

**Time resolved photoelectron spectroscopy with ultrafast
soft x-ray light**

by

Lora Nugent-Glandorf

B.S., Wheaton College, 1996

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Chemistry and Biochemistry

2001

This thesis entitled:
Time resolved photoelectron spectroscopy with ultrafast soft x-ray light
written by Lora Nugent-Glandorf
has been approved for the Department of Chemistry and Biochemistry

Stephen R. Leone

Prof. W. Carl Lineberger

Date _____

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Nugent-Glandorf, Lora (Ph.D., Physical Chemistry)

Time resolved photoelectron spectroscopy with ultrafast soft x-ray light

Thesis directed by Prof. Stephen R. Leone

Understanding the nature of chemical bonding in molecules has long been of fundamental interest, and manipulating specific chemical bonds has found practical potential in many areas, such as polymer chemistry, biophysics, and genetics. Photoelectron spectroscopy (using photons to eject electrons from a molecule to determine electron energies and bonding properties) has been a proven technique for gaining insight into the electronic structure of the simplest atoms to large molecules. Here, I describe experiments designed to investigate bonding in a simple molecule (Br_2) by measuring electronically excited molecular states and dissociative transient electronic states via time-resolved photoelectron spectroscopy with soft x-ray light. High-harmonic generation produces a novel, femtosecond source of soft x-rays by focusing an ultrafast 800 nm Ti:Sapphire laser into a rare gas jet. I outline the details of the experimental apparatus, including the optical layout, two-grating separation and compression of the high-harmonic pulses, and the magnetic bottle photoelectron spectrometer. The feasibility of using the generated soft x-ray pulses for photoelectron spectroscopy is established, and the spectral and temporal nature of the pulses are determined. The photoelectron spectrum of the bound excited B state of neutral Br_2 is measured and the issues involved in ionization from excited electronic states is discussed. The time-resolved dissociation of the excited C state of Br_2 is observed using a visible pump (400 nm) and a soft x-ray probe. Key results point to challenging new problems involving the cross-sections and shapes of photoelectron features arising from dissociating states, as well as understanding the role of cross-correlation processes versus dissociative wavepacket signals. UV-pump/soft x-ray probe photoelectron spectroscopy promises to offer a unique and powerful way to probe excited electronic states and dissociation dynamics of neutral molecules in the gas phase on ultrafast time scales.

Acknowledgements

First of all, I would like to thank my advisor, Steve Leone, who is largely responsible for making my graduate school experience a positive one. Not only was this project originally formed from his ideas, but has also seen success due to his advice, knowledge and experience. Steve has been a great advisor on all fronts, from the technical and conceptual realm to personal advice for career and life in general. For all this, and for his continuing support of me as a scientist, I am very grateful. Thanks also to Ronnie Bierbaum, my co-advisor, for her help and support.

I would also like to recognize OSEP, the Optical Science and Engineering Program at CU, for continuing financial support and the opportunity to do a research internship. I chose to do my internship with Dr. Richard Haight, an IBM researcher at the T.J. Watson Research Center in Yorktown Heights, NY. I am also indebted to Rich for his patience, advice, time and the opportunity to work for him. Funding for this project was received from the Air Force Office of Scientific Research, as well as additional equipment purchased with specific grants from the National Science Foundation.

Next, there are all the people who worked with me over the last 4+ years on this project. In the beginning, MK and Jen made a great team to work with as we attempted to make an empty room into some semblance of an experiment, as well as providing a great deal of comic relief. Next came Mike Scheer, whose brains and quintessential german-ness made the x-ray project into the great instrument it is today. The bulk of the data presented here was a result of Mike and I working together. During my absence in New York, I should thank Tobias Voss

for his work in the lab and for keeping Mike in check while I was away. Along the way we were happy to have Ed Grant and Xeuming Yang, both visiting professors to JILA, work with us while on sabbatical. Also thanks to Anneliese, a pre-grad student and a good friend for her work on Al_2Br_6 . Thanks also goes to David Samuels, the grad student who joined the project a year ago, for his hard work in the lab in the last months and for the new ideas he brings to the project. And to all the Leone group, past and present, thanks for all your free advice, patience and friendships. Other key players in the realization of this experiment were Hans Green, Blaine Horner and Dave Alchenberger from the instrument shop, and Paul Buckingham and James Fung-a-Fat from the electronics shop. To all the support staff at JILA, thank you for making this such a great place to do science!

