to 47.9 eV) from the valence-excited state and may represent a transition to a higher-lying orbital, e.g. 4d→σ* in the TS region.

In close analogy with the above example, the transients A and B in the photodissociation of allyl iodide are easily explained based on the same one-electron picture. In addition we find that to account for the origin of transient C, which is much more prominent in allyl iodide compared to methyl iodide, higher core-excited states (involving 4d→σ* transitions) must be invoked. Figure 4.12 shows a qualitative molecular orbital diagram of allyl iodide. The n(I) and σ*(C-I) orbitals represent the HOMO and the LUMO, respectively, as in other alkyl halides.41,42 The π (HOMO-I) and π* (LUMO+1) orbitals are built from C(2p) orbitals corresponding to the C2=C3 double bond and shown for the sake of completeness. The optical transition at 266 nm from the filled doubly-degenerate non-bonding n′(5pI) orbital to the vacant antibonding σ*0(C-I) orbital of allyl iodide creates partially filled n3 and σ*1 orbitals, the same as in CH3I. Therefore these are the lowest two orbitals available for a transition of a 4d core electron from the nσ* excited state surface. Although the potential energy curves in the A-band of allyl iodide are not known, the assignments are based on the premise that they are similar to methyl iodide.
along the C-I reaction coordinate. This assumption is justified by similar I/I* branching ratios and translational energy distributions observed in the I/I* channels (unimodal and bimodal for I* and I, respectively) for both molecules.\textsuperscript{34,43,44} In addition, the shape of the potential energy curves and the location of the \( ^3Q_0 \) \( ^1Q_1 \) conical intersection are found to be invariant across a series of linear/branched alkyl iodide molecules.\textsuperscript{35} In this context, given the equi-ergic valence excitation, 4d static XUV absorption, and product I atom resonances in both molecules, transients A and B in allyl iodide are assigned to \((4d_{5/2})^1\sigma^*\) and \((4d_{3/2})^1\sigma^*\) core-excited states, respectively, accessed via 4d\(\rightarrow\)n(I) transitions from the \( n\sigma^*\) state (i.e. similar to CH\(_3\)I).

Transient C, found on the higher energy side of the \( ^2P_{3/2} \) to \( ^2D_{3/2} \) I atom resonance, appears 3.1 eV higher in energy compared to transient A. The sum of the core-hole splitting of the I atom (\( ^2P_{3/2,5/2}, 0.95 \) eV) and I* (\( ^2D_{3/2,5/2}, 1.7 \) eV) spin-orbit states at the asymptote of the potential energy curve represents the maximum possible separation between transients borne out of 4d\(\rightarrow\)n(I) transitions from the \( n\sigma^*\) excited state surface. This value (~2.7 eV) does not encompass the empirical energy gap between transients A and C. The next available higher energy partially-filled orbital (\( \sigma^* \)) is therefore invoked to explain its origin. This particular core-to-valence excitation generates a state with three electrons in the n(I) orbital and two electrons in the \( \sigma^* \) orbital, i.e. with the electronic configuration \((4d)^1n^2\sigma^*\). In view of this assignment, it might then be argued that transient C should also be partnered with a spin-orbit counterpart \((4d_{3/2,5/2})\) that is \(1.7 \) eV lower or higher in energy (i.e. at \( \sim 46.7 \) eV or \( \sim 50.1 \) eV). However, these regions of the transient absorption spectrum coincide with the rising edge of the I* product absorption and the falling edge of the ground state depletion, respectively (as seen in Figure 4.9), and therefore no feature is observed in the experiment to corroborate the assignment to specific spin-orbit states. Transient C is therefore assigned to a 4d\(\rightarrow\sigma^*(\text{C-I})\) transition, leading to a \((4d)^{-1}n^3\sigma^*\) core-excited state, however, it remains unclear at present whether it corresponds to a \( d_{3/2} \) or \( d_{5/2} \) core-hole. It must be mentioned that the energies of these core-to-valence excited states are not known experimentally; however, the spectroscopic positions of the transients A, B, and C revealed in the femtosecond extreme ultraviolet transient absorption studies of methyl iodide and allyl iodide provide a benchmark for theoretical calculations on the nature of the core-excited states in alkyl iodides, especially in the TS region of the potential energy surface.

The differential absorbance of the new features observed in the transient absorption spectra of methyl iodide and allyl iodide provide the basis for a preliminary assignment of the transients observed to specific electronic states in the A-band manifold. The experimentally measured absorption intensities of transients A and B in methyl iodide (after deconvolution of the atomic absorption due to overlapping resonances) were found to be 10 mOD and 28 mOD (i.e. ratio of \( \sim 1 : 3 \)), respectively. A complete nine-dimensional potential energy surface calculation of methyl iodide provided the oscillator strengths of the n\(\rightarrow\sigma^*\) transition to the \( ^3Q_0, ^1Q_1, ^3Q_1 \) states as 0.81: 0.17: 0.02 at the ground state equilibrium geometry.\textsuperscript{45} However, the occurrence of nonadiabatic dynamics precludes the direct mapping of the measured peak intensities to computed oscillator strengths. Magnetic circular dichroism studies of CH\(_3\)I reveal that production of I atoms in the photodissociation is almost entirely due to the \( ^3Q_0 \) to \(^1Q_1 \) curve crossing (94% of the absorption strength between 260 and 262 nm is carried by the \( ^3Q_0 \) state).\textsuperscript{21} As the \( ^1Q_1 \) state contributes mostly in the red wing of the A-band absorption\textsuperscript{24} and has very low oscillator strength\textsuperscript{45}, it is omitted from the present discussion. Assuming that the oscillator strengths
for the 4d→n(I) transitions are not much different for the two valence-excited states (3Q₀ and 1Q₁), the XUV transient absorbance is expected to correlate directly with the transient population in each valence-excited state. Since the empirical intensity ratio of the transients approximates the known I*/(I+I*) branching ratio, the results are suggestive that transients A and B in CH₃I may correlate with the 1Q₁ and 3Q₀ surfaces, respectively.