To those teachers in the past who encouraged me in many ways, Mr. Warren Pettit, Dr. Brian Miller, Dr. Narl Hung, and Dr. Mark Niemchzeck, thank you for your influence on my life and career.

There is no room to thank all my friends who have helped me survive grad school in various ways, but I am overwhelmingly grateful to all of you. Special thanks and love to Paula, Allie, and Tara for great times at Tuesday lunches which kept me going, and to Jen and Sara for continuing to be good friends and always making me laugh. To Kitty, my only friend at IBM, thanks for helping me survive life away from home. And to the Bible study folks, you have been a great encouragement to me in my personal and spiritual life, which has helped me to be a better person.

Of course, I can't go without mentioning my husband Dave, who has provided me with unconditional love and support through our 5 years of marriage, and who is my inspiration. And to my family, my parents and sister and brother and their families, for always welcoming me home and for their constant encouragement and love, I am forever thankful for all of you.

Contents

Chapter

1	Introduction	1
	1.1 Background	1
	1.2 Time-resolved photoelectron spectroscopy	8
	1.3 Harmonic generation	11
	1.4 Coupling the high harmonic source and time-resolved photoelectron spectroscopy	13
	1.5 High-order harmonics and surface photoelectron spectroscopy	15
2	The Experimental Apparatus	19
	2.1 Introduction	19
	2.2 Laser System	20
	2.3 Optical layout	26
	2.4 Vacuum Chamber	32
	2.4.1 Pulsed Valve	32
	2.4.2 Two-grating separation and compression	37
	2.4.3 Photoelectron Spectrometer	38
	2.5 An instrument for ultrafast photoelectron spectroscopy of solids: IBM T.J. Wat- son Research Center	46
3	Characterization of high-order harmonics and static photoelectron spectroscopy	49
	3.1 Introduction	49

3.2	Harmonic generation	49
3.3	Photoelectron Spectroscopy with soft x-ray harmonics	55
3.4	Photoelectron spectroscopy of solid samples	62
4	Energy bandwidths of the harmonics	69
5	Photoelectron spectroscopy of the excited $^3\Pi_{0+u}$ B state of Br₂	80
5.1	Introduction	80
5.2	Excitation scheme	82
5.3	Photoelectron spectra	85
6	Pulse durations of pump and probe beams: Cross-correlation measurements	93
6.1	Introduction	93
6.2	800 nm + 400 nm	93
6.3	800 nm + 266 nm	94
6.4	17th harmonic + 800 nm	97
6.5	Harmonics + 400 nm	97
7	Photodissociation of Bromine	106
7.1	Introduction	106
7.2	Pump-Probe Photoelectron Spectra in Br ₂	107
7.3	Time-traces of cross-correlation and Br atom signals	113
7.4	Ionization of the excited state wavepacket	119
7.5	Ionization cross-sections of atoms and transient states	124
7.6	Conclusions	130

Bibliography	131
Appendix	
A Absorption spectrum of Bromine	137
B Rydberg wavepackets in Krypton	139

Tables

Table

4.1	Energy bandwidths for harmonics 7-55 generated in neon	75
7.1	A calculation of the enhancement of the atomic cross-section compared to the molecular cross-section for the 17th harmonic of 800 nm. Using 10,000 molecules as an arbitrary number, the raw photoelectron counts are used to calculate the ratio.	125
7.2	The corrections and final values for the enhancement of the atomic cross-section compared to the molecular cross-section for harmonics 13-21.	126
7.3	The percentages by total counts of the cross-correlation and transient photoelectron signals for three different scans and two probe wavelengths.	128

Figures

Figure

- 1.1 A simple molecular orbital picture demonstrating two atoms coming together to form two molecular orbitals. 2
- 1.2 **Top:** A pictorial representation of a valence electron being ejected from a valence or bonding orbital with an ultraviolet (UV) photon, and a core electron being ejected from an inner orbital with an x-ray photon. **Bottom:** The electron energy level diagram of the above pictures. On the left, the UV photon has sufficient energy to eject the 3π electron. On the right, a x-ray photon is needed to eject the 1σ electron. The dotted arrows represent the energy of the ejected photoelectron. Binding energy (B.E.) is defined as the energy with which an electron is bound to the nucleus. 4
- 1.3 (A) A schematic of an electrostatic analyzer where electrons are energy separated by their velocities. Objects shaded with dark gray represent the photon source and the light gray objects are the detectors. The dotted line represents the electron path through the analyzer. (B) A time-of-flight photoelectron analyzer where electrons are energy separated by their arrival time to the detector. 5
- 1.4 The photoelectron spectrum of HBr as a function of ionization energy. The Σ and Π labels are term symbols describing the final state of HBr^+ . Spectrum taken from ref. [1] 7