The appearance of the same transients (A and B) and an additional feature (C) in the photodissociation of allyl iodide offers additional insight into the origin of these transient features. The measured peak intensities of the transient features in allyl iodide were 6 mOD (transient A), 28 mOD (transient B, post subtraction of the asymptotic product I* atom absorption, as discussed later in Section E) and 13 mOD (transient C), i.e. in the ratio ~1: 5: 2. It must be reiterated that while transients A and B were both assigned to 4d→n(I) transitions, transient C was best assigned to a 4d→σ*(C-I) transition. The oscillator strengths in the A-band of allyl iodide are assumed to be similar to methyl iodide since the non-bonding and antibonding orbitals in both molecules are localized on the I atom and C-I bond, respectively. The experimentally measured I*/I branching ratio in allyl iodide is higher (9:1 measured by Fan et al. and 8.3: 1.7 measured by Sumida et al.), suggesting that non-adiabatic dynamics is less facile. Nonetheless, due to the curve crossing, the branching ratio of the reaction products is not expected to directly follow the oscillator strengths of the different surfaces involved in the valence excitation. It must be noted that even without considering the new transient feature C, the relative peak intensities of transients A and B in allyl iodide are found to be similar to those in methyl iodide (i.e. B > A), suggestive of their origin from the same valence-excited surfaces in both molecules. The feature C is observed for the first time in this work and although it most likely connects to a (4d)⁻¹σ* core-excited state, assigning it to a specific valence-excited state is not straightforward. Origin of transient C from the 1Q₁ state would be less likely, as this state has lower population in allyl iodide (~10%) compared to methyl iodide (~25%), and feature C is more prominent in allyl iodide. Thus, it possibly originates from the 3Q₀ surface, in line with the high I*/I branching ratio (signifying high population and consequently higher probability of detection) in allyl iodide. This initial assignment could potentially be tested by characterizing the transient peak intensities in other alkyl iodides with systematically varying I*/(I+I*) branching fractions at the same excitation wavelength (0.67 in C₂H₅I, 0.6 in C₂H₇I, 0.32 in C₆H₅I, 0.27 in C₇H₇I, and 0.22 in C₁₀H₂₁I). However, it must be mentioned that more thorough assignment of the transient species as a general feature of A-band photodissociation in halogenated hydrocarbons necessitates the availability of more quantitative information on the exact oscillator strengths of both the valence-excited and core-excited states, their slopes in the TS region, as well as the adiabaticity of the valence-excited states.

4.4.5 Temporal dynamics in the transition state region

In order to elucidate the temporal characteristics of the transient features, spectral lineouts are taken at their respective absorption maxima at a number of pump-probe time delays. Such a kinetic trace is shown in Figure 4.13. The transient features are observed to appear in a characteristic time-window between 0 fs and 180 fs after the n→σ* excitation initiated by the pump pulse, peaking at about ~ 60 fs. In contrast to the product I atom fragments, which rise in after time zero and plateau out at longer delay times (Figure 4.10),
these features are clearly 'transient' on the timescale of dissociation. Two points may be noted about these transient features. First, whereas transients A and C decay almost to zero at long time delays beyond 180 fs (Figure 4.13), transient B shows a finite non-zero absorbance. This is because the latter is overlapping with the high-energy wing of the $I^*$ resonance and the product absorbance manifests as a finite non-zero absorbance in the long delay time limit after the transient has decayed, just as in the case of methyl iodide. Second, within the energy and time resolution of the experimental set-up, no discernible spectral shift is noted in the absorption maxima of the transients as a function of time, as might be expected with varying slopes of the potential energy curves along the reaction coordinate; on the contrary, the transient features only appear with increasing and decreasing amplitude as a function of time. Higher energy resolution of the XUV spectrometer and shorter pump pulses might be required to follow energy shifts in the transient energy maxima with change in pump-probe time delay. The temporal behavior of the transients is fitted to a Gaussian function in order to determine the peak positions and the peak widths, as shown in Figure 4.14. The $I^*$ absorbance is deconvolved from transient B absorbance in order to extract its lifetime, using the same method described in the previous section on methyl iodide. Such a procedure was not required for transients A and C as they are well separated from the product fragment absorption peaks. The peak maxima for transients A, B, and C are obtained as $54 \pm 8$ fs, $64 \pm 3$ fs, and $59 \pm 3$ fs, respectively, whereas the peak widths (full width at half maximum) are obtained as $140$ fs, $67$ fs, and $93$ fs, respectively. The transients are found to decay completely by 145 fs to 185 fs, providing an estimate for the C-I bond dissociation time, which is also consistent with the rise times of the $I/I^*$ peaks shown in Figure 4.10. These time constants also agree well with femtosecond clocking experiments, which monitored the product I atom rise in alkyl iodide molecules of comparable mass.35 The lifetimes of the transients and C-I bond dissociation times in allyl iodide are found to be greater compared to the case of methyl iodide (as expected) by a factor of 1.6 to 2. This

Fig. 4.13 Time traces of transients A (gray squares), B (blue circles), and C (red diamonds) obtained by plotting the change in absorption intensity at the respective resonance positions as a function of pump-probe delay.

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is reasonable to expect from a simple square root of reduced-mass (of the dissociating R and I product fragments) dependence of the reaction time.\textsuperscript{51}

4.5 Concluding remarks

In summary, femtosecond transient core-to-valence absorption spectroscopy is used to noninvasively and directly probe the transition state region of the prototypical alkyl
iodide photodissociation reactions of methyl and allyl iodide. The XUV absorption spectra of methyl and allyl iodide captured at sub-100 fs time delays (e.g. 50 fs in Figure 4.5a and 70 fs in Fig. 4.11, respectively) provides a direct observation of the transient valence electronic structure in the transition state region leading to photoinduced bond-breaking of both alkyl iodide molecules. In the case of methyl iodide, this is the shortest-lived chemical transition state ever observed by core-level, X-ray or XUV spectroscopy. An intuitive one-electron transition picture closely approximates the experimentally-determined energies of the transient resonances in both cases. In the case of allyl iodide, three distinct peaks are identified as transients A (45.3 eV), B (47.4 eV), and C (48.4 eV) in the transition state region. While the first two peaks are both borne out of 4d→n(I) transitions (similar to CH3I), the third peak is attributed to a 4d→σ*(C-I) transition. While an analogous resonance is accessible in the case of methyl iodide, the longer dissociation time associated with allyl iodide makes this weak transient feature C easier to capture with the current temporal resolution of the experiment. In future experiments, with even better temporal resolution (e.g. using compressed 266 nm pump pulses below 10 fs and isolated attosecond XUV probe pulses), it may be possible to fully map the core-excited state potential energy surface along the C-I reaction coordinate. The results presented here provide a benchmark for future experiments and calculations aimed at leveraging the powerful advantages of XUV and X-ray core-to-valence absorption spectroscopy to expand our understanding of transition states of chemical reactions.

4.6 Bibliography

(3) Stöhr, J. NEXAFS spectroscopy; Springer, 1996.


(21) Gedanken, A.; Rowe, M. D. 1975, 34, 39.

(22) Loo, R. O.; Hall, G. E.; Houston, P. L. 1989, 90, 4222.


Chapter 5

Femtosecond x-ray spectroscopy of an electrocyclic ring-opening reaction

5.1 Introduction

The light-activated electrocyclic ring-opening of the 1,3-cyclohexadiene (CHD) chromophore is responsible for the crucial step in the photobiological synthesis of Vitamin D$_3$ in the skin$^{1-3}$ and provides the key activity in numerous optoelectronic technologies including optical switching and data storage,$^{4,5}$ photochromic devices,$^{6}$ and nanomechanical motors.$^{7}$ The photoinduced isomerization of this particular chromophore has also played a critical role in the development and corroboration of the Woodward-Hoffman rules that govern the stereochemical fate of pericyclic reactions.$^{8,9}$ The general reaction scheme of photochemical pericyclic reactions is postulated to involve non-adiabatic transit through an intermediate excited state of the same symmetry as the electronic ground state, implicating a complex interplay between nuclear and electronic degrees of freedom.$^{10}$

The photoinduced ring-opening mechanism of CHD, serving as a model of this ubiquitous process, is presented schematically in Fig. 5.1A. Following ultraviolet (UV) photoexcitation to an allowed 1B excited state by a strong $\pi\rightarrow\pi^*$ transition, the photochemical ring-opening reaction is thought to proceed onto a “dark” 2A excited state through a surface crossing, or conical intersection, between the 1B and 2A states (labeled CI1) after $\sim$55 fs and, subsequently, through the so-called “pericyclic minimum” in this intermediate state.$^{11-15}$ From an electronic structure perspective, the 2A state is described by a doubly-excited electronic configuration as shown in the intermediate orbital diagram in Fig. 5.1B.$^{10,14,15}$ As the photon energy is converted into nuclear dynamics along the reaction coordinate, the $\pi-\pi^*$ splitting is expected to be reduced near the pericyclic minimum, consistent with the narrowing gap between the ground- and excited-state potential energy surfaces. In this region, a conical intersection between the 2A excited-state and 1A ground-state potential energy surfaces (CI2) provides the critical outlet for the wavepacket to undergo non-adiabatic relaxation onto the 1A transition state region. From here, the wavepacket bifurcates toward either the 1,3,5-hexatriene (HT) photoproduct or back towards ring-closed CHD. The arrival time at the initial ring-opened HT photoproduct has been previously reported to be $\sim$140 fs.$^{11,14}$ A key to understanding this photochemical mechanism, which involves rapid exchange between electronic and nuclear motion, is to directly characterize both the time-evolving molecular structure and the coupled evolution of the valence electronic structure, especially through the crucial intermediate excited state.

Extensive time-resolved spectroscopic studies have allowed temporal tracing of the excited-state dynamics,$^{11-15}$ and recent femtosecond x-ray scattering experiments have even revealed the time-evolving molecular structure directly.$^{16}$ Nevertheless, a direct characterization of the transient valence electronic structure in the intermediate excited-state region has remained elusive. Here, we employ femtosecond soft x-ray absorption spectroscopy
near the carbon K-edge in combination with spectroscopic analysis from time-dependent density functional theory (TD-DFT) calculations of the x-ray spectra to directly capture the evolution of the valence electronic structure during the photochemical ring-opening reaction in real time. In particular, the direct x-ray spectroscopic signature of the key intermediate state near the pericyclic minimum is clearly distinguished in the experiment and characterized, in conjunction with theoretical spectroscopic analysis, to reveal transient overlap and mixing of the frontier valence orbital energy levels.

In general, x-ray absorption spectroscopy is a powerful tool to explore the electronic structure of molecules with element-specificity\textsuperscript{17} and, when applied with ultrafast pump-probe
techniques, can provide detailed information regarding the time-evolving oxidation states, spin-states, and chemical environments of specific atomic sites during photoinduced processes.\textsuperscript{18–28} In the present study, a 266 nm pump pulse is used to photoexcite the CHD molecules to the 1B state by promotion of an electron from the $2\pi$ highest-occupied (HOMO) to the $1\pi^*$ lowest-unoccupied (LUMO) molecular orbital, initiating the electrocyclic ring-opening reaction. We probe the ring-opening reaction of CHD directly through the carbon atomic sites via carbon K-edge (~284 eV) transient absorption spectroscopy, capturing broadband (~160-310 eV) absorption snapshots of the reacting molecule in real time.