- 1.5 Core level photoelectron spectra of HBr, Br₂, CH₃Br and CF₃Br showing the shifting of the 3d Br core levels due to chemical bonding (taken from ref. [2]). Fine structure splitting of the ion states is also present in the spectra. 9
- 1.6 A pictorial representation of time-resolved pump-probe photoelectron spectroscopy. The sample molecule is pumped into an electronically excited state with a visible laser pulse. At varying time delays after the pump pulse, a probe laser pulse ionizes the molecule and the photoelectrons are analyzed at each time delay. 10
- 1.7 An example of a time-resolved photoelectron experiment from ref. [3]. The photoelectron spectrum of I₂⁻(Ar)₂₀ clusters is shown at various time-delays between the pump and probe pulses. 12
- 1.8 A classical picture of high-order harmonic generation with an ultrafast laser. The coulomb potential of the atom is perturbed in the presence of the strong laser field, and tunneling ionization of the electron occurs. The free electron gains energy in the electric field (U_p , ponderomotive potential). As the optical field changes phase, the coulomb potential also oscillates and causes recombination of the electron with the atom, accompanied by the release of a high energy photon. 14
- 1.9 The process of imprinting circuitry on a Si wafer using a photomask. The mask is made of high-quality quartz with an image of the circuit deposited on the surface. Photons from a light source are incident on the mask and the pattern is written on the Si wafer. 17

- 2.1 A schematic of the Spitfire (two stage Ti:Sapphire amplifier). The seed pulse is first sent through the stretcher (1), and then into the first stage of amplification (Regenerative Amplifier, (2)) where it passes through a Ti:Sapphire crystal. After the maximum gain is achieved from the Regen, the pockels cell rotates the polarization, sending the pulse into the double-pass or Linear Amplifier (3). Finally, the pulse is directed into the compressor (4) and out onto the laser table. 21
- 2.2 A calibration curve for the Ocean Optics fiber-coupled CCD camera that is used to measure the bandwidth of the seed pulse from the Tsunami Ti:Sapphire laser. The points were measured by coupling light from a cw dye laser with known wavelengths into the fiber optic cable and recording the oscilloscope position. A linear fit to the data describes the relationship between wavelength and scope position in ms, allowing for measurement of the Tsunami bandwidth. 22
- 2.3 The temporal (left) and spectral (right) profile of the seed pulse from the Tsunami Ti:Sapphire laser measured with a commercial FROG instrument available in the JILA Keck labs. The dotted line is a measurement of the phase of the electric field across the pulse, or the amount of frequency chirp in the pulse. A flat phase indicates no frequency chirp across the pulse. 23
- 2.4 A schematic of the single-shot home-built autocorrelator used for determination of the temporal pulse width of the amplified output pulse. 25
- 2.5 The temporal (left) and spectral (right) profile of the pulse from the amplified Ti:Sapphire laser measured with a commercial FROG instrument available in the JILA Keck labs. The slight curvature in the dotted line (representing the phase of the electric field) indicates a slight frequency chirp from the amplification process as compared to the seed pulse. 27

- 2.6 The optical layout of the pump and probe beams. The output beam is split into pump and probe beams at the 80/20 beamsplitter (BS). The 20% reflected beam is sent into the doubler/tripler to frequency upconvert the pulse to 400 nm or 266 nm. The pump beam then passes through a 70 cm lens (L2) into the chamber, and after reflection from the mirror inside the vacuum chamber, comes to a focus at the slit. The 400 nm beam comes to an ~ 1 mm focal spot in the interaction region, with a power density of 2×10^{11} W/cm². The transmitted beam (80%) passes through a half-wave plate, a delay stage and is then focused with a 40 cm lens (L1) into the pulsed gas jet and the selected harmonic is directed and focused into the interaction region. The 17th harmonic, as an example, is focused to a 250 μ m spot with an estimated power density of 1×10^5 W/cm² in the interaction region. **Inset:** First the pump beam is sent through a telescope to reduce the beam size. For 2nd harmonic generation, the 800 nm beam is sent through a BBO crystal. For 3rd harmonic generation, the 800 nm beam is split into 2 beams where one arm is doubled in a BBO crystal and combined again with the second 800 nm arm in a BBO crystal cut for tripling to produce 266 nm output. 28
- 2.7 A ray tracing simulation of the 21st harmonic beam on the slit (right before the interaction region). The beam has a diameter of ~ 100 μ m in both directions. There is some ellipticity of the beam due to the toroidal grating surface. The toroidal grating was designed for a certain beam geometry, and the actual input beam deviates from that slightly with the addition of the spherical grating. The points represent 11 rays starting from different positions in the initial collimated beam. 30

- 2.8 A detailed schematic of the vacuum chamber, including the pulsed valve chamber, the two grating chambers, and the magnetic bottle photoelectron spectrometer. The probe laser beam is focused into the pulsed valve gas jet at (A) where the harmonics are created. The harmonic of choice diffracts in 1st order off of the first spherical grating at (B), then again off the second toroidal grating at (C), and enters the interaction region at (D) where it intersects the gaseous sample (E). Ejected photoelectrons are collected in the magnetic bottle time of flight (F) and detected with the MCP detector (G). The pump beam enters the chamber at (H) and reflects off of a mirror located slightly above the harmonic beam and crosses the harmonic beam at a small angle in the interaction region. 33
- 2.9 (a) A sketch of the pulsed gas jet used for harmonic generation. Gas is released out the 1 mm aperture when the center plunger is lifted by the puckering of the piezo crystal when a voltage is applied. Four adjustment screws hold the piezo crystal in place and the tension tunes the output profile of the gas pulse at a 1 kHz repetition rate. (b) A profile of the output gas pulse measured with a hearing aid microphone. The width of the pulse can be adjusted by the width of the driving voltage pulse. 34
- 2.10 An example of adjusting the backing pressure to the pulsed valve and recording the intensity of the harmonic signal from the Pt-electron multiplier using argon as the backing gas for the 9th harmonic of 800 nm. The maximum harmonic signal occurs at ~ 10 psi argon as shown by the arrow. The decrease in harmonic signal when going to higher backing pressures is due to ionization of the non-linear gas medium with higher gas densities. 36

- 2.11 Photoelectron spectrum of NO gas taken with the 9th harmonic of a long pulse, narrowband Nd:YAG laser, $E_{h\nu}=10.496$ eV. Here the inherent resolution of the magnetic bottle spectrometer is seen in the peak widths. The vibrational progression of the NO^+ ground state gives rise to the three peaks separated by ≈ 0.28 eV. 40
- 2.12 Photoelectron spectrum due to all harmonics simultaneously incident on a sample of He gas. The first harmonic energetic enough to ionize He is the 17th ($E_{h\nu}=26.4$ eV). Each subsequent harmonic is seen as another main ionization peak at increasingly higher energies. Note the decrease in resolution for the higher electron kinetic energies. 42
- 2.13 An energy calibration curve taken from the time of flight peak positions of Fig. 2.12 and the known photoelectron energies. The dotted line is a fit to the data from equation 7.1. 44
- 2.14 An energy calibration curve for very low photoelectron energy peaks (below 2 eV) taken from the time of flight peak positions of Fig. 2.11 and the known photoelectron energies. The dotted line is a fit to the data from equation 7.2. . . 45
- 2.15 A schematic of the instrumental apparatus used during my internship at IBM T.J. Watson Research Center, adapted from ref. [4]. The doubly amplified Ti:Sapphire laser is focused with a 40 cm lens into a pulsed jet of neon gas where high-order harmonics are created. The harmonics are frequency separated with a grazing incidence toroidal grating and focused onto the sample surface after passing through a small pinhole before the UHV chamber. Photoelectrons created from the surface are directed into a TOF drift tube with a parabolic mirror and detected with a multi-mode detector. 47