5.2 Experimental methods

The UV-pump, soft x-ray probe transient absorption experimental apparatus, shown schematically in Fig. 5.2, is an upgrade of an existing extreme-ultraviolet (XUV) transient absorption setup, which has been previously described.\textsuperscript{29,30} In the present work, two major changes to the previous setup have been implemented to extend the capabilities from the XUV regime into the soft x-ray regime. First, the spectrometer has been rebuilt to better detect and resolve photon energies up to ~1 keV. Specifically, a variable line spaced Hitachi grating with a nominal 1200 lines/mm (001-0660) was used at an $87^\circ$ angle of incidence to disperse the x-ray energies onto a translatable PIXIS:XO 400B x-ray camera.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig52.png}
\caption{Schematic representation of the ultraviolet pump, x-ray probe transient absorption experimental setup. The broadband x-ray probe pulses are produced by high-harmonic generation driven by 1320 nm laser pulses in a semi-infinite gas cell filled with ~630 Torr of Helium. The diverging x-ray beam is focused by a toroidal mirror (TM) into the sample target. The x-ray spectrometer consists of a concave, variable-line-spaced grating with a nominal 1200 lines/mm, which spectrally disperses the x-ray beam onto a translatable PIXIS:XO 400B x-ray camera.}
\end{figure}

Secondly, in order to generate soft x-ray pulses via HHG efficiently with photon energies up to and beyond the carbon K-edge, the fundamental 800 nm output of a Ti:Sapphire femtosecond laser source is converted to longer near-infrared wavelengths (1320 nm in the experiments presented here).

Briefly, the employed laser system (Spectra-Physics, Spitfire-ACE-PA) delivers 12 mJ pulses at 1 kHz repetition rate, 35 fs pulse duration, with a wavelength centered at 800 nm with a 45 nm full-width at half-maximum (FWHM) bandwidth. Using a 90:10 beamsplitter, the
output from the laser system is split into two arms, with the majority (90%) of the beam used for the HHG probe and the other 10% used for the generation of the 266 nm pump pulse. In the pump arm, the fundamental 800 nm beam is used to pump a home-built third-harmonic generator to generate 266 nm pulses of ~110 fs pulse duration. The 266 nm pulses produced are attenuated by an iris and focused by a lens (40 cm focal length) into a gas cell, which is continuously flowing with a pressure of ~15-20 Torr (1.9-2.7 kPa) of 1,3-cyclohexadiene (CHD). The gas-phase CHD molecules are photoexcited into the 1B state via one-photon absorption at 266 nm with ~4 μJ pulses. In the probe arm, the 800 nm beam is first used to pump a high-energy optical parametric amplifier (HE-TOPAS, Light Conversion). The TOPAS produces tunable mid-IR pulses with wavelengths between 1.2-2.6 μm. In the experiments described here, the TOPAS is tuned to generate a signal wavelength of 1.32 μm, which is separated from the idler beam using a dichroic wavelength separator. The transmitted idler beam is dumped into a beam block. The reflected 1.32 μm signal beam has a pulse energy of 2.8 mJ at 1 kHz repetition rate with a pulse duration of ~50 fs. The beam is first attenuated using an iris to a pulse energy of ~1.8 mJ before being focused by a 40 cm lens into a semi-infinite gas cell filled with 630 Torr of helium gas. The HHG process is sensitively dependent on the wavelength of the driving laser field and the precise phase matching conditions achieved in the gas cell. These conditions are tuned by adjusting the pressure, focal position, and incoming beam diameter (using the iris placed before the lens). With the present conditions, soft x-ray pulses with bandwidth ranging from ~160-310 eV are produced (Fig. 5.3). The residual IR beam after HHG is blocked by a 100 nm thick Al filter. The soft x-ray beam is transmitted and focused by a Toroidal mirror at 5° grazing
incidence into the flowing gas cell, where it overlaps the 266 nm pump beam at a 1° crossing angle.

After passing through the gas cell, the 266 nm beam is blocked between the sample chamber and the spectrometer. The soft x-ray beam is passed through a 100 nm thick Ti filter, which serves to protect the spectrometer from the sample gas and to block any scattered 266 nm light from the pump beam. Finally, the transmitted soft x-rays are spectrally dispersed by a grating onto an x-ray CCD camera, where the soft x-ray signal is measured as a function of the photon energy. For static absorption measurements, the pump beam is blocked completely before the sample chamber and the x-ray spectrum recorded with the sample gas flowing is referenced to another spectrum taken in the absence of the sample gas in order to obtain the absorption spectrum \( A = -\log \left( \frac{I_{\text{gas}}}{I_{\text{no gas}}} \right) \). All spectral regions are collected at once due to the broadband soft x-ray continuum (160-310 eV).

The energy axis calibration is established using known absorption resonances near the L\(_{2,3}\)-edge of Ar between 240-250 eV\(^{31}\) and the carbon K-edge of methyl iodide between 285-289 eV.\(^{32}\) The energy resolution of the instrument is estimated by fitting the Ar 2\(p_{3/2}\)4s resonance at 244.39 eV to a Voigt function incorporating the convolution of the natural Lorentzian profile of this resonance with a Gaussian profile representing the spectrometer resolution function (Fig. 5.4). By fixing the natural Lorentzian linewidth to the known value of 114 meV, the FWHM value (\( \Delta_G \)) of the Gaussian function that characterizes the spectrometer resolution is found to be \( \sim 350 \) meV.

Fig. 5.4 The 2\(p_{3/2}\)4s core-excited Rydberg state of Ar is fit to a Voigt profile incorporating the convolution of the natural Lorentzian profile of this resonance with a Gaussian profile representing the spectrometer resolution function. By fixing the natural Lorentzian linewidth to the known value of 114 meV, the FWHM value (\( \Delta_G \)) of the Gaussian function that characterizes the spectrometer resolution is found to be \( \sim 350 \) meV.