- 3.1 A spectrum of the harmonics of 800 nm created in a gas jet of neon (top) and argon (bottom). Detection of the harmonics was accomplished by irradiating a piece of Pt metal with the harmonic beam and detecting the ejected photoelectrons with an electron multiplier as the grating was rotated at a steady rate. Small shoulders on the low order peaks in the top panel are the 2nd order diffraction of the high harmonics reflected from the grating. Harmonics 13-65 are detected in neon, and 11-27 are detected in argon. Detector settings were 3.3 kV across the electron multiplier for the neon spectrum and 2.7 kV for the argon spectrum. 51
- 3.2 The intensity of the 9th harmonic generated in Ar as a function of the driving laser intensity in W/cm^2 . Two trends are observed, attributed to the increase of harmonic generation in a perturbative regime (dotted line) and then change in slope due to the laser intensity causing saturation (or ionization) of the non-linear medium at $\sim 7.1 \times 10^{14} W/cm^2$ (dashed line). 53
- 3.3 The intensity of the 9th harmonic generated in Ar as a function of the position of the driving laser focus in the gas jet. "Zero" on the x scale designates the center of the gas jet. The lens used to focus the 9 mm diameter beam has a 40 cm focal length. 54
- 3.4 (a) Photoelectron spectrum due to all harmonics simultaneously incident on a sample of He gas. The first harmonic energetic enough to ionize He is the 17th ($E_{h\nu}=26.4$ eV). Each subsequent harmonic is seen as another main ionization peak at increasingly higher energies. (b) A single harmonic (61st, $E_{h\nu}=95$ eV), selected by the grazing incidence grating, incident on a sample of He gas. Not only is the main ionization peak seen, but also the 1st and 2nd satellite peaks. 56

3.5	(a) The valence level photoelectron spectrum of Xe taken with the 11th harmonic (17.5 eV). (b) The photoelectron spectrum including 4d core levels of Xe taken with the 47th harmonic (73 eV). Resolution of the system is best at low photoelectron energies.	57
3.6	Photoelectron spectra in Xe with the 43rd harmonic, demonstrating the ability to tune the harmonic to an atomic Rydberg resonance. The bottom spectrum is the 43rd harmonic of 800 nm, while the top spectrum is the 43rd harmonic of 791 nm. By tuning the fundamental beam, the harmonic is tuned into a Rydberg level leading up to the 4d ionization threshold. The hole left by the excited electron causes an onset of Auger electrons (shaded area).	59
3.7	(a) The valence level photoelectron spectrum of Br ₂ taken with the 17th harmonic (26 eV), showing the X, A and B final states of Br ₂ ⁺ . (b) A section of the photoelectron spectrum of Br ₂ taken with the 49th harmonic (76.5 eV), showing the 3d _j core levels of Br ₂ ⁺	60
3.8	(a) The valence level photoelectron spectrum of Al ₂ Br ₆ taken with the 19th harmonic. (b) The core level photoelectron spectrum of Al ₂ Br ₆ with the 55th harmonic showing the bromine core levels. Al core levels were not observed.	61
3.9	The photoelectron spectrum of I ₂ taken with the 17th harmonic of 800 nm. The I ₂ spectrum has a similar structure to Br ₂ , except that the spin orbit splittings in the ion are more pronounced. The ² Π _g state at 9.3 and 10 eV binding energies, the ² Π _u state at 11 and 11.8 eV, and the ² Σ _g ⁺ state at 13 eV of the I ₂ ⁺ ion are observed [5]	63
3.10	The photoelectron spectrum of CH ₂ I ₂ with the 17th harmonic of 800 nm.	64
3.11	The photoelectron spectrum of GeBr ₄ with the 17th harmonic of 800 nm.	65
3.12	Photoelectron spectra of a GaAs (100) surface taken with harmonics 27, 41, 51 and 63 (top to bottom) of an 800 nm Ti:Sapphire laser. The 3d core levels of Ga and As are observed at 19 and 41 eV binding energies, respectively.	67

- 3.13 Photoelectron spectra of chromium metal on a Si(100) surface. The 3p core level is observed at 41 eV binding energy for three different harmonics (47, 55 and 59 from top to bottom). 68
- 4.1 Photoelectron spectrum of NO gas taken with the 9th harmonic of a long pulse, narrowband Nd:YAG laser, $E_{h\nu}=10.496$ eV (dashed line). Here the inherent resolution of the magnetic bottle spectrometer is seen in the peak widths. The vibrational progression of the NO^+ ground state gives rise to the three peaks separated by ≈ 0.28 eV. The solid line shows the same vibrational progression, but acquired with the 7th harmonic (centered at $E_{h\nu}=10.91$ eV) of the fs Ti:Sapphire laser. The broadening of the peaks is due to the energy bandwidth of the 7th harmonic. The height discrepancy in the highest binding energy peak between the Nd:YAG laser and the 7th harmonic of the Ti:Sapphire laser is due to the efficiency of the photoelectron spectrometer at different photoelectron energies. Though these peaks have the same binding energy, the dashed line peak at 9.8 eV corresponds to very low photoelectron energy, where the collection efficiency is quite low. 70
- 4.2 The relative energy width of photoelectron peaks from several different gases vs. their respective photoelectron energies. The higher energy photoelectron peaks converge to a relative width of 4-5%. For photoelectron peaks below ≈ 4 eV a new trend can be seen, where the ΔE of the peaks is due to the energy bandwidth of the harmonics. Target gas is He (\diamond), Ne (\times), Xe (\square), N_2 (\triangle), and NO (\circ). 73

- 4.3 (a) The absolute energy width of the harmonics derived from low energy photoelectron peaks (below 3 eV) are plotted as a function of the photon energy, or the harmonic used to ionize the electron from which the peak arises. The retarding grids in the electron flight tube were not used for this data set. (b) A more complete data set using the retarding grids to measure the bandwidths of all the harmonics from the 9th to the 55th. Comparison of (a) and (b) shows that no artificial broadening exists when utilizing the retarding grids. Target gases are He (\diamond), Ne (\times), Xe (\square), N₂ (\triangle), and NO (\circ), and the solid line is the average for each harmonic. 74
- 4.4 The photoelectron spectrum of NO gas with the 7th harmonic (left) and 9th harmonic (right), showing the vibrational progression of the NO⁺ ground state. The black spectrum represents the 70 fs unchirped pulse, while the light gray spectrum is taken with a positively chirped driving pulse and the dark gray spectrum is taken with a negatively chirped pulse. 77
- 5.1 A schematic of resonantly-enhanced excited state photoelectron spectroscopy of a generic molecule. Process (1): A single frequency photon used to resonantly excite an intermediate state and ionize it with a multi-photon probe. Process (2): A two-color REMPI process where one photon resonantly excites the molecule and a photon of a different wavelength is used to multi-photon ionize the molecule. Process (3): A two-color excitation-ionization scheme where one visible photon is used to resonantly excite an intermediate state and a VUV photon is used for single photon ionization. The dotted arrows represent the photoelectrons ejected from the three different processes. 81

- 5.2 Potential energy curves for Br_2 and Br_2^+ . Only the X and B states of the neutral and the X and A states of the ion are shown for simplicity. The 527 nm excitation laser pumps the neutral into the ${}^3\Pi_{0+u}$ excited B state, and the 17th harmonic photoionizes the excited molecules. The $v'' = 26$ vibrational level reached by the 527 nm photon is shown, creating a large region of Franck-Condon overlap in the Br_2^+ ion electronic states. The shading represents the accessible region of the X^+ and A^+ ion states with the probe photon. The intensities and energies of the photoelectrons will then be determined by the Frank-Condon overlap. 83
- 5.3 A molecular orbital diagram of the ground and excited states of Br_2 and Br_2^+ . The four molecular orbital levels shown result from combinations of Br atomic p orbitals (outer valence shell). The B and A states of the neutral have a similar configuration but differ in orbital angular momentum. 86
- 5.4 The photoelectron spectrum of gaseous Br_2 at 5×10^{-5} Torr taken with the 17th harmonic of 800 nm showing the final X, A and B states of the Br_2^+ ion. Solid black lines denoted ${}^3P_{2,1,0}$ are the known binding energies of the bare Br atom. 87
- 5.5 The photoelectron spectrum with the 17th harmonic only is shown in gray, while the photoelectron spectrum with the 527 nm + 17th harmonic is shown in black. Regions of small two-photon and atom signals are expanded for clarity. 88
- 5.6 An expanded photoelectron spectrum of Br_2 with (black) and without (gray) the 527 nm excitation laser. 90
- 5.7 A further expanded photoelectron spectrum of the $\text{B} \Rightarrow \text{X}^+$ transition in Br_2 (gray line=17th harmonic only). The dotted gray lines mark the photoelectron energies of the peak heights. 91