Lorentzian profile of this resonance with a Gaussian profile representing the spectrometer resolution function (Fig. 5.4). By fixing the natural Lorentzian linewidth to the known value of 114 meV,\(^{31}\) the FWHM value of the Gaussian function that characterizes the spectrometer resolution is found to be \( \sim 350 \) meV.

With the sample gas flowing, the x-ray differential absorption signal, \( \Delta A \), is obtained by measuring the soft x-ray signal in the presence of the pump pulse (\( I_{\text{on}} \)) at a given pump-probe time delay relative to the x-ray signal in the absence of the pump pulse (\( I_{\text{off}} \)): \( \Delta A = \)}
\(- \log \left( \frac{I_{on}}{I_{off}} \right) \). This is identical to subtracting the static absorbance spectrum taken with the pump beam blocked (\(A_{off}\)) from the absorbance spectrum taken in the presence of the pump beam (\(A_{on}\)) to obtain the change in absorbance (\(\Delta A\)). Note that \(A_{on}\) represents the absorbance of a mixture of both photoexcited and unexcited molecules, the concentration of each depends on the pump pulse parameters and absorption cross section of the sample at the pump wavelength used. At a specific time delay, the “I_{on}” spectrum is recorded and referenced to an “I_{off}” spectrum by utilizing an electronic shutter to block the pump beam before the delay stage moves to the next time delay. Several \(\Delta A\) spectra at each time delay are averaged by moving the stage through the progression of time delays multiple times and collecting both “I_{on}” and “I_{off}” spectra at each iteration. This procedure allows to correct for any long-term fluctuations in the x-ray flux. For a time scan, the differential absorption spectrum is recorded in 10-20 fs steps, averaging 32 scans. For every time step, the “I_{on}” spectrum is again referenced to a “I_{off}” spectrum by utilizing the electronic shutter and \(\Delta A\) is calculated. Each time step is recorded with an integration time of 1 s, corresponding to 1000 laser pulses. A full time scan is completed in ~1-1.5 hours.

5.2.1 Cross-correlation between UV and soft x-ray pulses

![Graph showing absorption vs. photon energy for Ar static x-ray absorbance and Ar x-ray absorbance with UV field](image)

**Fig. 5.5** Snapshot of the ponderomotive energy shift of the \(2p_{3/2}^{-1} 4s\) core-excited Rydberg state of Ar in the 266 nm field, at pump-probe temporal overlap (time-zero).

An independent in-situ cross-correlation between the UV and soft x-ray pulses is used to find time-zero and the instrument response function (IRF) of the experiment, as described in Chapter 1. Specifically, the ponderomotive energy shift of core-excited Rydberg states near the L_{2,3}-edge (~245 eV) of Ar is measured in the presence of the moderately intense 266 nm field as a function of UV-soft x-ray time delay. The soft x-ray pulse in this case acts as the pump pulse, exciting Ar to the \(2p_{3/2}^{-1} 4s\) core-excited Rydberg state at (244.4 eV), and the 266
nm pulse couples this state to the $2p_{3/2}^{-1}$ continuum (>248.2 eV), leading to a ponderomotive energy upshift of the resonance. Fig. 5.5 shows a snapshot of the ponderomotive energy shift of this resonance at pump-probe overlap (time-zero). In order to reach the appropriate 266 nm field intensities needed to observe the energy shift of the resonance with the current spectrometer resolution (~350 meV) at these x-ray energies, the iris, which is used to attenuate the 266 nm pump beam, is opened fully to allow ~17 μJ pump pulses to be focused into the sample target. Since the magnitude of the energy upshift scales linearly with the instantaneous 266 nm field intensity, the time-dependent energy upshift of the core-excited Rydberg state of Ar is exploited to directly map the femtosecond UV/soft x-ray cross correlation. The FWHM of the cross-correlation trace is measured at 120 ± 15 fs (Fig. 5.6). The obtained instrument response function is deconvolved from the time traces presented in section 5.3 to obtain the reported time constants.

![IRF = 120 ± 15 fs](image)

**Fig. 5.6** UV/soft x-ray cross correlation measuring the integrated change in absorption ($\Delta A$) over the $2p_{3/2}^{-1} 4s$ core-excited Rydberg state of Ar in the 266 nm field as a function of pump-probe time delay. The measured FWHM of the cross-correlation trace is 120±15 fs.

### 5.3 Computational Methods

C K-edge NEXAFS spectra were simulated using the restricted energy window (REW)\(^{35}\) linear-response time-dependent density functional theory (TDDFT)\(^{36,37}\) formalism as implemented in NWChem.\(^{38}\) The Tamm-Dancoff\(^{39}\) approximation is invoked within the REW-TDDFT calculations. All NEXAFS simulations employed the aug-cc-pvdz\(^{40}\) basis set in conjunction with the long-range corrected ω-Perdew-Burke-Ernzerhof (ωPBE) hybrid functional (LC-ωPBEH)\(^{41}\) with the short-range Hartree-Fock exchange and range-separation parameters given respectively by (C\(_{HF} = 0.2\)) and (ω=0.2 Bohr\(^{-1}\)). A rigid shift of 10.531 eV is applied to align the absolute energy scales of the simulated spectra and experiment. For simulating C K-edge spectra of valence-excited states of CHD we use a two-step approach whereby the maximum overlap method (MOM)\(^{42,43}\) is first employed to model a reference
valence excited state such as a HOMO→LUMO transition and the DFT eigenvectors and eigenvalues obtained from such a reference MOM calculation are then used in a REW-TDDFT calculation to obtain the corresponding NEXAFS spectrum. Molecular structures corresponding to various minima and conical intersections on the ground and first excited potential energy surfaces are taken from previous calculations by Lei et al\textsuperscript{44} that provided geometries optimized at the SA3-CASSCF(14, 8)/6-31G* level and were used as is without further optimization. NEXAFS spectra for all points on the ground state (S\textsubscript{0}) potential energy surface were calculated based on an electronic ground state reference while spectra for all geometries corresponding to points on the first excited (S\textsubscript{1}) surface were calculated on top of a valence-excited MOM reference state prepared by exciting one electron from the HOMO to the LUMO state. Wavefunction isosurface plots are generated using the VESTA-3 program.\textsuperscript{45}

5.4 Results and discussion

In Fig. 5.7A, the static near-edge x-ray absorption fine structure (NEXAFS) spectrum of CHD is plotted and compared to the TD-DFT calculation. The pre-edge resonances, labeled peaks X and Y, each consist of several overlapping transitions into unoccupied molecular valence orbitals. Peak X consists of carbon 1s→1π* LUMO transitions localized on the sp\textsuperscript{2} hybridized carbon sites, while peak Y consists of 1s→σ*(C–C), 1s→2π*, and 1s→σ*(C–H) transitions.\textsuperscript{46} UV photoexcitation promotes an electron from the HOMO (2π) of CHD to the LUMO (1π*), immediately modifying the electronic structure and, therefore, the NEXAFS spectrum. As the potential energy imparted by the photon is converted into kinetic energy of the nuclei, the electronic structure evolves accordingly as depicted in Fig. 5.1B, leading to further changes in the NEXAFS spectrum. In Fig. 5.7B, the change in the carbon K-edge NEXAFS spectrum (differential absorption, ΔA) following the 266 nm excitation of CHD is shown as a function of the pump-probe time delay. Three distinct temporal windows are marked off in shaded regions of Fig. 5.7B, namely 0-40 fs, 90-130 fs, and 340-540 fs, each of which show a unique differential absorption spectrum corresponding to a different step in the ring-opening reaction. In Figs. 5.8A-C, to clarify the interpretation of the evolving NEXAFS spectrum, the differential absorption spectra in these three temporal windows are converted to pure “pump-on” spectra (i.e. of the photoexcited molecules only) by adding back a scaled “pump-off” static spectrum based on the percentage of the molecules in the interaction region that are photoexcited. By this procedure, we find that ~13% of the molecules in the soft x-ray focal volume are photoexcited by the UV pump pulse, in agreement with an estimate from the absorption cross-section of CHD at 266 nm (8x10\textsuperscript{-18} cm\textsuperscript{2}, ε=2000 l/mol/cm) and the pump pulse fluence in the x-ray focus (0.27 mJ/mm\textsuperscript{2}), given the 4 μJ pulse energy.

The transient NEXAFS spectra in the 0-40 fs, 90-130 fs, and 340-540 fs time windows are plotted in Figs. 5.8A, 5.8B, and, 5.8C, respectively, and compared to the static “pump-off” spectrum. Each transient spectrum is an average over the designated time window. Due to the 120±15 fs IRF, the early time windows of 0-40 fs and 90-130 fs are not perfectly isolated. In the 0-40 fs time window (Fig. 5.8A), immediately following excitation, we observe a large depletion of the 1π* resonance (peak X) as well as a broad increase in absorption on the low energy wing (280–284 eV) of peak X and in the valley between peaks X and Y (~286 eV). In Fig. 5.8B, the most striking transient feature is observed in the 90-130 fs time window at 282.2
eV, which is a new resonance not observed in the NEXAFS of either ground state CHD or HT. Also in this time window, peak Y is broadened and shifts to lower energies, leading to increased absorption amplitude between peaks X and Y. In the final time window (340-540 fs...
in Fig. 5.8C), which represents the completed reaction, the transient resonance at 282.2 eV has decayed and peak X (1\pi* resonance) returns completely with even higher amplitude, but is broader and slightly red shifted by \sim 0.3 eV when compared to the 1\pi* resonance in the ground state CHD spectrum. Furthermore, peak Y has shifted back to higher energies, although a slight component remains on the low energy side. Lastly, in the 340-540 fs time window, a new broad feature at \sim 289 eV has risen in.

To elucidate the underlying physical processes that govern the evolution of the photoexcited NEXAFS spectrum, we perform TD-DFT calculations of the carbon K-edge spectra at different points along the reaction coordinate. In Figs. 5.8D, 5.8E, and 5.8F, the calculated NEXAFS at (D) the Franck-Condon (FC) region of the 1B excited state accessed via 266 nm excitation, (E) the pericyclic minimum of the electronically-excited 2A state, and (F) of an evenly distributed mixture of the HT isomers are shown. The calculated NEXAFS in the FC region, as shown in Fig. 5.8D, has a depletion of the 1\pi* resonance at 284.5 eV and a distinct new resonance at \sim 280.6 eV with carbon 1s→2\pi character (i.e. into the “optical hole” generated in the 2\pi orbital by 2\pi→1\pi* excitation). Previous femtosecond time-resolved studies have reported that the movement out of the FC region occurs on an extremely short timescale \sim 20-30 fs \cite{11,14}, which makes it very difficult to capture the transient NEXAFS expected in this region, given the IRF of our experiment. The TD-DFT calculations of the x-ray spectra along the reaction coordinate indicate that when the wavepacket reaches the 1B/2A conical intersection, the 2\pi and 1\pi* resonances begin to coalesce into a single resonance near 283 eV (Fig. 5.9). As the wavepacket moves down the steep 1B potential energy surface, the energy initially imparted by the 266 nm photon in the form of a 2\pi→1\pi* excitation (electronic potential energy), is converted to kinetic energy of the nuclei, which lowers the 2\pi-1\pi* splitting (schematically illustrated in Fig. 5.1B). From the perspective of the potential energy surface picture in Fig. 5.1A, this lowering of the 2\pi-1\pi* splitting is represented as the narrowing gap between the ground state and excited state, reaching the smallest gap near the pericyclic minimum of the 2A state. Any motion out of the FC region, therefore, will lead to shifting of the 2\pi resonance from 280.6 eV to higher energies and the 1\pi* resonance from 284.5 eV to lower energies.