6.1	A cross-correlation trace of the 800 nm fundamental pulse with the 400 nm pump pulse obtained by a 4 (400 nm photon) + 1' (800 nm photon) multiphoton ionization in Xe.	95
6.2	A cross-correlation trace of the 800 nm fundamental pulse with the 266 nm pump pulse obtained by a 3 (266 nm photon) + 2' or 3' (800 nm photon) multiphoton ionization in Kr.	96
6.3	Solid line: photoelectron spectrum of Kr gas with the 17th harmonic, showing the spin-orbit split doublet of the Kr^+ ion state. Dashed line: photoelectron spectrum of Kr gas when the 17th harmonic and an 800 nm dressing beam are overlapped spatially and temporally. The 800 nm dressing beam adds to or subtracts from the 17th harmonic ionization in an above threshold ionization process.	98
6.4	(a) A valence level photoelectron spectrum of Xe with the 17th harmonic showing the sidebands created by introduction of the 400 nm dressing pulse with spatial and temporal overlap. The sideband photoelectron peaks are exactly one 400 nm photon higher in energy than the main ionization peaks. (b) The time-correlation of the sideband photoelectron peaks.	100
6.5	Cross-correlation traces of the 17th harmonic + 400 nm in Xe. (a) Toroidal grating rotated to 1st order diffraction, concave grating at 0th order reflection, iris open (8mm), FWHM = 882 ± 105 fs; (b) as (a) except iris at 1 mm, FWHM = 449 ± 64 fs; (c) Both toroidal and concave gratings rotated to 1st order diffraction, iris open (8mm), FWHM = 440 ± 25 fs; (d) as (c) with iris at 1mm, FWHM = 288 ± 12 fs.	101
6.6	Cross-correlation trace of the 19th harmonic + 400 nm in Xe. The shortest soft x-ray pulse measured to date with the instrument described here. Some irregularity in the temporal profile may indicate an irregular spectral profile of the harmonic pulse.	103

- 6.7 The pulse widths of the 13th through the 21st harmonics measured by cross-correlation with a 400 nm pulse. Error bars designate the error in the pulse width given by the Gaussian fitting program. 105
- 7.1 A simplified potential curve diagram illustrating the pump-probe sequence and resulting photoelectrons. **Process 1:** Ground state absorption of the 17th harmonic resulting in photoelectrons leaving Br_2^+ in both the X and A state (B ion state not shown). **Process 2:** Two photon ionization with the 400 nm + the 17th harmonic centered at $t=0$. **Process 3:** Ionization with the 17th harmonic from the excited C state of Br_2^* at a positive time delay (but before dissociation is complete). **Process 4:** After the dissociation is complete, the Br atoms are ionized by the 17th harmonic. The total energy of the probe laser is decreased for simplicity and size of the diagram. 108
- 7.2 Three pump-probe spectra of Br_2 : $\Delta t=-500$ fs (background), -100 fs (cross-correlation signal), and $+500$ fs (Br atom signal). The spectra are displaced vertically for clarity. 109
- 7.3 An expanded region of the photoelectron spectrum of Br_2 at $\Delta t \sim 30$ fs (gray line) and background at $\Delta t \sim -300$ fs (black line) showing the cross-correlation features. The feature at 7.4 eV binding energy is the above threshold ionization resulting from the overlap of the 17th and 400 nm pulses where the Br_2^+ is left in the ground X state. The shoulder roughly centered at 9.4 eV is a similar signal, only the Br_2^+ is left in the excited A state. The signal at ~ 8.5 eV is attributed to the ionized excited state wavepacket as it is sliding down the dissociative curve. 111