In Fig. 5.8A, the transient NEXAFS measured in the 0-40 fs time window captures the immediate depletion of the 1\pi* resonance, but instead of a distinct resonance at 280.6 eV expected in the FC region, we observe a broad wing between 280.5-284 eV. This broad absorption wing represents the spread of the wavepacket significantly out of the FC region toward the 1B/2A conical intersection. To observe a continuous shift of the 1s→2\pi and 1s→1\pi* resonances, better temporal resolution would be required for the present signal-to-noise levels of this experiment. Nevertheless, we are able to address the population dynamics through the 1B state by plotting the time-dependent differential absorption at 284.5 eV, as shown in Fig. 5.10A, where depletion occurs immediately upon UV excitation. The subsequent decay of the depletion at the longest delay times is due to overlapping absorption with the HT photoproducts and vibrationally “hot” CHD molecules.

From the 1B state, a non-adiabatic transition onto the 2A state occurs and, at the minimum of the 2A state, the NEXAFS calculation in Fig. 5.8E shows that the merging of the 2\pi and 1\pi* resonances is complete, leading to a single resonance at 282.9 eV. The theoretical analysis reveals that this resonance involves carbon 1s promotion into a valence orbital of mixed 2\pi/1\pi* character (1s→2\pi/1\pi*). In the experimental spectrum, specifically the 90-130
fs time window shown in Fig. 5.8B, the calculated $2\pi/1\pi^*$ resonance is explicitly observed at 282.2 eV, representing a direct observation of the elusive 2A state pericyclic minimum. Furthermore, the clear coalescence of this resonance at an energy of 282.2 eV, in agreement with the theoretical prediction of the $1s\rightarrow 2\pi/1\pi^*$ transition, provides experimental

![Graphs and diagrams showing transient x-ray absorption spectra](image)

Fig. 5.8 (A-C) Transient “pump on” x-ray absorption spectra (i.e. of the photoexcited molecules only) measured in the delay time windows highlighted in Fig. 2B: (A) 0-40 fs, (B) 90-130 fs, and (C) 340-540 fs and compared to the scaled static x-ray absorption spectrum of ground-state (G.S.) CHD. Each transient spectrum is an average over the designated time window. As described in the main text, ~13% of the molecules in the interaction region are photoexcited. To directly compare the changes in the spectra induced by UV photoexcitation, the static CHD reference spectrum is scaled in accordance with the percent excitation. (D-F) Calculated x-ray absorption spectra at (D) the 1B state FC region of CHD, (E) the 2A state minimum, and (F) of an evenly distributed mixture of HT isomers. The valence orbitals involved in each of the major core-to-valence resonances in the pre-edge regions of the calculated spectra are shown. In the spectrum at the 2A state minimum in (E), a transient resonance appears at 282.9 eV, which involves C 1s promotion to a valence orbital of mixed $2\pi/1\pi^*$ character. This resonance is directly observed at an energy of 282.2 eV in the 90-130 fs experimental spectrum in (B).
confirmation of the strongly overlapped and mixed $2\pi$ and $1\pi^*$ frontier orbital energy levels in this region.

Since the transient resonance at 282.2 eV is maximized near the pericyclic minimum of the 2A state, the population dynamics through this intermediate region can be represented by the differential absorption at this resonance energy as a function of the pump-probe time delay, as shown in Fig. 5.10B. Note that there is a clear delay between the rise of the $2\pi/1\pi^*$ resonance at ~282.2 eV (Fig. 5.10B) and the depletion of the $1\pi^*$ resonance at 284.5 eV (Fig. 4A). The delay corresponds to the timescale required to arrive at the 2A state from the initially excited 1B state FC region and is measured to be 60 ± 20 fs. The subsequent decay of this state is fit to an exponential time constant of 110 ± 60 fs, which corresponds to the lifetime of the 2A state before the wavepacket relaxes non-adiabatically through the 2A/1A conical intersection. The error bars represent one standard error of the fitted parameter, calculated from the least squares fitting routine. Further analysis of the calculated NEXAFS spectrum at the 2A state minimum (Fig. 5.8E) also reveals an increase in oscillator strength and slight (~0.2 eV) red shift of peak Y to ~287.2 eV. The experimental spectrum in the 90-130 fs time window of Fig. 5.8B shows a larger ~0.5 eV red shift of peak Y, but no significant increase in absorption strength. The red shift observed at peak Y, which involves core transitions to unoccupied orbitals that do not participate in the 266 nm valence excitation, is attributed to nuclear dynamics. In the initial steps of ring-opening, the C=C and C-C bonds stretch and the ring is deformed $^{11}$. Bond elongations lead to red-shifting of core transitions to antibonding orbitals,

![Graph](image)

**Fig. 5.9** Comparison of the simulated x-ray absorption spectra at key regions of the potential energy surfaces involved in the photochemical ring-opening reaction. The black line represents ground-state CHD. The red line represents the FC region of the 1B excited state. The blue line represents the conical intersection between the 1B and 2A excited states (CI2) and the cyan line represents the 2A state minimum (i.e. the pericyclic minimum). Note that as the wavepacket moves from the 1B state FC region to the 2A state pericyclic minimum, the $2\pi$ and $1\pi^*$ resonances at 280.6 eV and 284.4 eV, respectively, coalesce into a single resonance at 282.9 eV with mixed $2\pi/1\pi^*$ character, at the energy observed experimentally.
1s→σ*(C-C) and 1s→2π*, which are underlying peak Y, due to the larger antibonding character of the final core-excited state compared to the valence-excited state.¹⁷

Lastly, crossing through the 2A/1A conical intersection along the reactive pathway leads to formation of highly vibrationally-excited HT. Although initially the HT molecule is produced in the all-cis conformation (cZc), the barriers between the different possible isomers

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**Fig. 5.10** Temporal evolution of the differential absorption amplitude (difference between “pump on” and “pump off”) at three different x-ray energies. (A) shows the temporal evolution at 284.5 eV, which is the peak energy of the ground-state CHD 1π* resonance. Note the immediate depletion (negative amplitude) occurring at this resonance, which follows the envelope of the pump pulse, and subsequent decay of the depletion at the latest time delays occurring due to the overlap with the 1π* resonant absorption of the HT photoproducts and vibrationally excited CHD molecules. (B) shows the temporal evolution at 282.2 eV, which is the peak energy of the transient 2π/1π* resonance and therefore represents the population dynamics through the intermediate 2A state region near the pericyclic minimum. The lineout is fit to a delayed rise (60±20 fs delay) followed by an exponential decay with a time constant of 110±60 fs. (C) shows the temporal evolution at 284.2 eV, representing the peak of the final 1π* resonance of the HT photoproduct and fits to a delayed rise at 180±20 fs.
are far below the internal energy present in the molecule,\textsuperscript{47} leading to a photoproduct that can take on any of its possible conformeric structures. In Fig. 5.8F, therefore, the calculated NEXAFS spectrum of an evenly distributed mixture of HT isomers is shown, which is an excellent match to the experimental spectrum measured in the long time-delay limit (340-540 fs), as shown in Fig. 5.8C. The close similarity between the NEXAFS spectra of each individual isomer, as shown in the calculated spectra in Fig. 5.11, precludes quantification of the contribution from each individual species. Here, in both experiment and theory, the $1\pi^*$ resonance of HT appears with higher oscillator strength and is slightly red-shifted compared to the analogous resonance of CHD. The experimental $1\pi^*$ resonance also appears much broader in the final HT spectrum due to the large excess of internal vibrational energy in the nascent HT molecules.

A key observation in Fig. 5.8C is the increase in the peak X ($1\pi^*$) amplitude, despite the significant broadening of the resonance, compared to the CHD ground-state spectrum. Since the $1\pi^*$ resonance of HT has a larger oscillator strength compared to that of CHD, as predicted by the calculations shown in Fig. 5.8F, the increase in peak X amplitude is caused by the production of ring-opened HT molecules. Peak Y in the experimental 340-540 fs transient spectrum also appears with greater amplitude and is red-shifted with respect to peak Y in the CHD spectrum, in agreement with the calculated spectrum of the HT isomers. We cannot explicitly distinguish the two species quantitatively to determine the precise HT:CHD branching ratio. Recently reported HT:CHD branching ratios include 60:40 and 30:70.\textsuperscript{13,16}

Lastly, the new broad resonance observed in the experimental spectrum at $\sim$289 eV in Fig. 5.8C is consistent with the calculated spectrum of HT isomers. There, a new broad resonance appears at 288.7 eV in HT, which is not present in the spectrum of CHD. However, we cannot specify possible changes due to vibrationally excited CHD. In order to clock the generation of HT photoproducts, the time-dependent differential absorption lineout at 284.2 eV is plotted in Fig. 5.10C, representing the rise in the peak of the $1\pi^*$ resonance of the HT isomeric mixture, which is red-shifted relative to the ground-state CHD $1\pi^*$ resonance (as seen in Fig. 5.8C and

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5_11}
\caption{Comparison of the simulated x-ray spectra of the individual isomers of the HT photoproduct, showing their close similarity.}
\end{figure}

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The lineout reveals a delayed rise at this energy, which reaches an asymptote in the long-time limit and signifies the formation of the ring-opened HT photoproduct. The rise of the HT signal is fit to a delayed step function centered at 180±20 fs.

5.5 Concluding remarks

The unique capabilities of carbon K-edge NEXAFS spectroscopy have been applied with femtosecond time resolution to characterize the evolution of the valence electronic structure during the prototypical electrocyclic ring-opening reaction of CHD. The analysis of transient carbon K-edge NEXAFS spectra, in combination with TD-DFT calculations of the core-to-valence absorption at critical points along the reaction coordinate, reveals that the frontier $2\pi$ and $1\pi^*$ orbitals are strongly mixed and overlapped near the pericyclic minimum. This transient electronic structure in the intermediate region is consistent with the Woodward-Hoffman framework describing the favorability of a “continuous” transition of the highest-occupied frontier orbital of the reactant into that of the product. In photoinduced reactions, the LUMO of the ground-state reactant is the highest-occupied orbital in the excited state and this orbital is thought to transform into the HOMO of the ground-state product. Providing direct evidence of this intuitive picture, the present results show that the frontier orbitals (i.e. the HOMO and LUMO of ground-state reactant) overlap energetically in the intermediate region between reactant and product. Complementary to recent x-ray scattering experiments, which directly image the evolving molecular structure, the measurements here provide significant new insight into the coupled motion of electrons and nuclei during a photochemical reaction. With ongoing increases in flux and stability, the continuing application and growing accessibility of “water-window” soft x-ray pulses on table-top setups promises to open new scientific directions in molecular photochemistry and photophysics, both in gas and condensed phases.

5.6 Bibliography

2015, 119 (33), 8832.


(17) Stöhr, J. NEXAFS spectroscopy; Springer, 1996.


(22) McCusker, J. K. Nat. Phys. 2014, 10 (7), 476.


(49) Henke, B. L.; Gullikson, E. M.; Davis, J. C. At. Data Nucl. Data Tables. 1993, pp 181–342.