- 7.4 Normalized, subtracted pump-probe spectra of Br₂ in the cross-correlation time region (left). The spectra are displaced vertically for clarity. The panel on the right shows the appearance of the Br atom peaks in the photoelectron spectra. The two peaks in the photoelectron spectrum are due to spin-orbit coupling in the final Br⁺ state. Numbers on the vertical scale are pump-probe delay in femtoseconds. 112
- 7.5 Total counts from the cross-correlation peak and the atomic peaks from Fig. 7.4 and additional time delay data not shown are plotted as a function of pump-probe delay between the 400 nm pump and the 17th harmonic probe. The cross correlation signal is fit with Gaussian function of width ~ 300 fs and the atomic rise is fit with a step function described in the text. The dotted line fit of the step function allows both τ_{step} and σ_{fwhm} to be variables, while the dashed line fit fixes σ_{fwhm} to 300 fs. The solid lines designate the time delay between the center of the cross-correlation trace and the 'step' of the error function used to fit the rise in atomic signal. 114
- 7.6 A similar plot as Fig. 7.5 except using the 19th harmonic as a probe. The cross-correlation signal has a FWHM of 204 ± 17 fs and t_0 of 0 ± 17 fs, and the fit to the atomic rise gives $\tau_{step} = 36 \pm 21$ fs and $\sigma_{fwhm} = 367 \pm 45$ fs (dotted line) and the dashed line is a fit holding σ_{fwhm} at 204 fs, and τ_{step} then becomes 30 ± 20 fs. 116
- 7.7 (a) The $C^1\Pi_u$ dissociate of neutral Br₂ given by equation 7.3 (b) A curve representing the integral of (a) in fs per \AA . The experimental result of 40 fs implies a bond distance of $\sim 3 \text{\AA}$, while a bond distance of $2R_e$ occurs at a time of 105 fs. 117

- 7.8 Time traces of the cross-correlation features in the Br₂ data (400 nm pump and 17th harmonic probe). Black line: signal from the ATI process leaving the Br₂⁺ ion in the ground X state. Dark gray line: signal from the ATI process leaving the Br₂⁺ ion in the excited A state. Medium gray line: transient signal from ionization of the excited state wavepacket. Light gray line: random background noise. 120
- 7.9 Time traces of the cross-correlation features in the Br₂ data (400 nm pump and 19th harmonic probe). Black line: signal from the ATI process leaving the Br₂⁺ ion in the ground X state. Dark gray line: signal from the ATI process leaving the Br₂⁺ ion in the excited A state. Medium gray line: transient signal from ionization of the excited state wavepacket. Light gray line: random background noise. 122
- 7.10 Long scans of the cross-correlation photoelectron energy region with the 19th harmonic as a probe. The shaded areas of the photoelectron spectra on the left correspond to the photoelectron energy regions giving rise to the time traces on the right. The photoelectron spectrum on the very bottom is a background, with no 400 nm pump beam, and from there the time delays step up from -33 fs to +165 fs in steps of 33 fs. 123
- 7.11 Photoelectron spectra of Br₂ at long time delays, after the atomic signal between 1 and 2 eV photoelectron energy has reached a maximum value. The atomic signal clearly increases as the harmonic number decreases. (The background signal in the vicinity of the atomic peaks is used for normalization.) 127
- 7.12 The cross-section enhancement factor plotted vs. the harmonic photon energy, demonstrating that the 17th harmonic probe was not sitting on a resonance for atomic Br, but the atom signal is similarly enhanced for several harmonics. . . . 129

A.1	Absorption spectrum of Br ₂ from ref. [6], with lines drawn at 400 nm and 527 nm.	138
B.1	An energy level diagram showing the excitation of a Rydberg wavepacket in Kr by a 3-photon absorption of 266 nm (black arrows). When an 800 nm pulse (gray arrow) is introduced, the Kr is ionized by a 1, 2, or 3 photon addition of the 800 nm photon. Note that the ionization of Kr with 4 photons of 266 nm is identical in energy to the 3+3' multiphoton ionization at t = 0.	140
B.2	Photoelectron spectrum of Kr with a time delay between the 267 nm pulse and the 800 nm pulse of 500 fs.	141
B.3	Time traces of the photoelectron signal resulting from the ionization of a Rydberg wavepacket in Kr. The black trace represents the total counts in the photoelectron peak at 0.8 eV, and the dark gray from the photoelectron peak at 1.5 eV in Fig B.2. The light gray line is the black trace normalized to the dark gray trace, showing the fast oscillatory structure.	143
B.4	The same time traces as in Fig. B.3, with the power of the 800 nm beam reduced to 200 mW average power.	144
B.5	Rydberg energy levels in Kr, showing the ns, nd _{3/2} and nd _{5/2} progressions. The energy of three 266 nm photons is designated by the solid black line. The dotted lines represent the energy bandwidth (FWHM) of the 266 nm pulse. . . .	145